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Goldschmidt | Streitberger

Basics of Coating Technology

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BASF HANDBOOK ON
Basics of Coating Technology

2nd revised edition

Foreword to the second revised edition

Glasurit's ”Paints and Coatings” manual has been a standard work in the field of coating materials since it was first published in 1934. Since then a number of editions in German were published. The latest edition being first time published also in English in 2003 was well received on a worldwide basis. This second revised and corrected edition was sponsored by BASF Coatings. Compared to the first edition based on the German edition of 2002 market data were actualized, some passages revised, more English references introduced and corrections made.

The manual starts logically with a brief historical summary of painting, its current economic and technical significance and the social framework underpinning the industry. This is followed by a chapter dealing with product composition, raw materials, principles of product formulation and the relevant production processes for these products. Descriptions are then given of the properties of the liquid and solid coating materials for the respective application types, after which a chapter follows that deals with theoretical aspects of coating compositions. Applications are then explained for the reader, taking due account of the current significance of the coating processes. In this chapter the substrate plays a major role because of its impact on the coating process and outcome. The demands on the environment, health, safety and quality as specified in the current legislation in Europe and Germany are dealt with in the next chapter. A journey is then undertaken through the various industrial sectors of the paint and coatings industry with the aid of a large number of examples and illustrations. This chapter is of particular interest for newcomers to the industry and practically-minded readers. Standard tables, general performance indicators, a selection of relevant websites, definitions of terms and a comprehensive index round off the book.

When reading the manual, please bear in mind that abbreviations are defined the first time they are used. In addition, you will find a complete list of all abbreviations used in the book in chap. 9.3. Environmentally compatible coating materials are introduced in chap. 5.8 referring to more detailed technical information on these materials in the individual chapters. In any case, the comprehensive index will help you get to the information you need quickly.

Literature references are cited to enable readers to obtain more in-depth information. These are assigned to the individual chapters and may therefore be repeated on occasion. Many comments and scenarios are based on experience gained by BASF Coatings and are therefore not necessarily assigned to specific quotations.

Statutory provisions and mostly DIN EN standards have been followed for the terms and units used. Readers will therefore find that many expressions traditionally used in the industry have not been employed. By using standardized expressions, however, we wish to contribute to a uniform specialist terminology and therefore to the prevention of ambiguity or misunderstandings. An appendix of acronyms is included for reference.

Manufacturers, users, the academic community, institutes and authorities have varied expectations for the manual. The publishers have attempted to address a broad range of topics, based on the response to the previous edition and on the current technical and social developments, but have consciously avoided the in-depth treatment of specialist aspects to prevent the book's scope from becoming too unwieldy.

The scope of the book nevertheless meets the objective of publishing a work of reference that provides satisfactory answers to paint-related issues for both newcomers and experts.

We wish to express our gratitude to the many employees of BASF Coatings AG who have contributed valuable suggestions and detailed information. Our special thanks go still to Klaus-Peter Löbbe and for the second edition to the management team of BASF Coatings and to Raimar Jahn. We also thank Dr. P. Bachhausen and Dr. W. Kreis for their assistance as well as the publishers for their patient advices.

Prof. Dr. A. Goldschmidt and Dr. H.-J. Streitberger
Wiedenbrück, July 2007

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1 Introduction

1.1 Definition, Tasks and Economic Importance

The task of coating technology is to provide surface protection, decorative finishes and numerous special functions for commodities and merchandise by means of organic coatings. Many everyday products are only made usable and thus saleable because of their surface treatment. To achieve this, relevant coating formulations, their production plant, the coating material and suitable coating processes for the product must be available. However, the quality to be achieved by means of the coating process is not the only function of the coating material used. The object to be painted or coated itself with its specific material and design and an appropriate application process are further variables which play a significant role. In addressing the ongoing tasks of quality optimization and rationalisation while minimizing the impacts for humans and the environment, it is vital that the dependencies mentioned above be not only recognized but also taken into account as the framework defining the conditions in which work is carried out from development to application. Coating technology, therefore, is an interdisciplinary subject. Paints and coating materials are not end products, but merely initial or intermediate products which, for the above mentioned reasons, require a skilled and conscientious user if they are to be converted into the actual end product, the coating itself. Only the cured coating, in many cases a system consisting of several individual coats, may meet the wishes invested in and the requirements demanded of the coated products.

Fig. 1.1.1
Coated objects of daily life

Two of the most important of the many functions which coatings have to meet are protection and decoration. Other noteworthy features are the informative tasks and the achievement of special physical effects. The conspicuousness of emergency service vehicles, the camouflaging of military equipment, and road or airport markings are just some of the informative tasks required of coatings. Color markings enable areas or spaces to be clearly signed or divided. Color coding helps to indicate the contents of containers or the material being conveyed in pipes. Optical effects induced by colored or metallic pigments lend a coating a particular optical attraction. Deliberately generated surface textures such as scars or wrinkles expand the range of effects which can be achieved. The use of color schemes for rooms and machines based on known physiological and psychological effects of colors also contributes in various ways to improved working conditions and enhanced safety. Functional pigments produce temperature dependent colors, for example as a result of their thermochromic properties, and therefore, indirectly permit the temperatures of objects to be measured.

The most important task for coatings, in economic terms, is surface protection. Thus coatings help to retain value and improve the usability properties of almost all products and are therefore, of huge economic significance. Particular mention should be made of the protection of goods made of metals which only gain lasting anticorrosive protection when they are painted.

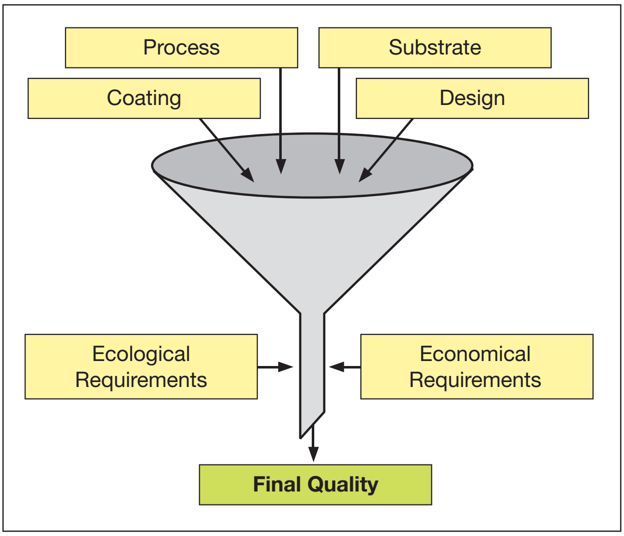


Fig. 1.1.2
Factors determining the quality of coatings

It is vital in this regard, for example, in the automotive sector, for the resistance of the coating system to external, sometimes aggressive natural and anthropogenic atmospheric influences such as tree resins, bird droppings, acids, alkalis, salts and organic solvents, to be guaranteed.

The protective function of paint on cars must not be impaired even under extreme mechanical impacts such as stone chippings thrown up from the road by traffic or by brush action in carwashes.

Furthermore, coatings must withstand combined, i.e. physical and chemical, effects to which objects are subjected, for example, in the different weather conditions. The interaction of sunshine, rain, heat and frost combined with emissions from heating systems and internal combustion engines, by ozone and saline fog makes great demands on a coating's resistance and protective properties.

However, a surface protection coating can also be applied in order to meet quite different requirements. Floors and steps can be made nonslip by means of rough or high grip coatings, thereby increasing their utility value. By contrast, surface friction can be reduced by use of smooth coatings to produce a high degree of nonadhesiveness. Flammable materials can be rendered safe by means of flame retardant coatings. Antibacterial coatings help maintain sterile surfaces in production and storage facilities in dairies and breweries or prevent the growth of barnacles and algae on ships' hulls. In the electrical engineering sector insulating coatings provide effective and lasting insulation for wire, windings and condenser materials. On the other hand, conductive coatings can be used to make insulating substrates electrically conductive or even to print electrical circuits. Furthermore, organic coatings can help to reduce noise pollution. Acoustical insulation coatings for machines and underbody protection coatings for passenger cars are examples of this.

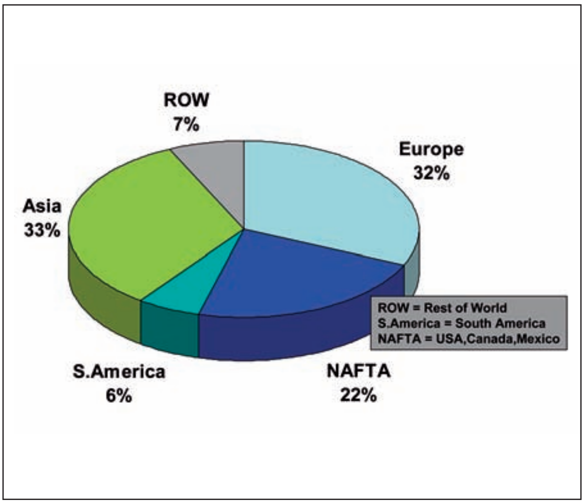


Fig. 1.1.3
World coatings market of 28.6 mio tons in 2006 by regions

This broad spectrum of requirements explains why no single coating material can satisfy every wish simultaneously and in the same way. The goal of providing coating materials for the durable protection, decoration and improvement of objects made of wood, metal, plastic or mineral materials at reasonable prices can only be met by adopting different formulations using a range of materials and material combinations. Each of these combinations targets a limited field of substrates, a selected application method and a specific profile of film properties.

Coating technology is used in metal processing, in the manufacture of plant and machinery and in the electrical engineering industry. All kinds of road and rail vehicles, ships and aircraft are important objects which require painting or coating. Effective surface protection by means of paints and coatings is also indispensable in the civil engineering sector, for steel and concrete structures and in wood processing. Even plastics and leather require coating in many cases. Modern paper, plastic or sheet metal packaging materials are inconceivable without the protection and decoration afforded by coatings.

The worldwide paint and coatings market reflects economic developments in the regions. It is most highly developed, for example, in the so called triade (North America, Europe, South East Asia). The per capita consumption of paints and coatings in these regions is approx. 4.5 kg. The growth in coating consumption is determined by the economic development in the individual regions or countries [1.3.1].

The broad field of applications for coatings and their widespread use are explained by the high value and great benefits which they offer. The fact that there are few objects which do not require coating is an indication of the enormous importance of coating technology. Calculating this importance merely in terms of the quantity of coating materials manufactured annually worldwide of 28.6 million tonnes in 2006 with a value of some 80 billion euros (fig. 1.1.3) gives an incomplete picture.

Although quoting the quantities of coating materials is not a direct indication of the added value of industrial commodities, it does permit the area which can be protected or decorated by means of coating materials to be calculated, taking due account of the film thickness to be applied. Assuming an annual production quantity of 28.6 million tonnes and a wet film thickness of 100 µm (0.1 mm), a surface area of some 315,000 km^2 can be coated. That represents about 3/4 of the surface area of Germany. A 10 m wide strip with a film thickness of 100 µm, on the other hand, coated using the same quantity of paint would stretch about 100 times from the earth to the moon or go round the world 600 times.

A more meaningful means of evaluation would be to use the value of the effectively protected and improved products. Assuming that an added value of 20% of the produced goods is achieved by painting or coating them in the form of an extended service life and increased attractiveness, this means EUR 200 billion for the German market in 2000. This represents 50 times the sales value of the paints and coatings.

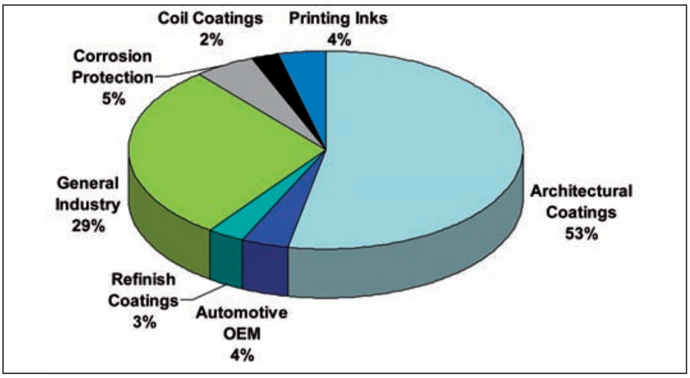


Fig. 1.1.4
Worldwide coatings market in 2006 by segments (source : VdL)

The division of the market into branches or segments is not uniform around the world. A number of breakdowns, however, seem agreed on using certain segments, such as decorative paints, general industrial paints, automotive paints, and printing inks.

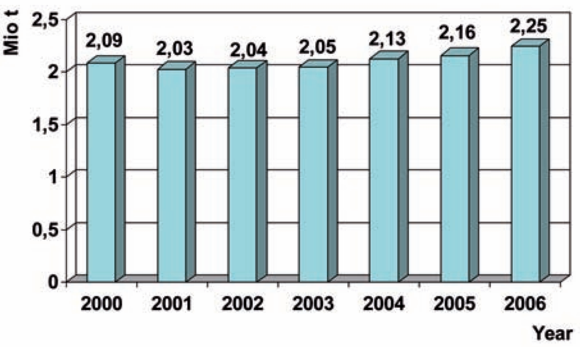
Decorative paints represent the largest market for paints and coatings at 53%. This is followed, at 29%, by the market for the industrial coating of a huge range of objects, from compact discs via plastic bumpers for cars to rail vehicles (see chapter 7). Automotive coating lines and refinishing bodyshops are each clearly defined segments with a high technological value, though of less significance in terms of volume sales. Printing inks represent approx. 4% of the worldwide demand for coating materials and are a separate segment in technological and marketing terms, though not from the point of view of their composition.

The size of the European market was 9.1 million tonnes in 2006. There is a slight shift towards industrial coatings and printing inks compared with the sectoral division in the rest of the world. Germany is the leader with a consumption of approx. 1.6 million tonnes ahead of Italy, France, the UK and Spain, which are all in the range between 0.7 and 0.8 million tonnes. The size of the Northamerican market was 21.2 Bio. US $ in 2002 served by about 835 companies [1.3.2]

The graphic below gives an overview of the economic development of the paint and coatings industry in Germany since 2000 which is closely linked to the country's overall economic development.

One of the characteristic features of coating technology in addition to coating consumption is the still high energy consumption for processing coatings which is estimated at approx. 200 billion kWh annually worldwide. This figure is the equivalent of the energy content of approx. 30 million tonnes of crude oil. If the raw materials required for paint production are also added to this figure in the form of crude oil equivalents, the result is a total crude oil requirement of approx. 100 million tonnes for the worldwide manufacture and processing of coating materials, or some 3 to 4% of the annual crude oil extraction worldwide.

The legal requirements imposed on environment compatible coating processes have resulted in greater use of appropriate coating materials in the last 20 years. These include, in particular, solvent free powder coatings, waterborne paints, in which organic



In more than 200 manufacturing plants with a total of 20,000 people about 2.3 million metric tons of coatings have been produced representing a value of 4.8 billion Euros in the year 2006.

Fig. 1.1.5
Production of coatings in Germany from 2000 to 2006

solvents are replaced in whole or in part by water, high solids paints and radiation curable paints, which are processed either in an aqueous solution or completely without conventional solvents with the aid of low molecular reactive thinners (see chapter 5). Statistics from the Association of the German Paint Industry (VdL) show that these coatings have achieved the greatest growth, with a 10% annual increase in the last 10 years.

Ongoing improvements in our knowledge of the toxicology of the raw materials entail a regular replacement of raw materials, which is associated with the corresponding development costs, if we wish to maintain the quality standard achieved.

As far as energy consumption is concerned, there is still a need to be more economical in the use of raw materials and energy. A proportion of the material is lost en route to the finished coating. Spray application, which is specified for many objects to be painted because of its optical attractiveness and range of colours, has a particular role in this regard. As far as coating wood and plastics is concerned, the more effective electrostatic spray methods have not yet found universal acceptance. In addition, the paintlines lose substantial quantities of heat energy. In recent years a number of developments have increased the efficiency of coating processes to such an extent that growth in the paint and coatings market in the industrially developed countries has been below the growth level of the gross domestic product (GDP).

As a result of the use of solvents as an application aid for coatings, an additional hydrocarbon emission load of approx. 200,000 tonnes is estimated annually in 2007 for Germany alone for the currently standard average organic solvent content of 50% [1.3.3]. Whereas the organic emissions from motor vehicles have been successfully reduced to less than 1/3 of their previous level in the last 20 years by the introduction of the catalytic converter, the successes in coating technology have been more modest to date by comparison. Despite the introduction of waterborne paints and powder coatings, approximately half of all the industrially processed coating materials used in Germany are still in the form of conventional, i.e. solventbased materials.

From a European perspective, the solvent processing industries, including the paint and coatings industry, are now the leading emitters of organic compounds and solvents. European legislators responded to this fact by issuing a 1999 EU directive (see chapter 5.3) in an attempt to force even small to medium sized companies to adopt more stringent measures to avoid emissions.

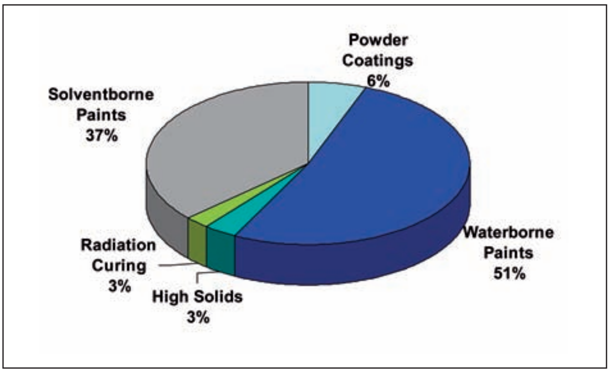


Fig. 1.1.6
German coatings market in 2006 by product classes (source : VdL)

Significant success has been achieved by manufacturers and processors of paints and coatings with regard to occupational health and safety. The chemical industry, for example, has led the accident statistics in Germany for the industry with the least number of incidents.

An analysis of this situation reveals that manufacturers and consumers of paints and coatings, though occupying different value added stages, are extremely closely connected. Manufacturers develop and supply coatings materials to the consumers who in turn modify the product while processing them in physical, physicochemical and chemical processes and convert them in this way into a bound, mechanically solid and, at the same time, flexible coating.

The path of chemistry from the raw material to the finished coating starts at the raw materials or paint manufacturer and is then consciously interrupted before it is taken up again during processing by the paint consumer.

Although the performance profile of a coating is initially shaped by the paint and thus by the paint manufacturer, it is the processor who actually generates the finished properties. The industrial scale coating of consumer goods is therefore a joint effort between paint and coatings manufacturers and processors.

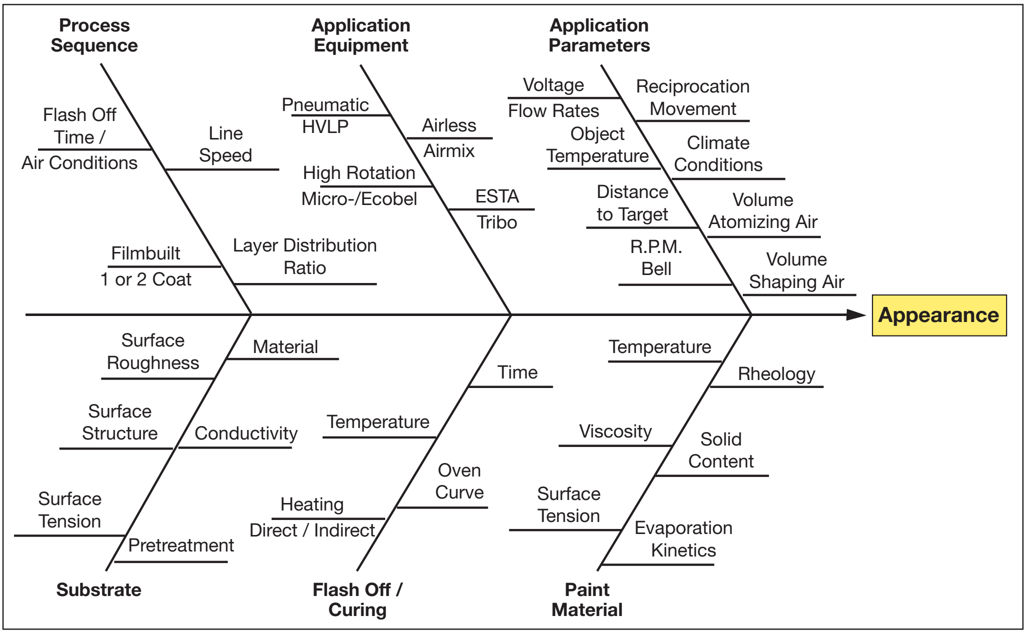


Fig. 1.1.7
Various factors determining the final coating result of the spray application process

Paint manufacturers who really know their job are nowadays responsible not only for developing, manufacturing and selling paint. Their task also includes providing the conditions for successful painting by their permanent technical presence and support. This relates primarily to materials and processes, though includes detailed environmental protection and occupational safety issues. Paint manufacturers offer a package, as it were, in which the material is just one component among many (see fig. 1.1.7). Apart from the technical tasks of manufacturing and processing coating materials, particular attention has to be paid to quality assurance methods.

Quality assurance links production with R&D and sales within a company. Production must be capable of reproducibly providing the quality demanded by the customer, while sales must identify the total costs to achieve the appropriate prices.

However, paint manufacturers are faced with specific problems since they are expected to produce constant material quality and at the same time paints with constant processibility. Only this provides the best conditions for achieving a uniform result in the painted article. This means that production paint and coatings entails more than merely manufacturing a product whose composition is identical to a defined standard. Rather, since physical variables can only rarely be applied as criteria for the practical properties of coatings, paint testing of necessity includes simulating the application method used by the processor of these materials. This gives rise to a large number of different test methods because of the very wide range of specification conditions and the different requirements on the coating process resulting from them. Standardising these tests and reducing their overall number is also a priority task for all concerned.

Quality and costs of a coating are defined, as mentioned earlier, not only by the paint material and an application method appropriate to it, but also and significantly by the substrate, i.e. by the material and the design of the object to be painted. It is therefore clear that it is extremely important to address surface treatment, material selection and its design properties during product design and to integrate these features in the overall planning.

Coating technology is therefore a complex marriage of chemical, physical, process-engineering, environmental, toxic and economic variables. This discipline is in constant move as a result of technical progress and further accelerated by legislative requirements. Companies are therefore called upon to link well known features with new knowledge. Industrial coating technology can only be fully understood if, in addition to detailed knowledge of paint processing, the properties of the coating material and of the object to be coated are known as well and also if all the quality shaping variables within the range of economic and environmental requirements are addressed.

1.2 Retrospective

The aim of the following look back at the materials and painting methods of the past is to highlight coating technology’s entangled paths by illustrating a few key events in order to make its progress more transparent.

The early coating materials were natural resins. *Dioscorides* and *Pliny* report, among other things, on the use of countless exotic natural resins from the time of the Greeks and Romans. Later papers describe the importance of colophony, copals, shellac and dammar. Later still, in the 12th century, come reports of the combination of hardened natural resins such as amber with resinifying, i.e. chemically hardening natural oils [1.3.4].

The application methods up to that point consisted solely of brushing or wipe techniques, without significant emissions, waste water or paint waste.

Rodgerus von Helmershausen, also called Theophilius, describes the manufacturing of coatings and gives detailled recommendations for formulas in chapter 21 of his book “Schedula Diversarium Artium“ around 1000 AC :

- Bring linseed oil into a small pot and add rubber, which is called “Forniß“ …
- In a different step collect 4 stones … over these put an empty pot and fill in the entire and mentioned rubber-“Forniß“, which is called „glassa“ in latin …
- Then bring carefully fire beneath until the rubber is melted.
- Have a third pot nearby on the coal in which warm linseed oil is filled …
- Pour the warm oil on top and stir with the iron …
- Related to the mass make sure that 2 parts are of oil and one third of rubber …

Fig. 1.2.1
First recipe of a coating material by Theophilius

The monk *Rodgerus von Helmershausen* reports in his book *Schedula Diversarium Artium* for the first time in detail around the end of the first millennium of the composition and manufacture of the then standard paint [1.3.5]. He is therefore, regarded as the person who specified the first relevant paint formulation with detailed production information.

Linseed oil and amber (then termed ”rubber” in German), are boiled together in a ratio of 2:1, with the hardened resin as a nonvolatile reactive thinner, and the linseed oil as a chemically crosslinking component. Solvents to regulate viscosity were not used at that time because of their insufficient availability.

In the 10th century it was the Arabs with the doctor *Abu Mansur* who taught the Europeans the art of distillation [1.3.6]. This art was then used in Europe for, among other things, extracting turpentine oil. When the *von Eyk brothers* extended *Rodgerus von Helmershausen’s* formulation, which was the first to be systematically described, by adding turpentine oil in the early 15th century, physical drying and thus emissions had been invented [1.3.7]. This outcome is noteworthy, on the one hand, because the use of painting expanded substantially as a result and, on the other hand, because the connected environmental problems are still tying up a considerable part of the paint specific research capacity to this day.

After the memorable ”invention” of emissions the „invention“ of waste followed very much later. By this is meant the introduction of the continuous production line by *Henry Ford* in the early 20th century which represents the start of industrial scale painting technology. The production line has brought the world huge benefits in terms of speed and therefore also economical production systems. However, full use could only be made of the faster coating processes which this required by employing quick drying paints and a new application method. The consequence of this was that the oil paints which took several weeks to cure were superseded by quick drying cellulose paints with solvent contents of up to 80%. At the same time the wastefree brush method which had been standard up to that point was replaced by the spray method. However, the introduction of the spray gun, which had been invented by *de Vilbiss* back in the 19th century, also ushered in a new problem because of its extremely poor material application efficiency of less than 50%: the generation of paint waste and, at the same time, a drastic increase in organic emissions because of the considerably higher solvent contents of the cellulose paints.

1920 introduced therefore a completely new situation in coating technology without an appropriate approach for the new problem. This approach had to be developed in the course of the following decades. The production line meant technical progress in the form of increased coating quality as a result of improved application and a more economical production system, though at the expense of the environment in the form of waste and emissions.

The introduction of the production line therefore shared the problems of emissions and waste which had been known since the time of the *van Eyk brothers* and was also the start of the metamorphosis of a craftsmenship into a segment of industrial production technology.

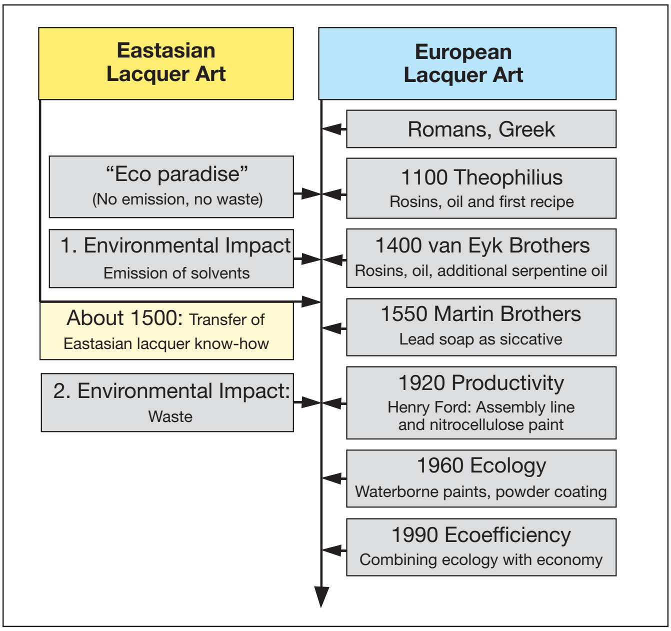


Fig. 1.2.2
Historical highlights in the evolution of coating technology

Until people finally became aware of this situation, resulting in appropriate concerted activity, government action was necessary in the form of environmental legislation. The innovations which occurred subsequently were no longer the results of individual ideas but were increasingly achieved thanks to cooperation among all those involved in the finished coating.

The first goal was to rationalise the processes and optimise quality on the basis of conventional, i.e. solventborne, coating technology. Later, from the 1960s onwards, research started in a new direction from several different locations simultaneously, initially separated but later with a common goal in view: the development of low solvent and low waste painting methods [1.3.7].

The results of this work are new waterbased materials, radiation curable systems and waste free powder coatings in association with new processing methods. Electrocoat painting, roller and curtain coating e.g. for coil coating and the application of solid powder coatings are the most noteworthy innovations of the last 50 years. Environmental protection, on the one hand, but occupational safety issues also, on the other hand, were beginning to become much more structured like the National Environmental Policy Act (NEPA) in USA from 1969. Research into environment compatible paint technologies was expanded to include the aspect of minimizing consumption of resources at the latest with the passage of Germany's Federal Environmental Protection Act in March 1974 and the oil crises.

The various trade associations and technical bodies of the American and European paint and coatings industries were also involved in this. The efforts in this direction were strengthened by the voluntary commitment ("responsible care") of the paint and coatings industry in almost every region of the world.

Successful examples of such a concerted approach to dealing with a problem by a number of different groups and bodies include the development of the new paint process for the Mercedes A-Class in which a paint manufacturer, a paint processor and a plant manufacturer cooperated, and also the "Expansion of the application fields for powder coating technology" research project funded by Germany's Federal Ministry for Education and Research (BMBF) and coordinated by the German Research Association for Surface Treatment (DFO) together with a total of 20 companies from the fields of paint production, paint processing, plant engineering, the raw materials industry and countless research institutes. The industry supported LEPC (Low Emission Paint Consortium) under the umbrella of USCAR (United States Council for Automotive Research) is another example [1.3.8].

The globalization of the world economy, particularly manufacturing industry, is currently confronting the paint and coatings industry with new challenges. Since quality requirements have been standardized worldwide as a result of consolidation, in the automotive industry for example, the major paint suppliers have recognized this and now guarantee the same quality standard for coatings everywhere. No end to this development is presently in sight. In addition, sales channels have been expanded for many paint suppliers by the introduction of e-commerce, the electronic transaction of purchases over the Internet. Of necessity, all aspects are steps in the direction of consolidation.

The quality requirements, particularly by the automotive industry in the form of ISO standards, VDA standards and the QS9000 series mean that the entire process from the product idea, via development, scale up, production and sale to the final application is falling more and more wholly within the paint and coatings companies' sphere of responsibility. It now seems that the entire process chain starting with the production of the paint materials to the finished (coated) article will become a key competency of the major paint companies.

It is therefore, guaranteed that the active players in this field will continue to grow closer together. Only in this way will it be possible to develop efficient processes for the respective sectors or applications.

The conditions for coating technologies with a zero environmental impact and making the most efficient use of resources are largely in place. Future success will depend on whether holistic concepts can be found. Product life cycle or ecoefficiency audits [1.3.9, 1.3.10] with the aim of achieving sustainable development will therefore provide the principles underpinning research and development programmes more and more frequently [1.3.11].

Soundly based knowledge is an essential factor in the successful introduction of environment compatible coating technologies with the simultaneous implementation of new ideas in processing technologies. This includes details on correlations and interdependencies between the individual scientific disciplines and thus of the various sectors involved in the paint process. This book has been written not least for this reason.

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2 Coating Material

In accordance with the old DIN 55 945 or with European standard DIN EN 971-1 which has been in force since 1996, and in general agreement with the English speaking experts the correct designation of materials for organic coatings providing surface protection is coating materials. Paints, on the other hand, is the standard term for coating materials featuring particular properties. In the English speaking world the term ”coatings” is often synonymous for paint, the layer on the coated products, as well as the painting process.

The standard defines paints as liquid, paste or powder coating materials which enable optically opaque coatings to be produced with decorative, protective and, if necessary, also specific technical properties. It should be noted that many terms in general use, such as varnish or vehicle, are different from the terms specified in international standards (see chapter 8). Paints are therefore just one part of the large class of coating materials, but nevertheless have to meet a broad spectrum of extremely different requirements. They can be sub-divided in accordance with various principles: by the function of the coating (clearcoat, metallic paint, solid paint), the particular layer in the coating system (primer, primer surfacer, topcoat), by the purpose of the paint (car paint, decorative paint, industrial paint), by its degree of environmental compatability (water based paint, high solids paint, radiation curable systems, powder coating), by the chemistry of film forming agent (alkyd resin paint, acrylic resin paint, cellulose nitrate lacquer) or by the processing conditions (baking enamel, oxidatively curable coating material), to name the major classification criteria.

The selection of the right coating materials for an optimum performance profile therefore depends equally on the quality requirements, the specified application conditions, the curing process, the design features and the various materials of the object to be painted. All coating materials, however varied their use may be, must have the same properties of wetting substrates, transforming into a closed film, flowing and then solidifying so that the desired mechanical and chemical protection of the object is achieved.

The performance profile of the paints therefore has to be adjusted not only to the application but also to the subsequent film formation. A fresh paint finish applied by spray gun must exhibit sufficient flowability so the droplets seal all pores. At the same time or subsequently it must equalize all peaks and troughs in the film surface caused by the application. Surface tension and viscosity are the most important paint parameters in this regard. Furthermore, special effects such as a high gloss finish, chroma and oriented reflection (metallic effect) may have to be achieved. Clearcoats for wooden panelling therefore have a completely different composition compared with those of anticorrosive paints or coating materials for color designs on leather.

2.1 Raw Materials

Resins as film forming agents, often incorrectly termed binders, additives, solvents, pigments and extenders are the usual ingredients of liquid coating materials. Binders in

accordance with DIN EN 971-1 are the pigment free and extender free parts of the dried or cured coating. They are, therefore, made up of the film forming agent and the nonvolatile part of the additives (see figure 2.1.1).
If there are no pigments and extenders, the material is a clearcoat, and if there are no solvents when higher molecular film forming agents are used, the coating material can be ground to produce a powder coating. If the film forming agents are lower molecular liquid products, it is also possible to dispense partially or wholly with the use of organic solvents. Water soluble resins or dispersions permit water to be substituted for the solvents.

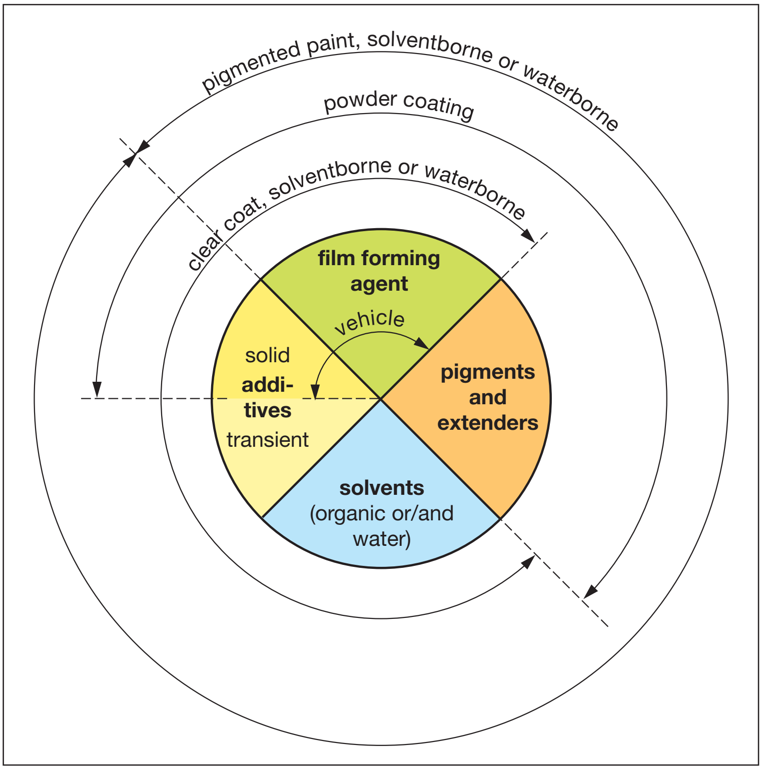


Fig. 2.1.1
Typical composition of coatings

Irrespective of the application, a **film forming agent** which solidifies as a result of physical or chemical processes is the indispensable component of a coating material. Classic film forming agents are exclusively oligomeric to polymeric organic materials because of the range of requirements relating to adhesion to the substrate, to mechanical strength with simultaneous elasticity and resistance to ambient effects. They can be manufactured from natural substances after chemical modification or by industrial synthesis.
Despite the existence of a broad range of synthetic resins, the natural substances or modified natural substances have lost little of their importance. Cyclorubber or chlorinated rubber, cellulose esters and alkyd resins based on natural fatty acids are just a few examples of the technically important group of renewable paint raw materials.

Film forming agents can be divided into two basic groups, irrespective on their derivation. The first group is the higher molecular, physically curing film forming agents such as cellulose nitrate, cellulose acetobutyrate, thermoplastic acrylates and also PVC copolymers. These resins set by giving off solvents, without undergoing a chemical change during film formation.

For high-grade decorative and industrial paints, on the other hand, chemically reactive film forming agents or film forming agent combinations are used. The crosslinking reaction initiated by heat or catalysts after application enables lower molecular and thus high solid base resins to be used. An example of this are baking enamels based on acrylicamino resin, alkyd amino resin or phenolic resin combinations. The oxidatively curing alkyd resins, incorrectly termed ”air-curing”, start to crosslink at room temperature, though much more slowly. Modern polyurethane and epoxy resin paints cure very quickly, even at room temperature. The latter can generally only be used in the form of 2-component materials because of their high chemical reactivity.

A coating material formulation usually also contains **solvents** in addition to a film forming agent. Only when the correct materials are selected and combined is it possible to achieve troublefree processing and film formation. The most common organic solvents are aromatic hydrocarbons such as xylene and solvent naphtha, aliphatic hydrocarbons such as mineral spirit or vernice, esters such as ethyl acetate or butyl acetate, alcohols such as propanol or butanol, ethers such as butyl glycol, ether esters such as ethyl or butyl glycol acetate and various ketones. Suitable combinations of the huge range of available solvents have to be chosen, depending on the resin type. It is especially important, with regard to the application process, to choose solvent combinations with the correct evaporation properties. Only in this way can a balance be guaranteed between the flowability and stability of paints freshly applied to vertical surfaces. Water as a solvent for environmental compatible paints plays a different role (see chapter 6.6.2).

Diverging from the classic principle of using solvents solely to regulate viscosity, they can also react chemically with the paint resins during film formation, i.e. have a role in addition to their function as a thinner. These socalled reactive thinners therefore remain in the solidifying film and thus contribute to a reduction in organic emissions. Paints which can be cured by means of UV or electron radiation also deserve to be mentioned in this context, as do unsaturated polyesters cured by organic peroxides.

The **pigments** used in the coating materials give the coating its chroma and hiding power. Extenders influence application properties, such as sandability and hardness, but also increase the nonvolatile proportion of the coating material. In many cases pigments and extenders prevent premature degradation of the substrate to be protected by painting and the polymer protective coating itself by the absorption of UV radiation. A further important task for certain special pigments is to optimize protection against corrosion. The many types of pigment are divided into organic and inorganic absorption pigments, metallic and interference pigments and anticorrosive pigments. The first two groups cited consist of extremely finely dispersed, generally crystalline solids. Titanium and iron oxides and the mixed-phase pigments are the most important among the inorganic pigments. There is a huge variation in the composition of organic pigments. Modern, synthetically manufactured organic pigments also offer excellent fastness to light and longterm outdoor exposure properties. Their particular strength lies in their brilliance and their high tinting strength. At high temperatures, however, with certain exceptions, they are inferior to the inorganic pigments in terms of heat stability.

Special optical effects are achieved by means of pearlescent, interference or metallic pigments. Coatings whose color or luminosity vary with the viewing angle are of particular interest in the automotive sector because of their attractiveness.

The final coating material components to be mentioned are the **additives** and **plasticizers**. With the exception of the plasticizers, these substances are added to the resin/solvent or pigment mixture in sometimes minute quantities. Despite this low concentration, they have a significant impact on the properties of coating materials and coatings. Additives can facilitate dispersion of the pigments during production. In the ready-to-use paint they suppress the tendency for the pigments to sediment, enhance flowability when the paint is applied, improve flow during film formation and improve the applied properties by influencing the surface smoothness or roughness. They prevent the pigments from floating to the surface, accelerate curing, also have an effect on the gloss, increase resistance to harmful UV radiation and reduce premature degradation by bacteria or mildew which attack paint.

2.1.1 Film Forming Agents

Whereas it is possible for a coating material to dispense with the raw materials such as solvents, additives or pigments mentioned in the first section, a film forming agent or a film forming agent combination is absolutely essential if the specified tasks as a paint are to be met. The film forming agent must meet numerous criteria. These relate essentially to adhesion to the substrate and the film's mechanical strength (cohesion) while retaining its elasticity at the same time. With such a range of requirements it is necessary to use macromolecular polymeric materials. Their molecular structure enables them to meet many requirements by mechanical linking of the molecular chains. It is just as feasible to achieve these properties with synthetically manufactured oligomeric or polymeric materials as with appropriate natural polymers, though the latter may require chemical modification to enable them to be used in practice. However, optimum coating properties can only be obtained if the film forming agent can wet the substrate as a resin solution, as a dispersion or as a molten powder coating and can be transformed into a visually attractive, smooth film by means of subsequent flow.

The mechanical strength can therefore be formed by the release of solvents (physical drying) or by molecular enlargement with simultaneous crosslinking of the film forming agent molecules (chemical hardening).

All film forming agents which solidify by physical drying, i.e. purely by releasing solvents, therefore remain sensitive to solvents and can be liquefied again by heat treatment. These film forming agents are thermoplastic. Consequently, coatings made using them are also thermoplastic.

Chemically reactive film forming agents, on the other hand, perform differently. These are chemically crosslinked with reactive groups of the resin molecules during film formation and thereby transformed into an insoluble duromeric film which also cannot be reliquefied.

Unlike purely physical drying, this supplementary chemical hardening also permits the use of low molecular film forming agents. This means that the amount of solvents necessary for processing can be significantly reduced in the chemically reactive systems. Chemically reactive systems therefore contribute to reducing solvent emissions compared with thermoplastic materials.

The varied shapes and sizes of the film forming agent molecules (see figure 2.1.2), but also the functional groups at the points of linkage within the polymer chains and those at the end of the molecular chains, determine the film forming agents' properties and thus the application for which they can be used.

Linearly structured molecules behave differently from branched ones in many respects. The large number of chain ends of dendrimers (tree-like polymers) permits a much higher functionality despite the low molecular weight compared with the former, thereby providing the necessary conditions for a high crosslink density [2.4.1].

The size or size distribution of these resin molecules has a particular impact on the processing properties, though also, of course, on the quality of the end product.

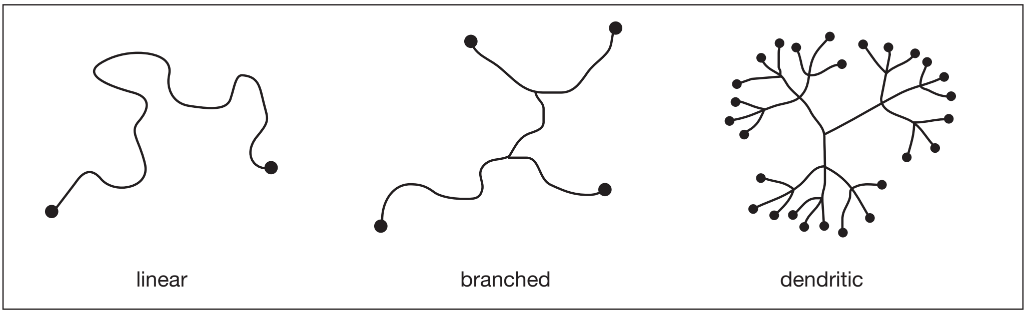


Fig. 2.1.2
Various forms of film forming molecules

The latter applies to the processing state but also to the structure of the molecular bond in the finished coating. In the case of thermoplastic materials, i.e. nonreactive film forming agents, this remains unchanged in respect of molecule size even after processing. With chemically reactive coating materials, on the other hand, considerable changes occur in the molecule size as a result of chemical crosslinking. When categorizing paint resins and their usability, therefore, the molecular weight and molecular weight distribution are important indicators of the molecule size.

Polymer chemists have developed numerous methods to determine these indicators Resin solution viscosity (viscosimetry), diffusability and the osmotic pressure (osmometry) which occurs when semi-permeable membranes are employed are used as indicators of the molecular weights. Methods involving chromatographic separation of the individual film forming agent molecules, which sometimes vary considerably in size, are more up-to-date and informative. Different dwell times in cavities of polystyrene gels enable average molecular weights and the molecular weight distribution to be determined simultaneously provided the appropriate equipment is available (see chapter 2.3.2). The molecular weight distribution is therefore particularly important as the applied properties cannot be specified merely by means of the average molecular weight.

Reactive end groups and the type of chemical link between the basic structural elements also help to shape properties. Information on the crosslinking capabilities of the resins and also their polarity can be obtained by determining experimentally the number of free carboxyl, hydroxyl or isocyanate groups in the form of the acid, hydroxyl or isocyanate values. Similarly, the iodine absorption value is an indicator of the presence of carbon double bonds which can, in turn, be used to describe the oxidative curing of alkyd resins (see chapter 2.3.2).

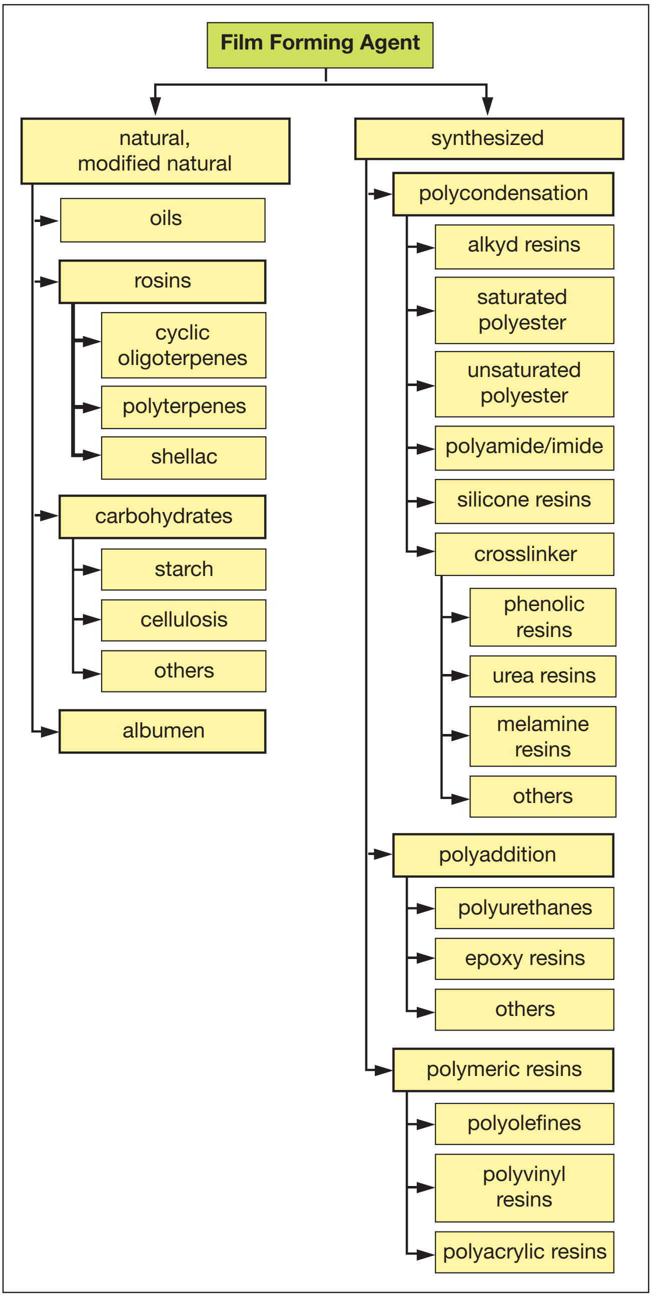


Fig. 2.1.3
Classification of important film formig agents

To understand the nature of the film forming agents' basic structural elements, wet chemical degradation reactions must first be conducted. Only then can the functional groups created be identified. This can be done either by determining the above resin indicators or by identifying and quantifying functional groups or characteristic molecular components using appropriate analytical instruments. These are divided into spectroscopic, thermal and chromatographic methods (see chapter 2.3.2).

The film forming agents which have proved their value over thousands of years for protecting and decorating objects are varied and belong to a huge range of classes of chemical substances. A number of different aspects can be used to classify them systematically. They can, on the one hand, be classified by the chemical principle of the molecular structure; there is also a method of dividing them into film forming agents which remain thermoplastic during film formation or are transformed into duromers. Another meaningful classification method is to distinguish between natural materials, modified natural materials and those which are obtained synthetically. Because a division into natural and synthetic products is a reflection of paint history, this chapter will also be structured in this way. Accordingly, natural oils which have been important for thousands of years should be mentioned first. They were combined at an early stage with hardened resins such as shellac to increase the initial hardness because of their very slow solidification which was a purely chemical process. Other important representatives of such hardened resins are colophony, copal, dammar and amber. They belong to the large group of natural isoprene derivatives. Latex milk which is produced from certain plants is also an isoprene derivative, in the form of 1,4-cis-polyisoprene (polyterpenes). It was used centuries ago as natural rubber to make water-repellent coatings. Later modifications to produce cyclorubber and chlorinated rubber gave access to those film forming agents which are still in use today for heavy-duty anticorrosive protection and the protection of damp rooms because of their hydrophobic properties.

Carbohydrates such as cellulose and starch which are produced in nature to excess by photosynthesis proved to be usable raw materials for paints in the form of organic or inorganic esters and ethers more than 100 years ago. Even in the 21st century cellulose nitrate and cellulose acetobutyrate are still technically important base resins for the woodworking and furniture sector, on the one hand, and the automotive sector, on the other.

Overall, natural materials have lost their pre-eminence because of their restricted availability and the merely limited adaptability of the material and processing methods with the invention or synthesis of artificial resins.

The economic breakthrough for synthetic resins came with the invention of phenolic resins and the combinations of amino resins featuring improved yellowing resistance with alkyd resins and saturated polyesters. The first synthetic resins also included the unsaturated polyesters which, when combined with chemically reactive solvents, enabled paints to be developed featuring high film thicknesses and low emissions because of the chemical bond between the film forming agent and the solvent. A degree of longterm outdoor exposure and chemical resistance which had not been possible previously was enabled by the invention of polyurethane and epoxy resins. The resistance to heat and longterm outdoor exposure of silicone resins permit coating materials to be designed with correspondingly excellent properties.

Polymer resins such as polyacrylates, polyvinyl chloride, polyvinyl ester and ether, polystyrene and copolymers are now used in all kinds of paint systems, e.g. as aqueous dispersions, radiation curing systems and powder coatings (see below).

2.1.1.1 Natural Materials

By far the most important natural materials used as film forming agents are the **natural oils** which are also known as fatty oils. They became extremely important as film forming agents for surface protection a considerable time ago as tri-esters of glycerine with polyunsaturated fatty acids because of their ability to transform from a low viscosity liquid into a solid by the interaction with atmospheric oxygen. This capability distinguishes them from fats based on saturated fatty acid esters. Fatty oils are pure

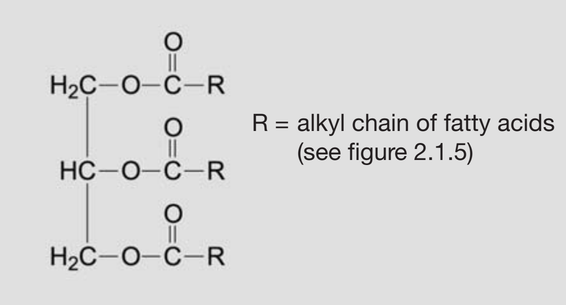


Fig. 2.1.4
Fatty oils in form of tri-esters of glycerine of unsaturated fatty acids

natural materials and are available in sufficient quantity as inexpensive raw materials for paints.

Even though the importance of natural oils has diminished more and more with the development of synthetic film forming agents, their fatty acid components are still used by raw materials suppliers for modern alkyd resins.

Numerous types of fatty oils are produced naturally by various plants and certain marine animals. If they are to be used successfully in technical applications they have to be isolated from seeds and fruits by cold- or warm-pressing and freed of impurities. These are mainly carbohydrates, proteins and lecithin which is of interest as a paint additive. Because of its tenside character, the latter is an important additive in

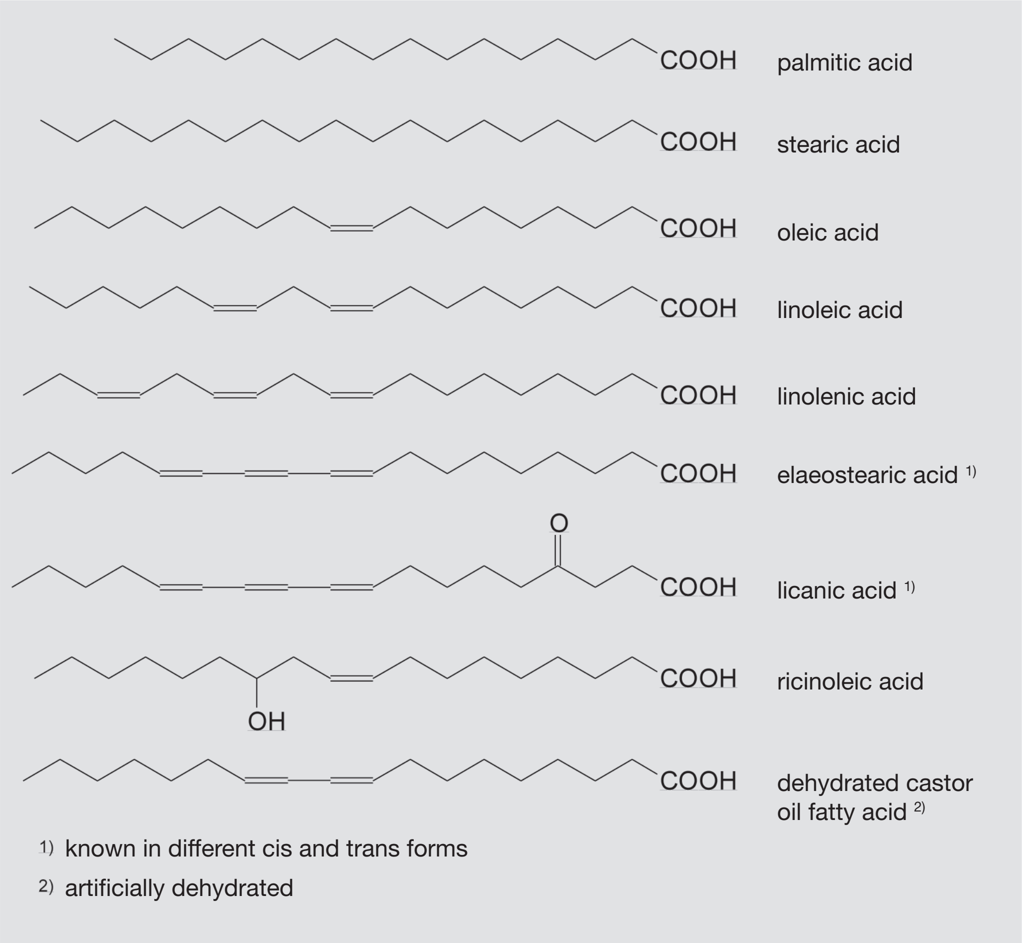


Fig. 2.1.5
Important natural fatty acids as components of fatty oils

paints for improving dispersibility of colored pigments in baking enamels. Because of its inhibiting effect on oxidative cross-linking of fatty oils it must be removed in quantity from them.

The large variety of oils which can be used in paint production, without exception esters of glycerine, stems from the wide choice of fatty acids available, the acid esterification component. These are produced naturally with varying chain lengths and, at the same time, a fluctuating number of double bonds and different cis/trans forms.

The fatty acids shown in figure 2.1.5, i.e. stearic and palmitic acid, cannot be cured by oxidation. Their analogue with a double bond in the cis position is oleic acid. Its ability to be crosslinked by oxidation is poor, which means that it cannot be used by itself in practice as a paint raw material. The C_{18} fatty acids with two or three double bonds are much more effective in terms of paint curing by means of atmospheric oxygen. In the former group the most important role is taken by the 9,12- and 9,11-octadecanoic acids. Unlike the 9,12 variant, linoleic acid, 9,11-octadecanoic acid does not occur naturally. It is obtained by artificial transformation (isomerization) of natural linoleic acid or by dehydration from castor oil or ricinoleic acid. Both double bonds occur proportionately in conjugate form and consequently give increased reactivity to the film forming agents in which they are chemically incorporated.

	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	$C_{18'}$	$C_{18''}$	$C_{18'''}$	$C_{20'}$	$C_{20''''}$	$C_{22'}$	$C_{22'''''}$
palmkernal oil	3–5	3–7	40–50	14–18	7–9	1–3	10–20	–	–	–	–	–	–
peanut oil	–	–	–	–	6–16	1–7	35–70	15–50	–	–	–	–	–
soja bean oil	–	–	–	–	7–11	2–6	15–30	40–55	4–10	–	–	–	–
sunflower oil	–	–	–	–	3–7	1–5	15–45	45–70	–	–	–	–	–
linseed oil	–	–	–	–	4–7	1	12–35	20–25	35–60	–	–	–	–
fish oil				6–8	15–20	2–4	10–18	1–3	0–2	2–8	15–30	1–8	5–20
fung oil					3–4	1–3	5–10	8–10	75–85*	–	–	–	–
oiticica oil					6–8	3–5	5–15	10–25	75–85**				
ricinene oil					1–2	1–2	85–90***	2–7	–	–	–	–	–

* α-eleostearic acid (conjugated double bonds)
** α-licanic acid (conjugated double bonds)
*** ricinolic acid

Fig. 2.1.6
Selection of important natural oils and their composition of fatty acids

Fatty acids with three isolated double bonds are even more reactive than those with two double bonds. Linoleic acid, with its three isolated double bonds as the main component of linseed oil, gives the oil an extremely pronounced oxidative curing capability which has been used since time immemorial. The reactivity of the elaeostearic acid contained in tung oil, which also has three double bonds albeit in a conjugate configuration, is among the highest of all fatty acids. Unfortunately, the highly unsaturated oils are less resistant to yellowing and therefore unsuitable for white coatings.

Among the large group of oils which are of importance in paint and coating technology special mention should be made of linseed oil, soy oil, tung oil, oiticica oil, groundnut oil, sunflower oil, cottonseed oil, dehydrated castor oil and fish oil.

It is also worth noting that tall oil, an important raw material for synthetic paint resins, is not actually an oil. It is not, as would be anticipated from its name, a triester of

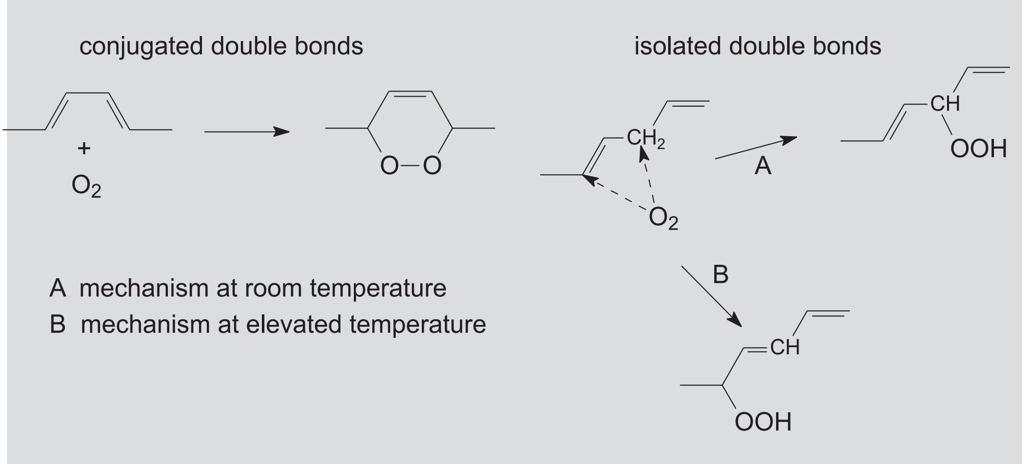


Fig. 2.1.7
First steps of the oxidative hardening of oils by forming of hydroperoxides and peroxides

glycerine, but rather is a mixture of various fatty acids formed during cellulose production by the alkaline saponification of oil-containing byproducts.

A proven indicator for the oxidative hardening of oils is the iodine value. This indicates the quantity of iodine which is added to the double bonds relative to 100 g substance. An iodine value > 150 is a pointer to rapidly hardening oils, a figure of 150 – 100 to ”semi-drying”, i.e. less reactive oils, and < 100 to nondrying oils. Although the latter react with atmospheric oxygen, they solidify only incompletely such that mechanical hardness cannot be achieved even after an extended reaction period.

The solidification caused by the action of atmospheric oxygen has been described by numerous authors [2.4.2]. It is now known that there is no single reaction mechanism which is valid for all oils in the same way [2.4.3]. Various reaction mechanisms have been identified as a function of the type of fatty acid and the number and configuration of the double bonds, but also as a function of temperature. Whereas it has been shown that the formation of cyclic peroxides is the first stage when conjugate double bonds are present, hyperperoxides are formed initially with isolated double bonds. The atmospheric oxygen acts either directly on the double bonds or on the activated methylene group between the double bonds as a function of temperature. Whereas at low temperatures it is primarily the activated methylene group where the action occurs, at higher temperatures the oxygen is added to a double bond and forms new conjugate double bonds at the same time (see figure 2.1.7).

When the peroxides and hydroperoxides decompose into radicals, the molecule-enlarging crosslinking process begins which then initiates radical polymerization. At the same time additional chain-transfer and recombination reactions start because of the high radical density.

This extremely complex process is also subject to numerous secondary reactions.

The chemical crosslinking process can be substantially accelerated by the use of specific catalysts, known as siccatives. Metallic soaps, whose cations accelerate peroxide decomposition by reversible valence change, are suitable as siccatives.

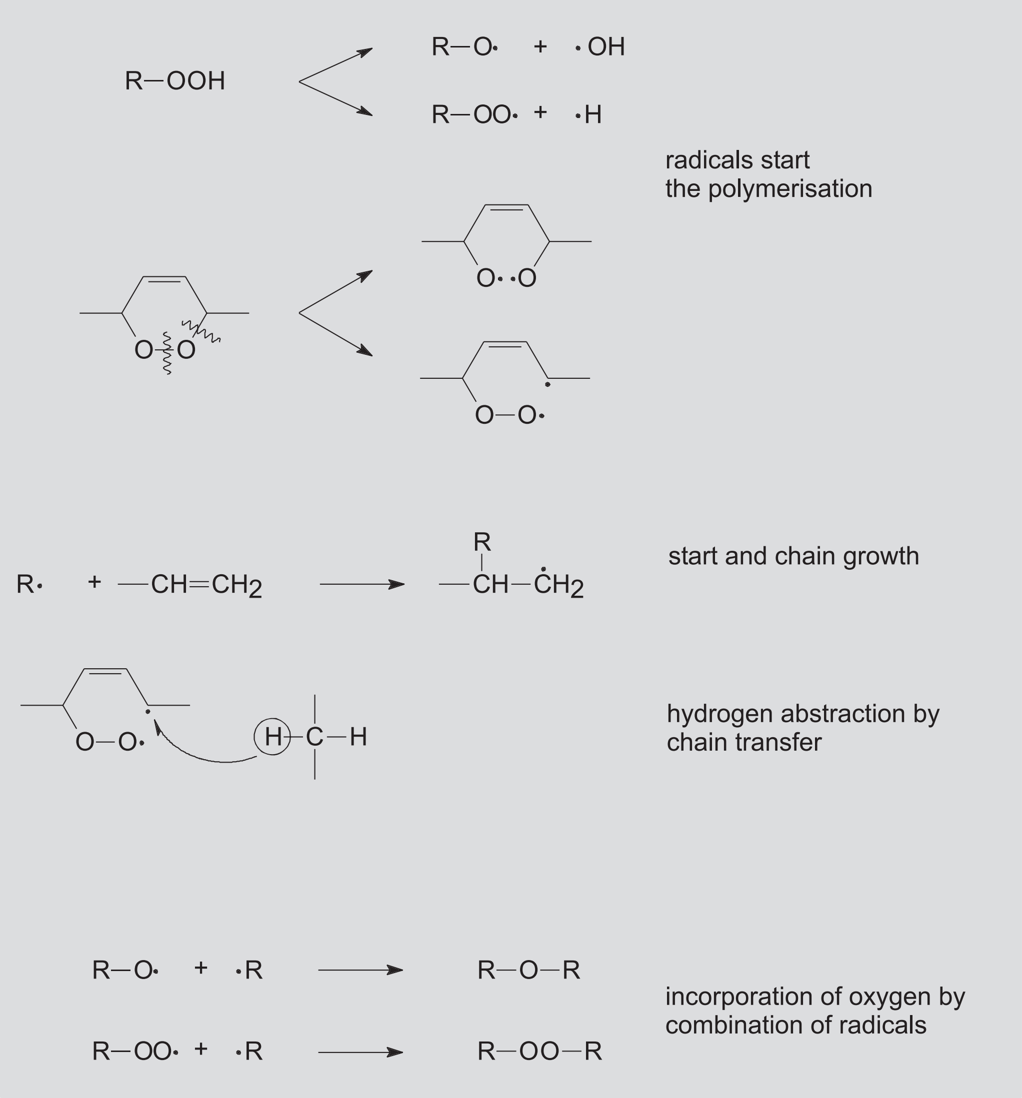


Fig. 2.1.8
Mechanism of oxidative hardening of unsaturated fatty acids

The hydrogen and hydroxyl ions formed by hydroperoxide or peroxide decomposition combine to form water. They shift the equilibrium towards the radicals and are therefore the driving force for the catalytic action.
The natural ”drying” oils, with a molecular weight of approx. 880, are relatively low molecular substances. In chemical terms, therefore, it is a long journey until the

$$\left.\begin{array}{l} Me^{2+} + ROOH \longrightarrow Me^{3+} + RO\cdot + OH^{-} \\ Me^{3+} + ROOH \longrightarrow Me^{2+} + ROO\cdot + H^{+} \end{array}\right\} H_2O$$

Fig. 2.1.9
Acceleration of decomposition of peroxides by siccatives

crosslinking caused by oxidative hardening produces a hard and, at the same time, resistant coating.

The natural oils' low molecular weight results in a low viscosity and consequently a high tendency to run on vertical surfaces. To remedy these shortcomings, various methods of preliminary, targeted molecular enlargement of the oils have been used to increase the viscosity. One such involves heating the oils in the absence of oxygen to temperatures of between 260 °C and 300 °C over a period of a few hours. This results in thermally induced polymerization reactions of the double bonds to form socalled stand oils with their higher viscosities. The goal of molecular enlargement can be achieved in the same time at temperatures of between 100 °C and 150 °C if the heating is carried out in the presence of oxygen. By contrast with the stand oils mentioned above, the increase in the molecular weight in the case of the oxidized oils is achieved by molecular enlargement via oxygen bridges.

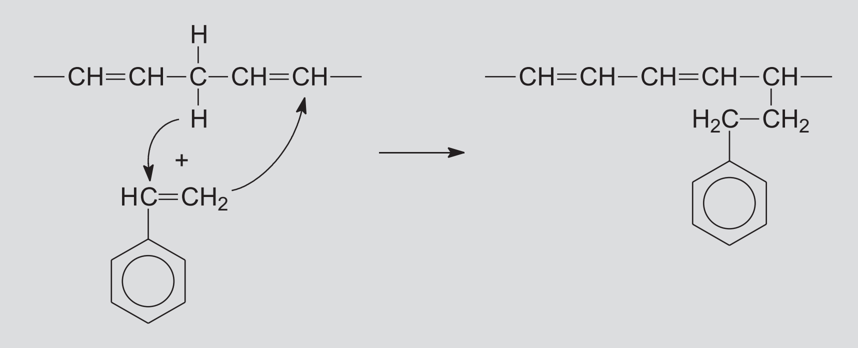


Fig. 2.1.10
Modified oils by reaction with styrene

The reaction of oils with styrene or cyclopentadiene also results in an increase in viscosity and thus to the faster formation of mechanically solid films.

One way of making natural oils more reactive is to increase the number of double bonds while, at the same time, increasing the proportion of conjugated double bonds. An increase in the number of double bonds is achieved by epoxydation of the double bonds in the fatty acids, followed by ring opening and dehydration.

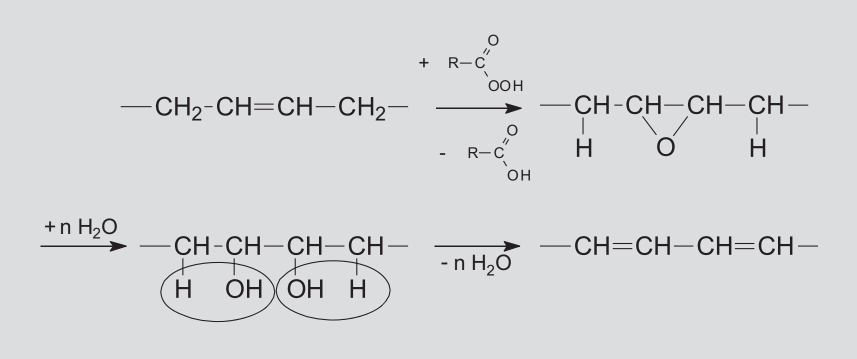


Fig. 2.1.11
Increasing conjugated double bonds of oils by epoxidizing

Fatty oils, particularly linseed oil, can also be converted into raw materials of interest for coatings by reaction with maleic anhydride. By adding maleic anhydride to the fatty acids' double bonds, splitting the ring with butanol and then neutralizing with amines, anionic and thus watersoluble paint raw materials are produced. Such modification products have proved very successful for many years as film forming agents for anodic electrocoating (see chapter 4.2.1).

Another means of improving the processing properties of oxidatively curing oils is to blend them with natural hardened resins. However, the resulting increased viscosity has to be lowered again by the addition of appropriate solvents. Hardened resins serve to accelerate physical drying, while the oils then ensure chemical crosslinking.

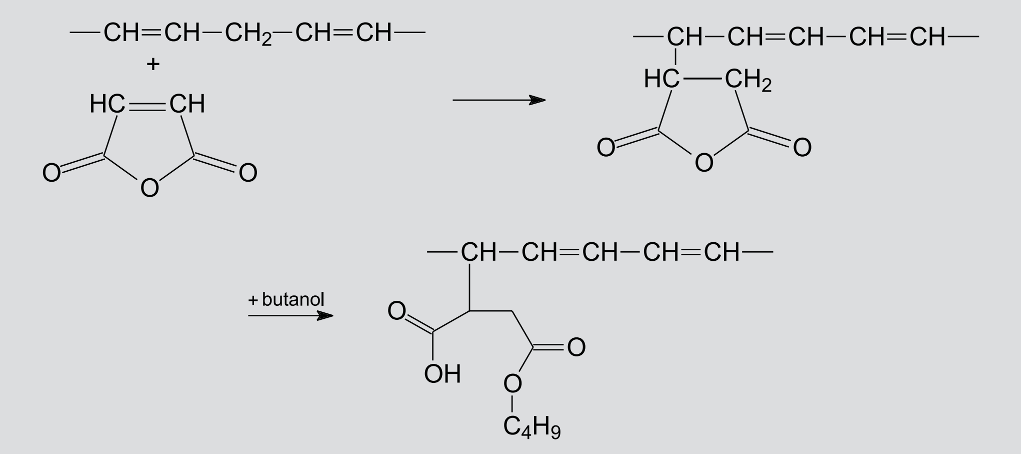


Fig. 2.1.12
Watersoluble resins by reaction of oils with maleic anhydride

Other important natural materials for paint formulations are the cyclic diterpenes and triterpenes (**rosins**). These include copals, amber, dammar and colophony. Because colophony still plays a very important technical role in printing inks, it is presented here as a representative example of the whole range of natural resins. It should not be forgotten that amber, which is now known solely as a material for ornamental objects, was used in the past as a raw material for particularly wear-resistant coatings. Whereas dammar and the copals have also become less important in coating technology, shellac, a natural polyester from cycloaliphatic, hydroxyl-functional polycarboxylic acids is still used today as a raw material for the surface treatment of furniture.

As just mentioned, colophony is by far the most important and is consumed in by far the most notable quantities of all the natural resins. Colophony is a constituent of conifers and is extracted from them as balsam by tapping. This involves cutting notches in the trees from which the balsam drips as a pourable compound. The raw material extracted in this way is a mixture of mono- and diterpenes, with numerous impurities.

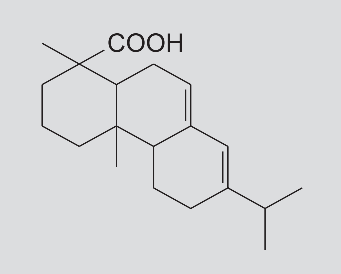


Fig. 2.1.13
Abietic acid as the main component of colophony

The balsam is separated into volatile turpentine oil, a blend of various monoterpenes including limonene and camphene, and the residue, colophony. Steam distillation was previously used for this, though fractionating distillation is now the preferred method. Its main constituent is abietic acid (see figure 2.1.13). Other sources of natural resins, corresponding to colophony in terms of composition, are tree stumps from cleared forests or the waste water from cellulose production.

Despite colophony's good compatibility with fatty oils, its softening point, which at 65 °C is too low, and the high level of acid groups are performance shortcomings, though these can be eradicated by chemical modification.

Increasing the softening point while simultaneously lowering the degree of acidity is achieved either by neutralization or by esterification with polyfunctional alcohols. Calcium oxide and zinc oxide have proved successful for salt formation, and glycerine and pentaerythritol for molecular enlargement by ester formation.

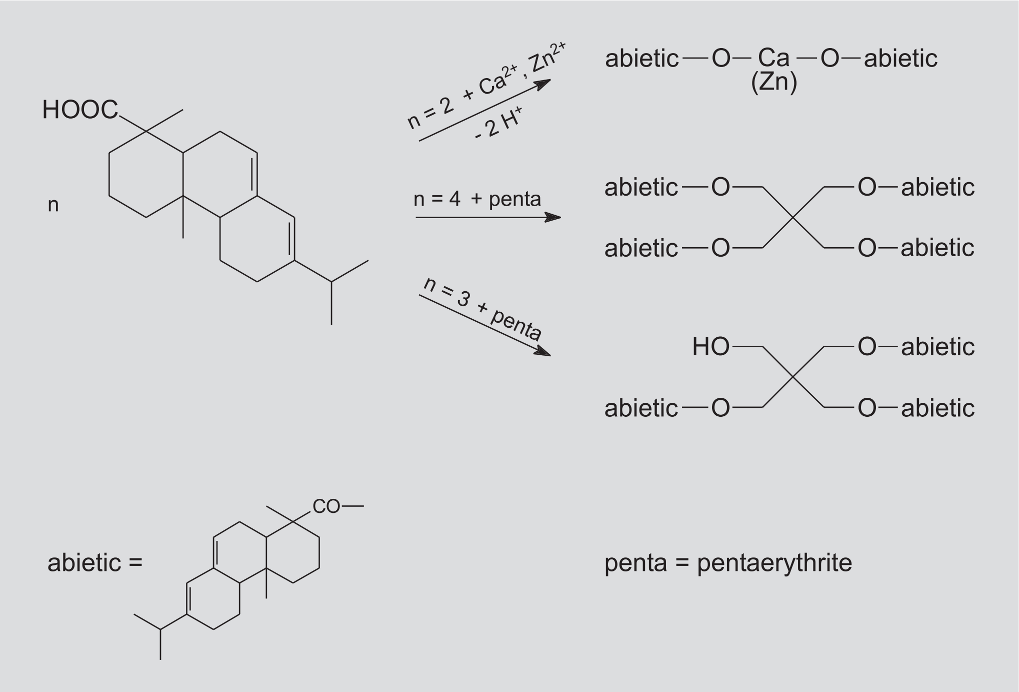


Fig. 2.1.14
Modification of colophony by neutralization or esterification

Esterification of the abietic acid can be carried out stoichiometrically, on the one hand, to produce nonpolar combination resins for oils (see figure 2.1.14) or can be carried out with excess alcohol, on the other hand, to produce polar modifying agents for cellulose nitrate.

While the salts of colophony have practically no technical significance any more, the products modified with maleic acid are still important in the printing ink sector. After thermal transformation of abietic acid to laevopimaric acid, the latter reacts with maleic anhydride in the form of a 1,4 Diels-Alder addition to form the intermediate stage of a tricarboxylic acid. This then reacts with polyols to yield maleic resins (see figure 2.1.15).

These maleic resins are light-colored, hard, high-melting, oxidation-resistant, readily soluble and advantageously combinable with many other film forming agents. They still play a significant role, particularly as additives for physically drying and oxidatively curing coating materials.

Nature is not just capable of synthesizing cyclic terpenes or terpenoids. In certain plants it can also join activated isoprene in a 1,4-polymerization stereospecifically to form macromolecules. 1,4-trans-polyisoprene has achieved less technical importance as guttapercha or balata than the isomeric 1,4-cis-polyisoprene, known as natural rubber i.e. caoutchouc (see figure 2.1.16). The latter is extracted as latex from notches cut in Hevea Brasiliensis which is grown in plantations specifically to harvest this raw material. After treatment of the aqueous dispersion crude rubber is then isolated.

Although 1,4-cis-polyisoprene is now manufactured synthetically, there is still a high proportion of natural rubber on the market.

While unmodified, natural rubber plays a major role as the raw material for rubber, the use of natural rubber as a film forming agent is only possible after chemical modification

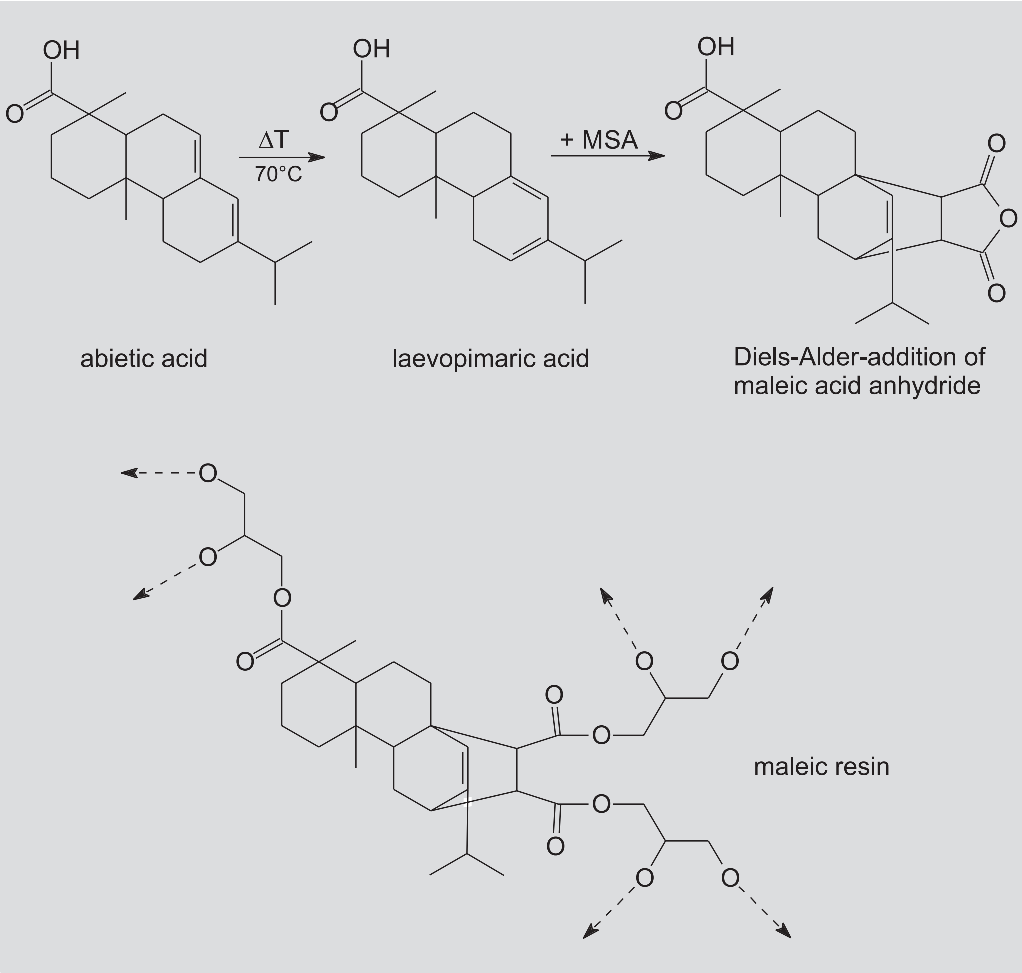


Fig. 2.1.15
Synthesis of maleic resins from colophony, maleic anhydride (MSA) and polyols

because of its insolubility in all commercial paint solvents and its lack of resistance to atmospheric oxygen.

The very high molecular weight and the double bonds, which become capable of crosslinking through atmospheric oxygen, can be effectively reduced by selected heat treatment in the presence of catalysts. New valency bonds are then formed by the initiation of hydrogen ions when the double bonds are split. The new bonds result in 6-membered rings within the molecules from the originally aliphatic molecular chain. This cyclization means that more than 80% of the previously existing double bonds are eliminated (see figure 2.1.17). If the reaction is appropriately controlled, the molecular weight of the resulting cyclorubber is also substantially reduced. The molecular weight of cyclorubber which can be used in coating technology is only 3,000 – 10,000 g/mol. This guarantees adequate solubility in aliphatic, cycloaliphatic, aromatic and terpene hydrocarbons. Cyclo-rubber is a hard resin with a melting point in the range between 130 °C and 140 °C, exhibits good compatibility with drying oils, alkyd resins and bituminous film forming agents. It has excellent chemical resistance because of the absence of saponifiable groups and also good compatibility with alkaline pigments because of the lack of acid groups. Its relatively good heat resistance enables the manufacture of coatings which will be subjected to thermal stresses. Cyclorubber is preferred for applications in heavy-duty anticorrosive protection, for underwater coatings and for coating vessels in dairies, breweries and other branches of the food industry. The low solid content of the coating

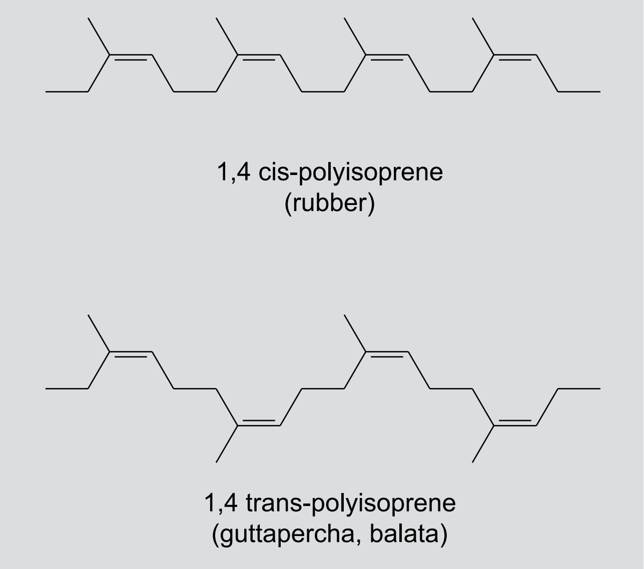


Fig. 2.1.16
Rubber and guttapercha as isomeric forms of 1.4-polyisoprene

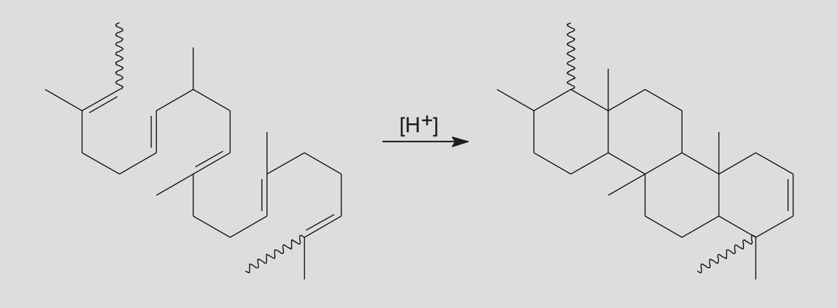


Fig. 2.1.17
Cyclization of caoutchouc (rubber)

formulations and the low resistance to light and longterm outdoor exposure have prevented it from being used more widely.

Another option for using caoutchouc for coating applications is to chlorinate it under the influence of UV light. In a synchronous reaction the chlorine is first attached to the double bonds, and then new double bonds are created when HCl is removed. Then chlorine is again attached to these new double bonds, and HCl is again removed and so on until complete chlorination of all the C atoms has been achieved in this way. The chlorination reaction is halted at a chlorine content of 66% and a density of 1.6 g/cm^3. By comparison with cyclorubber, chlorinated rubber is also only soluble in polar solvents because of its higher polarity. Leaving its lower heat resistance aside, chlorinated rubber has a similar performance profile to cyclorubber.

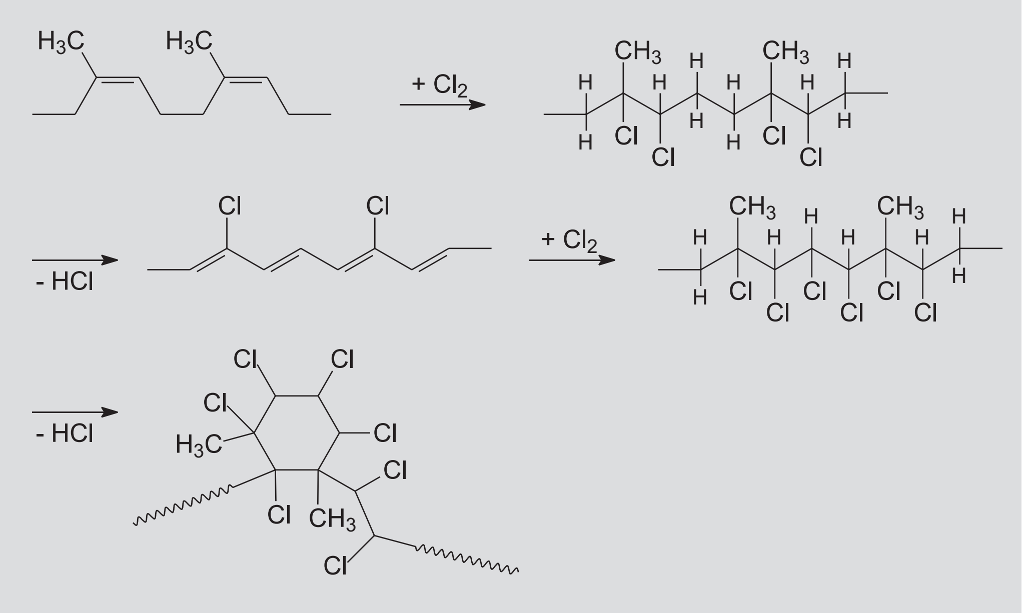


Fig. 2.1.18
Chlorinating of caoutchouc

Carbohydrates are also natural materials which have significantly influenced industrial coating technology in the form of numerous modifications. Cellulose nitrate and cellulose acetobutyrate are still in use today as film forming agents for wood and automotive paints. Because of their high availability in nature, the unmodified hydrocarbons are also presented below to increase understanding of them.

Carbohydrates are termed mono-, di- or polysaccharides, depending on the number of basic structural elements which are chemically linked to each other. The monosaccharides or sugars as the basic structural elements of this class of materials have the empirical chemical formula $C_nH_{2n}O_n$ or, using the older notation, $[C(H_2O)]_{n.}$ This also explains the name carbohydrates.

The monosaccharides synthezized by nature, principally with 5 or 6 C atoms in the aliphatic parent chain, are derived from glycerine aldehyde, the smallest base material in accordance with the definition of carbohydrates.

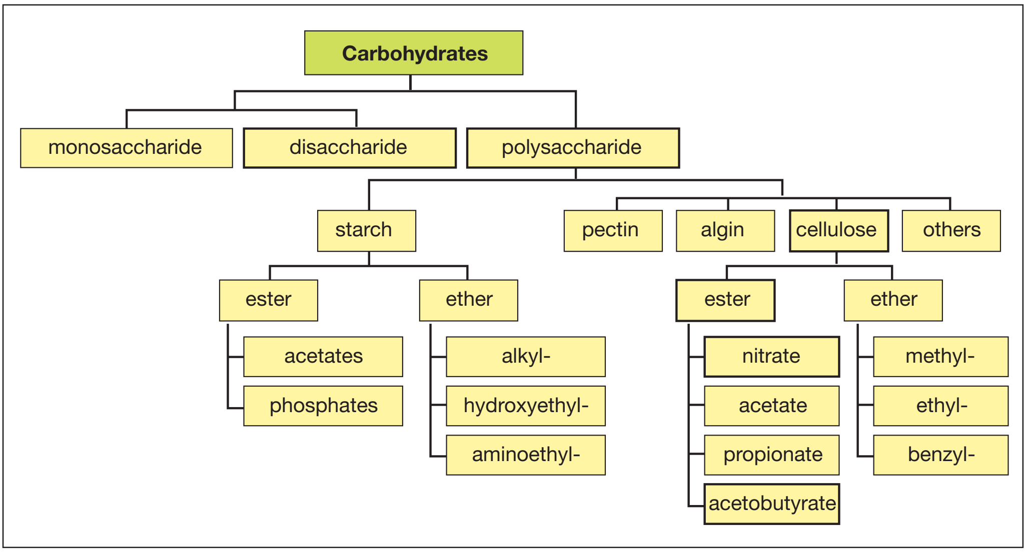


Fig. 2.1.19
Important carbohydrates for use in coatings

Glycerine aldehyde contains one aldehyde and two hydroxyl groups in the absence of an asymmetric carbon atom which gives the molecules stereoisomerism in the form of enantiomeric constituents, i.e. an isomer with its mirror-image isomer.

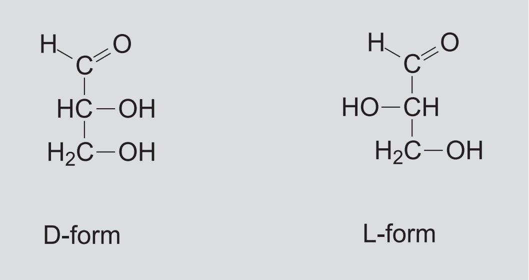


Fig. 2.1.20
Enantiomeric (D-,L-) forms of gylcerine aldehyde

Apart from their longer parent chain, the longer-chained pentoses containing 5 C atoms and the hexoses, which are based on 6 C atoms, also differ from glycerine aldehyde in the amount of asymmetric C atoms. The existence of enantiomers and diastereoisomers means that there is a variety of individual forms which is determined by the number of asymmetric atoms. If there are n asymmetric C atoms there will be 2^n different variants in the form of enantiomers and diastereoisomers. In the case of hexoses that means 2^4, i.e. sixteen variants comprising eight D- and eight L-forms.

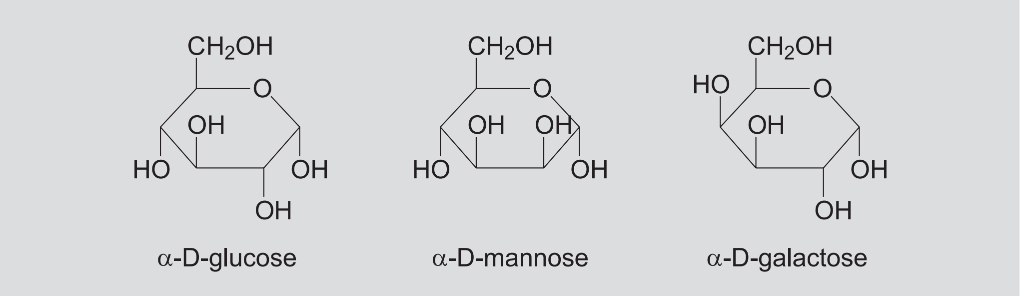


Fig. 2.1.21
Glucose, mannose and galactose as raw materials for resins

As far as coating technology is concerned, however, only the mannoses, the galactoses and the glucoses are important.

The degree of variety among the monosaccharides is increased still further by the position of the carbonyl group, but also by the ability to form hemiacetales intramolecularly with a simultaneous variation in ring size. Since there is a further asymmetric C atom as a result of the cyclizing formation of hemiacetale, the individual hexoses differ not only in their D- and L-forms, but also in their α- and β-forms depending on the steric configuration of the hydroxyl group of the hemiacetale. All monosaccharides are watersoluble, colorless, odourless and sweet-tasting because of their large number of hydroxyl groups.

In the context of their importance in coating technology it is worth noting that the terminal aldehyde and OH groups can easily be oxidized to hydroxyl-functional carboxylic acids either individually or jointly. Reduction of the carbonyl group is also easily possible. When glucose is reduced, for example, the result is sorbitol, a hexavalent alcohol which could become important, among other things, as a polyol for the production of long-oiled alkyd resins.

Among the disaccharides cane sugar, i.e. sucrose, is the most important substance with reference to coating technology. The total of eight hydroxyl groups, 3 primary and 5 secondary, can be converted into resin like esters using organic acids such as acetic acid, benzoic acid or mixtures of acetic and butyric acids. These are compatible with a large number of film forming agents and exhibit good solubility. As additives they increase hardness and increase the dependence of viscosity on temperature.

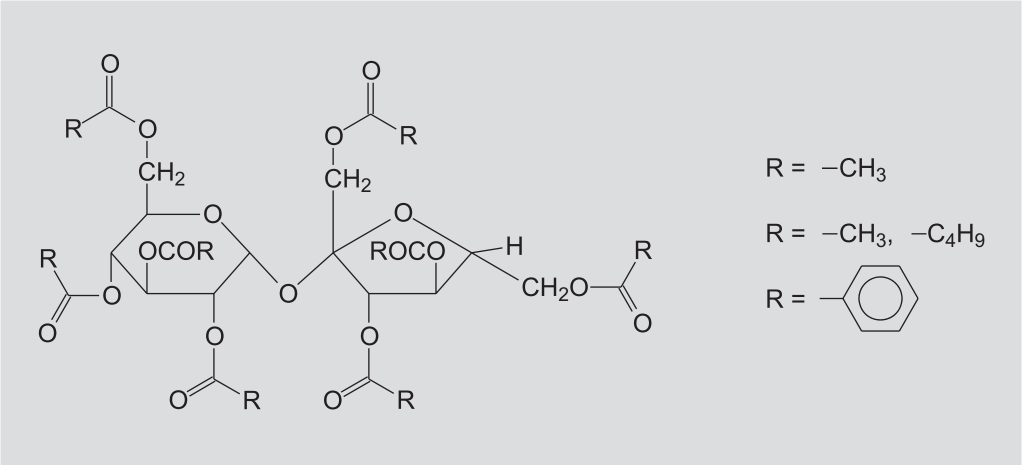


Fig. 2.1.22
Sucrose esters as raw materials for coatings

As the basic structural elements of carbohydrates, monosaccharides are capable of self-condensation to form longchain polysaccharides.

Starch and cellulose are produced naturally in huge quantities as highly polymerized forms of glucose and are therefore available for use as paint raw materials in sufficient volume. Despite their similar chemical structure their range of properties is extremely different.

Both starch and cellulose consist of longchain bonds of D-glucose units via the glycosidic hydroxyl group with the fourth C atom of the next structural element. The mere difference in the steric configuration of the glycosidic hydroxyl group results in the major differences in solubility and resistance to saponifying agents. While starch serves as an energy storage medium for plants and must, therefore, exhibit a certain solubility in water, cellulose as a skeletal material is absolutely insoluble in all usual solvents, especially in water.

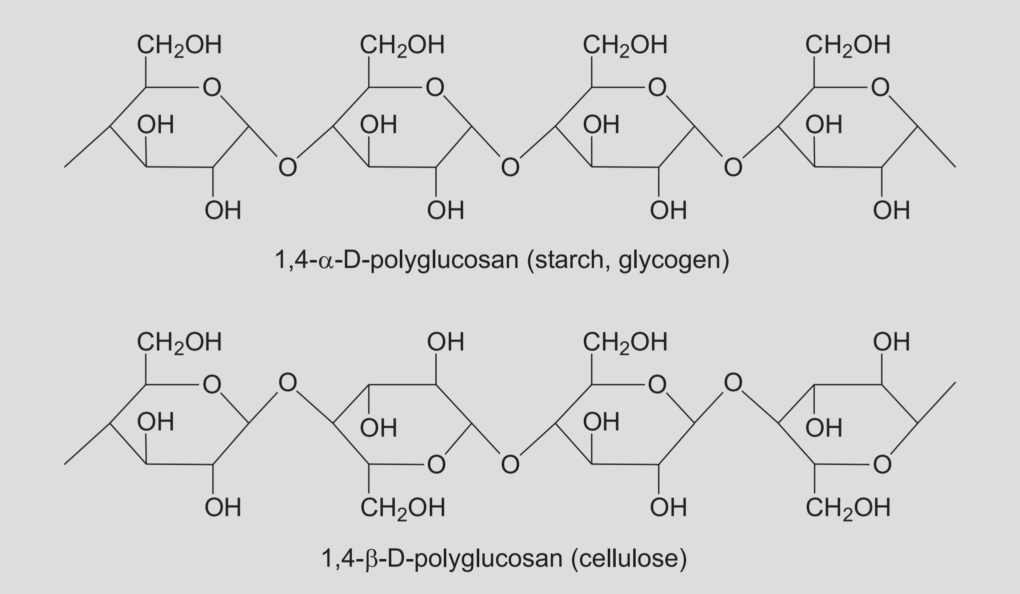


Fig. 2.1.23
Chemical structure of starch and cellulose

The various requirements are fulfilled by the different ways of forming intermolecular hydrogen bridging bonds caused by the α- and β-coupling of the structural elements.
The two products are only of any significance to coating technology in chemically modified form. Dextrines, i.e. partially hydrolysed starch, and also etherified and esterified starch have become important as physiologically harmless adhesives and film forming agents for paper coatings. Aldehyde starch occupies a special position because of its water resistance. It is obtained from starch by oxidation with periodic acid. The glucose structural elements are transformed into aldehyde groups without any significant reduction in molecular weight by splitting their parent chains between C2 and C3 with subsequent oxidation.
The derivatives of cellulose are of much greater technical importance. As with starch, the ethers and esters merit particular attention. In this regard the three hydroxyl groups per glucose unit can be substituted partially or completely.
Of the ethers, benzyl cellulose and ethyl cellulose are worth mentioning. Benzyl cellulose was used in the past as a film forming agent for heavy duty anticorrosive protection products because of its non saponifiable ether groups and its low water vapour permeability. Cyclorubber or chlorinated rubber coatings have succeeded in ousting benzyl cellulose in quantitative terms because of their lower cost.

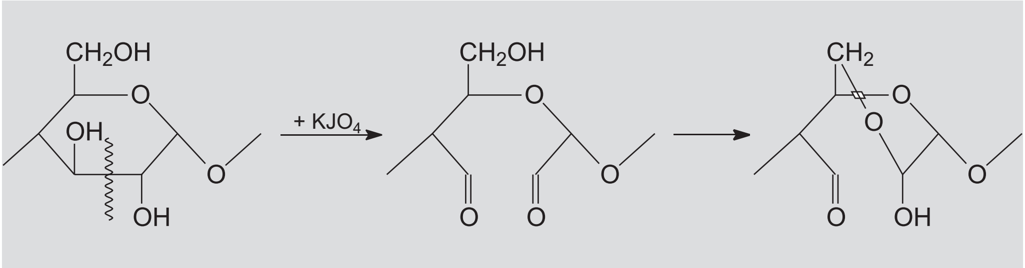


Fig. 2.1.24
Synthesis of aldehyde starch by degradation of starch by periodic acid

Ethyl cellulose suffered a similar fate. The commercial product, with an ethoxyl content of 45 – 50% which was easily soluble in alcohols and aromatic hydrocarbons, was unable to match modern synthetic resins because of its brittleness on exposure to UV light. Ethyl cellulose is still used to a limited extent today for paper films and printing inks for food wrappings.

The watersoluble variants of methyl or hydroxyethyl cellulose, however, continue to be successfully used as thickening agents for dispersions, as film forming agents for distemper and as wallpaper paste.

Cellulose can also be modified with organic and inorganic acids at varying esterification levels. The most important examples are cellulose nitrate, commonly known as collodion cotton or soluble guncotton, and the esters of acetic, propionic and butyric acids, though the latter are only used as mixed esters of acetic and butyric acids because of the decreasing hardness with increasing chain length of the esterification component.

Cellulose nitrate is produced from cellulose through the action of a mixture of nitric and sulphuric acid (nitride acid). Different esterification levels and a varying reduction in the original molecular weight are produced, depending on the reaction conditions. The target esterification level is achieved at a nitrogen content of between 10.6% and

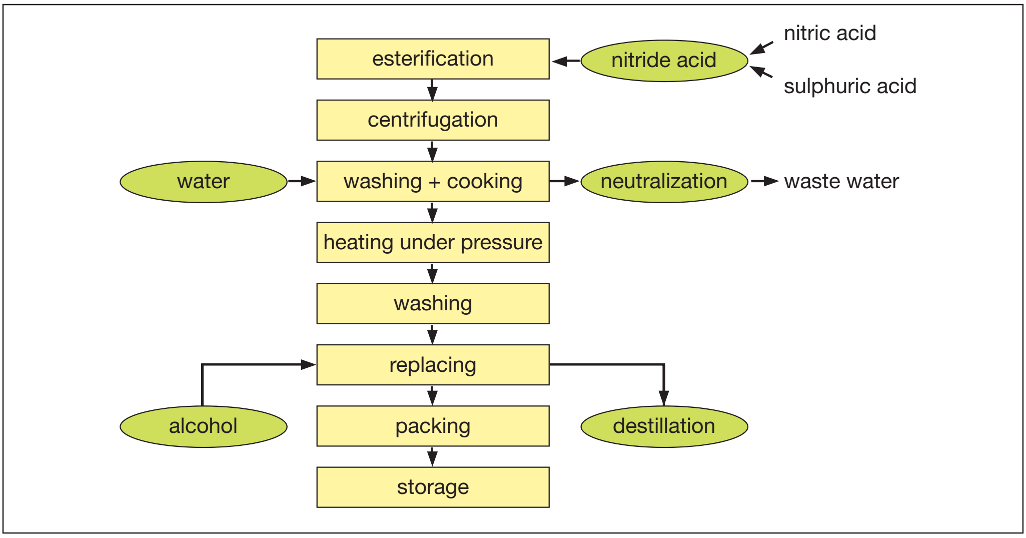


Fig. 2.1.25
Synthesis of cellulose nitrate

12.2% in the end product. Products with a lower nitrogen content lack the necessary solubility. The lower end of the nitrogen content range, from 10.6% to 11.2%, is made of up the alcohol-soluble products, known as alcohol-soluble cellulose nitrate, while the higher end, i.e. 11.8% and 12.3% nitrogen, comprises the ester-soluble products, known as ester-soluble cellulose nitrate. In the case of products with a higher nitrogen content, the blendability of the solutions with aromatic hydrocarbons causes problems. Furthermore, the reaction product has a pronounced thermal instability. All cellulose nitrate types used for the production of coating materials require special precautionary measures when handling because of their easy ignitability and high flammability. Thus they are never supplied as dry goods; instead they are usually delivered wetted in butanol in a ratio of 2:1. They can also be reliably transported in the form of chips processed with plasticizers or concentrated solutions in suitable solvents.

The properties which make cellulose nitrate stand out as an exclusively physically drying film forming agent are its extremely rapid drying and its ability to completely liberate its solvent. Coating materials based on cellulose nitrate meant that for the first time paints were available which were dry and could be sanded and polished within a few minutes of application, and could therefore keep pace with the short cycle times of modern industrial production.

Cellulose nitrate is combined with many other film forming agents to regulate the desired application properties. In addition to shellac and modified colophony, amino, amido and ketone resins can also be used (see elsewhere in this chapter). Alkaline pigments must not be combined with cellulose nitrate because of the latter's sensitivity towards saponifying agents.

The most important differences between the esters of cellulose with organic acids compared with cellulose nitrate are their improved fastness to light and reduced flammability. The favourable performance profile of cellulose esters made with organic acids is rounded off by improved resistance to extremes of temperature, their good electrical insulation ability and also by their resistance to water, oil, grease and sweat. Particular disadvantages of the esters of acetic acid are their limited solubility in organic solvents and a restricted compatibility with other resins. This disadvantage is not so marked in mixed esters of propionic and butyric acids.

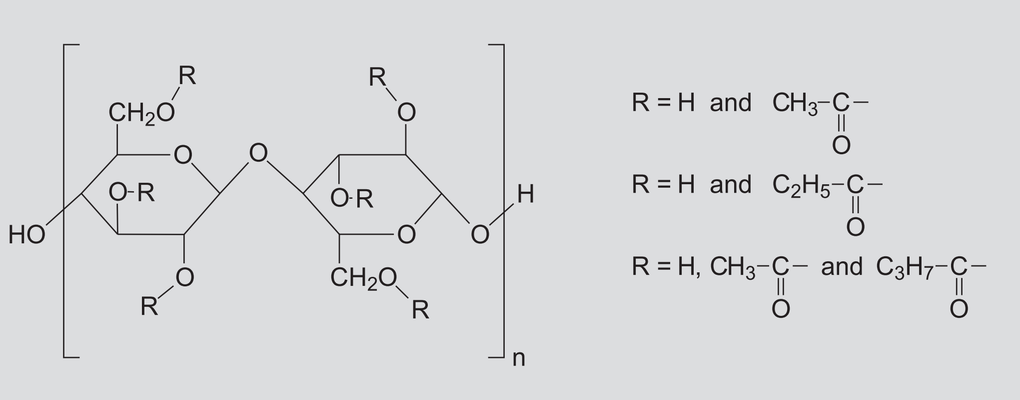


Fig. 2.1.26
Cellulose esters of organic acids

The cellulose acetate types used for paint manufacture have acetyl contents of between 38 and 40%. Cellulose propionate contains approx. 2.5 to 3.5% acetyl and 45% propionyl groups. In the case of cellulose aceto butyrate the acetyl content is between 2 and 30%, and the butyryl content between 15 and 53%. In all products the residual hydroxyl group content is between 1.6 and 5%.

The esters of cellulose produced with organic acids can be used, similarly to cellulose nitrate, to manufacture physically drying coating materials for a wide range of applications. The advantages are in the greatly improved resistance to light, water and heat, as already mentioned. The latter property enables cellulose esters from organic acids to be used as a rapidly drying component in baking enamels. During film formation, for example, the position of bronzes in metallic paints can be effectively stabilized.

For environmental reasons, however, no great future can be forecast for solvent-containing cellulose derivatives because of their solvent levels of up to 80%, despite their already mentioned advantages in terms of application technology.

Apart from natural resins, oils and hydrocarbons, nature also provides **proteins** as macromolecular substances. Based as they are on amino acids, these are polyamides in principle. They can occur either in isolation or in association with other polymer substances, e.g. polysaccharides. Products which merit attention for practical operations include collagens, casein, which is extracted from milk, and zein, which is obtained from corn. Collagens which are connective tissue proteins are transformed into bone glue by heating an aqueous alkaline solution via the interim stage of gelatine. This product, known as glutine, is compatible with fatty oils and is used for artists' paints, particularly watercolors

Casein, a calcium-containing phosphoprotein, is insoluble in neutral water and can be converted into highly viscous fillers, casein fillers, in reactions with calcium oxide. Zein has a similar performance profile, though with a different solubility. Unlike casein, it is readily soluble in alcohol.

Since some years the interest in renewable resources (see chapter 5.5) as raw materials for many type of coatings has increased, i.e. in some of the agricultural products as film forming agents or additives [2.4.4].

2.1.1.2 Synthetic Resins

The path from natural materials and chemically modified natural materials to the synthetic resins which are widely available today started in the early years of the 20th century. The most important reasons for the success of synthetic resins are, on the one hand, the opportunity to tailor products to a huge range of application fields with a significantly high reproducibility and, on the other hand, their unlimited availability.

In Germany the starting point in the systematic search for new resins, apart from the improved technical possibilities, was the political situation at the turn of the last century but one. Hardened resins such as copals, colophony, dammar and particularly shellac, all of which were foreign-sourced raw materials, were products which it was imperative to replace in the medium term by synthetic alternatives because their availability could not be guaranteed.

The invention of glyptal resins as hardened resins and the more fortuitous discovery of phenolic resins during the search for means of synthesizing shellac are just a couple of examples of noteworthy inventions from the pioneering phase of synthetic resin chemistry [2.4.5].

Whereas at the start of the new era a great deal had to be left to chance because of the lack of knowledge of how to produce large molecules and because soundly-based knowledge of the structure/property relations of resins did not exist, the situation changed at the latest when scientists were in the position to comment more precisely on the construction and structure of macromolecules. Systematic developments for specific product properties of tailor-made resins only became possible once scientists learned to produce linear, branched or even crosslinked macromolecules specifically by chemically bonding polyfunctional structural elements and when it became known that these could be formed into loops with each other because of the free mobility of chains, thereby guaranteeing elasticity and mechanical strength. It was the scientists *Staudinger*, *Carothers* and *Kuhn* who laid the foundations for modern polymer chemistry [2.4.6] through their detailed knowledge of the construction of macromolecules.

Thanks to a very wide range of analysis techniques we now have a detailed picture of the structure and properties of macromolecular materials. The desire at that time to develop or synthesize paint resins to meet the varied range of practical requirements has now become conventional technology.

The synthetic production of oligomeric and macromolecular materials is possible via chemical conversions of monomers if these are at least bifunctional. Classifying reactions as step and chain reactions in line with the type of molecular growth has proved useful. The first group includes polycondensation, which is accompanied by the formation of low molecular cleavage products, and polyaddition, which produces no cleavage products. The second group includes polymerization with the sub-groups of radical and ionic growth of the molecules during their production.

The synthesis of polyesters from dicarboxylic acids and diols by dehydration is an example of a typical polycondensation reaction, while the formation of polyurethanes from polyfunctional isocyanates and OH-functional reactants without the removal of molecular elements of low molecular weight is an example of polyaddition.

Polymerization as a chain reaction operates in accordance with a quite different mechanism. Using suitable starting radicals or ions, monomers – in by far the majority of cases basic structural elements containing C=C bonds – are activated and thereby enabled to attach further monomers to the growing chain. It is only when combined with another, also activated chain that molecular enlargement is halted during radical polymerization.

Simple reactive resins with low to medium molecular weights are manufactured using polycondensation and polyaddition reactions by different reaction mechanisms. Both types of reaction are important in synthesizing film forming agents for low solvent industrial coatings. Polymers, with the exception of the reactive acrylic resins, are generally higher molecular, nonreactive thermoplastic materials with relatively high organic solvent levels or are dispersed in water in the form of emulsion polymers (see chapter below).

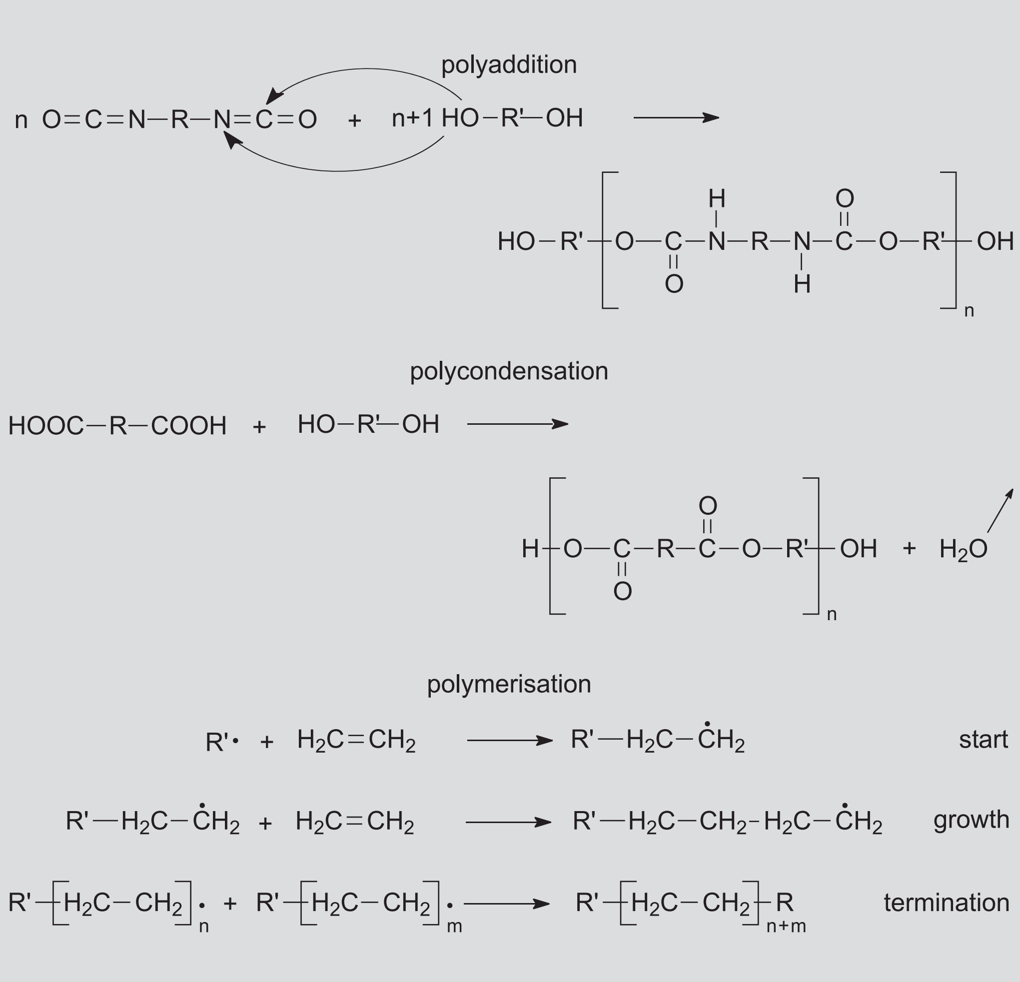


Fig. 2.1.27
Basic reaction for synthesis of film forming agents

For further details on the principles of macromolecular chemistry please refer to [2.4.7, 2.4.8].

Polycondensation resins

In the 1920s the esterification of glycerine with phthalic anhydride was achieved for the first time, which led to the first to some extend usable substitution products for natural hardened resins. However, these **glyptal resins** as they were known from the abbreviation of glycerine and phthalic acid tended to gel prematurely or resulted in incompatibilities with chemically curing oils, depending on the ratio in which the raw materials were mixed. Only later was it discovered that, because of their functionality based on bi- and trifunctional structural elements, reaction mixtures of phthalic acid or phthalic anhydride and glycerine either – as a function of the mixing ratio – crosslink during the synthesis process itself, and thus become unusable as film forming agents, or lose their compatibility with fatty oils because of their excessive polarity as a result of the excess of glycerine which breaks the chain.

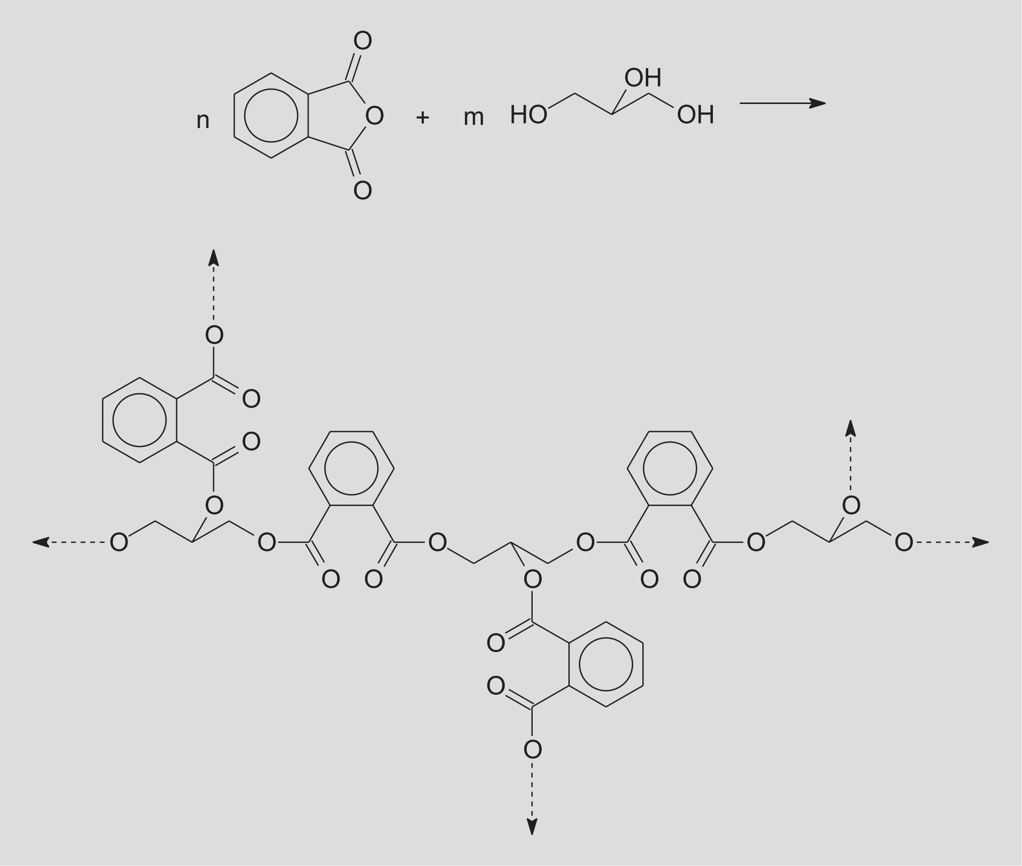


Fig. 2.1.28
Glyptal resins as replacement for natural resins

As a result of this knowledge, *Patton* formulated the so-called P_{gel} value as an easily calculated coefficient for reliably predicting the "cookability" of raw materials mixtures for polyester [2.4.9]:

$P_{gel} = m_0/e_a$

m_0 = sum of mols

e_a = sum of acid equivalents

The P_{gel} value, the quotient from the sum of the moles weighed and added and the sum of the acid equivalents (see chapter 2.3.2) should be as near as possible to 1. Usable resins can only be synthesized if this is so. If the P_{gel} value is too high, the manufacture of higher molecular resins is not possible; if, on the other hand, it is < 1, premature crosslinking, and thus gelling, occurs with higher degrees of conversion as a function of the raw material composition. The P_{gel} value represents the maximum permissible conversion. It enables a critical acid value to be calculated, below which gelling of the reaction mixture will occur.
Without this new knowledge *Kienle* successfully managed to unravel the Gordian knot represented by the tightrope walk between the tendency to gel and compatibility with oils as early as 1927. With immediate effect the lack of oil compatibility and premature

gelling of glyptals were immediately consigned to history once people learned to bond oils to them chemically.

This was the birth of **alkyd resins**, a class of substances which still heads the list of film forming agents for industrial coatings and decorative paints because of its balanced film properties and its price.

Two means of chemically bonding the physically drying, hard polyesters with the chemically crosslinking oils were developed: oils are either separated into their starting materials of glycerine, the polyol and fatty acids, i.e. monocarboxylic acids, by saponification, and then re-esterified jointly in the presence of phthalic anhydride and another polyol (fatty acid method), or the oils are converted by transesterification in the presence of polyols into a hydroxyl-functional intermediate stage which then reacts with phthalic anhydride to form the alkyd resins.

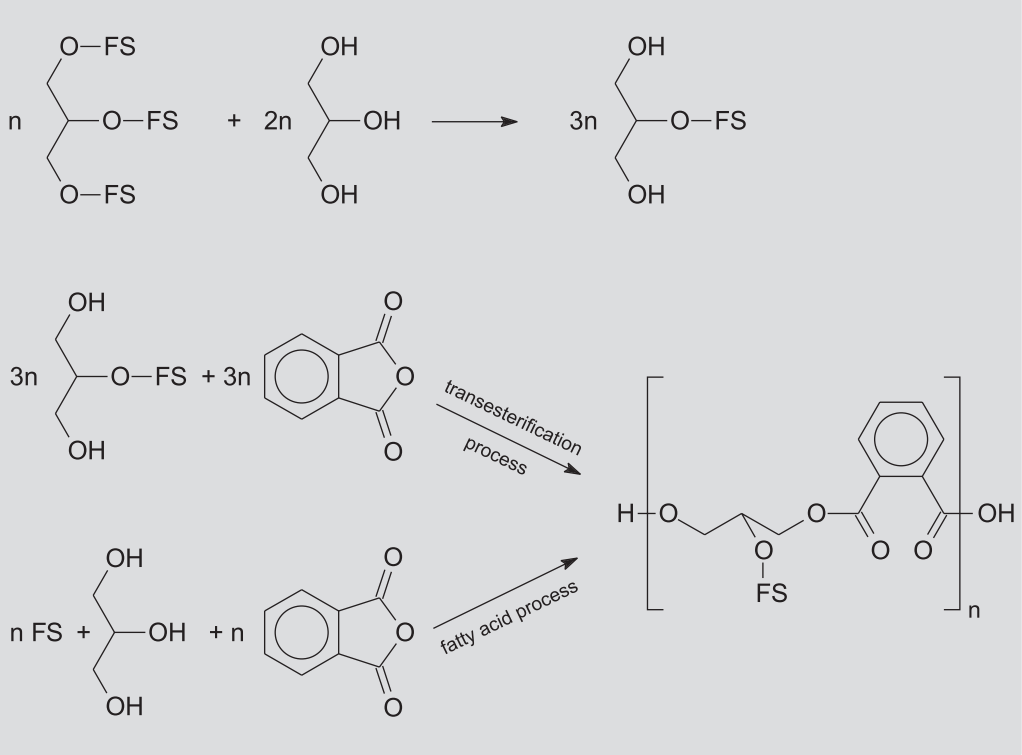


Fig. 2.1.29
Synthesis of alkyd resins by fatty acid method or transesterification (FS = fatty acid)

The essential reasons for the success of this class of substances are the simplicity of the synthesis processes, the availability of the raw materials with oil as a natural material and phthalic anhydride as an inexpensive product from the petrochemical sector, and the opportunities to meet many practical demands by varying the mixing ratios and using different types of oil.

It should be mentioned, to complete the picture, that after the inclusion of hydroxyl groups, the process of crosslinking, which originally occurred exclusively via the double bonds of the fatty acids, could also be carried out with corresponding complementary

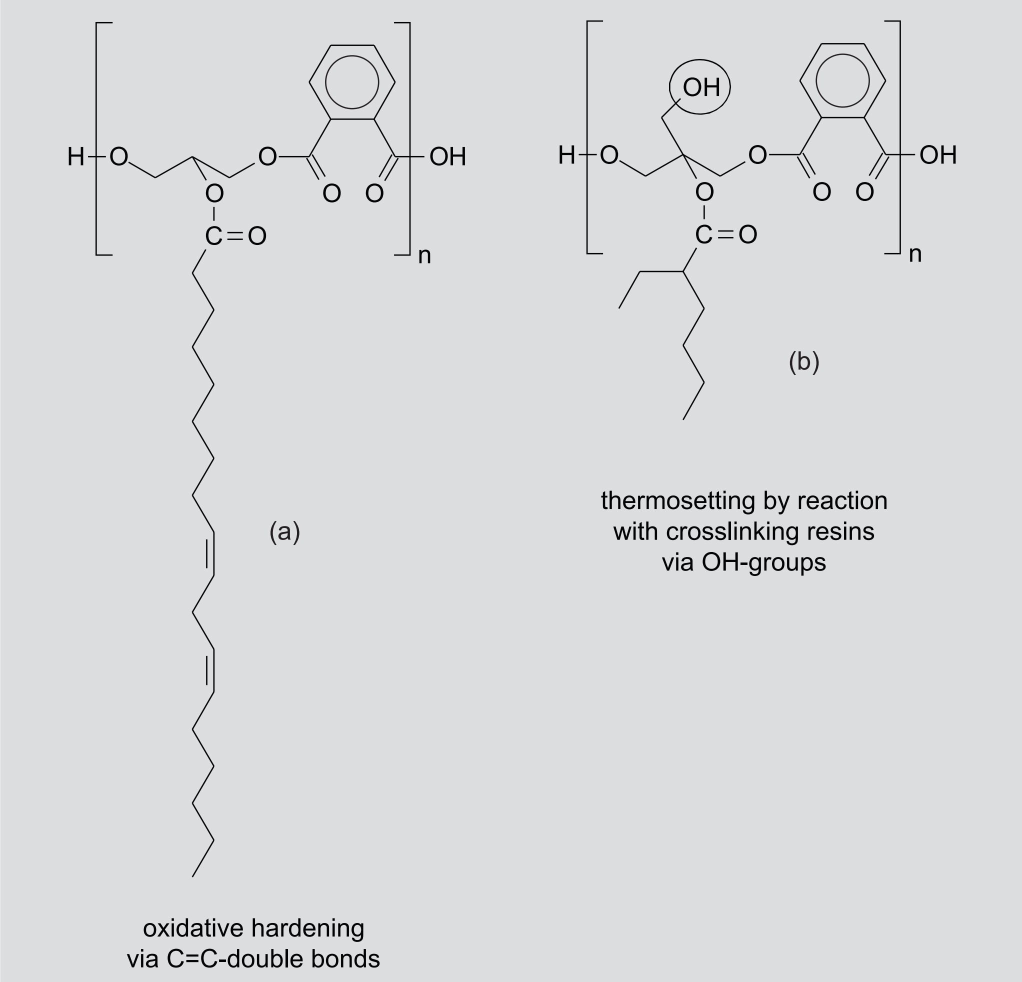


Fig. 2.1.30
Alkyd resins : suitable for oxidative hardening (a), for hardening with reactive partners at elevated temperatutres (b)

resins such as phenol or amino resins. The class of substances of the previously oxidatively curing alkyd resins therefore found itself with an important new member with such film forming agents for baking enamels.

The name alkyd resin is derived from the English terms alcohol and acid. Although the term alkyd resin makes no reference to the fatty acid component, alkyd resins are always understood as oil-modified polyesters which are sub-divided into long-, medium- and short-oiled alkyd resins, depending on the proportion of fatty acids or oils. The percentage of fatty acid which is esterified in imaginary fashion with glycerine is termed the oil length, irrespective of the polyol actually used by the resin manufacturers. The oil ratio and oil length are therefore only identical if glycerine is used solely as the polyol.

Alkyd resins as mixed esters of polyols, fatty acids and generally o-phthalic acid are in turn given a merely imaginary division into a physically drying, hard phthalate part and an initially soft, but chemically reactive oil part in order to describe their characteristics.

In line with the above definition, long-oiled alkyd resins have an oil length of more than 60%, medium-oiled 40 – 60% and short-oiled less than 40%.

In addition to the basic structural elements already mentioned, i.e. fatty acids, glycerine and phthalic anhydride, numerous mono- and dicarboxylic acids and polyols have now become accepted as supplementary raw materials or as alternatives for modifying, i.e. adapting properties.

The most popular of the dicarboxylic acids, measured in terms of quantities used, for the production of alkyd resins, is still o-phthalic acid or phthalic anhydride. It is manufactured by oxidizing o-xylene. It has a relatively low melting point of 131 °C.

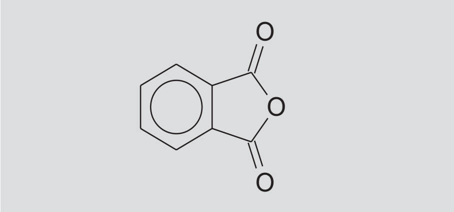


Fig. 2.1.31
Phthalic anhydride (PSA)

Isophthalic acid does not form an inner anhydride and only melts at 348 °C because of the resulting higher polarity. Preliminary esterification with polyols is therefore recommended.

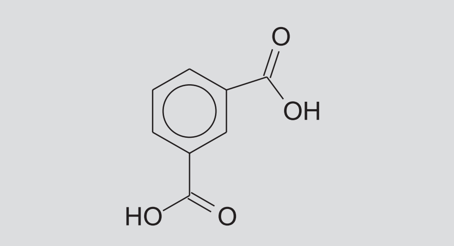


Fig. 2.1.32
Isophthalic acid

Because it tends less towards cyclic byproducts, isophthalic acid results in resins with a higher viscosity and is therefore of particular interest for long-oiled alkyd resins. Isophthalic acid alkyds have greater heat resistance because of their inability to form inner anhydrides.

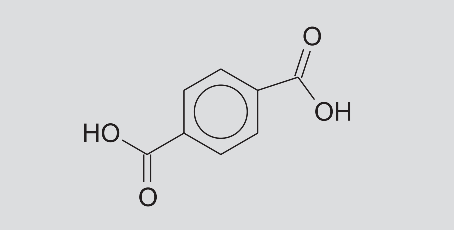


Fig. 2.1.33
Terephthalic acid

Terephthalic acid does not form an inner anhydride either and is primarily used, because of its even higher melting point and sublimation point, as a dimethylester which is liquid at room temperature. Its incorporation in the alkyd resin occurs via trans-esterification. Such alkyd resins are also thermally stable and are therefore important film forming agents for electrically insulating coatings.

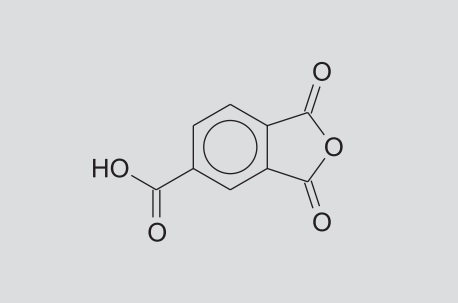


Fig. 2.1.34
Trimellitic anhydride (TMA)

Trimellitic anhydride is trifunctional. If only two carboxyl groups are esterified, and the remaining free acid group is neutralized with amines, watersoluble alkyd resins result.

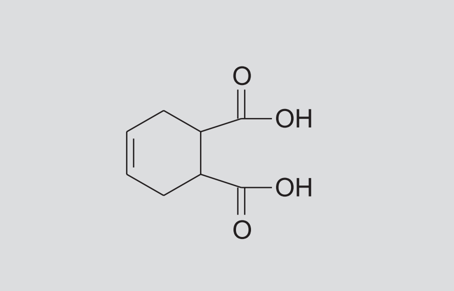


Fig. 2.1.35
Tetrahydrophthalic acid

Tetrahydrophthalic acid plays merely a subordinate role for alkyd resins. Its use in unsaturated polyesters is more important. It is used to reduce the inhibiting effect of atmospheric oxygen on film formation (see chapter 2.1.4 and 4.3.2).

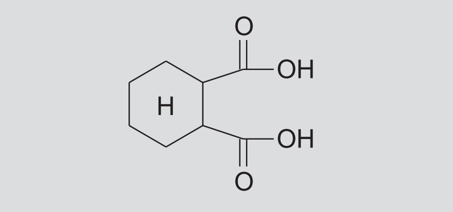


Fig. 2.1.36
Hexahydrophthalic acid

Hexahydrophthalic acid results in increased elasticity in alkyd resins with a simultaneous improvement in UV transmittance.

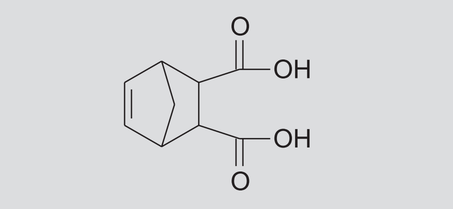


Fig. 2.1.37
Endomethylene tetrahydrophthalic acid

Endomethylene tetrahydrophthalic acid, a 1,4 *Diels-Alder* adduct made from cyclopentadiene and maleic acid, causes a reduction in oxygen inhibition, like tetrahydrophthalic acid.

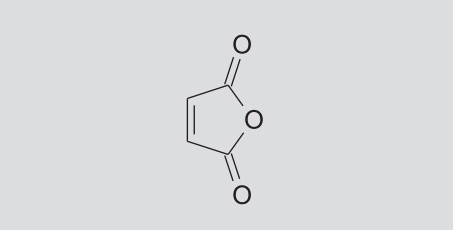


Fig. 2.1.38
Maleic anhydride (MSA)

Maleic anhydride is an essential raw material for unsaturated polyesters (see below). Since maleic anhydride reduces discoloration of alkyd resins during their manufacture, small quantities (< 2%) of it are added to the raw material mixture.
A proven means of elasticizing alkyd resins is to replace the aromatic or cycloaliphatic dicarboxylic acids proportionally with aliphatic dicarboxylic acids.

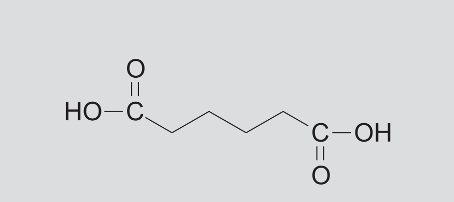


Fig. 2.1.39
Adipic anhydride

Adipic acid (C_6) and the longer-chain azelaic acid (C_9), which is accessed by oxidative cleavage of oleic acid, are among the most important aliphatic dicarboxylic acids.
In addition to glycerine, other polyols are also important as esterification components for alkyd resins and polyesters:

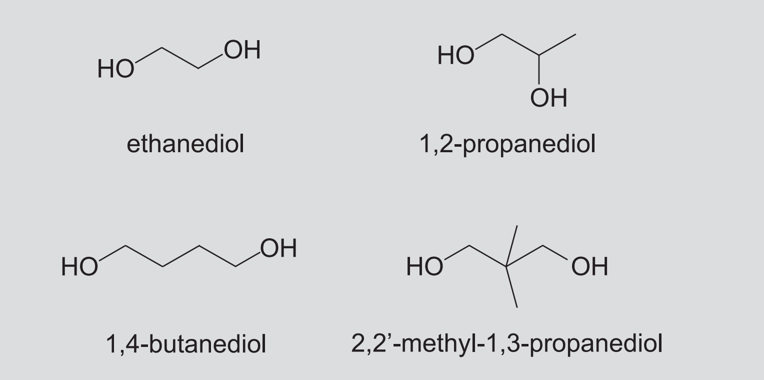


Fig. 2.1.40
Diols as components for esterification of alkyd resins and polyester resins

Diols such as ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,3-propanediol, 1,4-butanediol and 2,2-dimethyl-1,3-propanediol (neopentyl glycol) are mainly used to construct the basic chain of polyesters and less that of short-oiled alkyd resins.

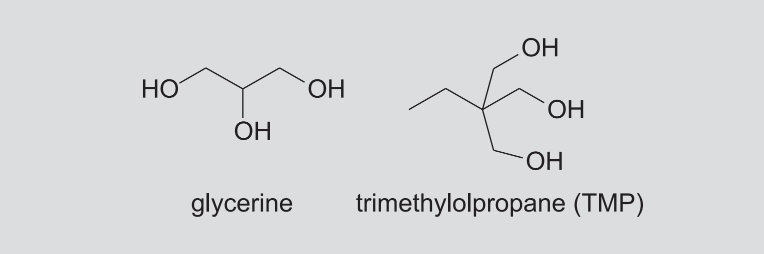


Fig. 2.1.41
Triols as components for esterification of alkyd resins and polyester resins

Glycerine is classified with the triols. However, it is only used nowadays in short- and medium-oiled, oxidatively and thermally curing alkyd resins.
Trimethylolpropane (TMP) and trimethylolethane are interesting alternatives to glycerine because of their three equivalent hydroxyl groups. TMP-based alkyd resins achieve improved compatibility with nonpolar solvents such as benzine compared with glycerine for the same oil length. They also can provide hyperbranched alkyd resins for use in high solid paints [2.4.10].

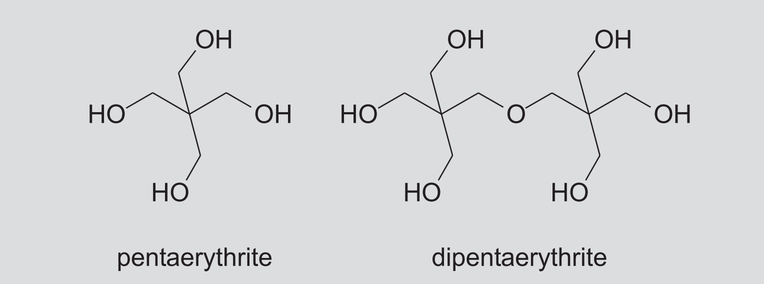


Fig. 2.1.42
Tetrols and higher polyols for alkyd resins and polyester resins

Pentaerythritol, with its four hydroxyl groups, is an important structural element for long-oiled alkyd resins. Dipentaerythritol, a byproduct of the manufacture of pentaerythritol, enables the oil length to be extended even further.
The range of natural fatty acids has now been expanded by a large number of synthetic monocarboxylic acids. While monounsaturated or polyunsaturated C_{18} acids are of particular interest for the oxidatively curing alkyd resins, thermally curing alkyd resins are generally manufactured using saturated, short-chain natural or synthetic monocarboxylic acids. By contrast with natural fatty acids, synthetic monocarboxylic acids feature greater purity and thus result in more consistent quality in the resins. The saturated monofunctional structural elements which are important for thermally curing alkyd resins are either unbranched short-chain C_4 to C_{12} acids obtained from natural materials or synthetic fatty acids which are branched to a greater or lesser extent.

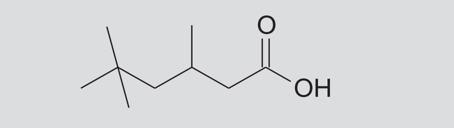


Fig. 2.1.43
Isononanic acid as an example for branched, primary and synthetic fatty acids

Isononanoic acid is highly branched in the alkyl group, but has a primary carboxyl group, nonetheless. Like the natural fatty acids, therefore, it is readily esterified, though equally readily saponified.

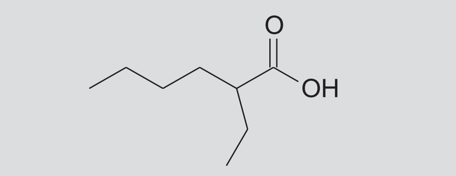


Fig. 2.1.44
α-ethyl hexanoic acid as example for branched, secondary and synthetic fatty acid

Although α-ethyl hexanoic acid, with a branch in the α-position to the carboxyl group, is harder to esterify, it is at the same time also harder to saponify. This means that coatings have a greater resistance to chemicals.

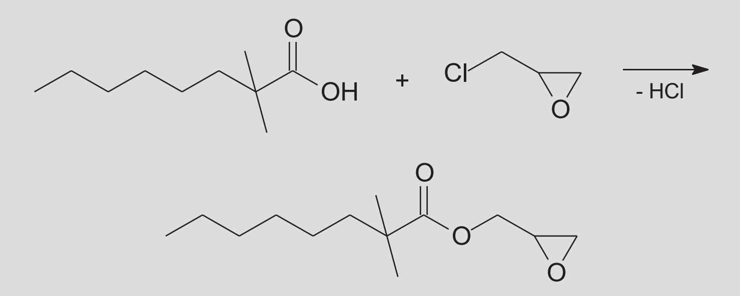


Fig. 2.1.45
Epoxy modified versatic acid as raw material for alkyd resins

Versatic acids with alkyl chains ($C_9 - C_{11}$) of varying length, have practically lost their ability for esterification as tert-carboxylic acids because of pronounced steric hindrance. They are therefore generally provided as glycidic esters with a reactive epoxy group. This behaves like a diol under the conditions prevailing during alkyd resin production.

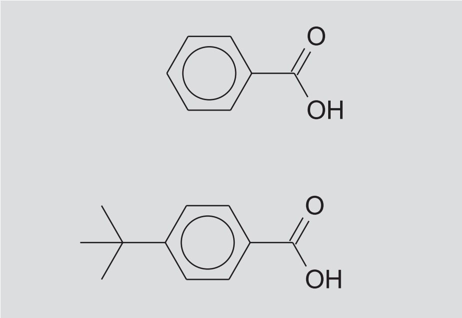


Fig. 2.1.46
Benzoic acid and p-tert-butyl benzoic acid

As a supplement to the aliphatic fatty acids, the aromatic benzoic acid and p-tert-butyl benzoic acid as monofunctional structural elements play a role as modifying agents to improve compatibility with other resins, in addition to their viscosity-regulating function.

Manufacturing processes

There are two different methods of manufacturing the alkyd resins. Either free fatty acids, dicarboxylic acids and polyols are reacted together in an appropriate mixing ratio (fatty acid process) or the actual esterification is preceded by a transesterification of the natural oils with appropriate quantities of polyols into bifunctional initial products. Only after this is esterification carried out with phthalic anhydride (see figure 2.1.29).

Unfortunately transesterification of the starting oils into bifunctional structural elements does not produce the desired quantities. In addition to measurable quantities of non-transesterified triglycerides, monofunctional and thus chain-breaking proportions are found in addition.

If mention is also made of the fact that the relatively high transesterification temperature

Fig. 2.1.47
Vessel for manufacturing alkyd resins

of up to 260 °C permits molecule-enlarging preliminary reactions via the fatty acids' double bonds, it will be clear that the different production processes cannot result in identical products. The molecule sizes and, in particular, the molecular weight distributions differ significantly at times, even if the formula ingredients have the same composition. Nevertheless, the two processes have not lost their technical importance to this day. Whereas in some countries the transesterification process is preferred, the fatty acid process is the more sensible method because of the greater flexibility in selecting the raw materials for customized film forming agents.

If alkyd resins are to be manufactured with uniform quality, it is imperative in the currently standard discontinuous batch process to monitor molecular growth during synthesis with appropriate measurement methods. The usual method is to measure the cleavage products arising from the polycondensation reaction which are removed by distillation, for a specified temperature curve, and also to record quantitatively the rise in viscosity and the reduction in the free acid groups (acid value) as corresponding performance indicators. In the case of thermally curing alkyd resins the number of free hydroxyl groups (hydroxyl value) must also be specified because of the later crosslinking with complementary resins (see chapter 2.3.2).

The **properties** of alkyd resins are mainly determined by the composition of the raw materials, the molecular weights achieved and the molecular weight distributions. In this context, the molecular weight distribution is influenced by the production process and the reaction conditions. The latter result in various secondary reactions which all have an impact on quality, as a function of the production temperature and the reactivity of the raw materials. Unwanted preliminary reactions of the double bonds, etherification, dehydration with simultaneous attachment of hydroxyl and carboxyl-functional molecule groups and unwanted cyclization are just some of the reactions which affect the molecular size and form.

Preparatory fractionation of the alkyd resin and specific merging of the individual fractions enable the effect of the varying size of structural elements on the application properties to be studied. This shows that, with the exception of unwanted residual monomers, all fractions contribute positively to the overall quality. While the high molecular portions ensure good, rapid physical hardening during film formation, it is the polar, low molecular structural elements which promote wetting during the intermingling of the pigments and thus their even distribution in the liquid matrix [2.4.11].

In long-oiled alkyd resins, the fatty acids used are primarily unsaturated, i.e. they give the resin the capability of oxidative crosslinking. Reactivity is closely correlated to the properties of the oil from which the relevant fatty acid mixture is derived and on the subsequent treatment (isomerization, dehydration) which it has undergone. A high oil content delivers good flow, results in high elasticity and easy processibility using workshop application methods. The slow curing of the film, and thus the mechanical sensitivity of the coatings shortly after processing, is a disadvantage. The most important alkyd resins in this class are based on linseed oil. These yellow very markedly, with the result that resins based on soya oil and tall oil fatty acids are preferred in the decorative paint sector for light coatings which have to resist yellowing (see figure 2.1.6).

Long-oiled alkyd resins should be used as sole film forming agents. Medium-oiled alkyds feature universal solubility and good compatibility with modified natural resins, cellulose nitrate and amino and amido resins. Short-oiled alkyds, both with oxidative crosslinking and also with saturated monocarboxylic acids, are among the most widely used film forming agents for baking enamels when used in combination with amino or amido resins, and frequently also with epoxy and phenolic resins. The performance profile is largely determined by the oil length and the type of fatty or monocarboxylic acids.

If saturated or only weakly unsaturated fatty acid mixtures such as those of coconut oil, castor oil or groundnut oil are added, the resulting alkyd resins do not crosslink oxidatively or do so only negligibly. They can, therefore, be used as plasticizing components in cellulose nitrate and acid-curing coatings.

The choice of suitable fatty acid or monocarboxylic acid mixture for particular applications therefore plays an important role for baking enamels, too. Baking enamel coatings with low baking temperatures of < 100 °C require oxidative secondary crosslinking. This is achieved with high levels of fatty acids with good resistance to yellowing and a high number of conjugated double bonds. Ricinoleic fatty acid, which is derived by dehydration from castor oil fatty acid, is ideal because this absorbs less atmospheric oxygen and tends less towards yellowing than the analogous isolenic acids. Hardness and chemical resistance are achieved by using branched synthetic fatty acids. The aromatic monocarboxylic acids which are sometimes also used in the fatty acid component of alkyd resins make it easier for solvents to be released from the liquid coating film and promote physical drying.

By contrast with the long- and medium-oiled alkyd resins, the emphasis of the crosslinking function with the short-oiled baking enamel alkyd resins is transferred to conversion of the hydroxyl groups and with watersoluble alkyd resins is also transferred to conversion of the carboxyl groups.

Despite the wide range of properties of alkyd resins, as a result of the type of oil, oil length, molecular weight, molecular weight distribution and free carboxyl and hydroxyl group content, numerous attempts have been made to adapt **alkyd resins** better to practical requirements **by chemical modification**.

The modification of alkyd resins with longchain polyaminoamides, made from dimerized fatty acids and aliphatic polyamines, results in **thixotropic alkyd resins** with the special feature of time- and shear-dependent flow (see chapter 2.3.2).

The originally incompatible components can be rendered compatible by means of transesterification and transamidation. At the same time, because of the formation of numerous intermolecular hydrogen bridging bonds, viscosity occurs as a function of the shear load in the form of pseudoplasticity and thixotropy. Since the thixotropy is also time-dependent, such resins open up new routes for formulating run-resistant coatings. It brings about a temporary reduction in viscosity during the high level of shear when spraying or during application by brush, which can then be reversed more or less quickly, depending on the level and type of thixotropy. Thixotropy is an important phenomenon and aid for troublefree film formation particularly on vertical surfaces. Alongside curing via solvent release or chemical crosslinking, it represents a third physical variable in film formation and harmonizes the flow and running of coating materials, particularly with waterbased paints (see chapter 5.6.2).

By analogy with the addition reactions familiar with the fatty oils, **styrene modified alkyd resins** result from the conversion of styrene or vinyl toluene with oxidatively curing alkyd resins. The chemical bonding of the styrene with the double bonds of unsaturated fatty acids can represent up to 50% of the oil component. Physical drying is substantially improved as a result. The good resistance of coatings made of styrenated alkyds to water and alkalis must be offset against a permanent sensitivity towards solvents.

The incorporation of acrylic acid or methacrylic acid esters results in **acrylated alkyd resins**. They also dry very quickly and provide coatings with good adhesion and excellent longterm outdoor exposure properties. They are also suitable for designing waterbased resins [2.4.12].

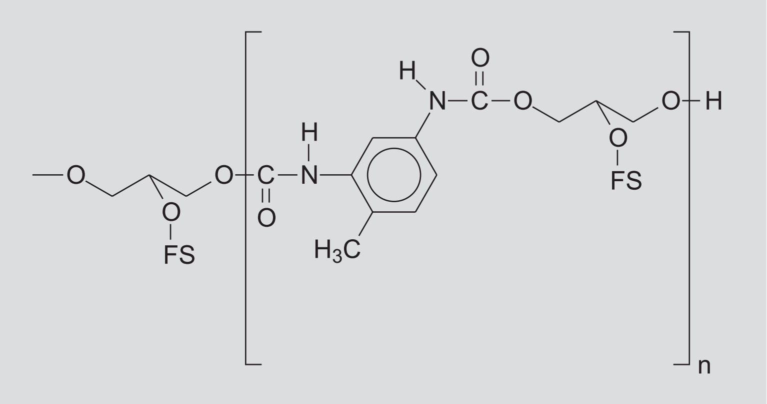


Fig. 2.1.48
Structure element of urethane oils on the basis of toluylendiisocyanate (TDI) and fatty acids (FS)

The partial replacement of the o-phthalic acid by diisocyanates results in the **urethane alkyds** group. These materials exhibit increased stability of the basic chain against saponifying agents, as a function of the degree of substitution. If the dicarboxylic acid is substituted quantitatively, the result is the **urethane oils** which are particularly wear-resistant and, at the same time, have better resistance to acids and alkalis. Aromatic diisocyanates impair the resistance to yellowing. Aliphatic modification agents, such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI), must be used to ensure the production of resins which are resistant to yellowing.

Modification with epoxy resins is also possible. This is based on the partial replacement of the polyol, which is necessary for the manufacture of the alkyd resin, by a suitable epoxy resin (see figure 2.1.49). During this process the epoxy groups and the hydroxyl groups of the epoxy resin act as the polyol component for the mono- and dicarboxylic acids.

Another way of modifying resins is the chemical bonding of epoxy resins with the finished alkyd resin. As expected, the modification results in a shift in the properties towards the modification resin. Improvements in the adhesion, resistance to saponification and hardness, on the one hand, but also impairment of the fastness to

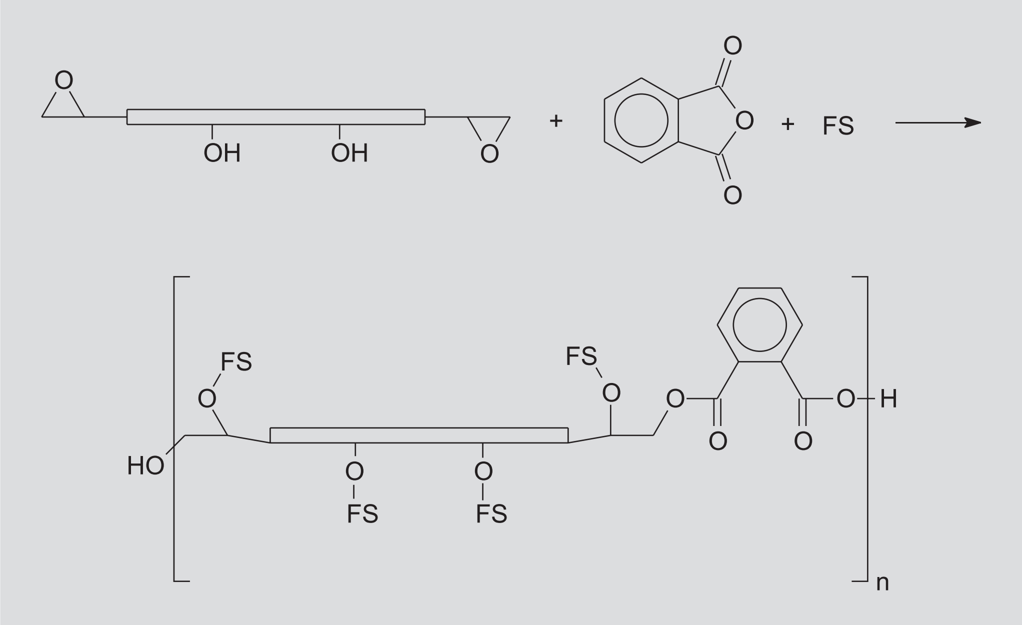
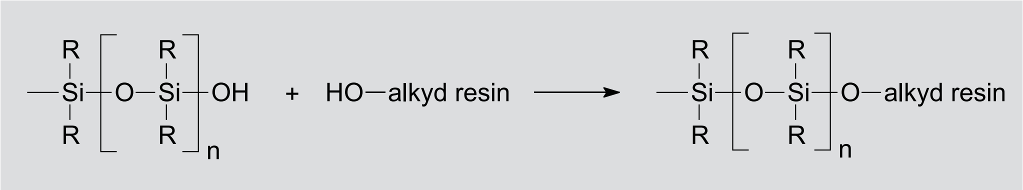


Fig. 2.1.49
Synthesis of an epoxy modified alkyd resin (FS= fatty acids)

light, on the other hand, are the outcome if aromatic ether types are used as epoxy resins.

Hydroxyl or methoxyl-functional silicone resins are also suitable for chemical bonding with hydroxyl-functional alkyd resins. Such **silicone modified alkyd resins** demonstrate effective improvements in heat resistance and longterm outdoor exposure properties of corresponding coatings, though only in the case of silicone resin proportions of 20% or more. Despite the associated high price, silicone-modified alkyd resins have established an important role, particularly where iso- or terephthalic acid is used.



$$-\underset{R}{\overset{R}{\mathrm{Si}}}-\left[O-\underset{R}{\overset{R}{\mathrm{Si}}}\right]_n-OH + HO-\text{alkyd resin} \longrightarrow -\underset{R}{\overset{R}{\mathrm{Si}}}-\left[O-\underset{R}{\overset{R}{\mathrm{Si}}}\right]_n-O-\text{alkyd resin}$$

Fig. 2.1.50
Structure of silicone modified alkyd resins

Oxidatively curing alkyd resins undergo a substantial improvement in through-hardening if they are made capable of forming complexes with organic aluminium compounds by means of chemical modification with diketenes. During oxidative crosslinking of the unmodified alkyd resins the forming film undergoes molecular enlargement caused by crosslinking, starting from its surface. A reduction in oxygen permeability is an associated feature. Good through-hardening therefore requires only slow surface hardening. Thus if both properties need to be combined, further crosslinking mechanisms must be sought. The already mentioned conversion of the alkyd resins' hydroxyl groups with diketenes results in acetoacetic ester groups, which cause the additional through-hardening of the **metal supported crosslinked alkyd resins** during film formation by transformation of an Aluminium acetylacetone complex which is added as a liquid component. The acetylacetone is released and then escapes. In the search for coating materials which can be processed in an environment compatible manner **water soluble and water emulsifiable alkyd resins** have proved to be inexpensive film forming agents. In order to achieve solubility in water or the ability to form stable emulsions in water, polar functional groups corresponding to the polar nature of the water must be integrated in the film forming agent. Free carboxyl and carboxylate groups have proved suitable in practice. Depending on the number of carboxyl and carboxylate groups dispersion or emulsification, i.e. heterogeneous distribution in the form of extremely fine resin droplets in water or conversion into a homogeneous solution, is possible.

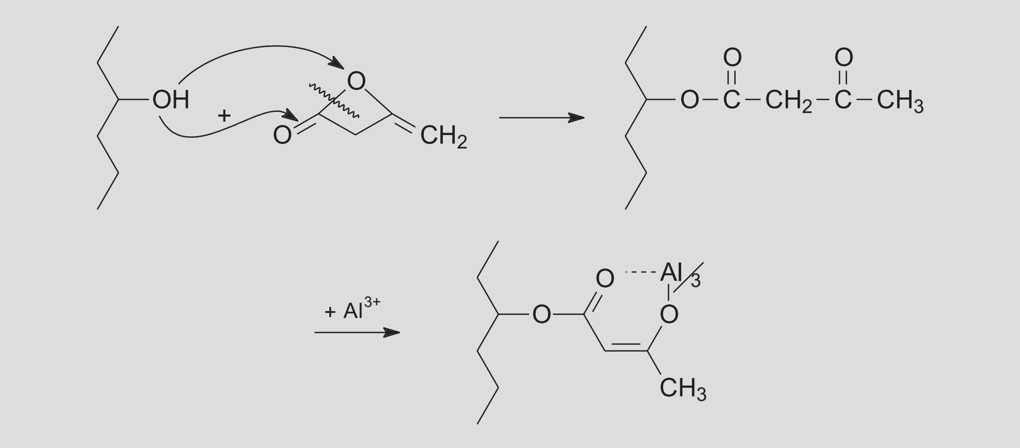


Fig. 2.1.51
Film forming of metal supported crosslinked alkyd resins

Neutralization of the polar carboxyl groups with amines increases their polarity and enables the manufacture of stable emulsions and solutions as a function of the quantity of amines and the supplementary solvents used, i.e. the cosolvents, which can be mixed with water. Glycol ether and classic alcohols in volumes ranging from 5% to 15% have proved successful as cosolvents for aqueous solutions. The watersoluble alkyd resins obtain the necessary number of carboxyl groups for hydrophilization by partial or complete substitution of the usual o-phthalic acid by trimellitic acid. This is the only way in which the demands for a sufficiently high molecular weight and a sufficient number of carboxyl groups to ensure solubility in water can be met. Compared with solutions, emulsions offer the advantage of being able to cope with a smaller number of polar groups and significantly lower levels of cosolvents.

The environmental benefit of reduced emissions during the processing of oxidatively curing alkyd resins dissolved or emulsified in water must be offset in the form described thus far against the disadvantages of the polar carboxyl or hydroxyl groups which thus impair the film resistance. If, as in the film formation of classic alkyd resins, physical

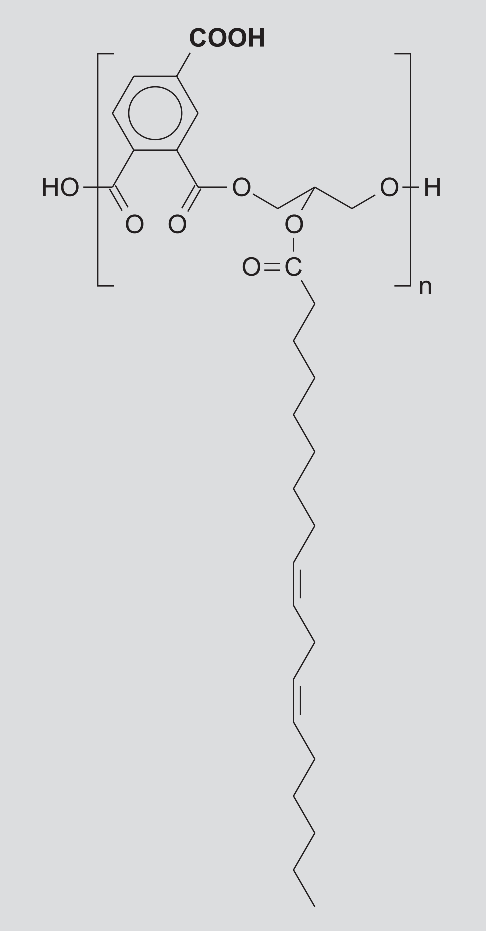


Fig. 2.1.52
Structure element of alkyd resins for water soluble resins

curing is followed by oxidative curing, the carboxyl groups remain in the cured film. By contrast, the carboxyl groups in the thermally curing alkyd resins react with complementary resins. Initial problems with the resistance of emulsions by saponifiable ester groups were overcome by displacement into the interior of the emulsion droplets.

The starting point for the success of oilfree **saturated polyesters**, which are now becoming more and more important, are the glyptals which were controversial at the time of their invention. In the early days they could only be manufactured with difficulty and were often incompatible with nonpolar partners. In addition, the alkyd resins first synthetically manufactured by *Kienle* with their short-oiled variants exhibited yellowing to a greater or lesser degree when subjected to thermal loads, light or longterm outdoor exposure. Only when fatty acids were completely dispensed did it prove possible to manufacture nonyellowing resins.

Usable resins were produced by replacing the glycerine with neopentyl glycol, trimethylol propane or pentaerythritol and substituting isophthalic acid or terephthalic acid for phthalic anhydride. The elasticizing which is now necessary because of the lack of fatty acids is achieved by internal plasticizing by incorporating adipic acid or sebacic acid in the resin. Any solubility in water which is desired is obtained, as in the classic alkyd resins, by replacing the dicarboxylic acids by the trifunctional trimellitic acid or tetrafunctional pyromellitic acid. The molecular form and the molecular weight, and therefore the solubility and compatibility with other resins, are affected by the overall functionality of the raw materials and the degree of conversion.

The success of saturated polyesters is due in part to their ability to meet specific properties for powder coatings or coil coatings. In both cases thermal resistance associated with the high requirements in terms of application properties may be mentioned. As a result, saturated polyesters have established themselves as the base resins for sophisticated polyurethanes in addition to their standard applications as baking enamels.

Saturated polyesters, whether they are purely hydroxyl-functional or are also carboxyl-functional as special resins for waterbased paints and powder coatings, are exclusively

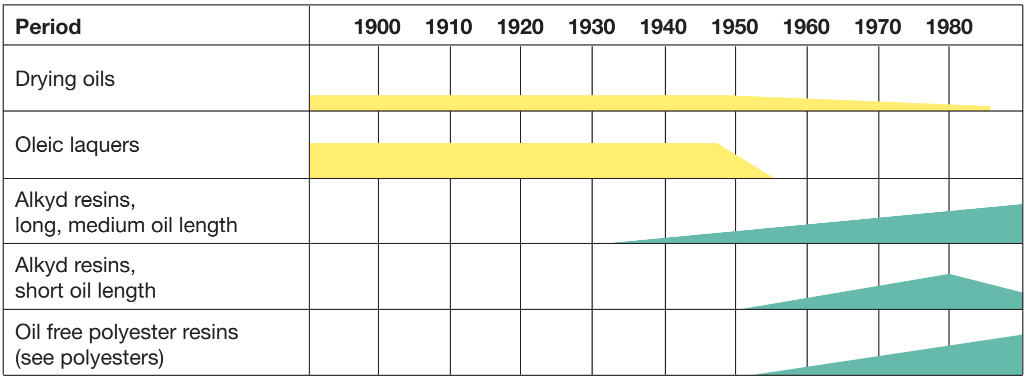


Fig. 2.1.53
Qualitative graph of the development of the saturated polyester market in comparison to other resin types

polar representatives, compared with their fatty acid-containing rivals, and are therefore also only compatible with correspondingly polar complementary resins. Low molecular melamine resins highly etherified with methanol have proved successful. The high degree of etherification promotes the mutual crosslinking of the melamine resin with the saturated polyester. Quality-diminishing self-curing, as occurs in melamine resins with a low etherification level, is thus prevented (see below).

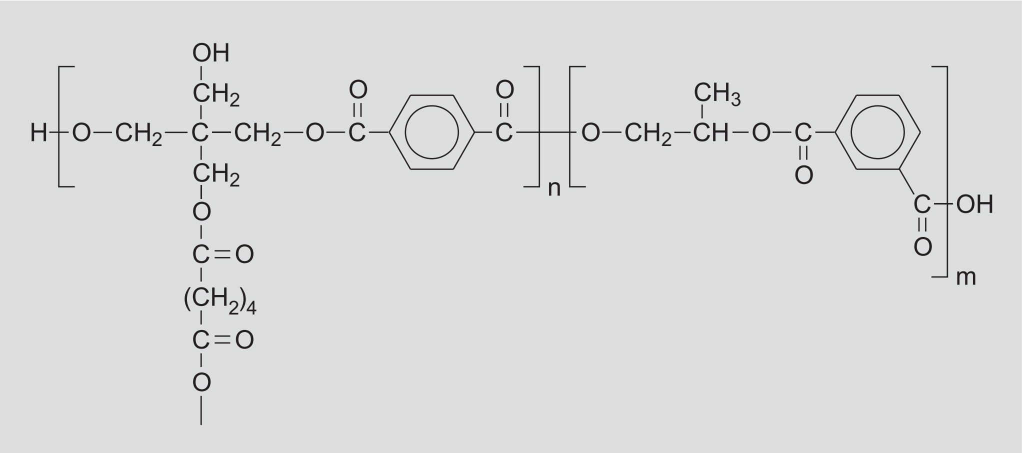


Fig. 2.1.54
Example of a typical structure element of a saturated polyester resin

Despite having a lower number of basic structural elements by comparison with alkyd resins, there is a broad range of saturated polyester products available. The solvent-containing polyesters with molecular weights up to 25,000 g/mol should first be mentioned. As linear or branched products they are OH-functional and therefore suitable for crosslinking with melamine or isocyanate resins.

Solvent free polyesters with similarly high molecular weights are used as solid resins, again OH- or carboxyl-functional for powder coatings. Representatives which have hydroxyl groups are combined with polyisocyanates, while the carboxyl-functional types were previously combined with triglycidyl isocyanurate (TGIC), though this has now been replaced by isophthalic acid, trimellitic acid glycidylester or N,N,N',N'-tetrakis-(2-hydroxyethyl)adipamide (Primid) or similar β-hydroxyl alkylamides because of the proven mutagenic effect of this crosslinking component [2.4.13].

The basic reactions b) and c) in Fig. 2.1.55 are in the form of polycondensation reactions with the disadvantage that with relatively large film thicknesses, the removal of the cleavage products which occur during crosslinking can result in faults in the film.

Hydroxyl- and at the same time carboxyl-functional resins with acid values of 40 – 80 mg KOH/g (see chapter 2.3.2) become watersoluble after neutralization with amines, though only in conjunction with cosolvents in the lower range of the acid values quoted. Waterbased baking enamels can be formulated for the automotive and coil-coating sectors and for industry in general by combining them with watersoluble, highly etherified melamine resins.

Low molecular hydroxyl-functional polyesters with molecular weights of 1,500 – 4,000 g/mol can also be processed into 1-component high solids coating with solid contents of up to 70%. Even higher solid contents are possible if the molecular weights are reduced still further and crosslinking is carried out with low molecular isocyanate hardeners. The only slight increase in viscosity after application as a result of physical drying has to be equalized by pseudoplasticizing or thixotroping.

There is a further application for saturated hydroxyl-functional polyesters if the hydroxyl groups at the ends of the polyester chains are esterified with acrylic acid. This makes it possible to use high-energy UV or electron radiation for curing (see chapter 4.3.2).

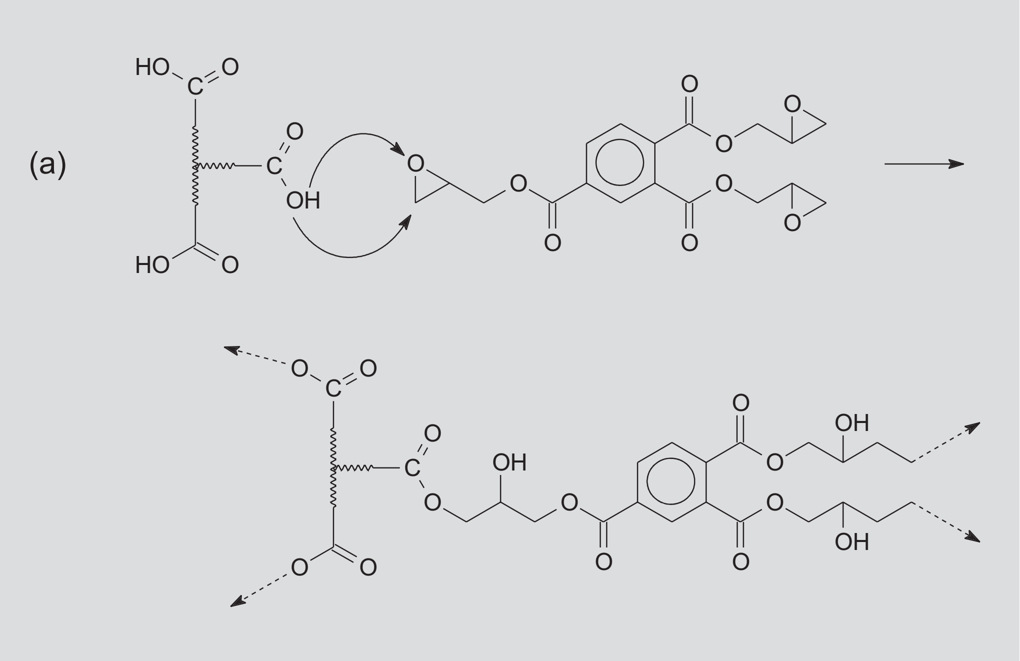


Fig. 2.1.55
Crosslinking reaction of polyester resins for powder coatings
(a) with trimellitic glycidylester, (b) with β-hydroxyl alkylamides, (c) with blocked isocyanates
(to be continued on next page)

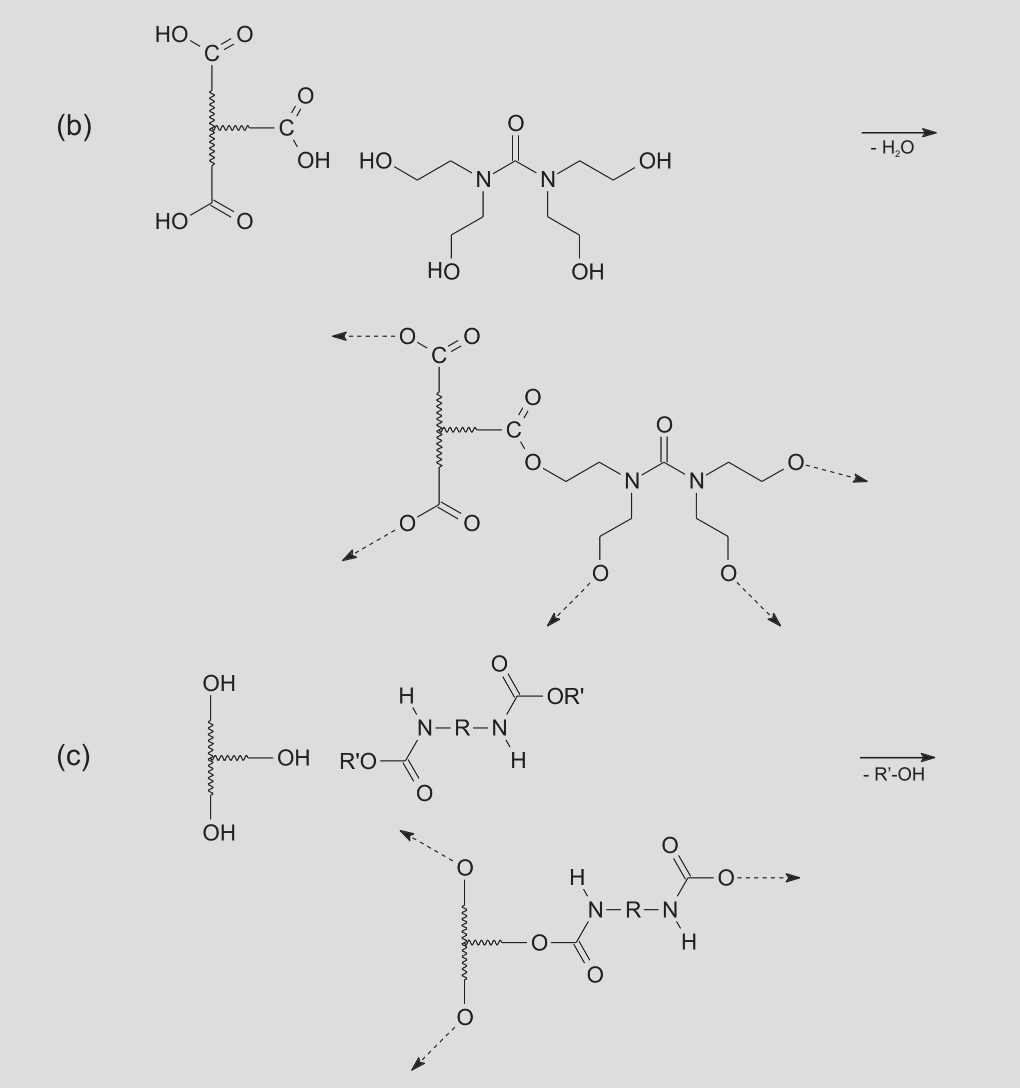


Fig. 2.1.55
Crosslinking reaction of polyester resins for powder coatings
(a) with trimellitic glycidylester, (b) with β-hydroxyl alkylamides, (c) with blocked isocyanates
(continued from last page)

Such resins can also be copolymerized with acrylic acid or methacrylic acid monomers, which results in the general incompatibility of polyesters with acrylic resins being overcome.

Modifications of saturated polyesters with silicone resins also result in interesting film forming agents for coatings with extreme longterm outdoor exposure properties if they are made to react with melamine resins in polycondensation reactions or with aliphatic/ cycloaliphatic polyisocyanates in polyaddition reactions.

Saturated polyesters generally feature a high level of hardness combined with pronounced elasticity. High crosslink densities and mobile segments in the basic chains are the reasons that these are suitable for coil coatings which have to withstand extreme deformation without suffering damage. Good gloss, excellent build, resistance to yellowing when overbaked and good chemical resistance are other noteworthy properties.

Unsaturated polyester resins are semi-finished products which are transformed into a duromeric coating on the basis of incorporated double bonds which copolymerize with styrene or vinyl toluene as a chemically reactive solvent. Unsaturated polyesters belong to the group of the polycondensates or condensation polymers because they are manufactured from dicarboxylic acids and diols in polycondensing reactions.

The special feature of this class of substances, when compared with the saturated polyesters, lies in the linear structure of the resin molecules and the proportion of maleic anhydride used. This makes crosslinking with the solvent styrene possible. In this process the ratio of maleic acid to phthalic acid in connection with the quantity of styrene determines the crosslink density of the cured film and thus the solvent resistance and the mechanical/technological properties.

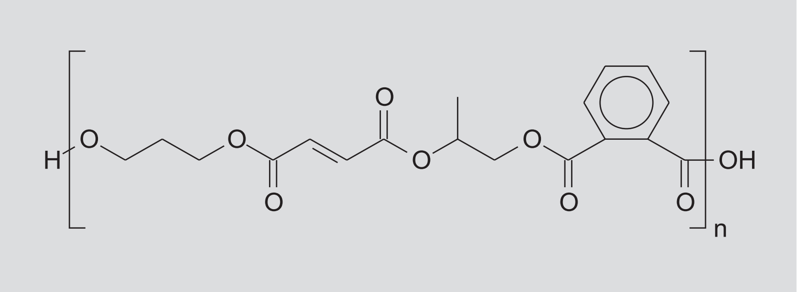


Fig. 2.1.56
Structure element of an unsaturated polyester

Since the styrene as a reactive diluent does not leave the paint film on curing and, in addition, no volume-reducing cleavage products are formed, unsaturated polyesters can be processed into high film thicknesses without causing any problem. They therefore have important applications for coatings with high film thicknesses in the wood and furniture sectors, but also as resins for automotive repair fillers.

In addition to the ratio of maleic anhydride to phthalic anhydride, elasticizing basic structural elements can also affect the mechanical/technological properties. On the dicarboxylic acid side these are adipic acid or sebacic acid. On the polyol side the standard components ethanediol and 1,2-propanediol are partially or wholly replaced by1,3-propanediol, neopentyl glycol, diethylene glycol, 1,4-butanediol or triethylene glycol.

When synthesizing unsaturated polyesters trouble free esterification is only possible under the exclusion of atmospheric oxygen at reaction temperatures of 190 – 210 °C and with the addition of inhibitors because of the risk of premature crosslinking.

Radical scavenging products such as hydroquinone or quinone in volumes of 0.001% to 0.1% have proved successful as inhibitors. If unwanted curing has started, they can halt it again by chain transfer. The ready-to-use unsaturated polyester is a mixture of the actual polyester resin, styrene and hydroquinone as a stabilizer to increase storage stability.

Since the inhibitor retains its inhibiting properties when initiators are added to harden the coating, it affects the starting point of the curing process and the crosslinking rate. Manufacturers make use of this fact by varying the inhibitor quantity to adjust the pot life to operating conditions.

Not all application techniques can be used to apply unsaturated polyesters to the object to be coated. Spraying is not an option because of the huge increase in the material surface area during application and the resulting acceleration in the evaporation of the reactant styrene. Roller or curtain coating remain as usable processing methods. Both methods are used solely for planar objects such as coils or wooden and plastic panels.

Since the solvent styrene is also a reactant in the curing process and therefore cannot leave the forming film, no thermal processes may be used to accelerate crosslinking of the film. The mutual bonding of styrene with the double bonds of the basic chain of the unsaturated polyester resin can therefore only be induced by the ”cold” formation of starting radicals.

These can be derived from the catalytic decomposition of peroxides and hydroperoxides or using the high-energy radiation of photoinitiators (see chapter 2.1.4). Whereas the

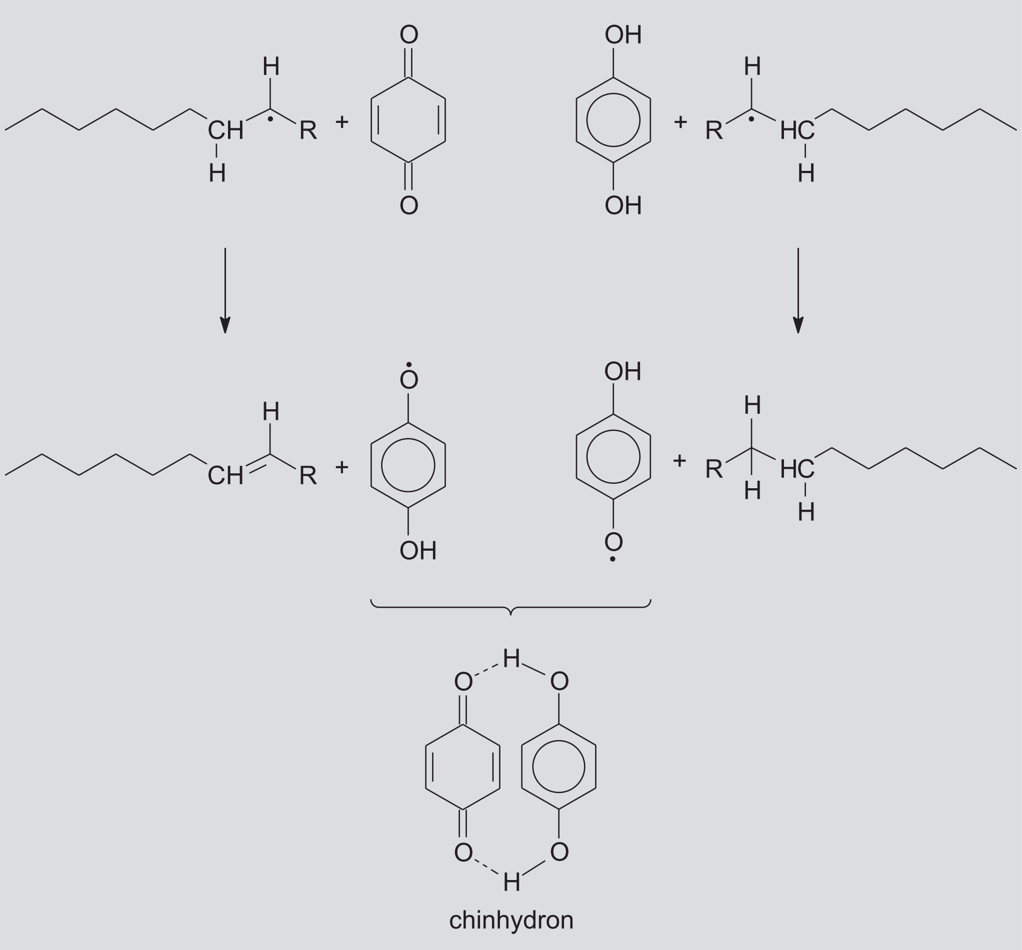


Fig. 2.1.57
Chemical effect of the inhibitors quinone and hydroquinone on radicals

first option results in 2-component paints with a limited pot life, processing into 1-component paints is possible when curing with UV radiation. The 2-component paints consist of the base with unsaturated polyester, styrene, inhibitor, accelerator and the peroxide containing hardener.

Decomposition of peroxides or hydroperoxides is achieved by catalytic action with certain metallic soaps. Cobalt salts can successfully be used to accelerate radical formation because of their ability to change valency. Dibenzoyl peroxide, cumyl hydroperoxide and t-butyl perbenzoate may be cited as examples of the broad range of commercially available radical initiators.

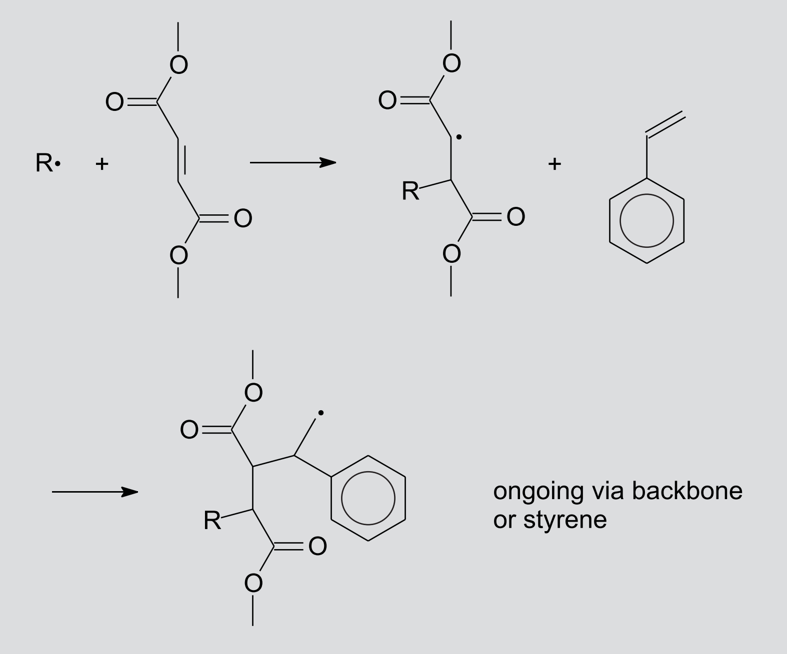


Fig. 2.1.58
Crosslinking reaction of unsaturated polyesters with styrene

Tertiary amines are alternatives to cobalt salts. Their effect is based on radical-forming hydrogen transfer.

Both product groups of accelerators have proved successful in practice. Whereas the highly reactive amine is gradually used up by the curing process, thereby diminishing its effect, the cobalt salt acts purely catalytically with relatively low initial reactivity but better through-hardening. Blends of the two product groups are therefore used to ensure the best processing properties. The amines' tendency to yellow is a disadvantage to note in light coatings.

The chemical destruction of the inhibitors after decomposition of the initiators and the subsequent exothermic crosslinking reaction result in a restricted pot life. Manufacturers have two performance indicators to enable them to make a quantitative evaluation. The gelling time is defined in DIN 53 184 as the time which passes until the temperature of the reaction mixture has risen as a result of the crosslinking reaction heat by 10 °C. The curing time is the time taken to reach the maximum temperature.

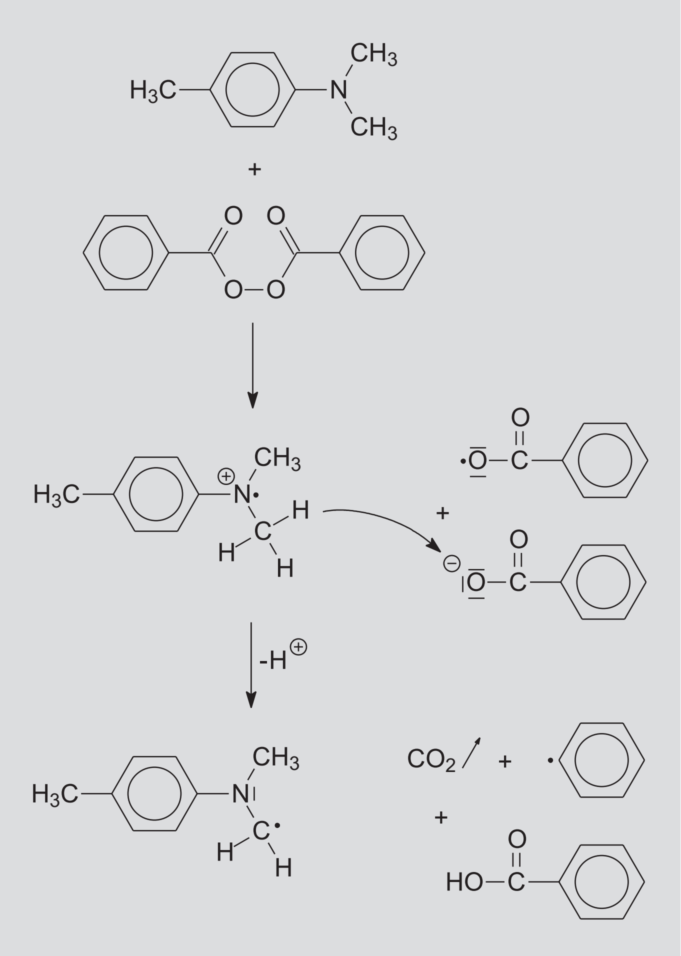


Fig. 2.1.59
Mechanism of catalysis by amines for the decomposition of peroxides

Because of the limited pot life and at the same time the relatively slow curing of unsaturated polyester resins additional curing methods have developed. The process of generating radicals by means of photoinitiators under the simultaneous effect of UV radiation has been in use since the 1950s. The advantage of the now no longer limited pot life was then supplemented by a significant acceleration of the curing process. Photoinitiators or sensitizers are benzoin derivatives, benzil ketals, α-halogen ketones or benzo phenone derivatives. The latter do not decompose into radicals, but abstract hydrogen atoms from suitable synergists which are then transformed into radicals (see chapter 2.1.4).
Mercury vapour lamps are the radiation source for the curing process, supplying the necessary energy in the form of short electromagnetic waves from low pressure and high pressure lamps. Curing by electron radiation results in a further reduction in the crosslinking time while also enabling photosensitizers to be dispensed with. Accelerated electrons are capable of forming radicals or radical ions by direct interaction with the coating resins (see chapter 4.3.2).

Intensive research in the field of radiation curing brought new understanding of the mechanism of photopolymerizing curing. The ratio of the rate of the growth reaction to chain termination is of particular importance in ensuring a high degree of crosslinking and thus for the degree of hardness in the coatings. Out of the huge range of different classes of substances special acrylicresins proved advantageous in this context, and as a consequence more than 60% of radiation curable coatings contained acrylic resins as their base resin by 1995 (see below).

Irrespective of the processing method used, atmospheric oxygen inhibits the crosslinking process. It intervenes in the molecule-enlarging chemical reactions as a biradical at a high concentration and terminates radical chains. All the standard resins described thus far therefore have the drawback of not achieving optimum curing on the surface which is associated with a permanent stickiness. There are two different approaches to eradicating this problem. Either the interaction of the oxygen with the forming coating must be stopped by adding floating waxes, or the chain terminating effect of the oxygen must be prevented by the chemical insertion of special groups into the polyester resin, i.e. incorporating these groups in the coating formulation via additives. However, the first method requires an additional working stage to remove the floating layer of wax by polishing.

The chemical route succeeds either by adding hydroperoxide-forming and thus oxygen-activating structural elements during production of the polyester or by subsequently including additives which contain allyl groups. Possible substances for the first case are tetrahydrophthalic acid and endomethylene tetrahydrophthalic acid.

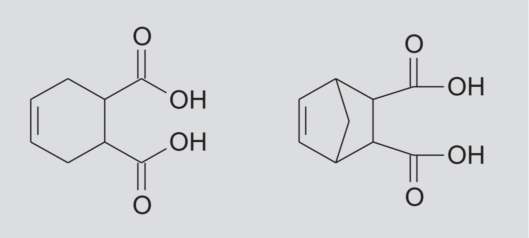


Fig. 2.1.60
Dicarbonic acids for unsaturated polyester resin based coatings featuring no inhibition by oxygen

The paints formulated according to these principles can be safely applied with high film thicknesses using the low waste generating curtain and roller coating processes. As a result these methods are still widely used in the wood and furniture sector to this day.

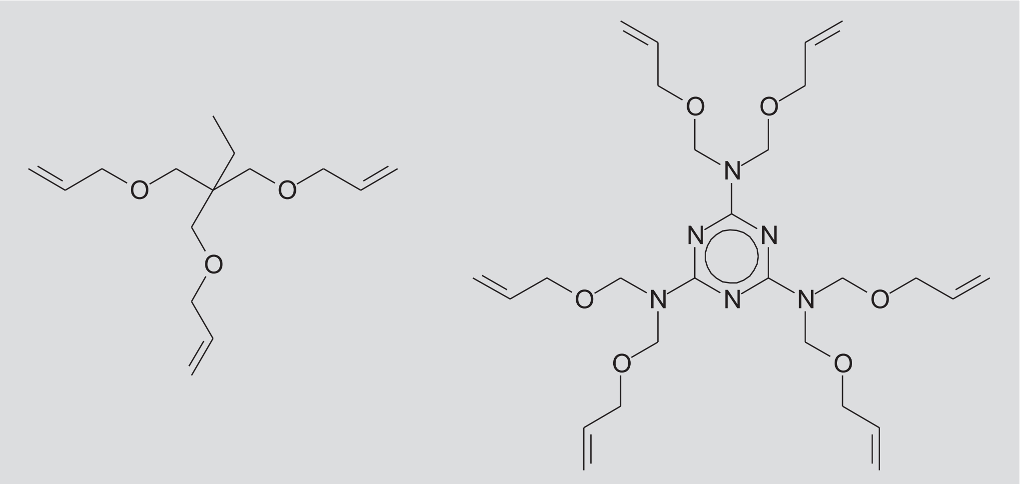


Fig. 2.1.61
Examples for additives to reduce inhibition by oxygen

Polyamides are polymer compounds in which the basic structural groups are bonded to each other via acid amide groups. Despite being related to polyesters, polyamides are only of negligible importance in coating technology terms.

Synthesized by *Carothers* in the US in 1929 and *Schlack* in Germany in 1935 from aliphatic dicarboxylic acids and aliphatic diamines or ω-aminocaprolactam, they were originally used as synthetic replacements for the then expensive Japan silk because of their chemical similarity to natural silk [2.4.14, 2.4.15].

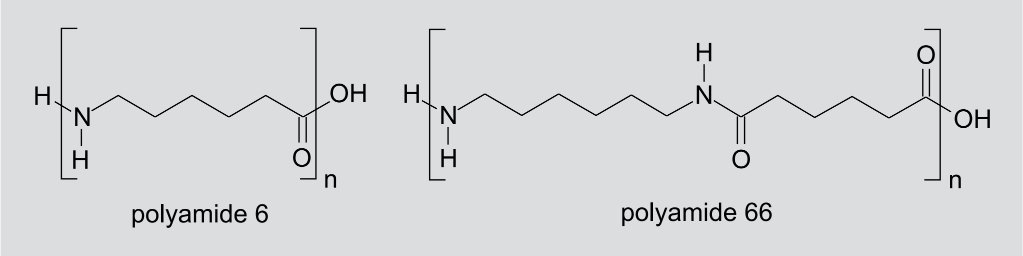


Fig. 2.1.62
Structure elements of polyamide-6 and polymaide-66

It was later that methods of manufacturing polyamides from other basic structural elements too were developed. The greatest significance in terms of coating technology may be ascribed to polycondensates of dimerized fatty acids and aliphatic polyamines. Polyaminoamides have proved successful, depending on the mixing ratio of the initial components, as thixotropic agents for alkyd resins or as hardeners for epoxy resins. If an excess of dicarboxylic acids is chosen, the initial materials for providing thixotropy are obtained. With excess amines the then liquid polycondensates become raw materials for flexible epoxy resin coatings.

The polyamide manufactured from ω-aminoundecanoic acid merits mention as a base resin for thermoplastic powder coatings processed using the fluidized-bed method. The amino acid is made available by thermal decomposition of ricinoleic acid to the resulting product of which amino groups are attached.

Like the related polyimides, polybenzimidazoles and polybenzimidazopyrrolones, polyamides are proven initial products for thermally stable plastics and coatings.

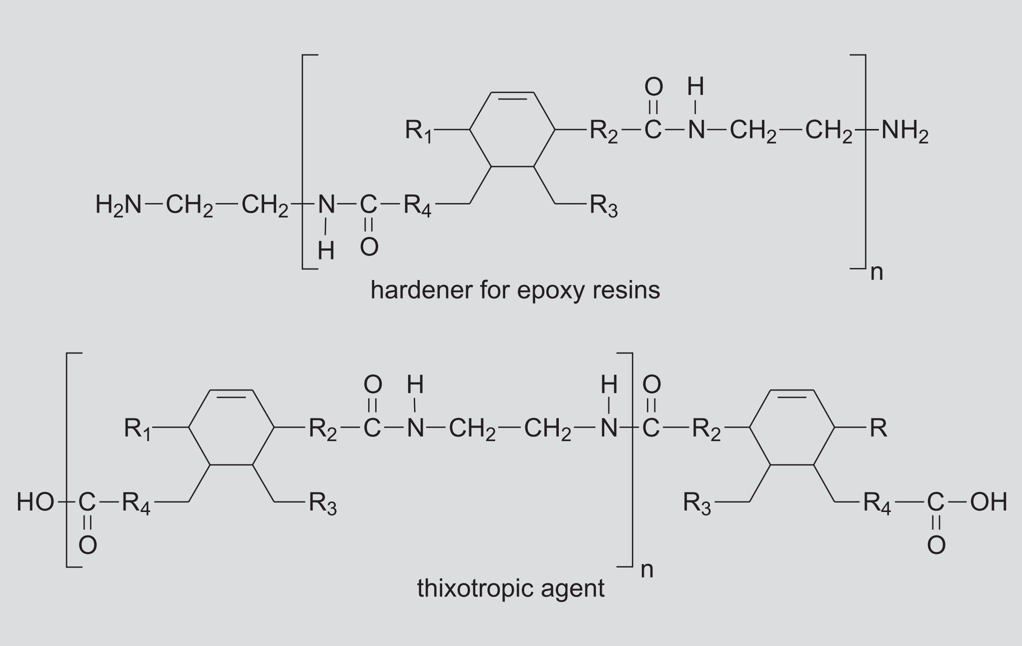


Fig. 2.1.63
Polyaminoamides as thixotropic agents and haredeners for epoxy resins

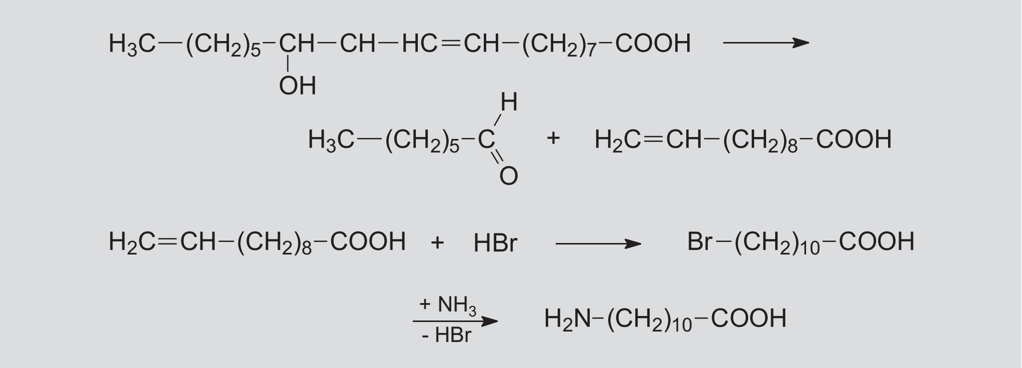


Fig. 2.1.64
Synthesis of ω*-aminoundecanoic acid from ricinolic acid*

Because of the low mobility of the rigid monomers which cannot form coils, the entropy changes only minimally during synthesis or decomposition. Consequently, the quotient of the change in enthalpy and entropy has a relatively high value.

$T_c = \Delta H/\Delta S$

T_c = ceiling temperature
ΔH = reaction enthalpy
ΔS = reaction entropy

The variable given as the ceiling temperature T_c is the temperature at which the rates of polymer formation and polymer decomposition become the same. Because of a relatively small ΔS in the above polyamide derivatives, these have exceptional heat resistance.

Polyimides are manufactured from aromatic tetracarboxylic acids with aromatic diamines via the intermediate stage of acid polyamides.

Heat resistances of more than 250 °C for continuous exposure and up to 600 °C for transient heat exposure are obtained in this class of substances.

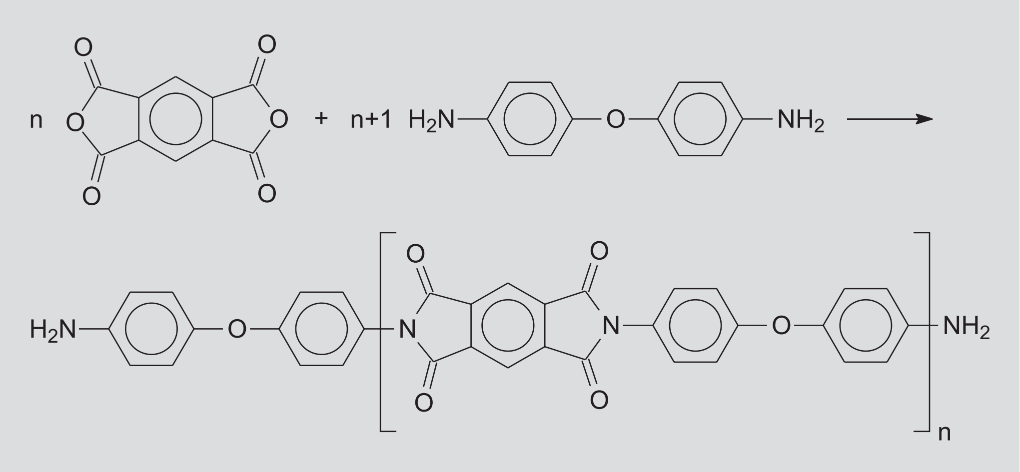


Fig. 2.1.65
Synthesis of polyamides from pyromellitic acid and diaminophenylic ether

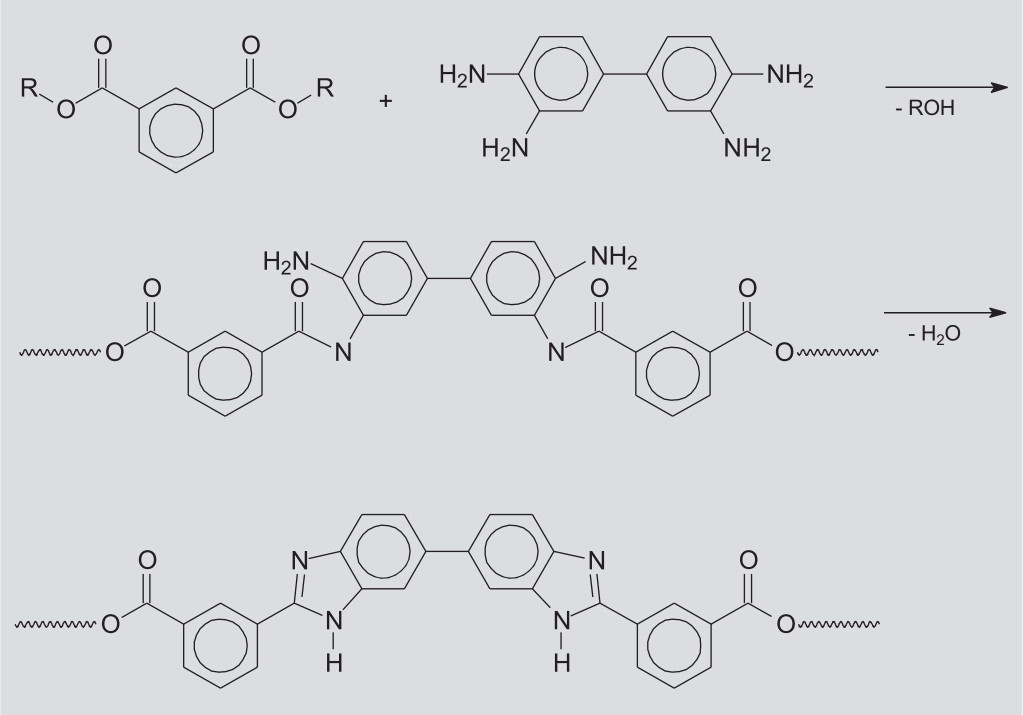


Fig. 2.1.66
Polybenzimidazoles from isophtalic acid phenylester and tetraaminobiphenyl

The solubility which is necessary for use as coating materials is obtained by substituting diphenyl endomethylene cyclohexane tetracarboxylic acid for the pyromellitic acid, though this results in a gradual reduction in the heat resistance.
If the tetracarboxylic acid is replaced by the bifunctional isophthalic acid phenylester with simultaneous substitution of tetraaminobiphenyl, a 4-functional structural element, for the diaminophenylether, the result is the polybenzimidazole class of substances via the intermediate stage of a polyamide.
The deficient resistance of polybenzimidazoles to atmospheric oxygen can be eliminated by the partial replacement of the amino groups by mercaptan groups, i.e. by converting the imidazoles into thiazoles. Only exotic solvents can be used for processing as coating materials with dimethyl sulphoxide.
A further increase in the molecular stability when exposed to heat can be achieved by polycondensation of the 4-functional pyromellitic acid with the equally 4-functional tetraaminobiphenyl to form the polyimidazopyrrolones (see figure 2.1.67).
Apart from a further improved heat resistance, this class of substances also has excellent stability against the effect of high-energy radiation. The polymeric azopyrrolones are therefore resins for special aerospace applications.
Polyimides cannot be crosslinked, are difficult to dissolve and are therefore used as a raw material only for special coatings, particularly where high temperature resistance is called for.
By contrast with the film forming agents discussed so far which essentially consist of carbon chains, the skeleton-forming elements in the **silicone resins (polysiloxanes)** are

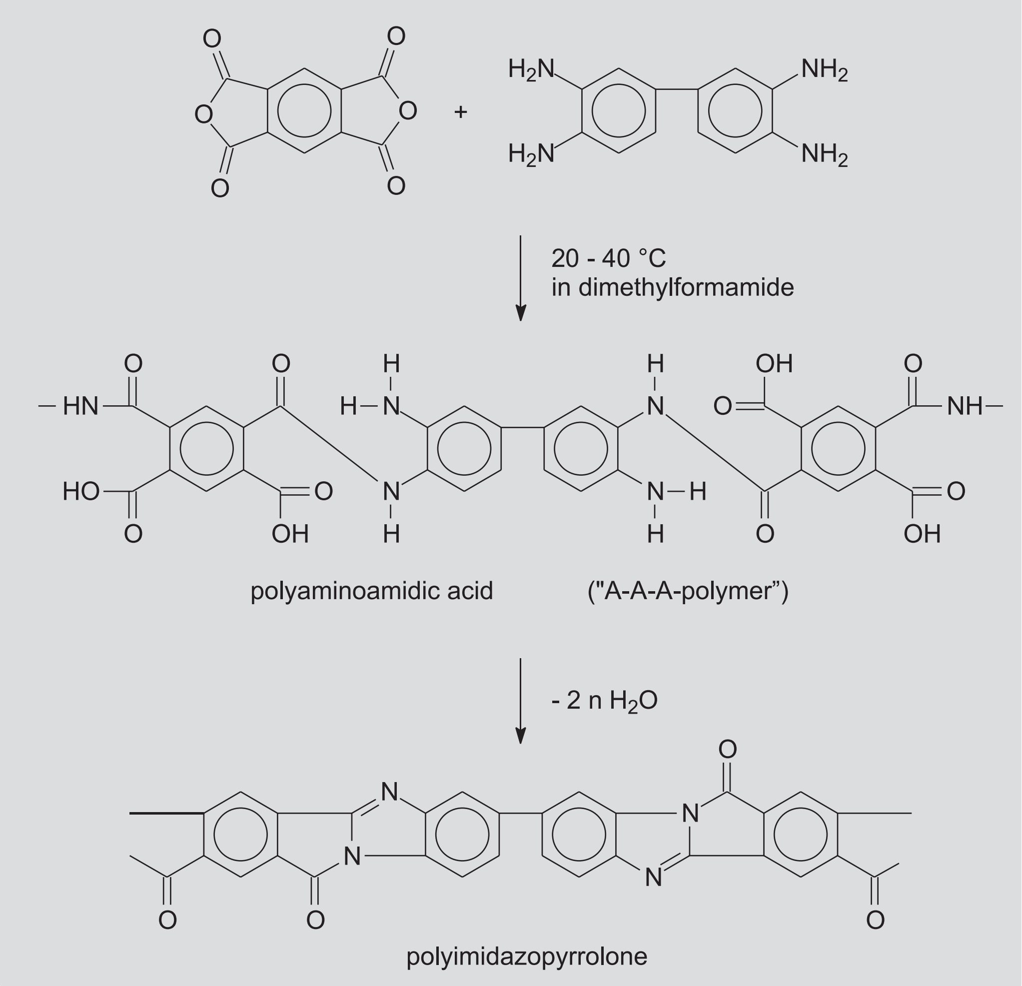


Fig. 2.1.67
Polyimide azopyrrolones from pyromellitic acid and tetraaminobiphenyl

silicon and oxygen. Hydrocarbon groups are found only as substituents in the side chains. Greater stability is achieved because of the higher bond energy of 375 KJ/mol in the alternating silicon/oxygen bonds compared with 340 KJ/mol for the carbon/carbon single bond. The organic alkyl or aryl groups attached to the basic skeleton are always directly connected to the silicon. Depending on the type of basic structural elements, different product groups can be synthesized. This class of substances ranges from liquid to paste-like silicone oils or silicone greases via elastomeric silicone rubbers to solid silicone resins.

Because of their good resistance to longterm outdoor exposure, chemicals and damaging atmospheric effects combined with excellent mechanical/technological properties silicone resins have always proved successful where particularly high demands are made of the coating.

They are important components for coil coatings. Particularly demanding heat resistances are specified in this application because of the high coil speeds and the associated high baking temperatures.

Polysiloxanes are now manufactured exclusively using the *Müller-Rochow* synthesis method [2.4.16]. Extremely finely-ground elementary silicon is reacted with alkyl halides with a cuprous catalyst to form mono-, bi- and trifunctional organosilanes. The individual components are then separated by distillation, before being rejoined in defined mixtures for molecule enlarging hydrolysis, depending on the chemical goal.

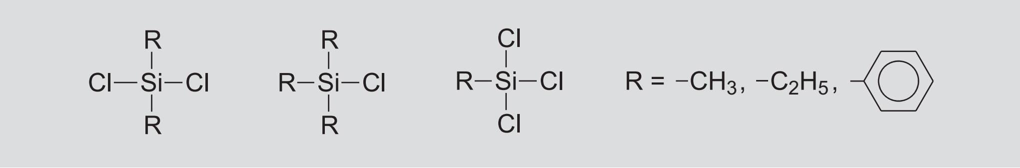


Fig. 2.1.68
Basic components for the synthesis of polysiloxanes

The mixing ratio of the mono-, bi- and trifunctional basic structural elements determine the molecular size and form. Monofunctional chlorosilane terminates chains and thus limits molecular growth, while trifunctional silanes, on the other hand, cause molecules to branch.

The polysiloxanes can be divided into various types, depending on the organic residues bonded to the basic chain. If only the chlorides of methane are used for conversion with silicon, the extremely nonpolar macromolecular silicone oils are obtained. They are neither chemically reactive, nor do they achieve mechanical strength, regardless of their molecular weight. Because of their very low surface tension of 20 mN/m silicone oils or silicone pastes fulfil important roles as additives for wetting, improving flow and defoaming. Their incompatibility with almost all coating resins is also specifically used to create surface textures, such as a hammer finish.

If the bulky and, at the same time, polar phenyl groups are substituted for some of the methyl groups, and steps are taken at the same time to ensure that reactive groups occur at the ends of the chains, compatibility with the standard coating resins improves. The hydroxyl functional chain ends can undergo cocondensation with other hydroxyl-functional reactants either directly or after etherification with methanol. Precondensation with saturated polyesters or OH-functional acrylicresins may be noted in this context. Final hardening can then be carried out with the usual crosslinking resins.

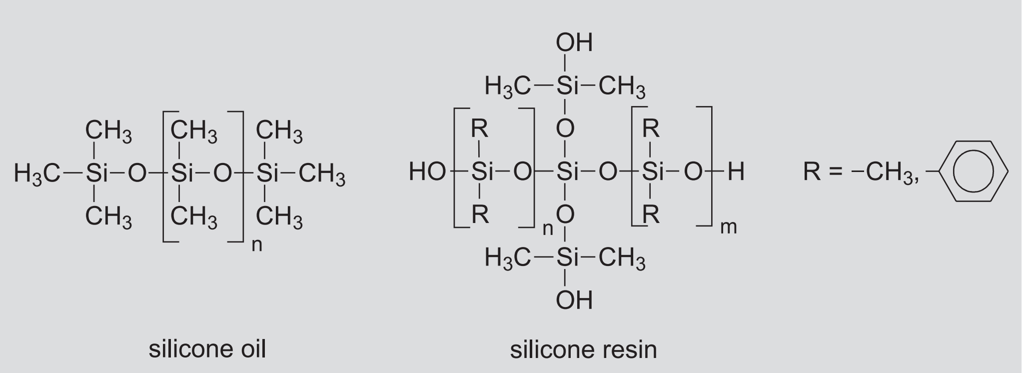


Fig. 2.1.69
Structure elements of silicone oils and silicone resins

Apart from the good properties already described, silicone resins have a continuous heat resistance of between 180 and 200 °C. Even transitory peak temperatures of up to 600 °C can be withstood without any quality impairments.

A further increase in the resistance of polysiloxanes can be achieved by crosslinking with isocyanates. To do this, however, the acidic SiOH groups of the classic silicone resins must be replaced by neutral Si–CH_2–CH_2–OH (see below).

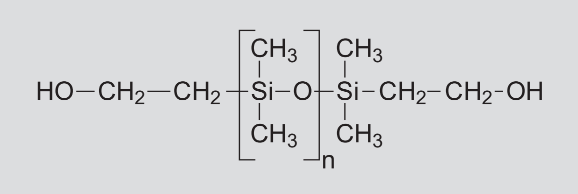


Fig. 2.1.70
Polysiloxanes for hardening with isocyanate crosslinker

Silicone resins are also frequently modified with resins from other classes of substances because of their high price. The mutual chemical bonding of the silicone resins with the modification resins takes place at an early stage of the production process. Important examples of the modified products are silicone polyesters, silicone alkydes, silicone-reinforced epoxy resins and silicone acrylates.

The properties of the modified resins are determined by the initial resins and the proportions in the resin combination. Where the silicone ratio exceeds 50%, the character of the silicone resin is dominant. In these cases the modification results in improved application properties over pure silicone resins with only a slight deterioration in the heat resistance. In the case of silicone resin proportions below 50% the partner's character prevails. Thus the oxidative crosslinking of the paint film consisting of an alkyd resin modified with 30% silicone takes scarcely any longer, assuming standard drying, than with unmodified alkyd resins.

The price of silicone resins limits the use of pure polysiloxanes to applications in which a high resistance to heat and/or longterm outdoor exposure is indispensable. With the exception of certain branches of the electrical industry, this is restricted to the manufacture of ovens, stoves and other goods subjected to extreme temperatures. Recently a further application field has been added, namely the coating of cladding elements which are mounted on façades of high-rise buildings which are difficult to access.

Many of the paint resins described require a reactant to obtain the desired coating properties via crosslinking. **Crosslinking agents** are generally low molecular and high-functional resins. Important crosslinking resins for polycondensation reactions include phenol and amino resins, with the subgroups of urea and melamine resins. Another group of crosslinking agents are the polyaddition isocyanate resins which are described in greater detail elsewhere.

When the chemist *C. H. Meyer*, an employee at *Louis Blumer*, received an order from his brother-in-law, a merchant, to manufacture shellac synthetically, but at the same time also received the incorrect information that shellac as a vegetable product also had to contain phenol and formaldehyde, he could not possibly have known that, despite being given inaccurate information, he would succeed in manufacturing a resin that was extraordinarily similar to shellac, i.e. a secretion from an insect known as a lac and thus demonstrably an animal product. Despite the fact that the product was synthesized on a completely incorrect basis, the supposed imitation shellac was to go down in history as the first synthetic coating resin [2.4.17]. Not by Mr. *Meier*, however, but by the Belgian *Baekeland* who, after refining the synthesis of the phenolic resin class of substances under the name Bakelite, was able to introduce the world to the first solid plastic [2.4.18]. Although a few decades earlier, under different circumstances and with a different objective, *Adolf von Bayer* had failed to synthesize phenolic resins [2.4.19], *C.H. Meier* succeeded in isolating a chemically inert synthetic resin which was soluble in polar solvents by mixing phenol with a mistakenly low volume of formaldehyde. The new coating was named Novolak. Today it is regarded as the original resin in a now large class of resins with important descendants in coating technology.

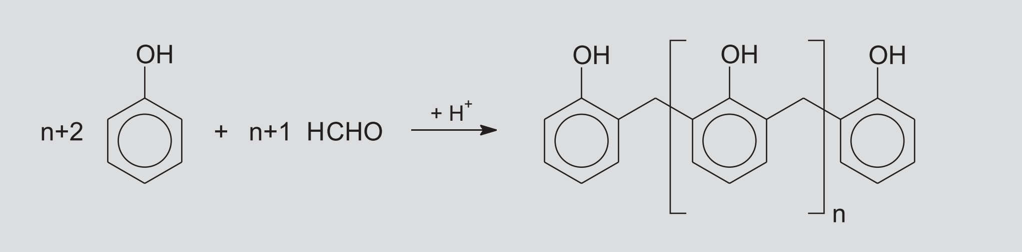


Fig. 2.1.71
Synthesis of novolak from phenol and formaldehyd

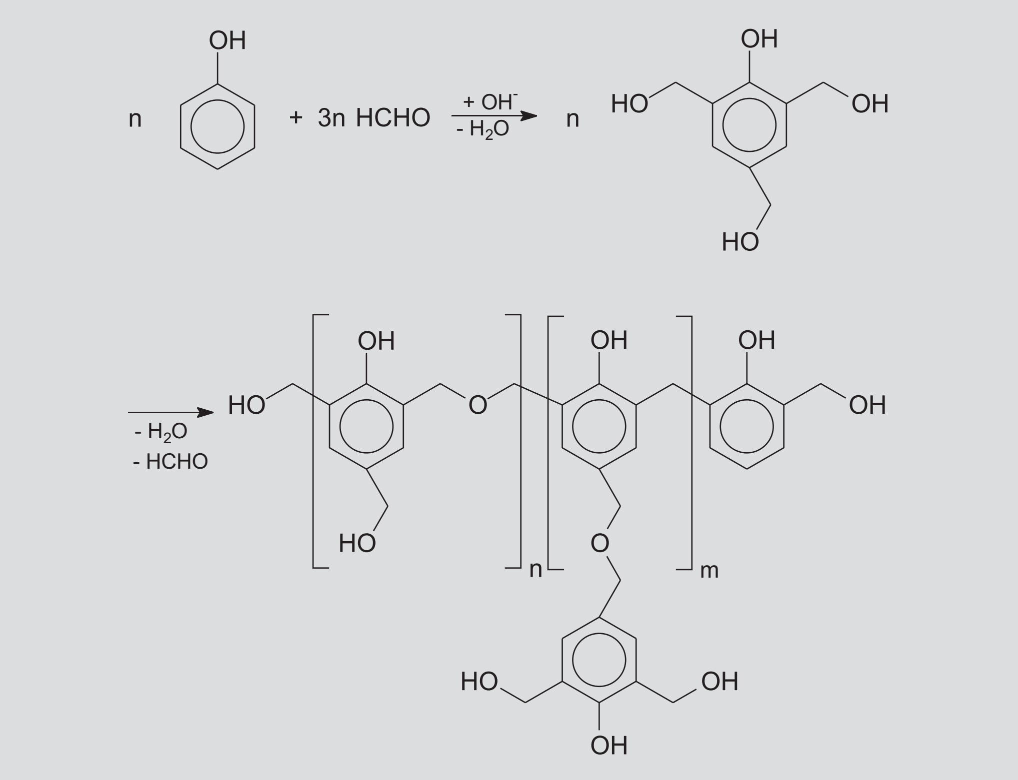


Fig. 2.1.72
Synthesis of resols from phenol and formaldehyde

The synthesis of Novolaks from phenol and formaldehyde succeeded despite the high reactivity of the reaction mixture because the reactants' mixing ratio only permitted a limited molecular size.

The electrophilic addition of formaldehyde to the phenol body is continued by a subsequent polycondensation stage to form Novolak.

If the proportion of formaldehyde is increased during the synthesis process, this results in premature crosslinking and the product therefore becoming unusable because of the trifunctionality and high reactivity of the phenol in the acid environment.

Only when scientists learned to slow the reaction rate down by increasing the pH value such that intermediate stages of the polycondensation processes could be stabilized by premature cooling, was the now more important subgroup of the resols invented.

Resols contain hydroxymethylene groups and are therefore reactive resins which can self-cure to become resites by heating or acid catalysis.

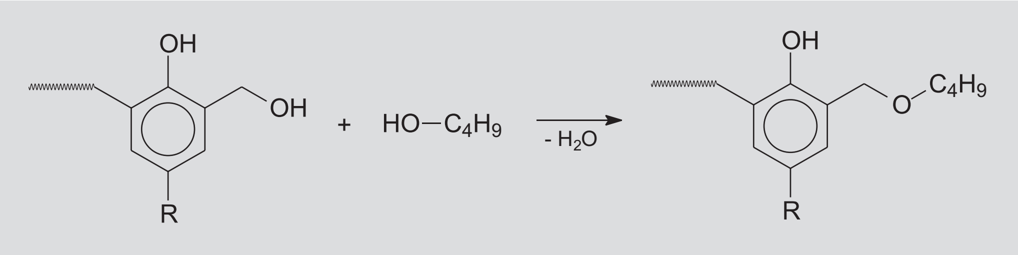


Fig. 2.1.73
Etherification of resols with butanol

Phenolic resins are less suitable for use as sole film forming agents because of their poor elasticity. However, an additional modification is needed if they are to be mixed with elasticizing OH-functional alkyd resins or saturated polyesters.

To improve compatibility, reduce the tendency to self-condensation and to achieve addition elasticity phenolic resins must be etherified with aliphatic alcohols.

The variety of phenolic resins commercially available today is the result in part of the different types and levels of etherification. These determine reactivity, compatibility with other resins and solubility. Moreover, there has been no shortage of attempts to manufacture further variants by using additional raw materials and modifying the base resin.

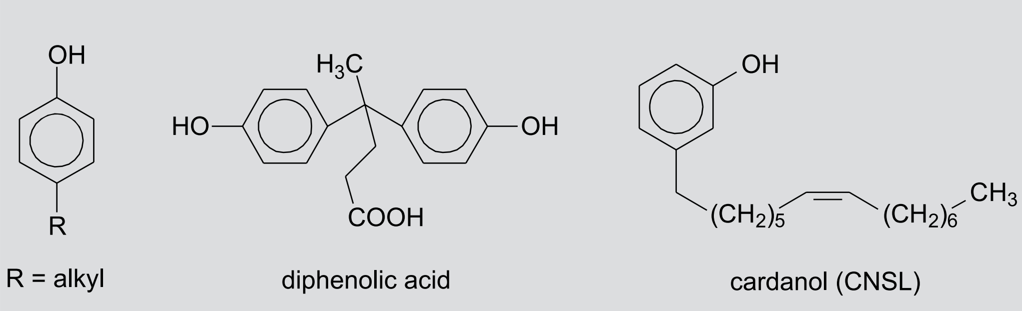


Fig. 2.1.74
Phenolic derivatives as components for phenolic resins

Replacing phenol with alkylphenol results in a reduction of functionality and, depending on the type, position and length of the alkyl groups, permits the polarity to be lowered. The improvement in compatibility with nonpolar oils should also be noted in this regard. An opposite effect is achieved by incorporating diphenolic acid (DPA), a conversion product from laevulinic acid and phenol. Such products are converted into phenolic resins which are watersoluble but, at the same time, are stable when stored after neutralization of their carboxyl groups.

After modification with cardanol, a natural material from cashew nuts (CNSL = cashew nut shell liquid), phenolic resins even have oxidatively curing properties.

The conversion products of resols with colophony or maleic resins, termed artificial copals, which are modifications of already manufactured phenolic resins, are worth noting.

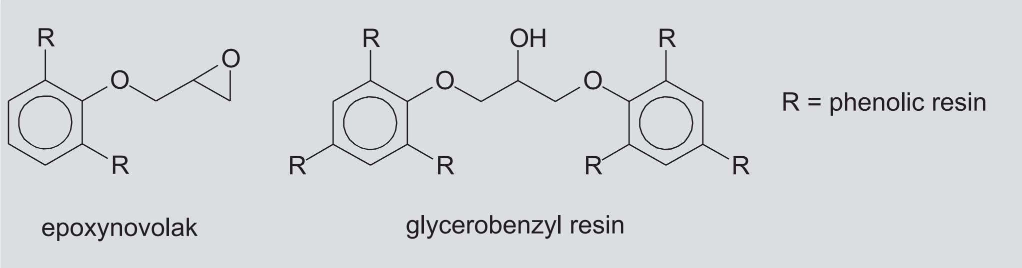


Fig. 2.1.75
Alkali resistant phenolic resins by modification of the phenolic group

During the production and processing of phenolic resins the acidic phenol group remains chemically unchanged. Despite chemical crosslinking, therefore, films made of cross-linked phenolic resins are alkali-unstable. Alkali stability can be generated by chemical inactivation of the phenol group. Transesterifications with acetyl chloride or trans-etherifications with epichlorohydrin have proved successful. The latter result in epoxy novolaks containing epoxy groups or in the hydroxyl-functional glycerobenzyl resins, as a function of the stoichiometric ratio of the reactants.

In general, phenolic resins today are found in numerous applications because of their good acid stability, hardness, adhesion and electrical insulation capability. They deserve mention both as coatings for receptacles and for their watersoluble variant for electrocoat

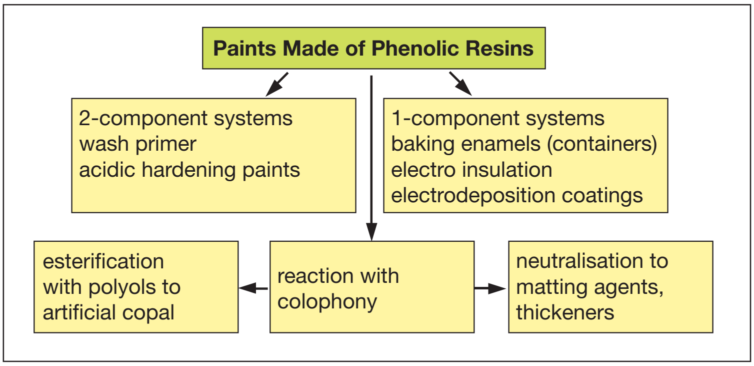


Fig. 2.1.76
Application of phenolic resins

paints. When combined with polyvinyl butyral (see below) and phosphoric acid they are known as wash-primer and offer effective anticorrosive protection as primer coats for untreated steel or ground areas. In combination with alkyd resins and epoxy resins they are also important film forming agents for baking enamel primers and primer surfacers processed on an industrial scale.

Since phenolic resins require relatively high baking temperatures of 180 °C and they display marked yellowing at the same time, there has been no shortage of attempts to develop more reactive and, at the same time, more color-stable alternatives. Urea, melamine, benzoguanamine, various urethanes and recently also glycoluril are the preferred materials from the broad range of products tested to replace phenol in reaction with formaldehyde. They are all nitrogen-containing compounds with reactive amino or amido groups and can readily be converted to corresponding methylol compounds with formaldehyde. Molecular enlargement can be achieved, if required, by subsequent self-condensation. The reactivity of aniline and alkyl-substituted benzoles with formaldehyde has also been investigated, but these materials remain only suitable for exotic niche markets because of their different chemical properties.

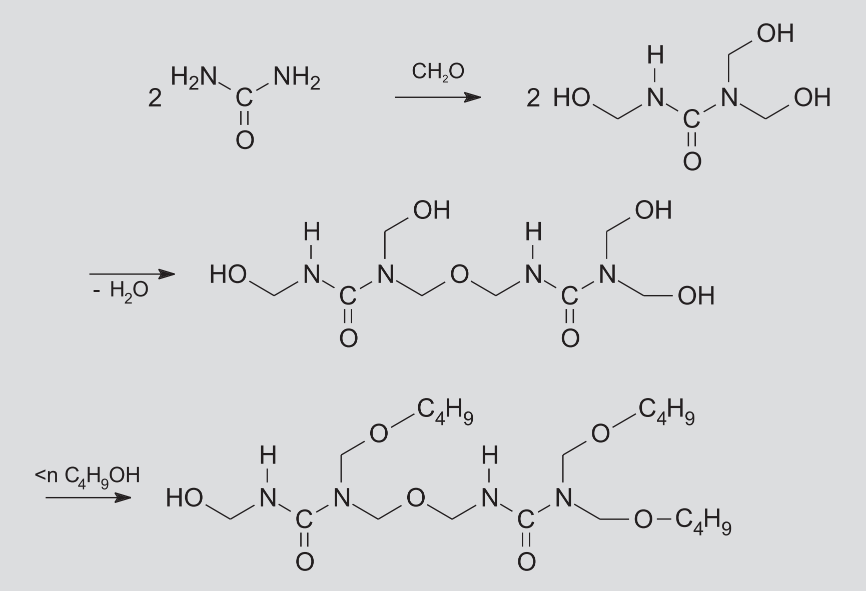


Fig. 2.1.77
Synthesis of partially etherified urea resins

Urea resins, which are mostly highly etherified at varying levels with butanol and have varying degrees of methylolation by formaldehyde, generally occur in solution in butanol. Commercially available urea resins are relatively low molecular products with molecular weights < 1000 g/mol.

Intramolecular dehydration and following ring formation resulting in hexahydrotriazine as a secondary reaction during manufacture is the reason that the functionality of the urea resins is lower than would be anticipated from the chemical structure of the urea.

Urea resins are not used as sole film forming agents because of the brittleness of their films and because of a lack of resistance to water. These properties together with the

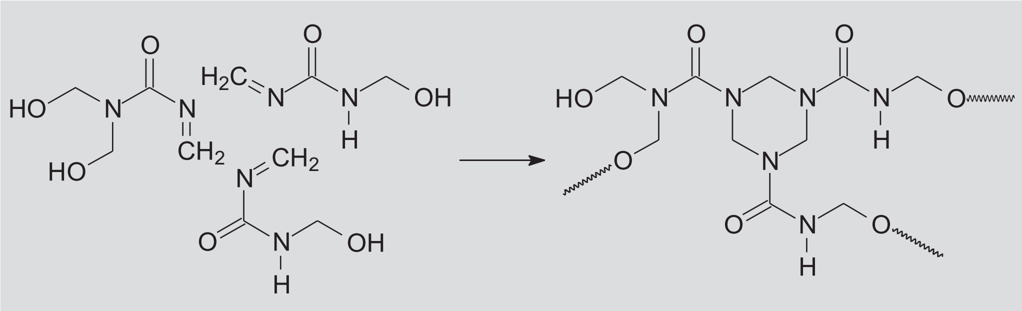


Fig. 2.1.78
Side reaction during synthesis of urea resins

fastness to light and sandability are improved when combined with soft resins and cellulose nitrate. When used in acid-curing paints, plasticizing is generally carried out with alkyd or polyester resins. The most common partners of etherified urea resins in baking enamels are lean to semi-fatty hydroxyl-functional alkyd resins.

Urea resins can be elasticized while improving their compatibility at the same time by precondensation with saturated polyesters. This results in the plasticized urea resins which can be used in all relevant application fields which require acid-curing or thermally reactive products, and can also be used as sole binders.

Urethane resins, which are similar to urea resins, are reaction products of esters of carbamic acid. Because of the bifunctionality of the initial materials only linear structures are possible. They remain soft and elastic up to high molecular weights. Their plasticity increases with the chain length of the carbamic acid ester. Urethane resins are only used as modifying agents in combination with other resins, for example as elasticizing agents for acid-curing urea resins.

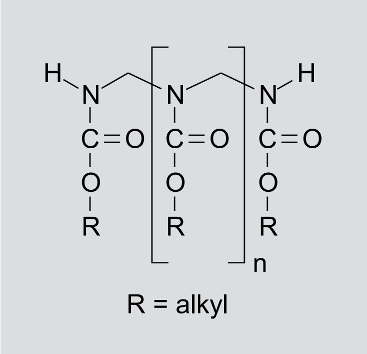


Fig. 2.1.79
Chemical structure of urethane resins

A higher crosslink density compared with the urea resins can be obtained by replacing urea with its maximum functionality of four by the hexafunctional melamine. This is readily obtained by conversion of urea with carbon dioxide and is thus an inexpensive raw material.

The target properties during the production of melamine resins are influenced by the mixing ratio of melamine to formaldehyde, usually between 1:3 and 1:6, the etherification alcohol and the degree of etherification.

Different molecular weights occur as a function of the reaction conditions.

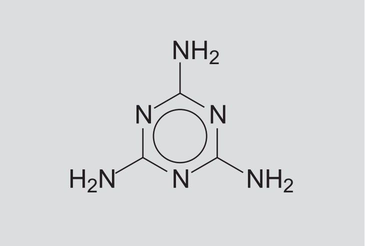


Fig. 2.1.80
Melamine (2.4.6-triamino-1.3.5-triazine)

Whereas polynuclear classic melamine resins are condensation products which consist of 5 to 6 melamine structural elements and are partially etherified only with butanol to achieve a sufficiently high reactivity and compatibility with standard solvents, a different route is followed with regard to molecular structure with today's melamine resins.

A new generation of low molecular, in the most extreme case even mononuclear, products which are highly etherified with methanol has been created to improve compatibility with polar saturated polyesters up to watersoluble reactants. Because of their low molecular mass they are liquid and at the same time they are soluble in both organic solvents and in water.

High solid and waterbased paints are therefore formulated with these melamine resin variants.

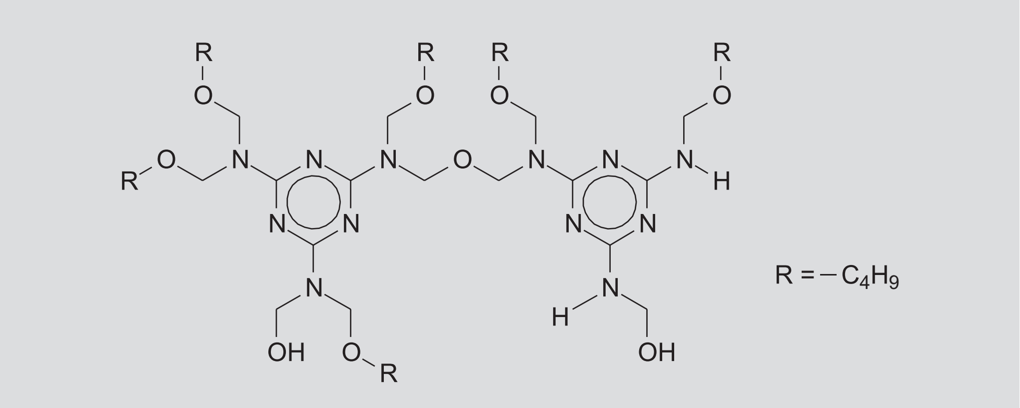


Fig. 2.1.81
Condensated melamine resin for crosslinking OH-functional base resins

If we add that a high etherification level lowers the unwanted selfcondensation during crosslinking with hydroxyl-functional reactants, the importance of the new melamine resin class such as hexamethoximethyl melamine (HMMM) is underlined from a quality perspective, too.

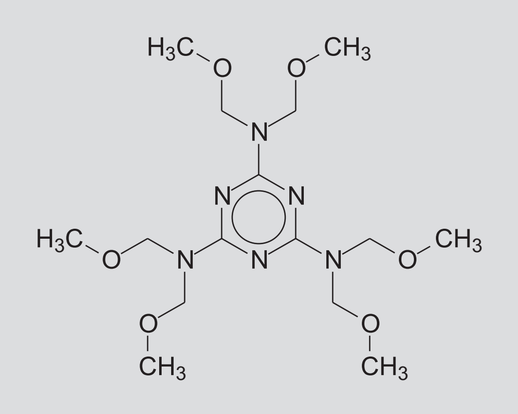


Fig. 2.1.82
Hexamethoximethyl melamine (HMMM)

The lower reactivity which is a consequence of the high etherification level must be equalized by acid catalysis with carboxyl groups of the reactant or by separately added acids.

Since the important baking enamels processed on an industrial scale are exclusively melamine resin combinations with short-oiled alkyd resins, saturated polyesters or OH-functional acrylicresins whose crosslink density determines the quality, particular attention must be paid to the etherification level. While the capability for external crosslinking increases with rising etherification level, the thermal reactivity shows a marked deterioration.

A low etherification level results in stability problems during storage because of the tendency towards self-condensation.

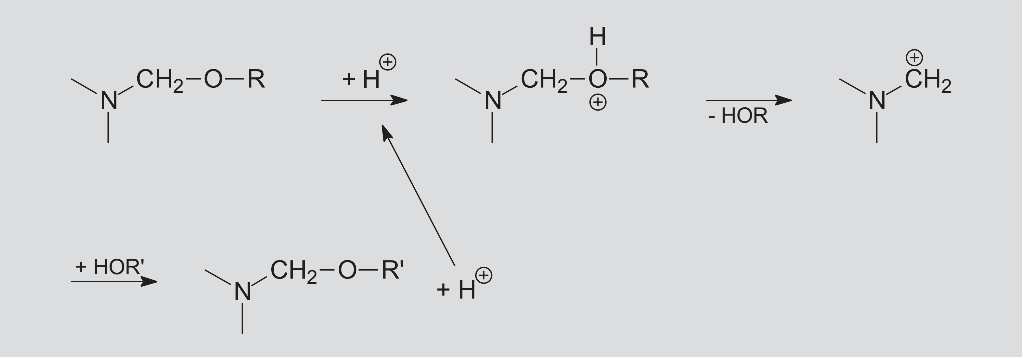


Fig. 2.1.83
Reaction scheme of crosslinking highly etherified melamine resins with OH-functional resins

If watersoluble reactants are used as the reactants for melamine resins, it is important to ensure that the carboxyl groups resulting in solubility in water react with the melamine resins during the baking process to improve longterm outdoor exposure properties. Only if this is the case a quality level can be achieved with the coatings which is comparable to that of classic solventbased coatings.

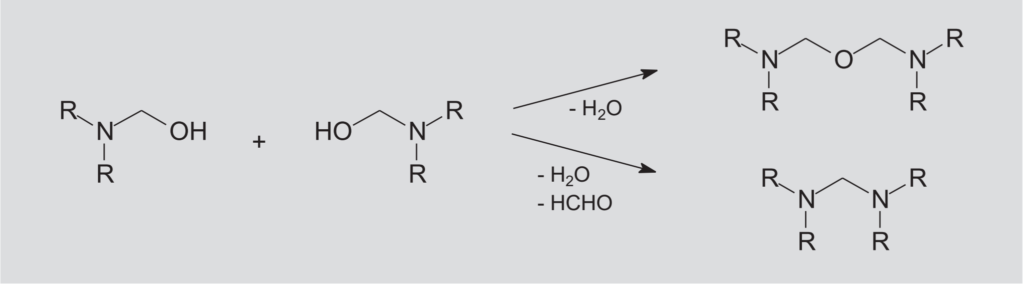


Fig. 2.1.84
Selfcondensation reaction of melamine resins

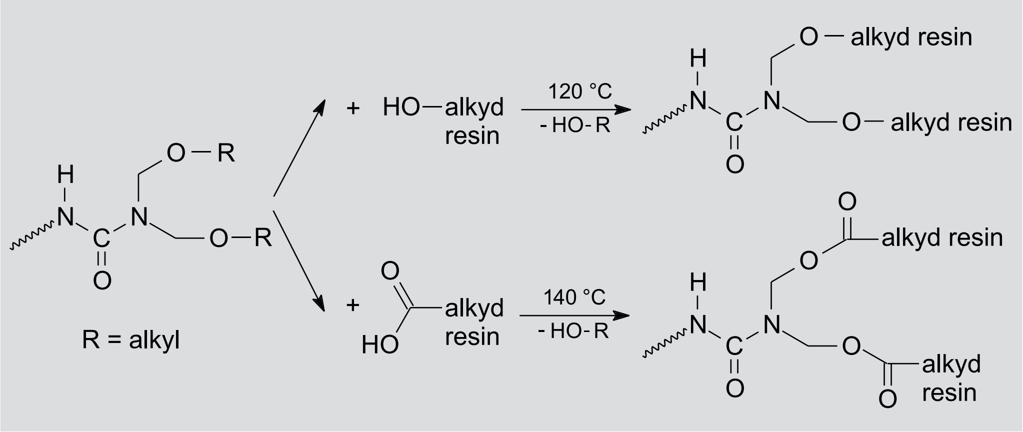


Fig. 2.1.85
Crosslinking of melamine resins with OH-functional resins and acidic resins

Since, however, the activation energy for the conversion of melamine resins with carboxyl groups is significantly higher than for conversion with OH groups, higher baking temperatures must be set when baking waterbased materials.

Measurable quantities of formaldehyde are released during the thermal crosslinking of melamine resins. In partially etherified melamine resins up to two per cent of the melamine resin content can be formed by free formaldehyde. With the more highly etherified alternatives it is now possible to reduce this formaldehyde cleavage to less than 0.1%. A concomitant feature of this is the reduction in the overall quantity of cleavage products during the baking process, which in turn results in a fall in the formation of gloss-reducing microstructures in the surface of the coating. The outcome is an improved appearance.

In general, coatings with melamine resins result in improved longterm outdoor exposure, water resistance, gloss retention, resistance to saline fog and excellent hardness because of their higher crosslink density with, at the same time, a lower baking temperature compared with urea resins.

New application found melamines as reaction partners for carbamate functional acrylic resins. The thermal crosslinking leads to polyurethane groups avoiding isocyanate precursors. Due to the excellent weatherability characteristics and mechanical properties of the films together with the simple use as 1-component paints those systems gain increasing interest in the automotive industry [2.4.20]

Usable resins can also be synthesized for coatings from **benzoguanamine** or **glycoluril** in corresponding fashion to the manufacture of phenolic resins, by conversion with formaldehyde. Compared with classic melamine resins, benzoguanomine resins improve the flow, gloss and adhesion of the coating, though at the same time causing a deterioration in the longterm outdoor exposure.

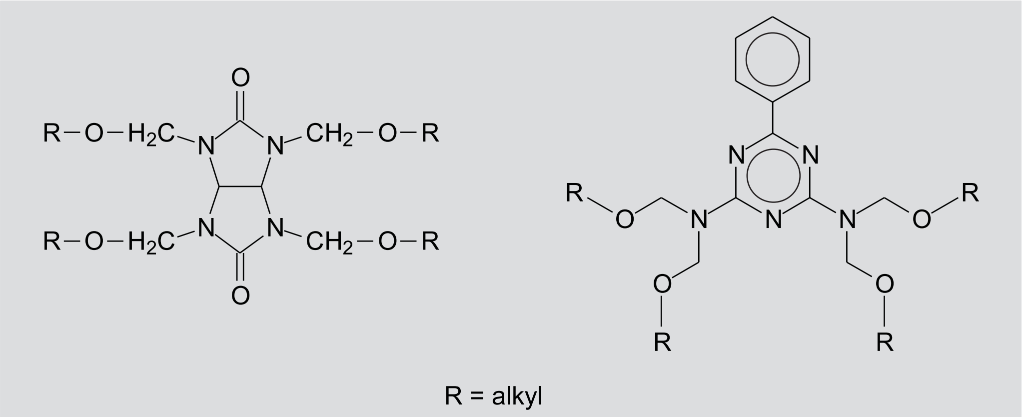


Fig. 2.1.86
Glycoluril and benzoguanamine resins

Glycoluril, a reaction product of glyoxal and urea, permits the synthesis of mononuclear, highly etherified crosslinking resins with good storage stability and excellent adhesion to metallic substrates. Less formaldehyde is released during processing, and anticorrosive protection improves at the same time.

Other, admittedly exotic, reactants for formaldehyde are sulphonamides and alkyl-substituted benzene bodies. While, for example, toluene-p-sulphonamide reacts in accordance with expectations in the first reaction stage with formaldehyde, there then follows a practically quantitative trimerization to a stable sulphonamide resin which is principally used as a modifying resin because of its fastness to light, solubility and compatibility with other paint resins.

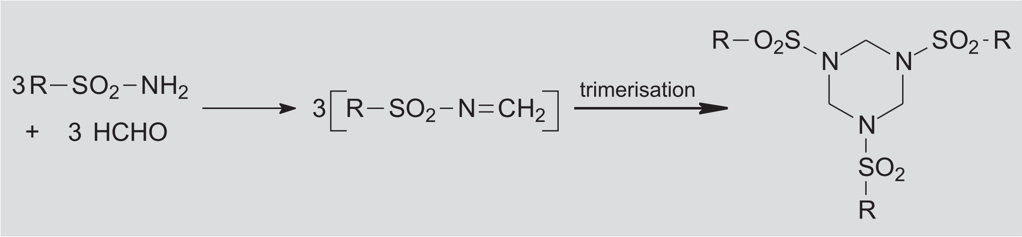


Fig. 2.1.87
Trimerization of methylolated sulphonamide resins

The reactivity scheme of aniline is similar. Here, too, triazine rings are first formed as a result of the action of formaldehyde. By contrast with sulphonamide resins these can be opened by a thermal load above 140 °C with the formation of long chains. The reaction product remains thermoplastic, is lightfast and displays interesting dielectric properties. These products are therefore mainly used for electrical insulation.

If, on the other hand, substituted benzenes such as toluene or xylene are converted with formaldehyde, the result can be the substitution of reaction products in the ring under extreme reaction conditions. These have similar properties to phenolic resins. These products are used almost exclusively as modifying agents in the printing ink sector.

Ketones, too, which contain activated methylene groups next to the carbonyl group, can be converted with formaldehyde. These resins are primarily used as binders for adhesives and printing inks.

In addition to conversion with formaldehyde, cyclohexanone can also be transformed into usable paint resins by self-condensation. Converting the oxygen in the carbonyl group with the reactive hydrogens in α-position also results in lightfast and, at the same time, nonsaponifiable resins with good compatibility.

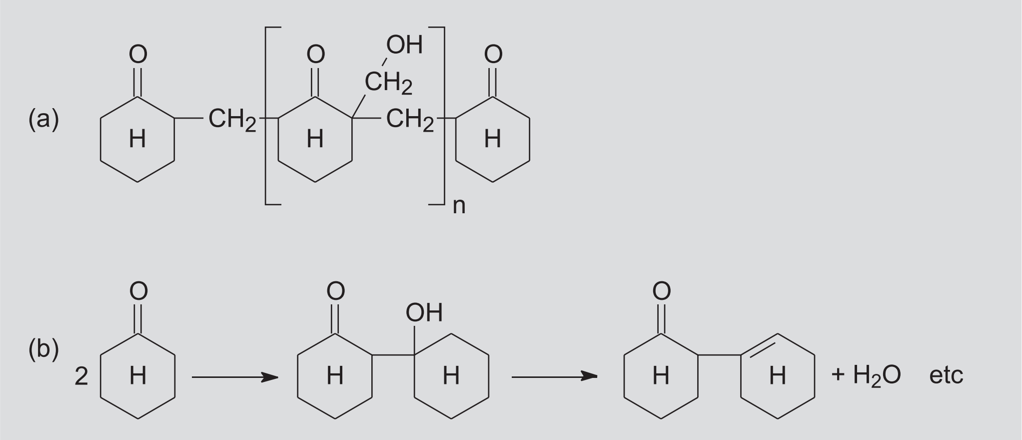


Fig. 2.1.88
Ketone resins from cyclohexanone with (a) and without (b) formaldehyde

Polyaddition resins

Polyaddition is a step reaction in which the reactants join to form macromolecules without, by contrast with polycondensation, releasing low molecular fragments. Molecular enlargement is achieved by transferring a hydrogen atom to the reactant while forming new bonds at the same time. Such polyaddition resins from only two classes of substances have achieved any technical importance. These are the **polyurethanes**, which can be formed from OH-functional and isocyanate-containing structural elements, and the **epoxy resins** which react with amines or carboxylic acids.

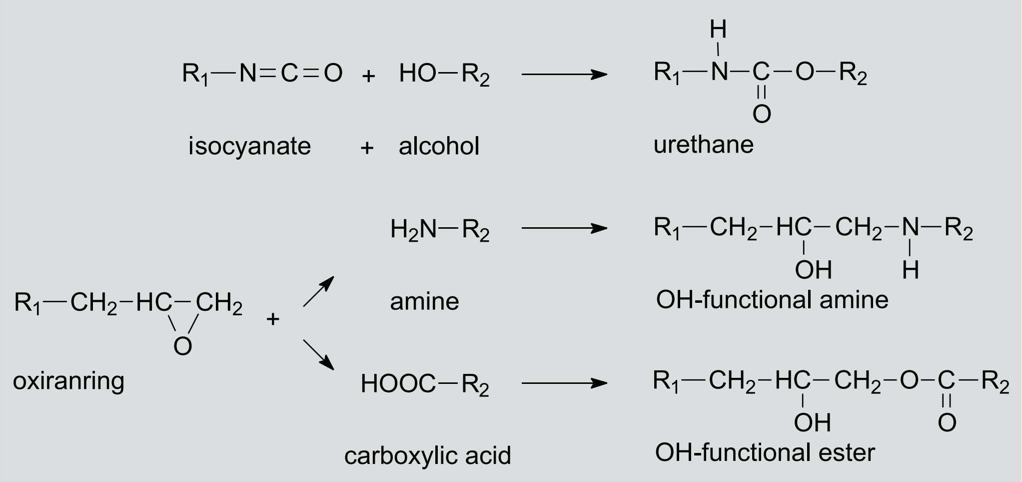


Fig. 2.1.89
Basic reaction of the most important polyaddition resins

After molecular mixing of the two components both classes of substances can react and enlarge their molecules at room temperature. Coating materials made from them are mostly formulated as 2-component systems.

When *O. Bayer* transferred the reaction of ethanol with ethyl isocyanate described as long ago as 1849 by *Wurtz* to polyfunctional structural elements in 1940, he laid the foundation for the new class of substances known as the **polyurethanes** [2.4.21]. They exceeded the quality levels in terms of elasticity and resistance to saponification of the polymers known at that time and were consequently able to establish themselves quickly for use in plastics, adhesives and coatings.

The conversion of resins containing hydroxyl groups with the isocyanate hardener results in the formation of urethane groups. Because of the high reactivity of the isocyanates, the manufacture of polyurethanes also incorporates numerous secondary reactions, depending on the reaction conditions and the choice of raw materials.

In the event of an excess of the isocyanate hardener, this can continue to react to form allophanates because of the active hydrogen in the urethane group. Isocyanates also react with ambient humidity. The resulting unstable carbamic acid is transformed by decarboxylation into a primary amine. This in turn is able to form urea or biuret structures in the event of an excess of isocyanate hardeners. When acid resins, for example polyester resins, are used, account must also be taken of the carboxyl groups which are reactive with isocyanates. The adduct which is first formed quickly

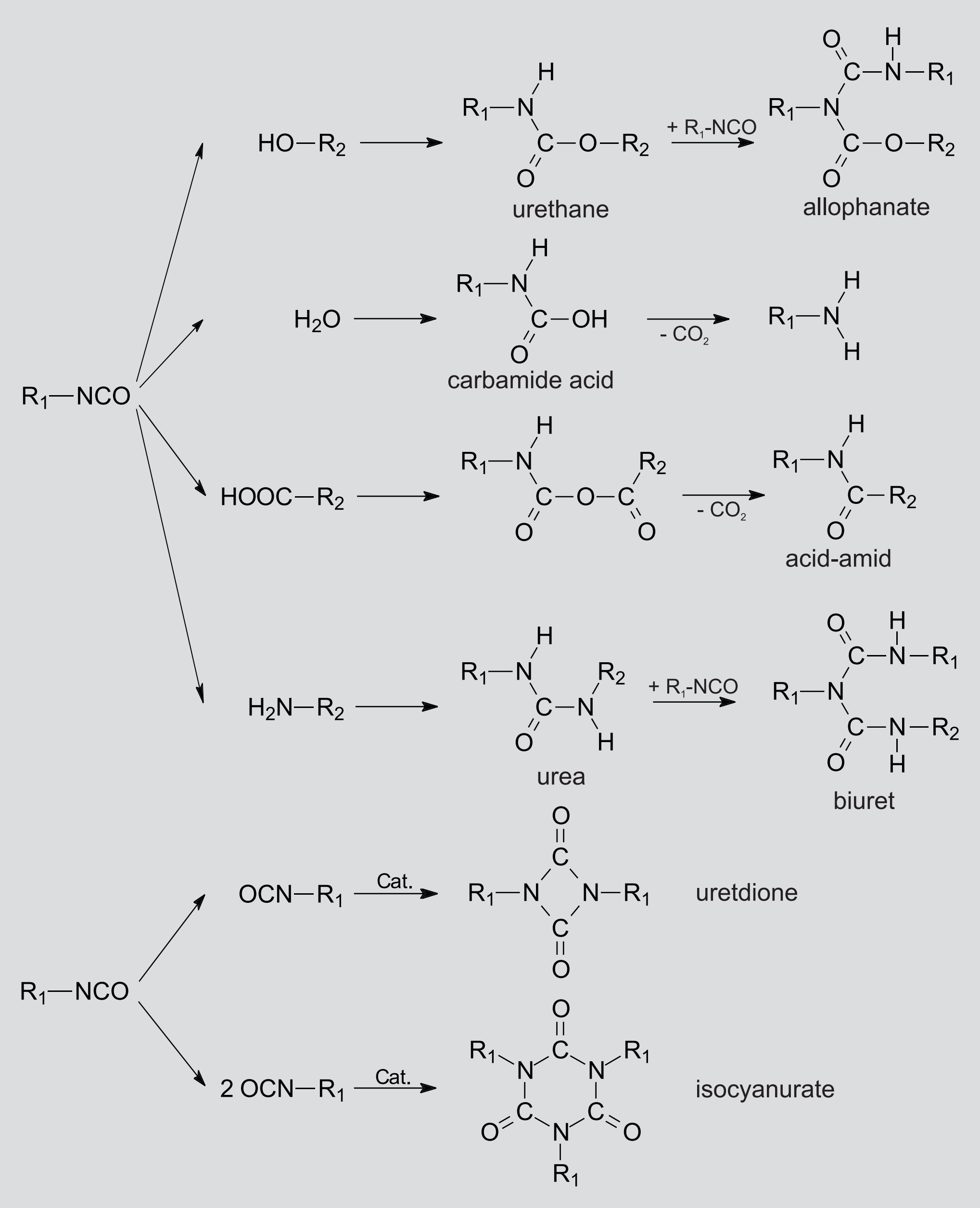


Fig. 2.1.90
Main and side reactions during manufacturing of polyurethanes

decarboxylates into an acid amide. It is therefore recommended that polyesters with as low an acid value as possible be used. Two further isocyanate reactions result in commercially available hardeners. This is because, depending on reaction conditions and the type of catalyst, isocyanates can trimerize into uretdiones or isocyanurates into diuretdiones. Whereas the isocyanurate ring is only split back into its initial materials at temperatures > 300 °C, the uretdione is split at temperatures > 140 °C. Uretdiones are therefore proven thermoreactive reactants for OH-functional resins (see figure 2.1.90).

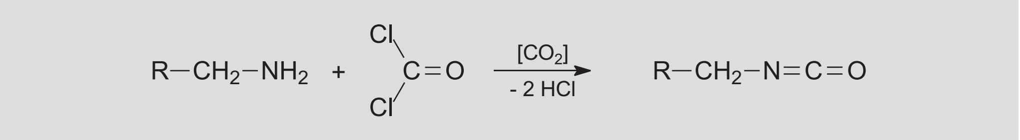


Fig. 2.1.91
Synthesis of isocyanates from phosgene and amines

Large-scale synthesis of isocyanate hardeners is generally achieved by converting primary amines with phosgene using CO_2 as a catalyst.
Because of moves to replace chlorine processes, phosgenefree synthesis processes are gaining in importance. They are based on the thermal decomposition of appropriate carbamic acid or urea derivatives [2.4.22].

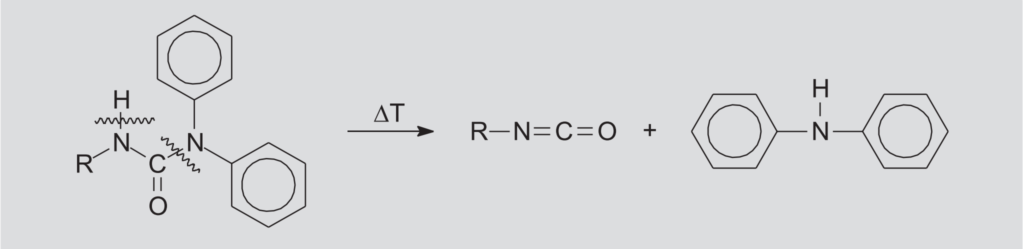


Fig. 2.1.92
Synthesis of isocyanates by thermal degradation of derivatives of urea

The rate of curing of polyurethane coatings is essentially determined by the reactivity of the isocyanate group. The electrophilic property of the carbon in the isocyanate group is the deciding factor. The first attack is by the electrophilic carbon of the isocyanate on the OH group of the reactant. The urethane group is formed by the subsequent transfer of the hydrogen atom from the hydroxyl group to the nitrogen in the isocyanate group. Since aromatic rings on the nitrogen of the isocyanate group increase the carbon's electrophilic property through electron attraction, aromatic isocyanates are substantially more reactive than aliphatic ones.

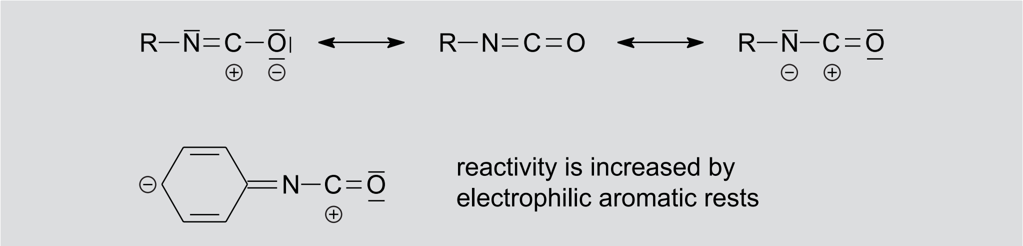


Fig. 2.1.93
Structural impact for the reactivity of isocanates

By contrast, the influence of the OH-functional resin component on the reaction rate can be rated as low. The reactivity of secondary hydroxyl groups, which is higher in principle, is frequently overcompensated for with reference to the primary groups by steric hindrance.

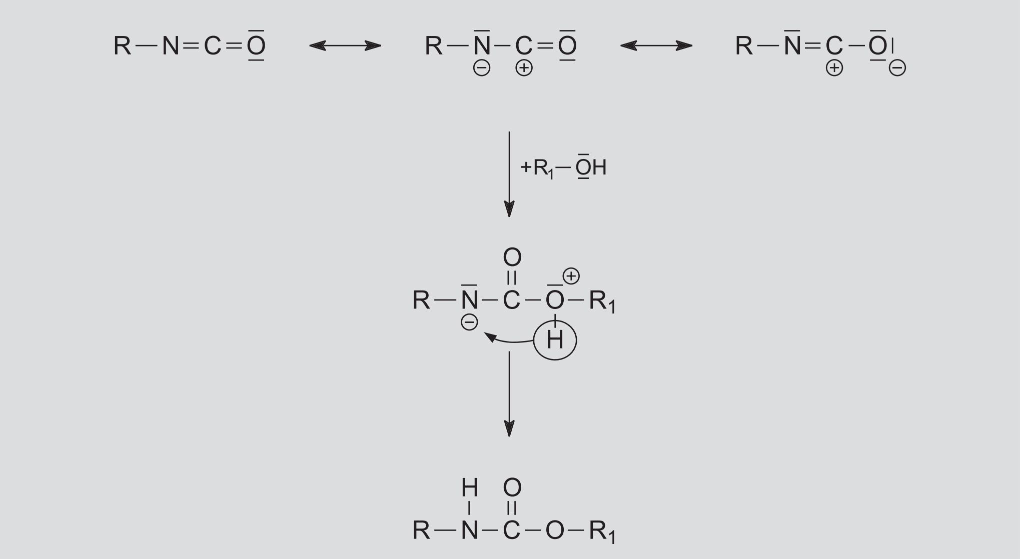


Fig. 2.1.94
Reaction scheme of crosslinking isocyanantes with OH-groups

Countless types of hardener are available commercially because of different requirements of polyurethane paints. These in turn are manufactured from 2-functional basic structural elements by molecular enlargement with a simultaneous increase in functionality. Important basic materials for aromatic hardeners are toluylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) and xylilene diisocyanate (XDI).

The manufacture of aliphatic or cycloaliphatic hardeners usually involves hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) or H_{12}MDI, a hydrated variant of MDI.

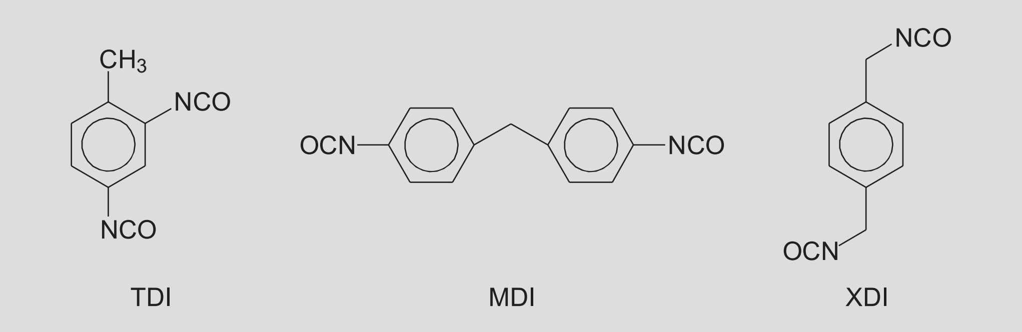


Fig. 2.1.95
Aromatic diisocyanates as basic compounds for crosslinkers

The disadvantage of the lower reactivity of aliphatic isocyanates can be more than equalized by appropriate catalysts.

The isocyanates described cannot be used as raw materials for paints because of their low molecular weight, high vapour pressure and the associated potential physiological hazard, e.g. an occupational exposure limit (OEL) for HDI of 0.01 ppm (see chap. 5.4).

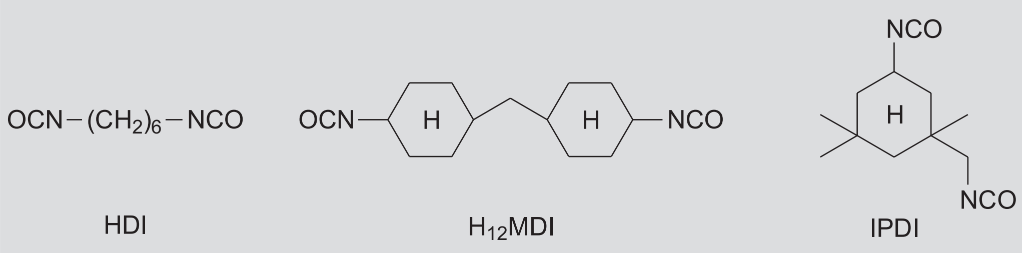


Fig 2.1.96
Aliphatic diisocyanates for nonyellowing and weather resistant polyurethane coatings

An additional molecular enlargement step should therefore be carried out. This can be done using appropriate reactants or by adduct formation with itself. Practical examples include the conversion products of TDI with trimethylolpropane (TMP) or the triadduct of HDI after its partial hydrolysis with water.

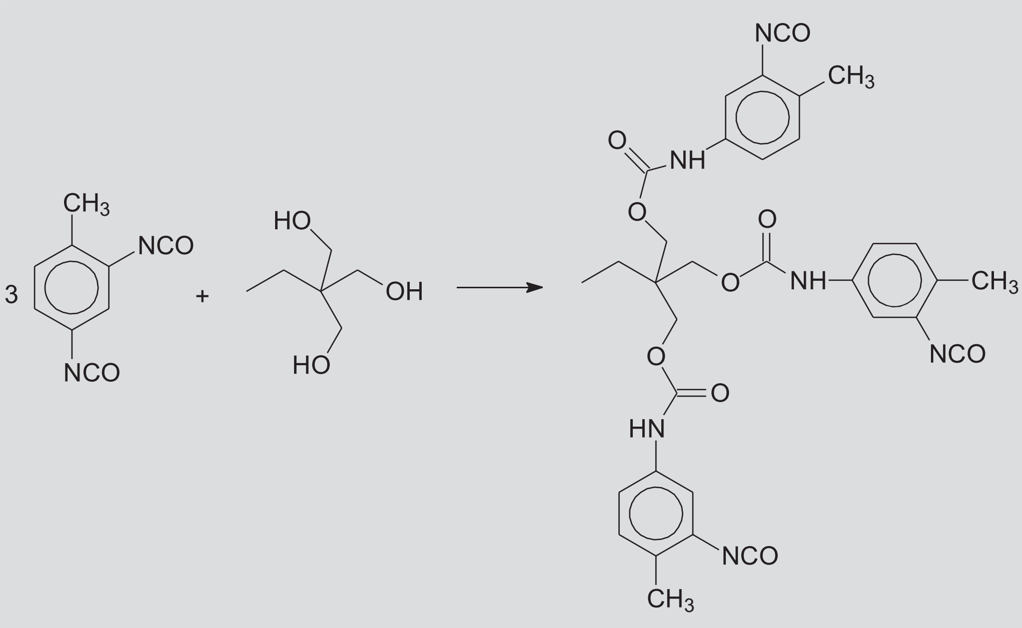


Fig. 2.1.97
Synthesis of higher molecular weight isocyanate crosslinker by forming adducts with trioles

Important adducts from a coating perspective also include the isocyanurates of HDI or IPDI as well as those formed from mixtures of HDI with TDI.

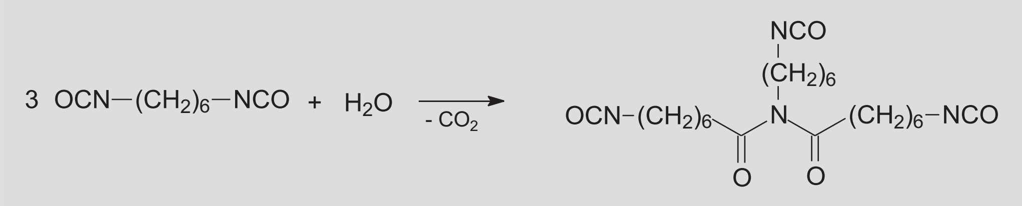


Fig 2.1.98
Growth of molecular size by partially saponification of hexamethylen-diisocyanates (HDI) with water

Saturated polyesters and polyacrylates are of similar technical importance as resins for the OH-functional parts of the generally 2-component paint formulations, known as base-paints. To further improve the chemical and weather resistance of the already excellent polyurethanes, the polyols required to manufacture the hydroxyl-functional base resins can be achieved with fluorine groups. Provided no extreme demands are placed on the resistance to yellowing, even alkyd resins are appropriate partners as oil modified polyesters.

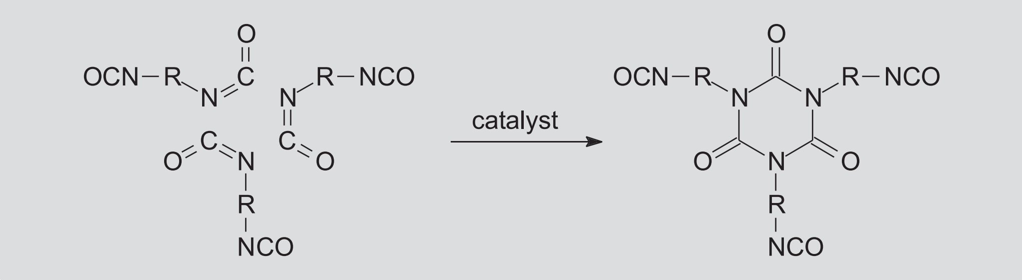


Fig. 2.1.99
Growth of molecular size of isocyanates by trimerization

Because of the reactivity of the isocyanates and the chemical reaction between mixtures of the base-paints and hardener which therefore begins even at room temperature, common polyurethane coatings have only a limited pot life. A proven performance indicator is the time taken for the processing viscosity to double.

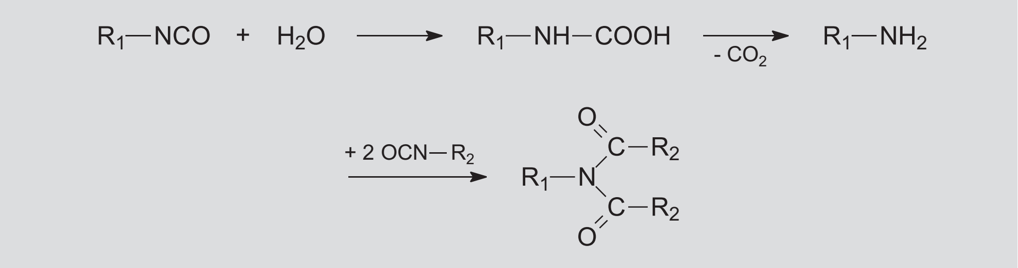


Fig. 2.1.100
Classical hardening reaction of polyurethane resins by water

Both components of polyurethane coatings in the preparation for a 2-component system must be extremely accurately metered and homogenized for processing. So if large quantities of materials are being processed, suitable metering and homogenization systems are required (see chapter 4.2.1). This additional expense is more than compensated for in many applications, e.g. for automotive refinish paints or aircraft paints, by the advantage of rapid curing at room temperature

Because of the technical input and the additional sources of errors when metering and homogenizing, countless attempts have been made to process polyurethanes as 1-component coatings too. One means of achieving storage-stable 1-component systems consists of involving the ambient humidity in the film formation of resins which have no OH groups. The isocyanate groups are partially hydrolyzed by water and converted through decarboxylation into amines with which excess isocyanate crosslinks.

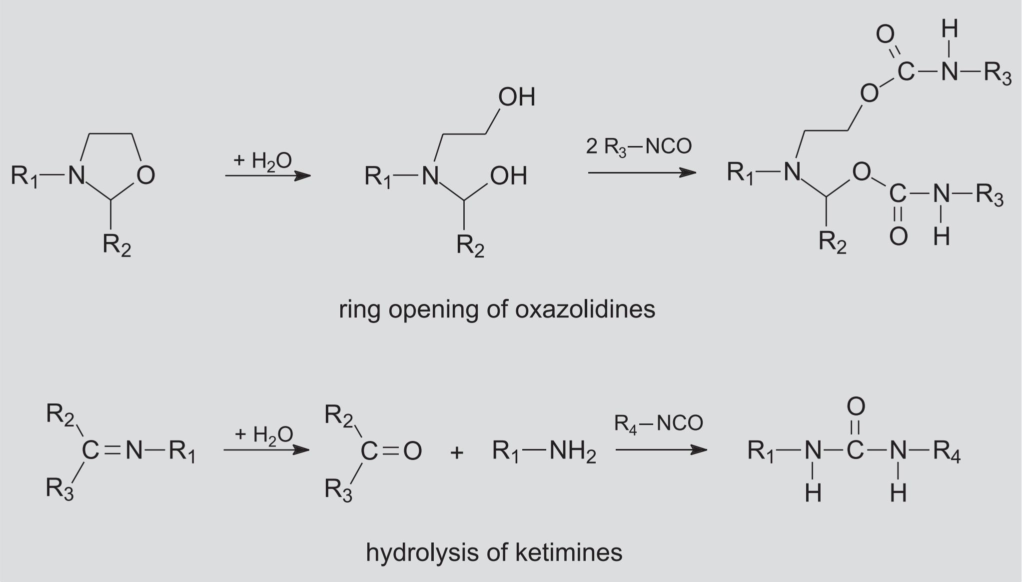
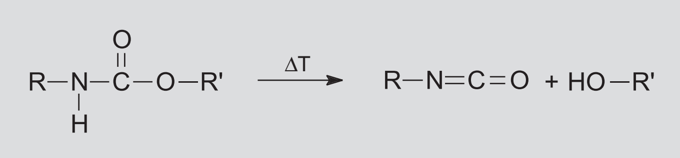


Fig. 2.1.101
Hardening reaction of polyurethane resins with water in presence of oxazolidines or ketimines

In addition to these classic systems a new generation of humidity-hardening polyurethane coatings has been developed. Since ketimines, aldimines and also oxazolidines react more quickly with ambient humidity than the isocyanates, but are not reactive with isocyanates because of a lack of active hydrogen atoms, corresponding paints can be processed as 1-component systems. The ambient humidity which is permitted access to the film after processing does not now cause any hydrolysis of isocyanates and thus does not form CO_2 either; instead it opens the oxazolidine ring or splits the imines. Both cases give rise to the necessary hydrogen for crosslinking in the form of OH or NH_2 groups.
Another method of designing 1-component coatings consists of carrying out a preliminary conversion of the isocyanates into chemically inert intermediate stages which can, however, be reactivated by heat action. As already mentioned, such blocking can be carried out with the material itself or with external materials. These are separated again, i.e. unblocked, in the event of thermal reactivation and then have an impact on air flow and consumption in the drier as volatile cleavage products (see chapter 4.3.1).



$$R{-}NH{-}C(=O){-}O{-}R' \xrightarrow{\Delta T} R{-}N{=}C{=}O + HO{-}R'$$

Fig. 2.1.102
Deblocking reaction of capped isocyanates

Classic blocking agents for isocyanate groups are phenols and ε-aminocaprolactam. Because of the relatively high cleavage temperature of 160 – 180 °C oxims or CH-acid compounds such as acetoacetic ester, acetylacetone or malonic ester have been successfully tested as blocking agents. Other blocking agents which also resplit materials at around 140 °C are 1,2,4-triazole and dimethylpyrazole [2.4.23].

The blocked, thermally curing 1-component polyurethane paints occupy a special position in that they exhibit better chemical resistance and elasticity with greater hardness at the same time than the classic baking enamels with amino resin crosslinking agents. Representatives blocked with ε-aminocaprolactam are used to meet special demands for coil coating and can coating, for sterilization-proof coatings on the insides of cans for aggressive foodstuffs and on cans for fuels and oils. Blocked isocyanate crosslinking agents are also used in electrical insulation coatings because of their high heat resistance and their constant electrical properties.

In powder coatings the blocking agent ε-aminocaprolactam (a) is being replaced more and more by the more reactive 1,2,4-triazole (b). Furthermore, isocyanates of the trimeric HDI and IPDI blocked with methyl ethyl ketoxim (c) are being incorporated in baking primer surfacers for automotive paints.

Isocyanate hardeners blocked with ethyl acetoacetate (e) or diethyl malonate (f) have proved successful for reactive topcoats and clearcoats because of their low baking temperatures. 3,5-dimethyl-1,2-pyrazole (d) also recently became available for similarly low reaction temperatures.

Blocked isocyanates are also used in cationic electrocoat paints for a high crosslink density.

The formation of cleavage products of blocked isocyanates is a disadvantage which does not occur when the already mentioned uretdiones are used. After heating, the uretdiones are activated by ring opening or cleavage, as a function of temperature, without the formation of cleavage products. In the case of ring opening, allophanates are formed after addition of the OH-functional reactant, while with cleavage, classic

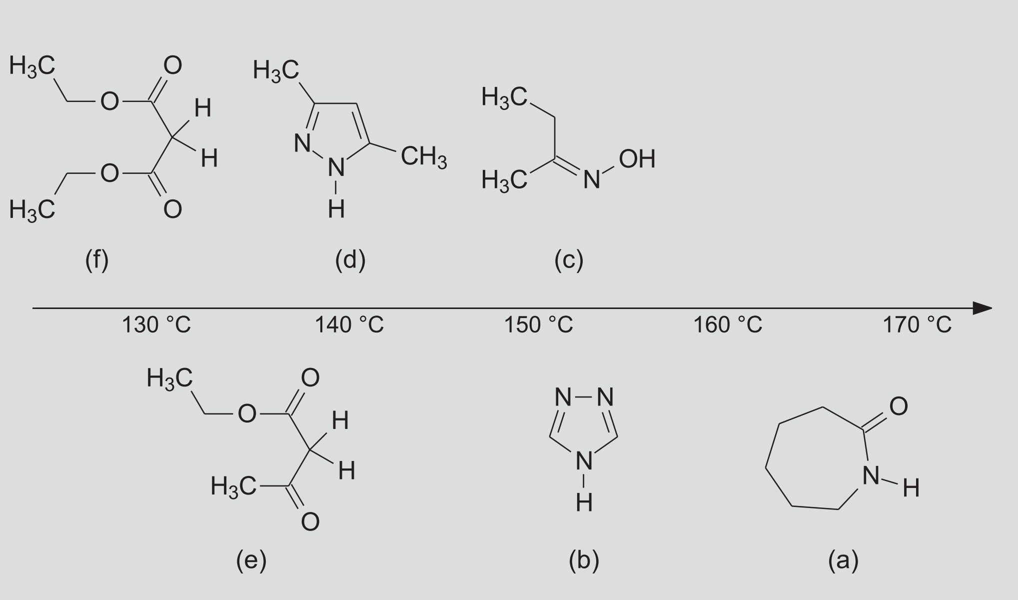


Fig. 2.1.103
Capping agents for isocyanates crosslinker and their respective deblocking temperature

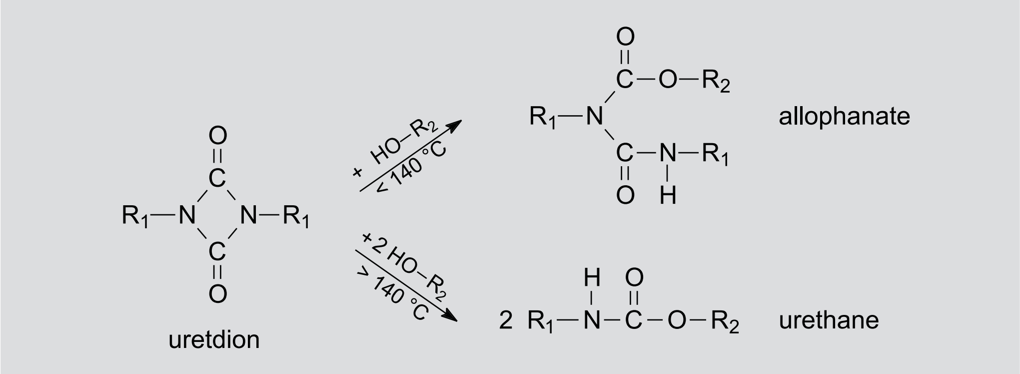
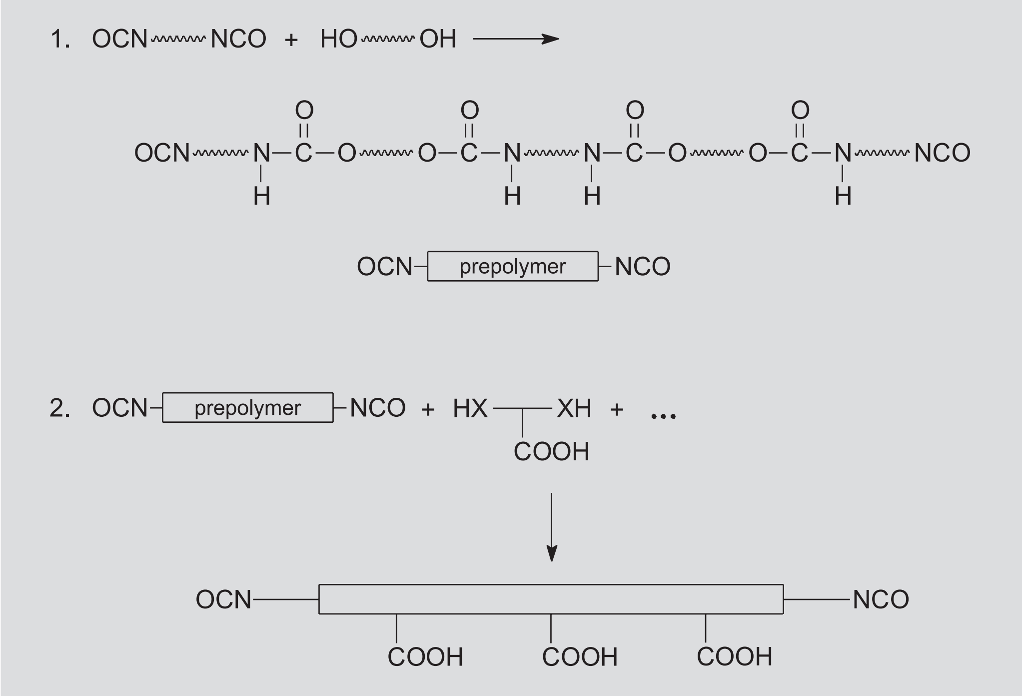


Fig. 2.1.104
Uretdiones : hardeners for OH-functionalized resins by thermolysis

urethanes are formed. This has enabled 1-component polyurethane paints to be formulated which have already proved successful as powder coatings [2.4.24].

Because of the reaction of isocyanates with water and the associated destruction of the crosslinking functions precautions must be taken when designing waterbased polyurethane paints to prevent this preliminary reaction of the isocyanate groups. This



3. Transfer into a waterbased dispersion:
The melted polymer + neutralisation agent + water result in a water in oil emulsion. Further addition of water provide a phase transfer (oil in water) and a chain extension by hydrolysis of isocyanate groups.

Fig. 2.1.105
Chemical steps for manufacturing waterbased polyurethane dispersions

can involve either, as just described, blocking the isocyanates or using the reactive groups before the film formation with the specific intention of constructing the basic chains.

The latter method is used with anionically stabilized polyurethane dispersions. Their manufacture involves diisocyanates, diols and sterically hindered dihydroxycarboxylic acids being converted to prepolymers, neutralized with amines and then transformed into a fine dispersion. Steric hindrance of the carboxylic acids prevents them from reacting with the isocyanates. They are thus retained for anionic stabilization.

Analogous cationic and nonionic polyurethane dispersions have been developed in the meantime. The resin molecules containing amino groups are converted with acids, usually acetic acid, into the watersoluble form.

By comparison with emulsion polymers, polyurethane dispersions have the advantage that they are particularly fine and dry physically to form dense, homogeneous, glossy films. The films are tough and elastic because of their elastomeric character and the resulting hydrogen bridging bonds. The dispersions can also be combined with other

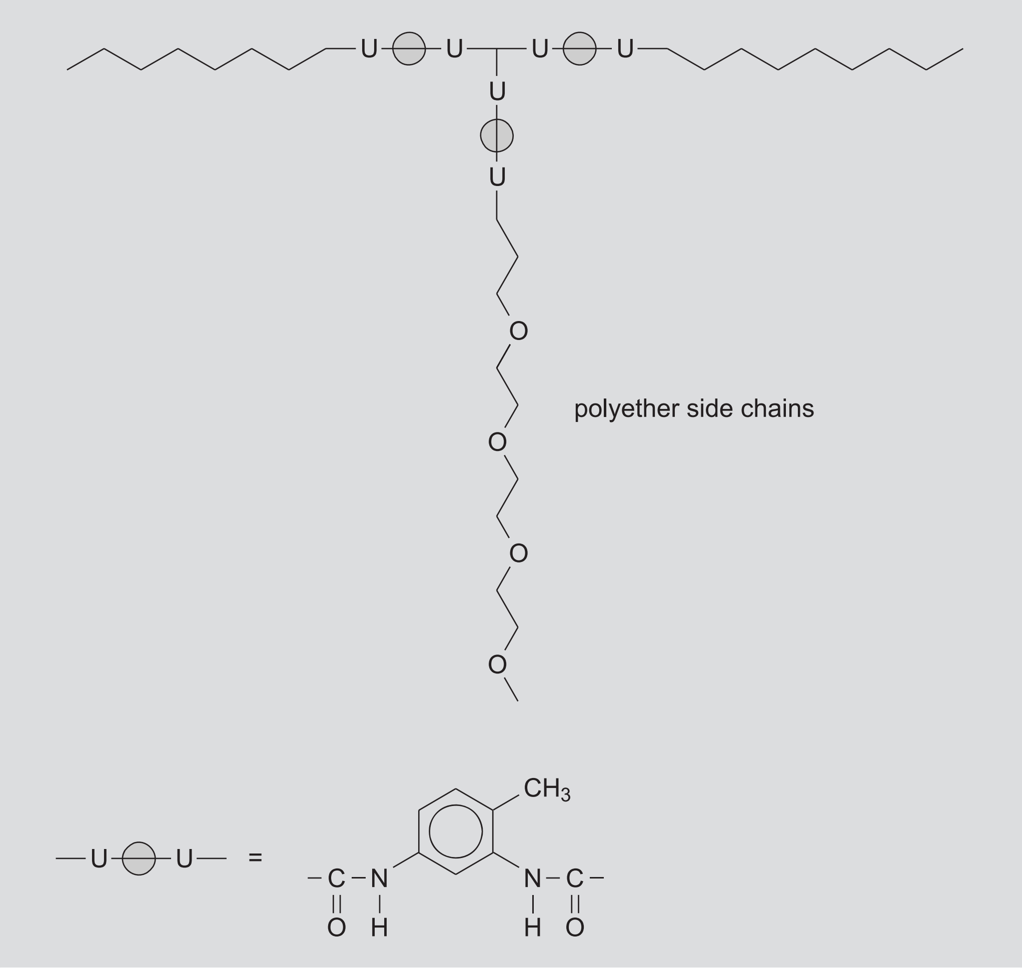


Fig. 2.1.106
Example of a structure for a nonionic polyurethane dispersion

water dilutable binders. For this reason they are particularly suitable for water-borne primer surfacers and basecoats, one-coat topcoats, plastic coatings, wood and foil coatings. They can also be combined with primary acrylic dispersions to form water based decorative paints. The result is diffusion resistant, glossy films (i.e. for painting windows).

In addition to the synthesis of physically drying dispersions, chemically reactive polyurethane dispersions incorporating OH-groups have been successfully manufactured which can be converted to duromer films by crosslinking with melamine resins dissolved in the aqueous phase. The HMMM resins have proved extremely suitable for this group of water based polyurethane baking enamel systems. Such dispersions are used, among other things, for base coats and primer surfacers in the automotive sector [2.4.25].

Contrary to the assumption that OH-functional water based polyurethane dispersions with isocyanates cannot be processed as 2-component coatings, both chemical and process engineering methods have been developed to improve the resistance of the hardener against the aqueous environment. Improved emulsibility involving the incorporation of polyether groups, reduced reactivity and a suitable dispersing system have brought the desired success. Mixing takes place directly prior to processing by means of jet dispersion of the hardener in the base paint, with the result that hydrolysis can only take place very slowly. Acrylic or polyester polyols containing OH-groups are combined with an isocyanate containing hardener using appropriate metering and emulsifying equipment. A relatively coarse primary emulsion is first obtained; this is then so finely distributed in a downstream dispersing machine that the necessary molecular mixture is achieved during film formation by diffusion [2.4.26, 2.4.27].

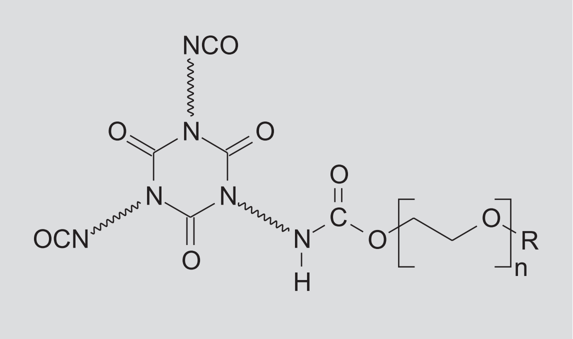


Fig. 2.1.107
Isocyanate crosslinker for waterbased 2-component paints

Despite the heterogeneous distribution of the components and the reduced reactivity, the possibility that some of the isocyanate groups are split hydrolytically as a result of the effect of the water at the dispersion interface cannot be excluded. To ensure optimum crosslinking, therefore, it is necessary to remove the water quickly from the film and also to provide excess hardener. Even if coatings made of water based 2-component polyurethane dispersions have not yet been able to match the performance profile of solventborne polyurethanes, they have attained a quality level which justifies their use in the wood and metal coatings sector [2.4.28].

The range of possible applications for polyurethane paints is as wide as the available variety of raw materials. Pigmented and unpigmented polyurethanes for a huge range of substrates with an impressive list of benefits are in use in the individual industries. These benefits include their good adhesion, wear resistance, longterm outdoor exposure properties, hardness with a high degree of elasticity at the same time and a high resistance to chemical agents such as acids, alkalis, household chemicals, solvents and fuels. 2-component PUR systems are very successful as automotive refinish paints. Their use on automotive coating lines has also advanced greatly in recent years for the above mentioned reasons. Polyurethanes have had a dominant role for quite some time now when it comes to coatings for large vehicles such as buses, commercial vehicles, road tankers, passenger and freight carriages on the railways and also aircraft. They have also proved successful for coating in the wood and furniture industry. Other applications include coatings on masonry, concrete, asbestos cement, plastics and even on rubber.

Humidity-hardening polyurethane paints yield finishes with excellent mechanical properties and good resistance to the effects of water, acids, alkalis and solvents. They are therefore used on highly stressed wooden parts such as parquet and hall floors, plastics, fabrics and often also on concrete surfaces. In the latter case they largely protect concrete structures against penetration by moisture, road salt, oil contamination and other critical materials.

Polyurethane paints are now used in all environment-compatible coating systems such as powder coatings, waterbased, solvent free, liquid and radiation curable coatings.

The second important group of polyaddition resins from a coatings perspective is that of the **epoxy resins**. Even though the first successful attempts at manufacturing epoxy compounds took place more than 100 years ago, it nevertheless took more than 35 years until the first technically usable paint raw materials became available [2.4.29].

Today epoxy resins have a secure place among the high-performance polymers because of their excellent adhesion to metallic substrates and good mechanical/technological properties as adhesives, plastics and coating materials. As with the polyurethanes group, the epoxy resins are generally processed as 2-component paints.

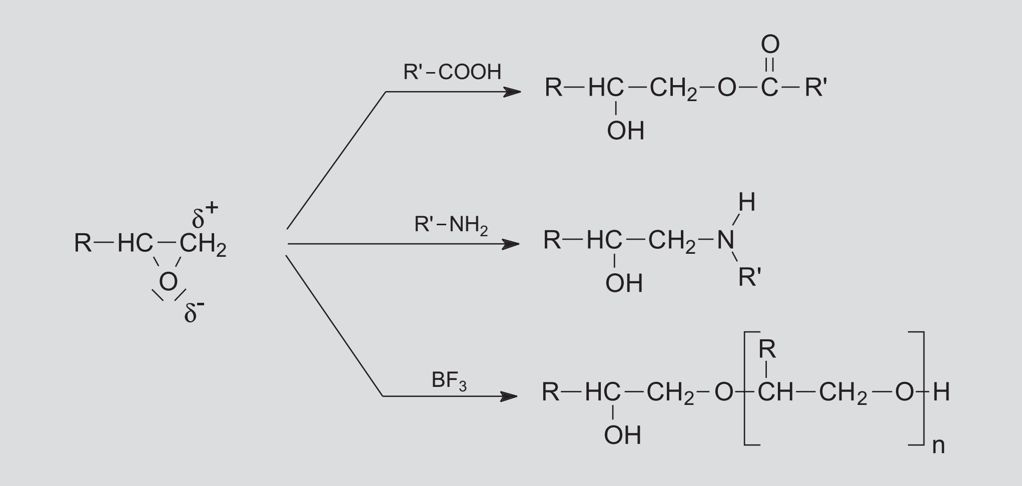


Fig. 2.1.108
Crosslinking reactions of epoxy resins

The oxiran or epoxy group is characteristic for epoxy resins. It consists of a three-membered ring containing oxygen with a high ring strain. The reactivity is further enhanced by the electronegativity of the oxygen and the resulting polarity of the epoxy groups. The carbon atoms of the three-membered ring which are starved of electrons

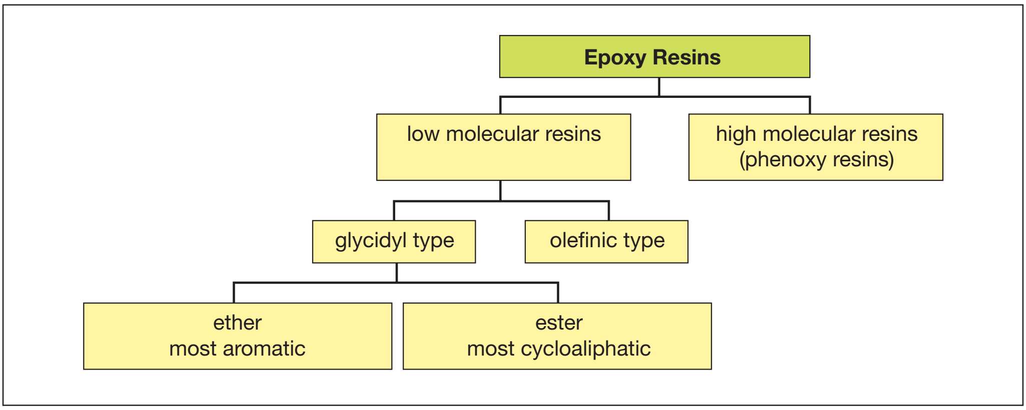


Fig. 2.1.109
Classification of common epoxy resins for the coatings industry

therefore become electrophilic and can take part in addition reactions with numerous nucleophilic partners. The reactions with amines and carboxylic acids are of particular importance for practical operations. The oxiran group can also be polymerized such that the ring is opened even without reactants. The reaction initiated by *Lewis* acids, such as BF_3, or ferrocene complexes splitting under UV radiation, results in technically important polyethers.

By far the most important group among the epoxy resins is formed by the aromatic glycidyl ether types. They are manufactured by polycondensation from epichlorohydrin and bisphenol A. The molecular weight of the individual representatives of this group is determined solely by the mixing ratio of the reactants. If a molar ratio for epichlorohydrin to bisphenol A of 2:1 is chosen, the outcome is the smallest representative of this resin class. If the ratio is increased to 3:2 or even further towards 1:1, higher molecular products will be synthesized. They differ from the first representative described in having additional hydroxyl groups. As a result the epoxy resins become of interest for all partners which are reactive with OH groups in addition to the reactivity via epoxy groups.

If a mixing ratio close to 1:1 is chosen, the resin molecules become so large that the terminal oxiran groups lose more and more importance in respect of crosslinking. Such high molecular phenoxy resins therefore only have a role as hydroxyl-functional resins. The light-unstable ether groups formed by the reaction of epichlorohydrin with bisphenol A restrict the use of this resin group to primers and primer surfacers. Ester types must continue to be used for lightfast topcoats. Technically important examples are the glycidyl esters of hexahydrophthalic acid and isophthalic acid or trimellitic acid. Triglycidyl isocyanurate (TGIC), formerly the standard hardener for acid reactants in powder coatings, may now only be used if appropriately labelled because of its toxicity. The resulting decision to dispense with TGIC in many cases has caused problems in the field of powder coatings. Today, in addition to the isophthalic acid and trimellitic acid esters of epichlorohydrin, there are other alternatives, albeit ones which crosslink in polycondensing reactions, for the acid acrylic or polyester resins. Noteworthy glycidyl group free crosslinking agents include hydroxyl-functional adipic acid amides which were largely able to supersede TGIC (see above).

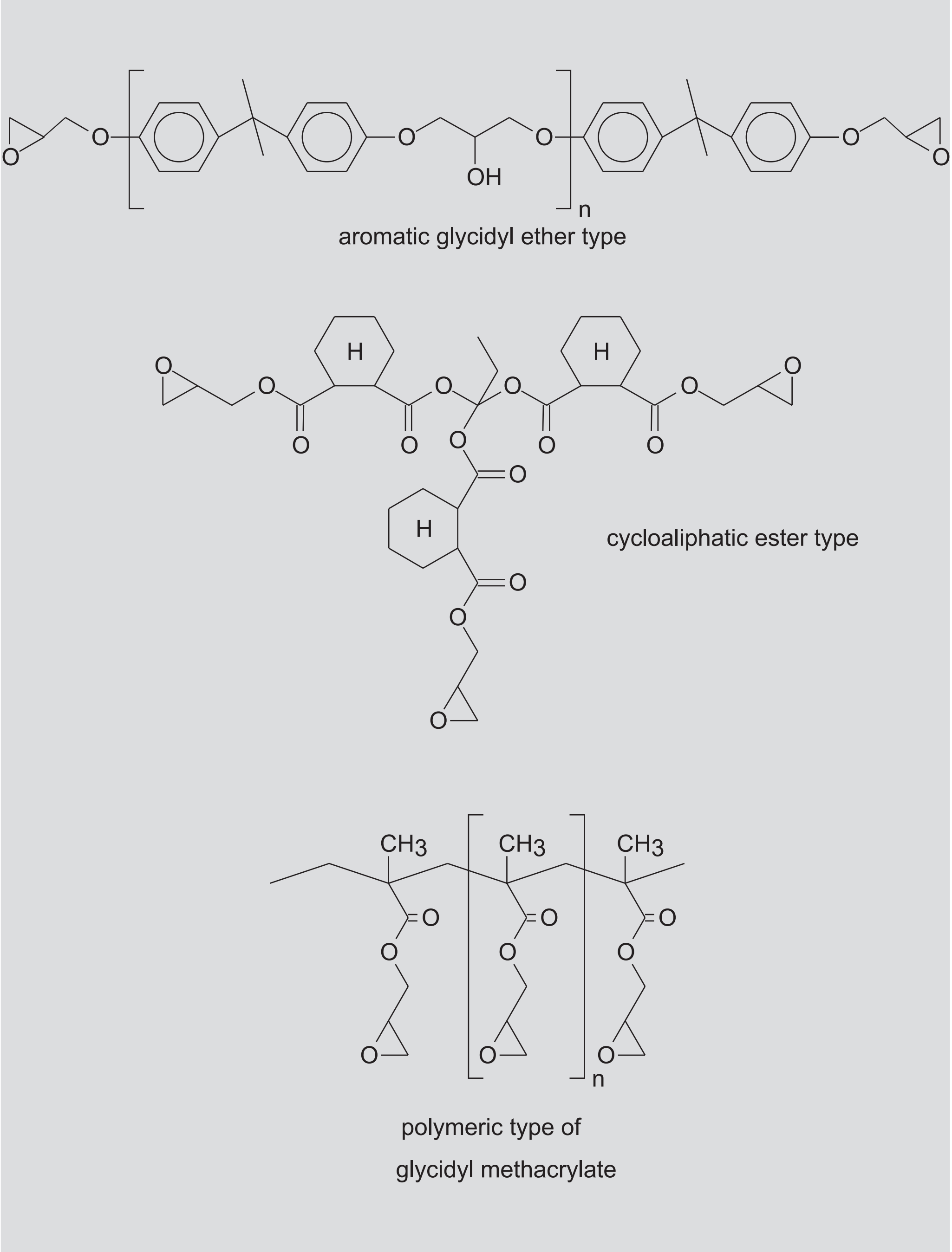


Fig. 2.1.110
Chemical structure of important epoxy resins

Other yellowing-resistant epoxy crosslinkers with good longterm outdoor exposure are the 2- and 3-functional reactants of epichlorohydrin with isophorone diisocyanate or hydantoin, where hydantoin also has the benefit of a higher heat resistance.

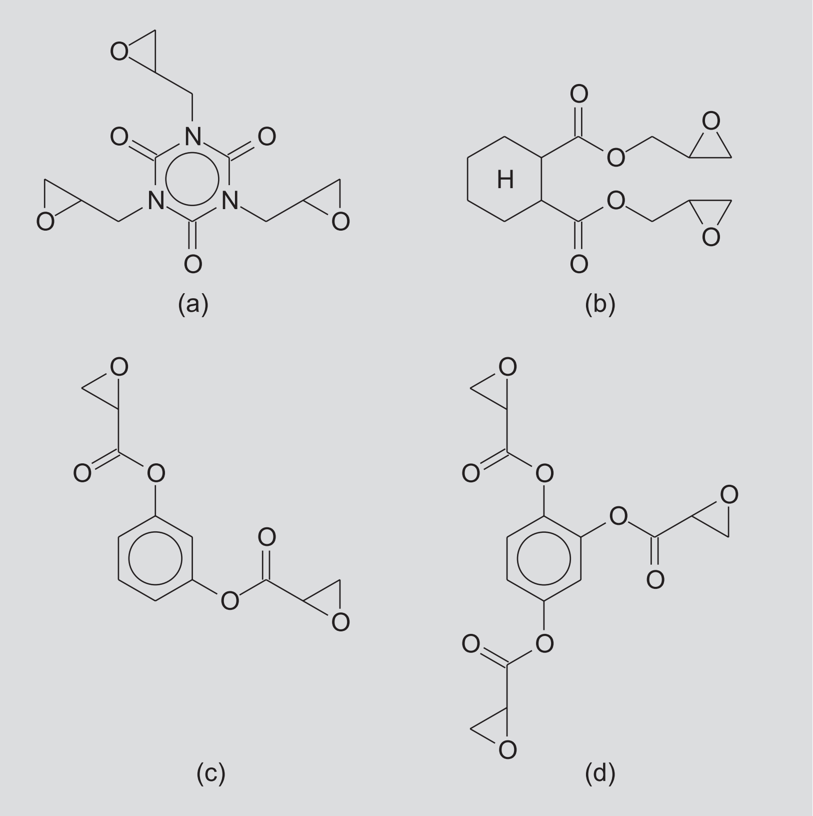


Fig. 2.1.111
Triglycidylisocyanurate (TGIC : a) and alternatives (b–d)

A completely different approach to epoxy resins involves the epoxidation of carbon double bonds. This results in so-called olefin types. The reaction of tetrahydrostyrene with peracetic acid, for example, results in a bifunctional cycloaliphatic, though only low molecular epoxy resin. These solvent free, low viscosity structural elements have proved their value as reactive diluants. As solvents they have a pronounced viscosity

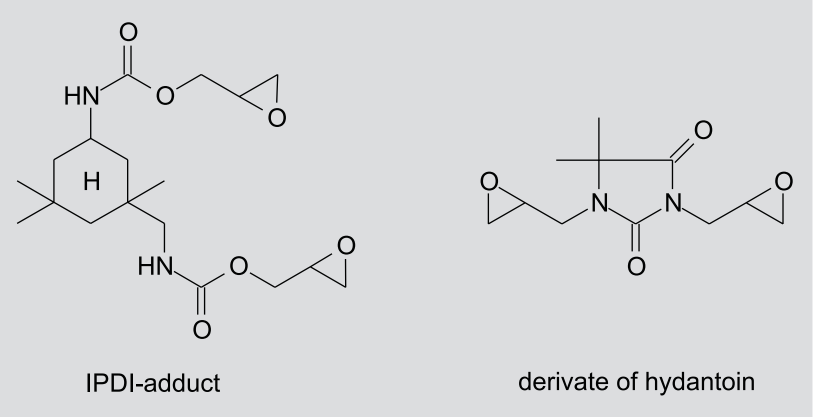


Fig. 2.1.112
Heat resistant and nonyellowing epoxy crosslinker

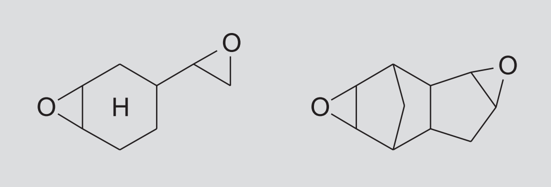


Fig. 2.1.113
Olefinic types of epoxy components as reactive diluants

lowering effect, though are also involved in the polyaddition process of crosslinking during curing. So they do not leave the film and therefore contribute to reducing organic emissions.

As outlined in principle above, the crosslinking of epoxy resins can take place, depending on the reactant, either exclusively at the oxiran groups or additionally at the less reactive hydroxyl groups. Consequently, epoxy resins can be cured as 1-component or 2-component coatings.The usual method of curing epoxy resins involves amines, acid anhydrides or carboxylic acids. In addition, mercaptane hardeners are also used as reactants for special applications.

The reaction rate of amine curing depends on the type of amino group. Different processing or curing times are determined by the basicity of the amine hardener in association with the steric configuration of the amino group. The most reactive with a pot life of 15–30 minutes are the short-chain aliphatic polyamines (ethylenediamine,

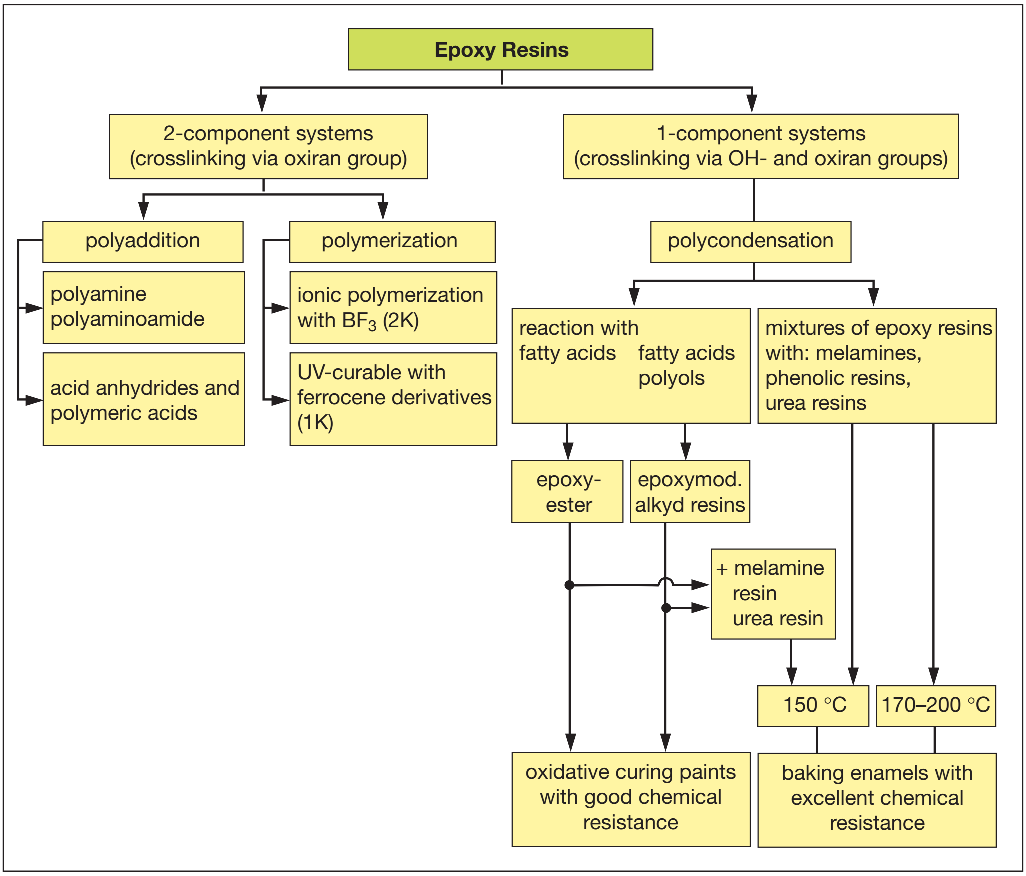


Fig. 2.1.114
Summary of applications of epoxy resins in coating formulations

diethylenetriamine etc.). The longer chain polyaminoamides are less reactive and result in more elastic films. Mixtures of epoxy resins with cycloaliphatic or aromatic amines must even be heated briefly to 120 – 140°C because of their inadequate reactivity. Dicyandiamide occupies a special position among the amine hardeners. The product, which is solid at room temperature, is incompatible with epoxy resins and forms two phases from homogeneous melts when solidifying by cooling. The reaction takes place only at the common interface and is therefore so slow that the mixture is ground and can be used as a powder coating which is stable in storage. However, the reaction of dicyandiamide with the epoxy groups proceeds differently from the reaction familiar from the classic amines. Primary adducts are rearranged into acid amides and urethanes,

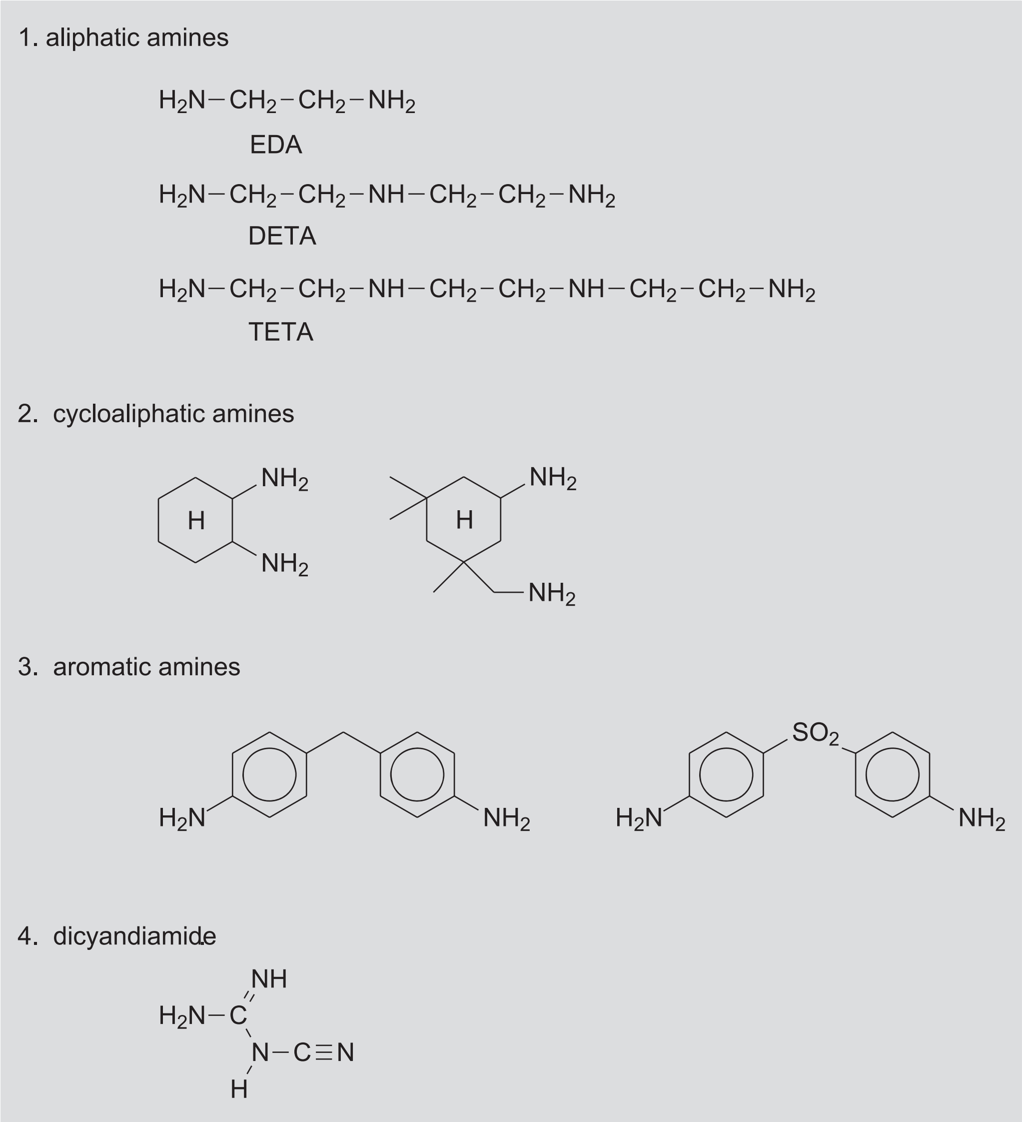


Fig. 2.1.115
Amine hardeners for epoxy resins (EDA = ethylenediamine, DETA = diethylenetriamine, TETA = triethylenetetramine)

among other things, by secondary reactions. Dicyandiamide is, therefore, not, 4-functional, as would be anticipated from its chemical structure but only 3-functional [2.4.30]. The second, no less important, route for industrial coating technology to highly crosslinked and adhesive coatings involves the reaction of epoxy resins with acid anhydrides.

Because of the lack of active hydrogen atoms acid anhydrides cannot react directly with epoxy resins. Only once the reaction of the anhydride ring with the hydroxyl groups of the epoxy resin chain has been initiated by heat action does this result in opening of the ring and the simultaneous formation of a carboxyl group. If the ring-opening OH groups are absent, reaction of the acid anhydride with the epoxy resin by the addition of catalytic quantities to butanol is possible because a new OH group is formed for each bond between a carboxyl group and an epoxy ring.

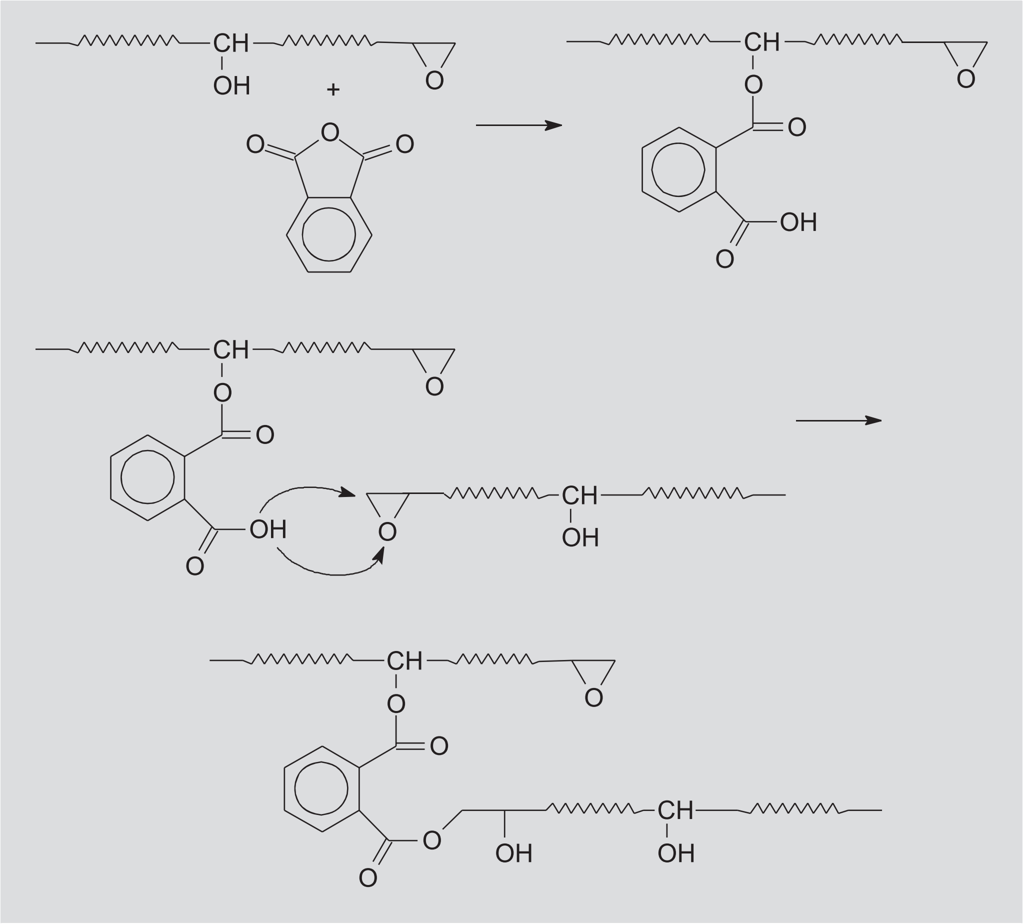


Fig. 2.1.116
Crosslinking of epoxy resins with anhydrides, for example phthalic anhydride

If the performance profile of anhydride-cured and amine-cured epoxy resins is compared, it will be noted that the systems differ significantly in their acid and alkali resistances. The amine-hardened films are sensitive to acids, while the acid-hardened esters are more susceptible to saponification by alkaline compounds.

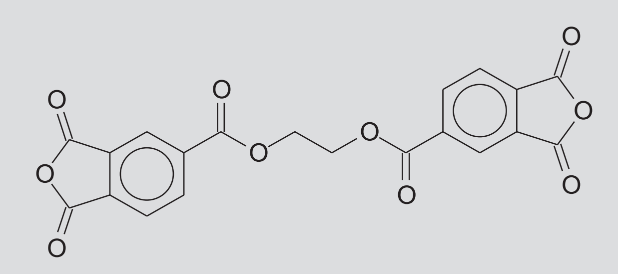


Fig. 2.1.117
Example of an anhydride hardener as a reaction product from trimellitic anhydride and 1.2-ethandiol

If aliphatic or cycloaliphatic epoxy resins are used in place of aromatic ones during acid curing, the resulting coatings feature improved electrical insulation properties, even when subjected to continuous heat treatment.

Because of the ring tension in the epoxy group, epoxy resins can be polymerized to polyethers with the assistance of suitable starter ions such that the ring can even be opened without supplementary reactants. The reaction is particularly rapid if the starter ions are provided by the *Lewis* acid, boron fluoride. One method of successfully extending the pot life is to form a complex of boron fluoride and amines. The boron fluoride can then be released again by means of thermal decomposition at the time of film formation.

This reaction sequence is used on a large scale for the production of polyethylene glycols from ethylene oxide. Depending on the degree of polymerization, the polymer is available in liquid or wax-like (carbowaxes) form and serves as a plasticizer or dispersant in waterbased paints.

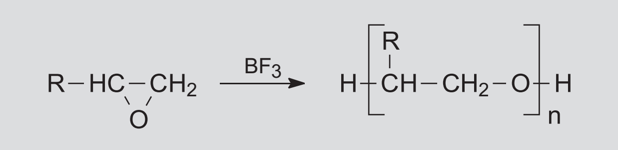


Fig. 2.1.118
Polymerization via ring opening of epoxy resins with BF_3

In the search for high-quality 1-component systems the experience of blocking gained with the polyurethanes was successfully transferred to epoxy resins. Inactivated amine hardeners in the form of ketimines or aldimines achieve a pot life of more than 200 days if stored correctly, for a curing time of less than 16 hours. The ketimines and aldimines hydrolyse as a result of the ambient humidity and release the amines required for crosslinking (see figure 2.1.101).

The simple mixing of epoxy resins with amino resins or phenolic resins also yields usable, thermally curable 1-component coatings. Such combinations feature excellent resistance to a wide range of aggressive chemicals.

The reaction of epoxy resins with fatty acids to form epoxy resin esters results in a resin class in which the excellent adhesion and hardness values of the epoxy resins are combined with the elasticity and good flow properties of the oils. Furthermore, it is possible to engineer purely oxidative curing or, in conjunction with amino resins, thermal curing, depending on the type of fatty acids used.

Epoxy resin esters are therefore important basic structural elements for high-quality primers and primer surfacers for industrial coatings.

If the epoxy resin esters are modified via the double bonds in the fatty acids with maleic anhydride and if the incorporated anhydride ring is opening in similar fashion to the maleinized oils with butanol and neutralized with amines, the result is watersoluble resins for anodic electrocoating.

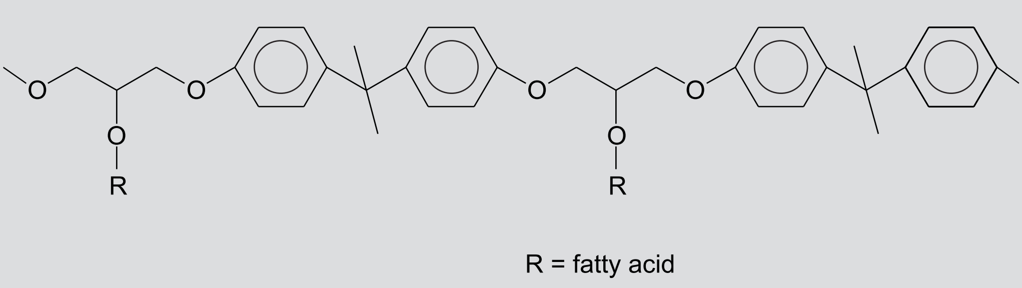


Fig. 2.1.119
Structure of epoxy resins modified with fatty acids

Bisphenol A epoxy resins are also used for the manufacture of resins for cathodic electrocoat paints which are significantly more important today (see figure 2.1.121). The cations which are required for dispersion in water are obtained by adduct formation with amines and subsequent neutralization with acetic acid.

The important electrocoat primers in the automotive industry and its supply industry are based on resins which consist of polyester nuclear segments and added epoxy resins. The epoxy end groups are then converted with amines as described. Crosslinking takes place mainly with added blocked isocyanates which then react with the OH and NH groups of the base resin after thermal unblocking [2.4.31].

Apart from their importance for solventbased 1- and 2-K systems and as a base resin for electrocoat paints epoxy resins have developed a broad range of applications for waterbased systems and powder coatings for primers. In waterbased systems the oxiran-group containing resins stay in the hydrophobic micelles while the amines are in the continuous waterphase. Reaction occurs when evaporation of water has been taken place. With polyesters epoxy powder can be used as topcoats.

The good film properties in conjunction with the potential of lower baking temperatures without emission of cleavage products have made polyaddition coating resins particularly attractive.

Several product groups can also be considered as further polyaddition crosslinking materials. The addition of active methyl-ene

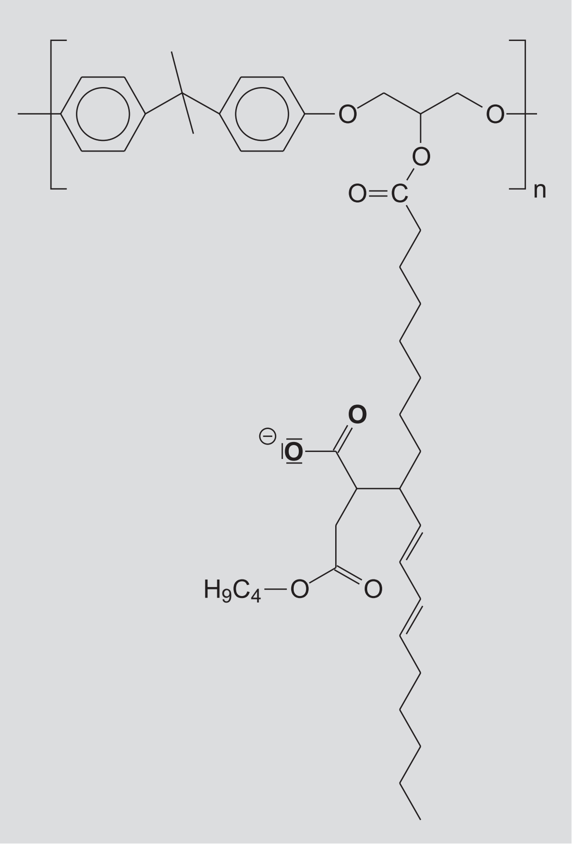


Fig. 2.1.120
Structure of maleinized epoxy polyester resin for anodic electrodeposition process

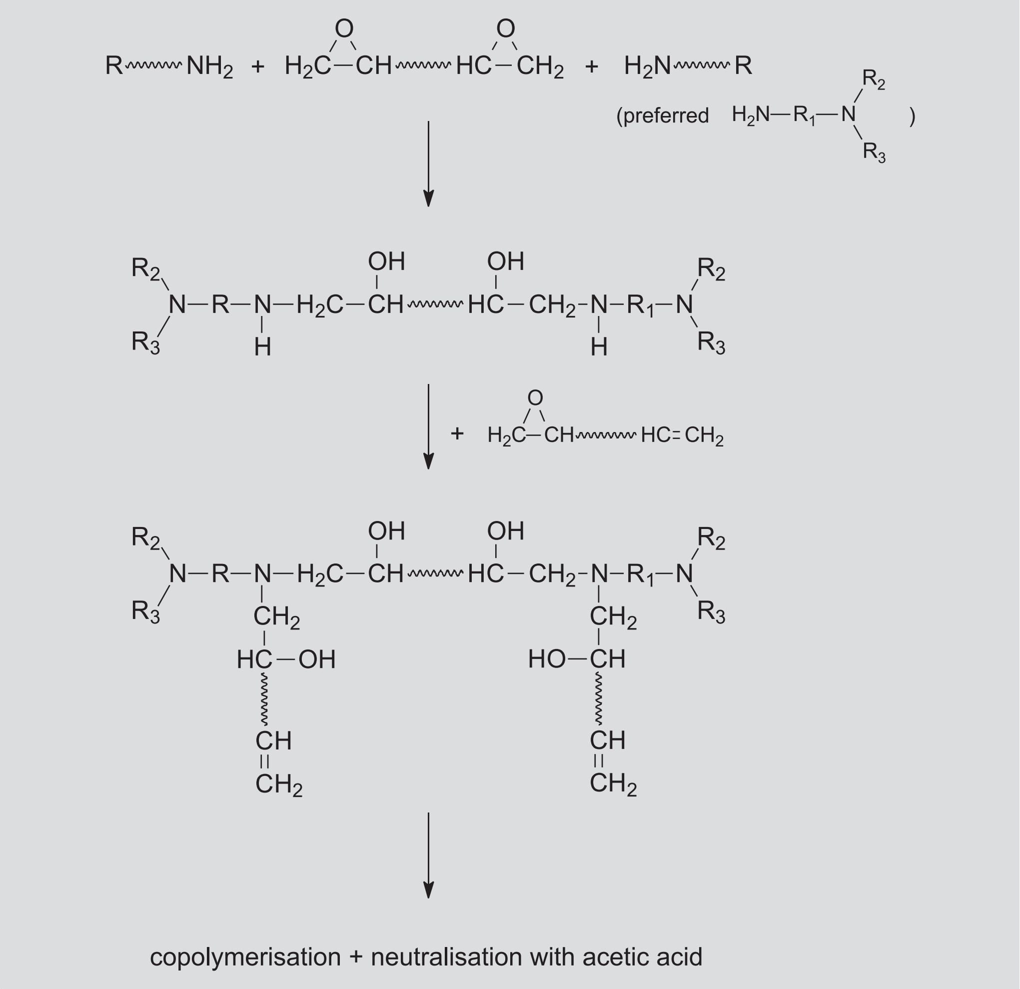


Fig. 2.1.121
Example of a chemical structure of a cathodic electrodepositable resin based on epoxy resins

and amino groups to vinyl ketones or acrylic esters, the reaction of carboxylic acids with carbodiimides and the varied reaction options for oxazolines with carboxylic acids, carboxylic acid anhydrides and with itself are just some of the novel crosslinking reactions which are worth noting. An example which merits a special mention is the *Michael* condensation of malonic acid esters or polyamines with acrylic ester containing resins. The discovery of catalysts means that the crosslink temperatures can be reduced

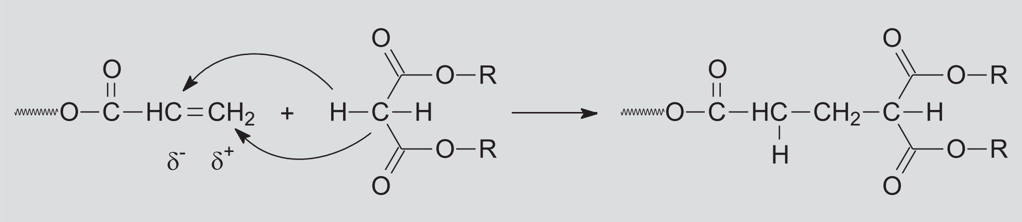


Fig. 2.1.122
Michael addition of malonic acid esters to acrylic acid derivates

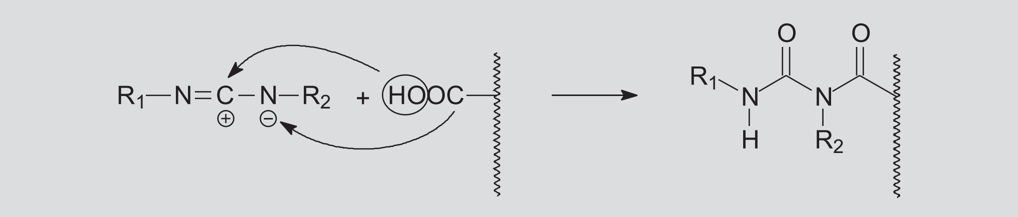


Fig. 2.1.123
Reaction scheme of the addition of organic acids to carbodiimides

to as low as 70 °C, as a result of which new options are opening up even for thermally sensitive substrates and for the automotive refinishing sector [2.4.32].
Carbodiimides, which have been known for many decades as a mild condensing agent in the chemistry of natural products, can be used as paint resins if they are reacted with carboxyl group containing film forming agents such as acid polyesters or polyacrylates.

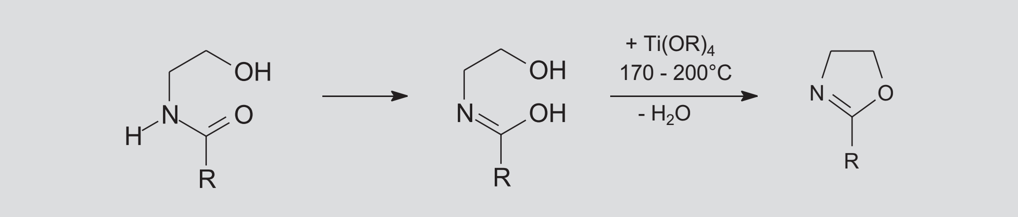


Fig. 2.1.124
Synthesis of oxazolines from β-hydroxy-acidamides

Oxazolines, which have been known for their role in the emulsification of alkyd resins for decades, are experiencing renewed interest. Their synthesis works by the intramolecular dehydration of hydroxyl-functional acid amides or by removing NH_3 from reaction products of ethanolamine with nitriles.

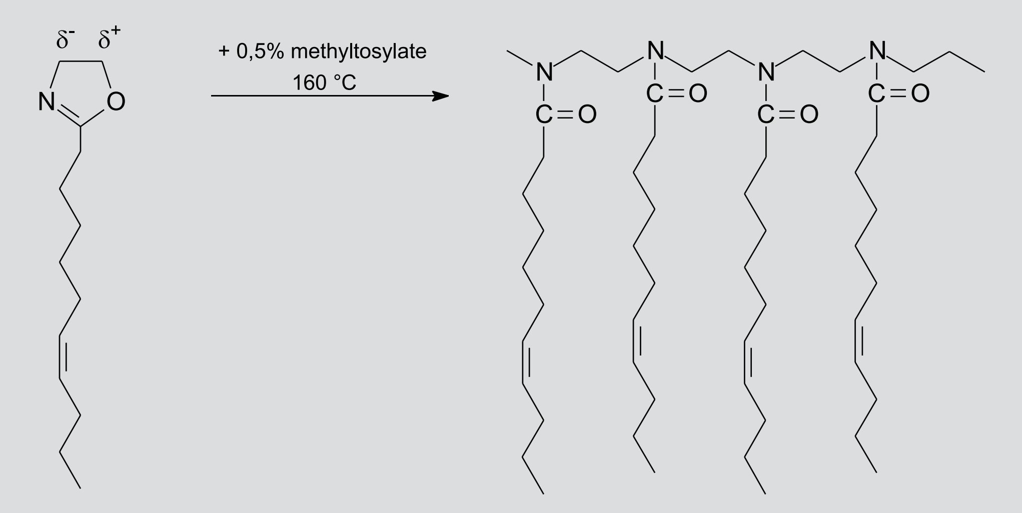


Fig. 2.1.125
Ring opening polymerization of oxidative hardening oxazolines

Oxazoline, made from analogous unsaturated fatty acid amides, are eminently suitable for the synthesis of oxidatively curing polyamides if they are polymerized with ring opening in the presence of appropriate catalysts.

Oxazoline group containing film forming agents are also partners for acid polymers. They react with carboxyl groups at temperatures above 180°C, resulting in opening of the ring, formation of esters and, at the same time, formation of acid amide groups.

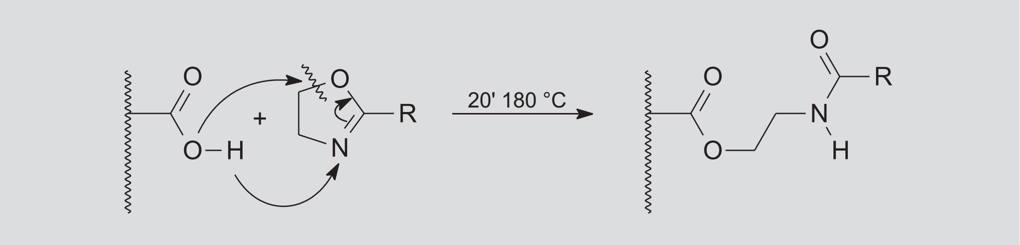


Fig. 2.1.126
Crosslinking reaction of oxazolines with organic acids

A reaction with acid anhydrides is also possible. For example, maleinized epoxy resin esters can be converted with oxazolines to stable esterimides.

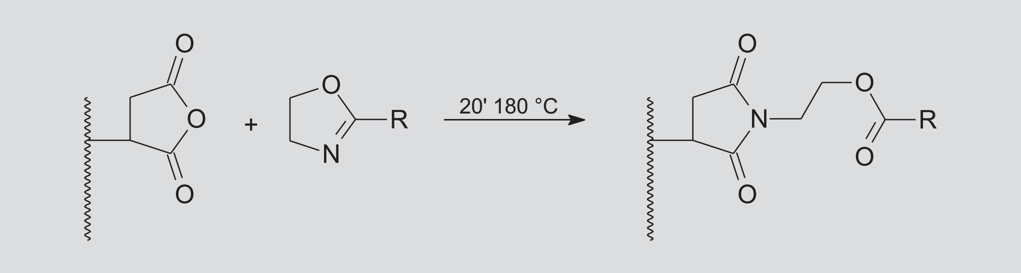


Fig. 2.1.127
Crosslinking reaction of oxazolines with acid anhydrides

Cyclic carbonic esters can also be used as crosslinking resins. Cyclic propylene carbonate reacts with primary and secondary amines are low temperatures to form polyurethanes.

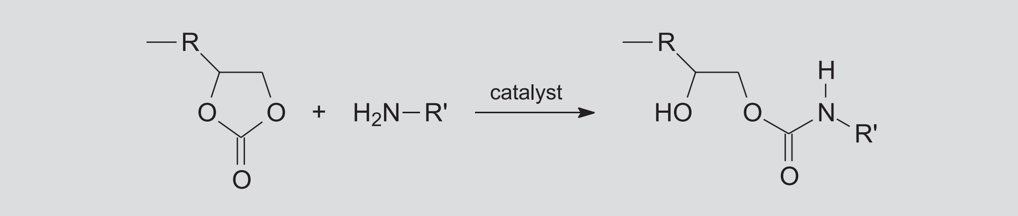


Fig. 2.1.128
Scheme of crosslinking reaction of carbonic acid esters with polyamines

Resins by polymerization

The polymerization reaction has become by far the most important type of reaction for the manufacture of synthetic materials. As a result of the mechanism and kinetics of the reaction polymers generally have substantially higher molecular weights than condensation resins which are more suitable for paint purposes. Since a high molecular weight in a film forming agent is associated with reduced solubility, increased viscosity in the paint solutions and thus a low solid content, the use of high molecular polymers in dissolved form faces considerable environmental problems. As solventbased paints, therefore, they are of fading importance.

A way out of this problem is offered by processing as a dispersion, or also as a powder coating. The aqueous emulsion polymers play a very major role. They serve as the basis for dispersion coatings, fillers and synthetic resin putties. Acrylic or polyvinyl acetate dispersions for coating external façades or interior surfaces can be particularly mentioned in this regard. Dispersions, in which solvents or plasticizers act as the fluid phase instead of water, include particularly the organosols and plastisols which are used as baking enamels. The plastisols contain plasticizers, while the organosols contain still volatile nonsolvents in addition. The polymers which are important in coating technology are divided into polyolefins, polyvinyl compounds and polyacrylates.

The classic **polyolefins**, such as polyethylene, polypropylene, i.e. those which are no longer accessible to chemical crosslinking during film formation, have failed to gain any technical importance as film forming agents because of their insolubility in standard solvents and their tendency to crystallization. Polyisobutylene, obtained by ionic polymerization, partially soluble in hydrocarbons and with excellent cold resistance, has proved a successful elasticizing component for bitumen and for flexible coatings of food wrappings and textiles.

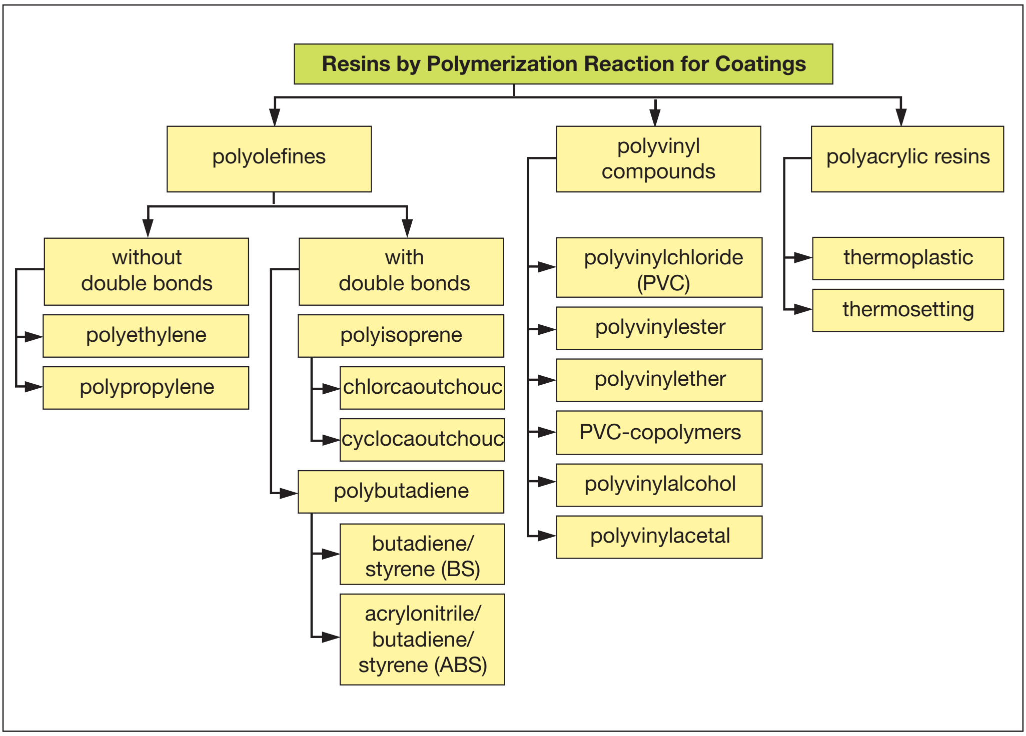


Fig. 2.1.129
Groups of important resins by polymerization for coatings

Low molecular polyethylene wax dispersions are additives to influence the surface smoothness and effect formation of metal effect coatings. After sulphochlorination they perform special tasks as film forming agents. There is a different situation with polyolefins which still contain reactive double bonds after their manufacture. Polybutadiene and polyisoprene belong to this product group. Low molecular polybutadiene oil, like fatty oils or oxidatively curable epoxy resin esters, is maleinizable and thus a proven film forming agent for anodic electrocoating [2.4.33].

The most important members of the **polyvinyl resin** group are polystyrene, polyvinylchloride (PVC) and various polyvinylesters and polyvinylethers.

Polystyrene, a homopolymer, is not suitable for use in coatings because of its inability to absorb pigmentation and its high degree of brittleness. Only when copolymerized with acrylonitrile (better color absorption) and butadiene (elastic properties) is the resulting acrylonitrile-butadiene-styrene copolymer (ABS), which is processed from an aqueous dispersion, of interest for coating, among other things, surfaces at risk of chipping.

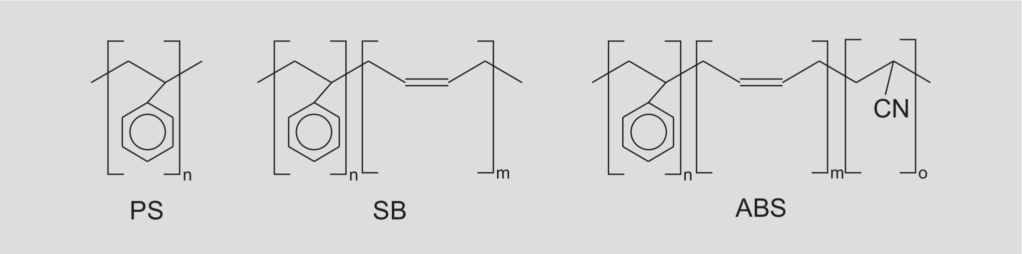


Fig. 2.1.130
Polystyrene(PS) as a homopolymeric compound as well as styrene-butadiene (SB) and acrylonitrile-butadiene-styrene (ABS) as copolymeric compounds

The copolymers of butadiene with styrene in the form of aqueous dispersions have acquired another application field. Because of their residual C = C double bonds the films are capable of oxidative secondary crosslinking. This helps to increase hardness and resistance to water, chemicals and detergents. Latex paints are manufactured with styrene-butadiene copolymers. They are suitable for internal and external application, particularly on mineral substrates and, in some cases, also on metals.

PVC is not usable as a film forming agent without modification, either. Its poor solubility and sensitivity to light are the most serious shortcomings from the coatings perspective. Only post-chlorinating the raw material, which already contains 56% chlorine, to a chlorine content of approx. 65% improves solubility and thus permits the manufacture of physically drying film forming agents. These were used in the past, in combination with tar and bitumen, for heavy-duty anticorrosive protection.

PVC attains much greater importance when used as a dispersion in plasticizers. Such plastisols can be processed in an emission free manner. They then gel by heat action to form a highly elastic mass which is processed in thick films. Underbody protection and seam protection sealants in the automotive sector are important applications for PVC plastisols. PVC plastisols are also processed as topcoats in the coil-coating sector.

Coatings made of nonplasticized polyvinyl chloride have a high surface hardness, wear resistance and above-average resistance to water, solvents, chemicals and fuels. As a result they are particularly suitable for cladding containers, storage tanks and similar objects.

Their weakness in fastness to light and heat resistance can be overcome by the use of stabilizers. Good adhesion to iron can only be achieved by the use of special self-etch pretreatment primers.

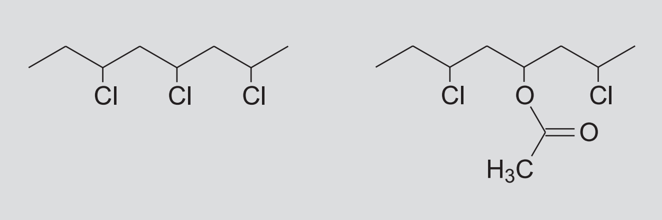


Fig. 2.1.131
Molecular segments of polyvinylchloride (PVC) and a copolymerisate with vinylacetate

Aqueous PVC dispersions are also used to coat textiles, leather and synthetic leather. PVC-based powder coatings are only of interest for the fluidized-bed process (see chapter 4.2.2). A widely used method of obtaining film forming agents with better solubility, adhesion and compatibility properties is copolymerization of the vinyl chloride with vinyl acetate, vinyl propionate, vinyl isobutylether or in smaller proportions also with free acrylic and maleic acids. The amount of ester- and ether-type comonomers ranges from 5% to 50%, while that of the adhesion-enhancing acid components is of the order of 1%. Apart from the molecular weight, the type and proportion of comonomers used has a defining effect on the solubility and compatibility of the resins, but also on the properties of the coatings made using them.

With few exceptions, the copolymers of vinyl chloride are physically drying film forming agents. Important applications for PVC copolymers include internal coatings of beverage cans, heat-sealable coatings on aluminium foils for lamination and bonding, high-adhesion coatings on hot-galvanized substrates and aluminium sheets. PVC copolymers are also used to protect concrete floors and for road-marking paints. When combined with alkyd resins they serve as primers and high-build anticorrosive coatings.

The homopolymer **polyvinyl acetate** is a waterwhite, lightfast, odourless and tasteless coating resin. It is available in a wide range of different molecular weights. The molecular weight is not only important for the viscosity of solutions, but also for compatibility with other paint raw materials and for the mechanical properties of the dried films. In all cases polyvinyl acetate has good adhesion, even on difficult substrates. The preferred solvents for polyvinyl acetate are esters and ketones. There is good compatibility with cellulose nitrate, acetobutyrate, chlorinated rubber and polyacrylates.

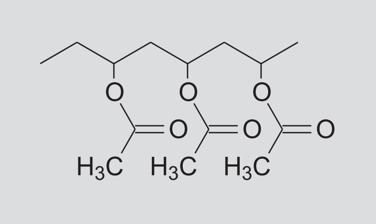


Fig. 2.1.132
Molecular segment of polyvinyl-acetate

Carefully coordinated combinations increase the bonding strength and build. Despite their good barrier effect against gases, polyvinyl acetate films are extremely permeable to moisture. This permits the exchange of moisture between the coated substrate and the atmosphere.

Aqueous polyvinyl acetate dispersions with solids contents of 50 – 60% have incomparably more important uses than the solventbased types. For the homopolymers the minimum processing temperature, i.e. the minimum film forming temperature (MFT), is 15 °C which is too high for central European climate conditions. To reduce this and thus to guarantee film formation even at lower temperatures, the material has to be plasticized. Plasticizing can be achieved by the addition of plasticizers or by copolymerization of the vinyl acetate with plasticizing monomers. Materials which can be considered for use as plasticizing monomers are esters of vinyl alcohol with lauric or stearic acids, but also alkyl esters of maleic and fumaric acids.

Polymers of vinyl propionate have greater resistance to alkalis. The high inherent elasticity of **polyvinyl propionate** means that for many applications it is necessary to raise the product's hardness by copolymerization, e.g. with vinyl chloride.

Aqueous dispersions (see below) of polymers of vinyl acetate and propionate manufactured by emulsion polymerization have worked successfully as the basis for dispersion paints for decades. They are very widely used in the manufacture of coatings for buildings, wood coatings, coatings for wallpaper and textiles and of fillers and synthetic plasters. The numerous advantages of good compatibility with many other film forming agents, their physiological safety, their fastness to light and the film gloss that can be achieved with polyvinyl acetate must be weighed against the disadvantages of their tendency to swell with water and the saponifiability of the ester groups.

Polyvinyl alcohol cannot be manufactured from its monomer because of the instability of the vinyl alcohol which immediately rearranges into acetaldehyde. Polyvinyl alcohol therefore has to be obtained indirectly by saponification of polyvinyl acetate. As a technical material it is used as a thickening agent and as the initial material for polyvinyl acetals.

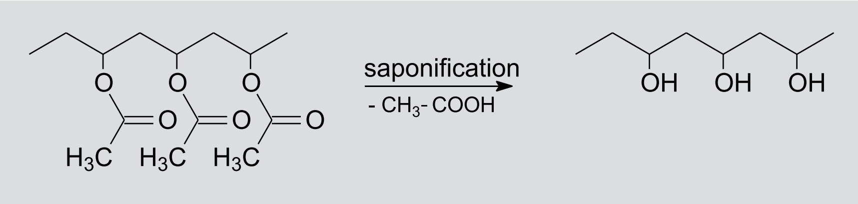


Fig. 2.1.133
Saponification of polyvinylacetate to polyvinylalcohol

Polyvinyl acetals are reaction products of polyvinyl alcohol and aldehydes or ketones. Polyvinyl formal is produced by the reaction of formaldehyde with polyvinyl alcohol, while polyvinyl butyral, which is more important from a coatings perspective, is the outcome of the reaction with butyraldehyde. Because polyvinyl alcohol is manufactured from polyvinyl acetate it contains residual nonsaponified ester groups. There are also hydroxyl groups which escaped acetalation. Apart from the molecular weight, the defining factors for the products' solubility properties and compatibility are the relevant proportion of residual acetate and hydroxyl groups to the acetal groups formed.

Polyvinyl butyral is compatible with all phenol and urea resins, and in part also with alkyd resins and cellulose nitrate. Low molecular types serve as plasticizing components in baking enamels based on phenolic resins and in acid-curing coatings based on urea or melamine resins. Medium-molecular types are often blended with epoxy and phenolic resins and have an important role in corrosion control in reactive mixtures with phosphoric acid as wash primers.

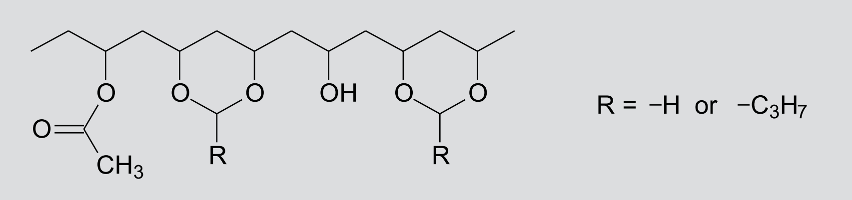


Fig. 2.1.134
Molecular segment of polyvinylacetal

Other polyvinyl compounds worthy of note are the polyvinyl ethers which are more resistant to saponification than polyvinyl esters but are not lightfast. The copolymer of **polyvinyl isobutylether** and PVC is the most important commercial product in this class of substances and is excellently suited for physically drying primers because of its good adhesion on nonferrous metals.

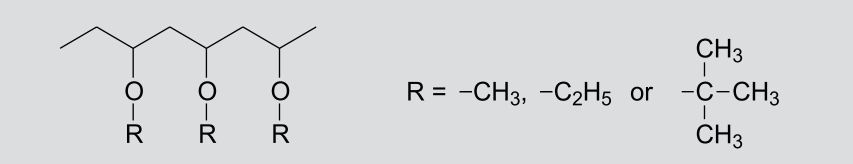


Fig. 2.1.135
Molecular segment of polyvinylether

Most of the polymers described thus far are processed as aqueous dispersions when used for coatings. Their **manufacture** is mainly by means of emulsion polymerization [2.4.34, 2.4.35].

In this manufacturing process the monomer structural elements to be polymerized are first transformed into a coarse aqueous emulsion stabilized by tensides. Excess tensides aggregate in the polar aqueous phase to form micelles. These are small nests with polar particles of the tenside facing outwards while the less polar particles face inwards.

The hydrophobic monomers which have poor solubility in water ultimately migrate into the hydrophobic cores of the micelles. Water soluble starting radicals R· initiate a polymerization reaction in the micelles. As a result of the tenside and radical concentration it is possible to control the growth of the particles in the micelles such that the desired particle size is reached when the monomer has been fully used up (see figure 2.1.136).

Acrylic resins

The term acrylic (acrylate) resins, which are also called polyacrylates or polyacrylics, refers generally not just to the polymers of the pure acrylic acid derivatives, but rather to the copolymers of the esters of acrylic and methacrylic acids and styrene. The individual monomers can be incorporated in almost all mixing ratios in the polymer chains in random distribution with each other. The group transfer polymerization (GTP) and other techniques have gained some importance for producing acrylic backbones with designed hydrophilic-lipophilic balance (see chapter 2.1.3) i.e. usefull as dispersants [2.4.35].

The character and properties of the acrylic resins are defined by the monomer mixture used and also by the molecular weight. Thermoplastic acrylic resins with molecular

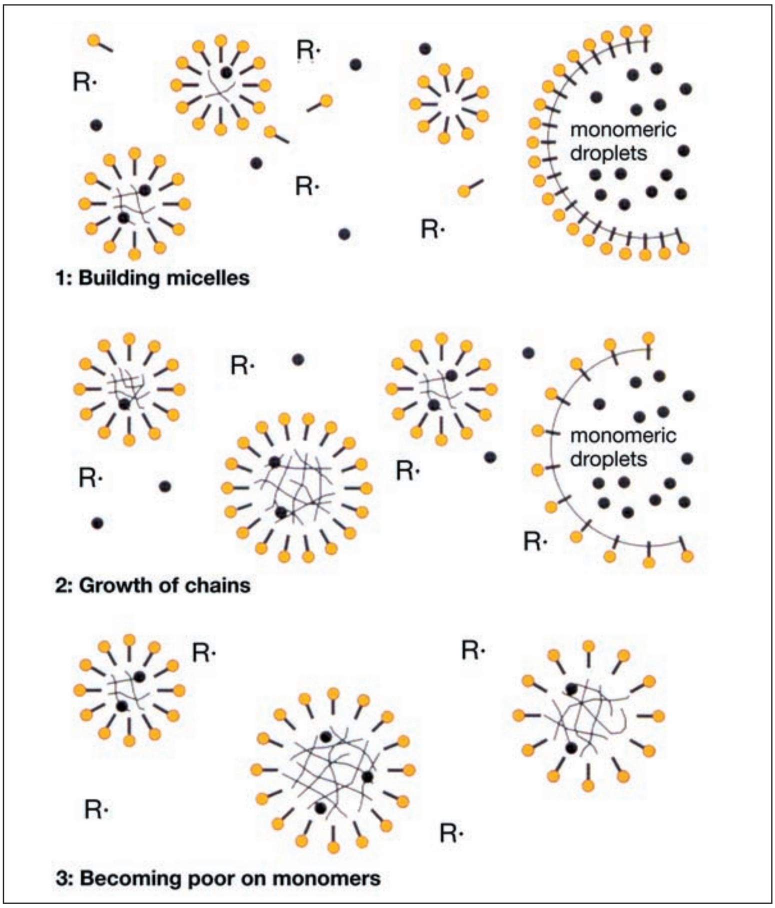


Fig. 2.1.136
Scheme of emulsion polymerization

weights of more than 100,000 g/mol and which have no reactive groups have found their niche in coating technology just as much as low molecular chemically reactive types with molecular weights of less than 20,000 g/mol. Thermoplastic polyacrylates are mainly processed in aqueous dispersions nowadays (see above). For environmental and economic reasons the proportions of genuine organic partial solutions are low. The

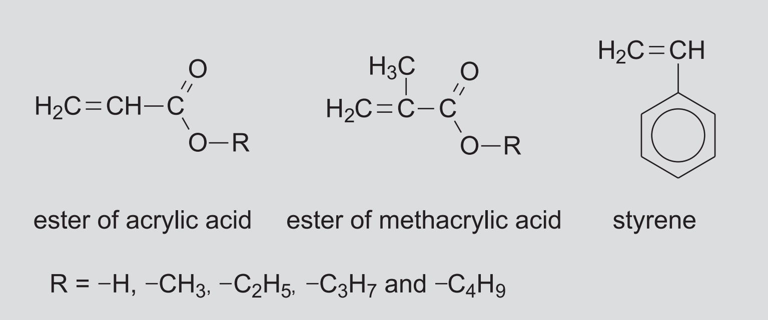


Fig. 2.1.137
Basic components for thermoplastic acrylic resins

chemically reactive variants are used in conjunction with crosslinking agents such as melamine resins as 1-component paints or with isocyanate hardeners as 2-component materials.

Important monomers for thermoplastic coating materials include ethyl, methyl and butyl acrylates and analogous esters of methacrylic acid and styrene.

Thermally curing coating paints, known as ”thermosetting paints”, use resins which also contain proportions of free acrylic acid, hydroxyl-functional acrylic esters, acrylamides, glycidic esters of acrylic acid and corresponding methacrylic acid derivatives.

The film properties and chemical reactivity can be controlled by the number and type of functional groups. In addition to hydroxyl and carboxyl groups, amino or amido groups also merit a mention in this regard. The latter can occur free, mixed with formaldehyde and also etherified.

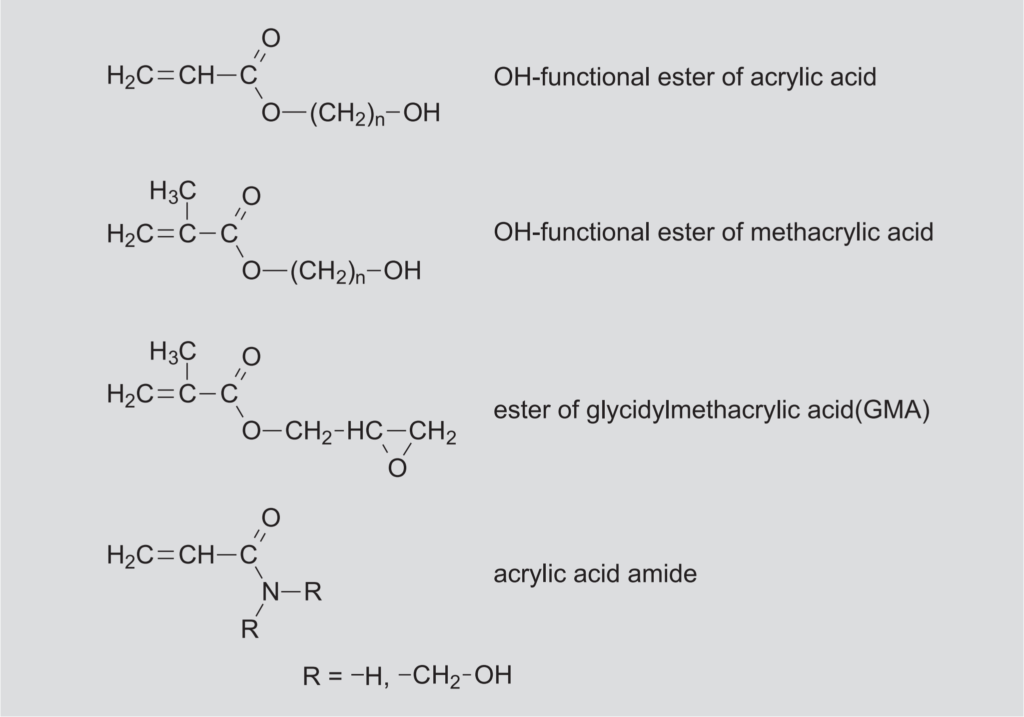


Fig. 2.1.138
Basic components for thermosetting acrylic resins

The mixing ratio of the randomly copolymerizing basic structural elements affect the softening point, also termed the glass transition temperature (see chapter 3.2.5) and thus also the minimum film forming temperature for aqueous dispersions. The methyl side groups of the methacrylic esters stiffen the molecular chains in similar fashion to the aromatic groups in styrene. Polymethacrylates or styrene-containing polyacrylates are, therefore, harder than the corresponding pure polyacrylates. The softening point of the polymers is also affected by the length of the alcohol group of the acrylic or methacrylic esters. For comparable molecular weights of the polymers, the butyl esters are relatively flexible whereas the methyl esters are rigid and hard. The length of the alcohol group affects the mechanical properties, the solubility in solvents and the compatibility with other resins.

A characteristic feature of the performance profile of acrylic resins, irrespective of whether they are thermoplastically or chemically reactive, is the very high degree of saponification of the polymeric acrylic and methacrylic esters. They are, therefore, proven film forming agents for coating concrete, plastics and nonferrous metals such as copper, silver, brass or chrome-plated iron. Aqueous thermoplastic acrylic resin dispersions have now also gained access to the wood coatings field because of the relatively rapid evaporation of the water.

However, the high molecular weight and the associated poor pigment absorption prevents them achieving peak performance in terms of gloss level and hiding power. Despite such difficulties thermoplastic acrylic resins have achieved a certain importance as rapidly drying automotive refinishing paints for spray cans because of their excellent resistance and at the same time good polishing properties. They allow flaws and contamination to be eliminated by sanding during refinishing work without any additional secondary coating since the coating merely needs to be heated to enable it to flow again and create a smooth, glossy film. This method, known as the ”reflow” process, was used for a time the US in the 1970s on automotive coating lines.

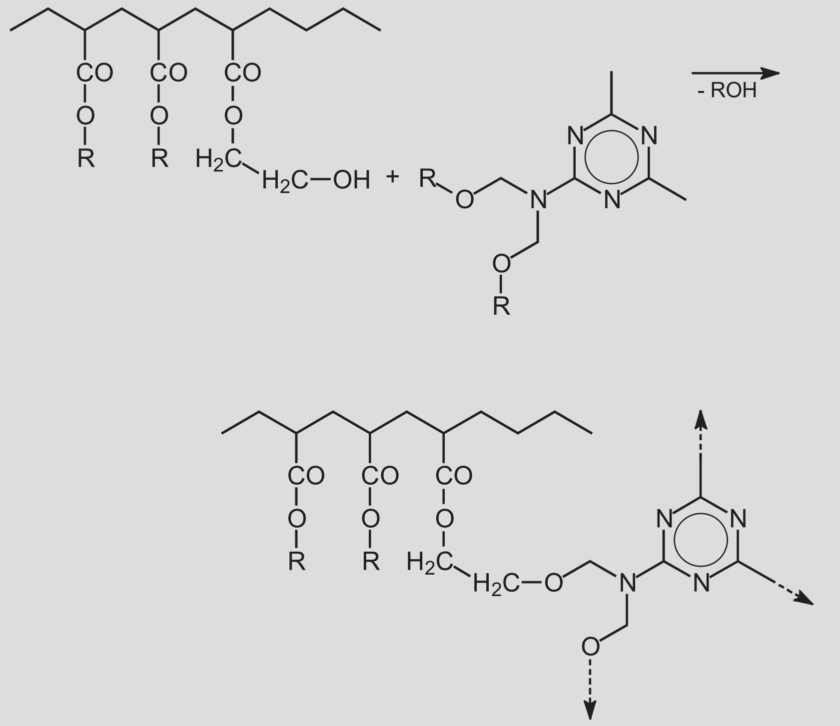
Functional polyacrylates, combined with melamine resins or isocyanate hardeners to achieve crosslinking, are widely used on industrial coating lines and for refinishing. Because of the benefits they bring, they have largely superseded the topcoats based on alkyd/melamine resin combinations which were previously used as standard. To ensure high crack resistance (see chapter 3.3.2) under extreme climatic conditions clearcoats based on externally crosslinking acrylic resins are formulated for metallic base coats.

If glycidyl acrylate or glycidyl methacrylate are used proportionately in the manufacture of acrylic resins, such special resins can also be made to react with acid polyesters or acid acrylic resins via the epoxy groups which are now present in the molecule. This crosslinking reaction is used in powder coating technology, among others (see figure 2.1.139).

If a specific modification is carried out, self-curing acrylate resins can be produced. One of the many options that these resins contain in their chain molecules, in addition to the hydroxyl groups, are amino groups formed by copolymerization with acrylamide. These can be methylolated and also etherified with butanol. Starting from the modified amino groups a duromer network is attached to the hydroxyl groups during baking without requiring the presence of a foreign resin. These are the base resins for detergent-proof single-film coatings of household appliances, dishwashers and refrigerators.

If the proportion of the hydroxyl- and particularly the carboxyl-functional monomers is increased in the monomer mixture, this results in special products which become water soluble after the addition of amines as polymer anions and which can therefore also serve as resins for anodic electrocoating. Cathodically depositable acrylic resins can also be manufactured from acrylate esters with amino groups in the esters by polymerization. After the addition of blocked isocyanates and neutralization with organic acids the mixture can be dispersed and used for topcoats with acceptable longterm outdoor exposure properties. For further improvement in weather and UV-resistance fluorinated acrylics can be used [2.4.36].

1. polycondensation with melamine resins



2. polyaddition with isocyanates

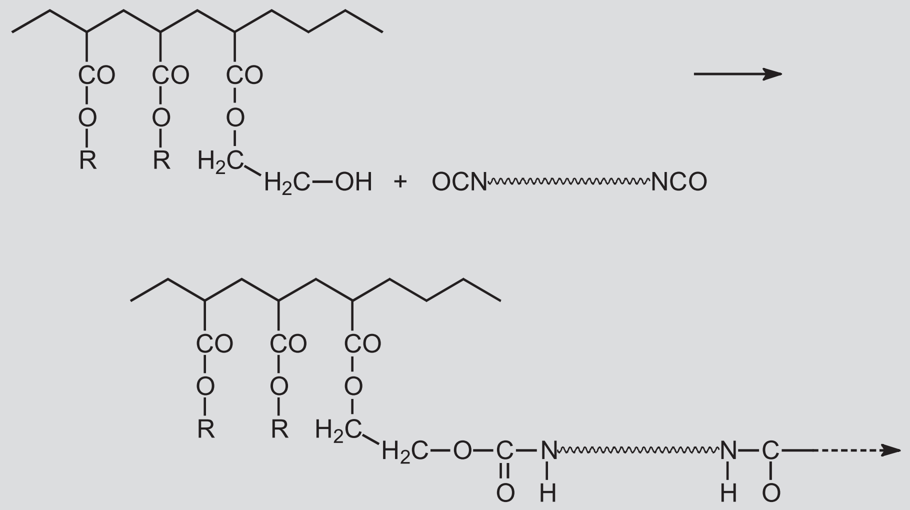


Fig. 2.1.139
Reaction schemes of crosslinking of acrylic resins with other compounds (to be continued)

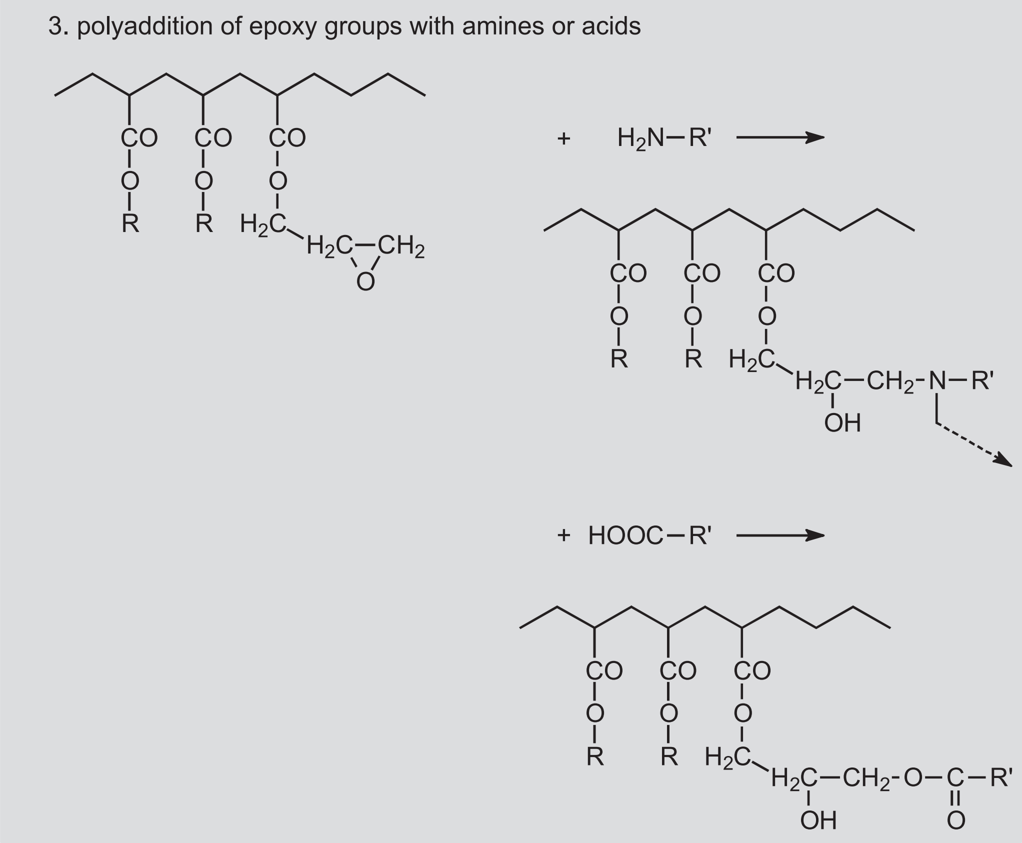


Fig. 2.1.139
Reaction schemes of crosslinking of acrylic resins with other compounds (continued from last page)

The **radiation curable acrylic resins** have a completely different chemical constitution from the film forming agents described thus far. By contrast with the classic acrylic resins radiation curable resins still contain carbon double bonds. These are inserted by the incorporation of terminal acrylic ester groups. They are, therefore, not genuine acrylic resins, but rather acryl-modified film forming agents from a huge variety of origins.

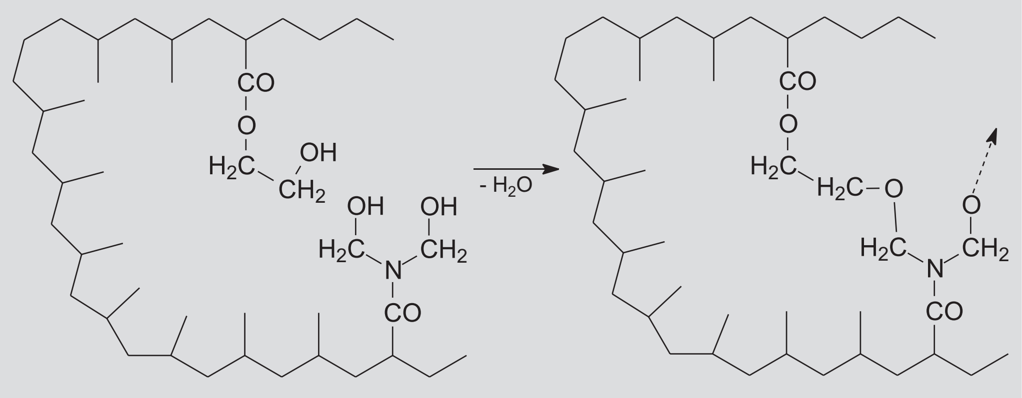


Fig. 2.1.140
Example of a reaction scheme for self crosslinkable acrylic resins

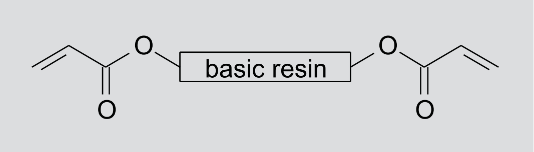


Fig 2.1.141
Acrylic acid modified resin for radiation curing

Such resins contain terminal active double bonds and consequently differ in respect of their suitability as film forming agents for radiation curable coatings from the styrene-containing unsaturated polyesters used as standard previously by having a better ratio of growth to breakage during their curing. They result in higher molecular networks and as a result are more resistant to chemical and mechanical stresses. The excellent scratch resistance resulting from the very high surface hardness should be emphasized.

Various prepolymers, which are enabled to bond chemically with acrylic acid via either the terminal epoxy or hydroxyl groups, are used to manufacture the acrylic acid-containing film forming agents.

The first commercially available resins were acrylic acid-modified epoxy resins. Since one OH group is created per reaction stage by the addition to the epoxy groups, this can also be made to react with acrylic acid chloride with the release of HCl. The resulting increased functionality yields even higher degrees of crosslinking and thus to even greater resistance to chemicals with improved hardness at the same time.

The manufacture of modified polyester or urethane resins is similar to that of acrylic acid-modified epoxy resins. Polyesters are bound to acrylic acid via terminal OH groups in a condensing reaction, while isocyanate-containing resins are bound to OH-functional acrylic esters in a polyaddition reaction.

In keeping with the characteristic properties of the prepolymers, the radiation curable systems dominate specific application fields. The reactive epoxy acrylates result in high chemical resistance, while polyester acrylates are extremely lightfast and therefore

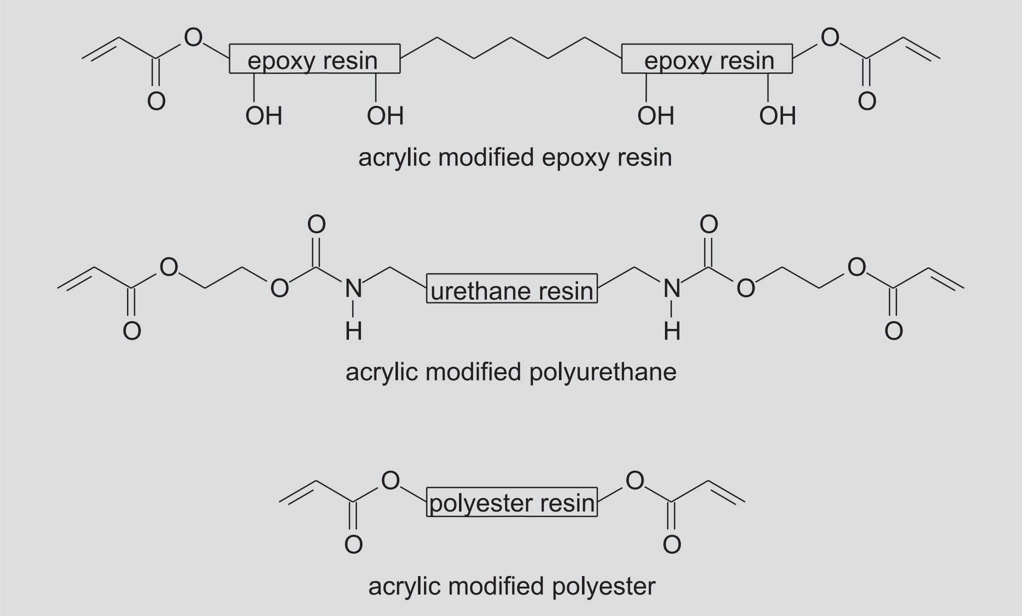


Fig. 2.1.142
Examples of radiation curable, acrylic acid modified film forming agents

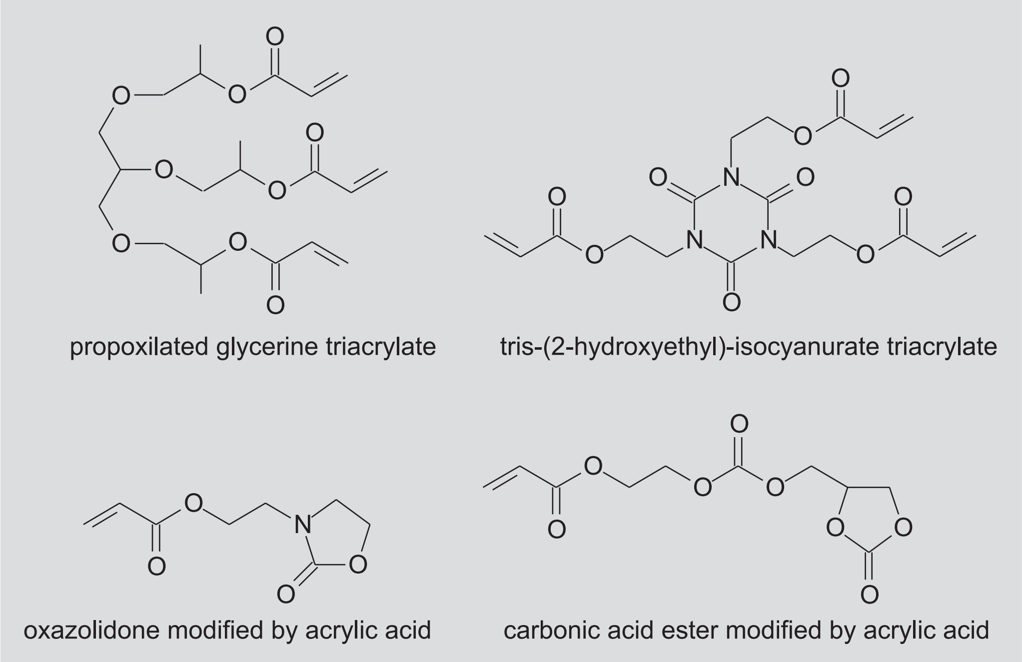


Fig. 2.1.143
Reactive diluents for radiation curing and following thermal crosslinking

suitable for packaging material coatings and for wood treatment materials. Urethane acrylates are particularly suitable for coating plastics and wood because of their toughness, their good adhesion and wear resistance and are also suitable for coating leather and for printing inks.

If special demands with regard to heat resistance are made of the coating with good longterm outdoor exposure and mechanical/technological properties at the same time, silicone acrylates are the ideal initial products.

Coating materials for UV curing made purely of modified acrylic resins are generally too viscous to permit them to be processed without difficulty. They are therefore dissolved in solvents. However, the practice of using proportionately low molecular reactive diluents copolymerizing with the base resin has become widely accepted Such formulations are practically emission free. The acrylic esters of trimethylolpropane and pentaerythritol have been superseded by propoxylated glycerine triacrylate or tris-(2-hydroxyethyl)iso-cyanatotriacrylate because of irritation on contact with the skin. New reactive thinners which are regarded as safer include acrylic acid-modified carbonic esters and oxazolidones.

One of the other ways of influencing the rheological properties during processing consists of transforming the prepolymers into a watersoluble or water-dispersible form. However, radiation curing is only possible once the water has completely evaporated. Although interest in this relatively new variant of radiation curable coatings is growing, it has yet to find an important market.

As with unsaturated polyesters and coatings made from them, photoinitiators are absolutely essential to initiate hardening by UV radiation, despite the higher reactivity of the acrylate functions (see chapter 2.1.4 and chapter 4.3.2).

A new variant of radiation curable film forming agents are the resins with terminal acrylic acid groups manufactured from **dendritic polyesters**. Crosslinking requires only minimal quantities of photoinitiators. It is even possible to dispense with them completely if there is adequate radiation energy in the presence of amine synergists. The synergists, i.e. amines with a methylene group close to the nitrogen, generate radicals and reduce the oxygen inhibition. They are then incorporated in the film forming agent.

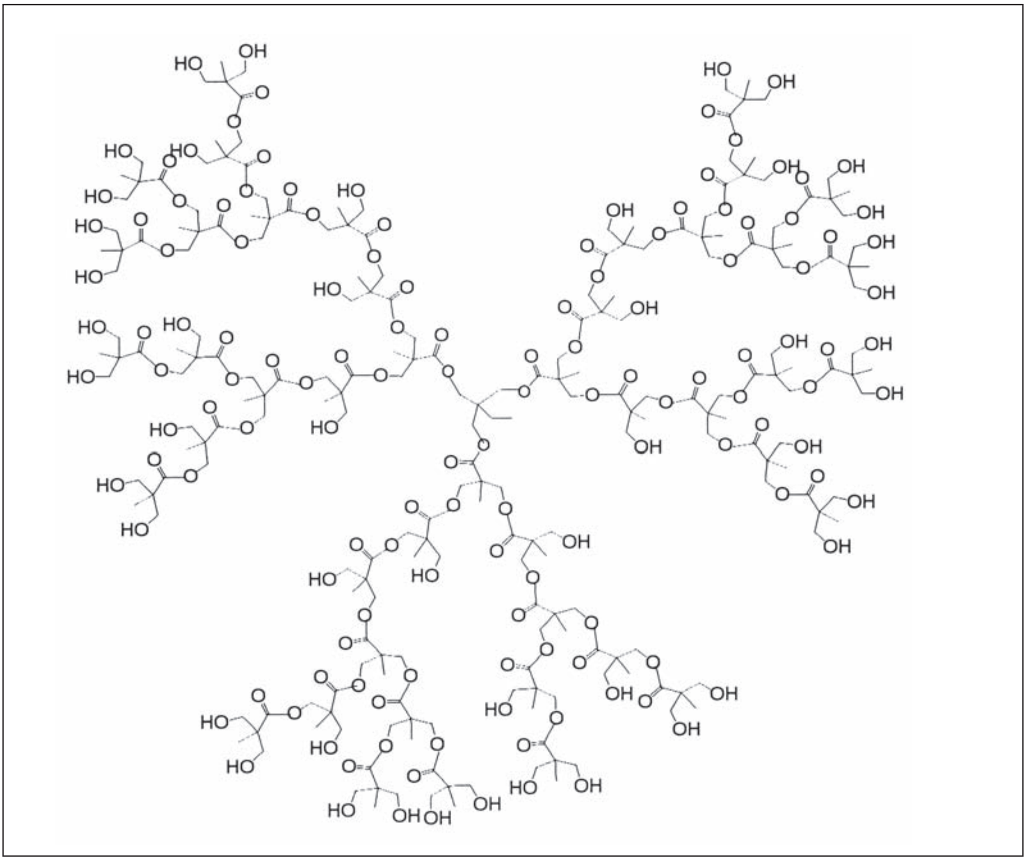


Fig. 2.1.144
Structure of dendritic polester resins (dendrimere)

The special molecular form of the dentritic polyesters results in low viscosities even at high molecular weights. The high functionality results in extremely high crosslink densities and thus to scratch and chemical resistance of a level which could not otherwise be achieved [2.4.37]. Other interesting properties of dendrimeric film forming agents are their extraordinary curing rate and also extremely low shrinkage during crosslinking because of their particular molecular form.

2.1.2 Solvents

Solvent, as defined in DIN EN 971-1, are liquids comprising one or more components that are volatile under the specified drying conditions and can dissolve film forming agents purely physically without chemical reactions.

Solvents, as low viscous substances, are the exceptions among all the raw materials of coatings. They perform a special task in that they merely provide assistance during the processing of coating materials. When this task is done, they should be removed again as quickly and completely as possible. They are thus unlike the reactive thinners, additives and plasticizers which also affect the consistency of the material. Whereas reactive thinners combine chemically with the resin, the chemically inert plasticizers and most additives remain in the film as very low volatility substances.

Ideally solvents should result in a uniform liquid phase for all components in the resins. By contrast, other formulation methods are followed for colloids, gels, emulsions and dispersions. Despite variation in their formulation, the aim remains the same, i.e. to guarantee the processibility of the coatings from the liquid phase.

In the case of solutions the interaction with the film forming coating resins can result in varying configurations of the film forming agent molecules, depending on compatibility with the solvent, and thus in varying coiling of the macromolecular chains during film formation. Variations in the mechanical strength of the film are associated with this. The latter impacts on the crack resistance and impact strength. This effect is particularly pronounced with physically drying coating materials. The selection of the solvents for the particular coating system is, therefore, limited, not just in terms of the application method, but also for mechanical/technological reasons.

However, the effect of the solvents on the film forming process and thus also on the properties of the coating goes well beyond the coil expansion of the resin molecules. The surface tension of solvents which is generally lower than that of the more polar coating resins promotes the wetting of the substrate. To this can be added the fact that the lowering of the viscosity by the solvents also aids improved processing, i.e. better sprayability, coatability, rollability or also dippability. The solvent composition should enable the rheological properties during the entire transition from the liquid coating material via the application to the viscoelastic coating including the drying and hardening phases to be modified such that good flow is achievable without runs or without running away from edges, setting is completed without blisters and craters, good overspray absorption is possible and at the same time an optimum effect formation is obtained with metallic or pearlescent effect coatings (see chapter 6.2).

The influence of the solvents on the substrates must not be forgotten. In the case of plastics, for example, the ability of the substrates to swell and the associated impairment of the visual properties during solvent discharge and bonding must be taken into account.

Mixtures of solvents are often used because of the need to coordinate the interaction with the resin molecules and the associated evaporation rate during processing and film formation. They should be capable at any time, under permanently changing circumstances, of guaranteeing the optimum film properties. Despite their environmental problems, therefore, solvents are necessary for coatings.

In recent decades considerable efforts have been made to replace organic solvents by the physiologically safe alternative of water or, as in powder coatings, to dispense with them completely. Because of the specific requirements of complex coating processes, the use of organic solvents will undoubtedly continue to be necessary for the foreseeable future to some extend.

Since current legislation now only permits solvent emissions in significantly restricted form, the operators of coating plants are compelled to reduce emissions by secondary measures or by using low solvent coatings (see chapter 5.3.1).

Coating	Typical Solvent Content [%]
Powder coatings	–
Silicone paints and -plasters	–
Interior dispersion paints	0 – 2
Exterior dispersion paints	3 – 5
Plasters	3 – 5
Waterborne primers	3 – 5
Electrodeposition coatings	1 – 3
Waterborne paints	8 – 18
High Solids	25 – 30
Conventional paints	45 – 65

Fig. 2.1.145
Typical solvent content of different paints as delivered

Solvents can also be hazardous materials for those people involved in the manufacture and processing of coatings. They are, therefore, substances which must be equally critically evaluated from the points of view of occupational health and the environment. Numerous toxicological studies in the last few decades have provided comprehensive information on the hazards of handling solvents. Research projects are continually in progress to replace or reduce solvent use. Furthermore, classifications and labelling of standard solvents for coatings simplify their selection and correct handling (see chapter 5.4).

The colloidal solutions mentioned earlier, whose film forming agents are no longer uniformly distributed, are clear to slightly opalescent liquids. As a sign of the inhomogeneity which is gradually taking effect, they scatter light. The cause of this lies in the aggregation of a number of individual molecules. However, the solvents act fully on them. Dispersions, whose use has grown more and more in recent years, are heterogeneous systems with a high degree of light scatter. They are milky liquids consisting of a continuous liquid phase and a discrete phase. This can be solid or also liquid. The discrete phase must be electrostatically or entropically stabilized (see chapter 2.2.3).

2.1.2.1 Theory of Solubility

During the dissolving process solvent molecules penetrate the matrix of the film forming agent and surround its individual molecules with solvent shells. They solvate the resin. As a result of the solvent shells, the interaction between the resin molecules themselves is reduced to such a degree that a molecular distribution of the dissolved materials occurs.

The strength of the solvatation is equally dependent on the intermolecular interactions of the film forming agent molecules and those of the solvents themselves.

The coherence of the solvent, quantified by its cohesion energy ΔE, can be calculated from the enthalpy of evaporation ΔH_V. The cohesive energy related to the molar volume, the cohesive energy density ΔE/V, is a specific figure for each solvent. It can be used to estimate the solvent power, provided corresponding figures for the film forming agent to be dissolved are also available. In ideal solvent mixtures the joint value for the mixture is the geometric mean of the cohesive energy densities of the individual components. The square root of the cohesive energy density is designated as the solubility parameter δ. Solvents with similar δ-values have comparable molecular interaction forces and thus also a similar solvent power. They therefore mix together well. Mutual solubility should therefore always be guaranteed if the differences do not exceed 6 $[J/cm^3]^{1/2}$. In a good fit with this thesis the table for several pairs shows that the actual solubility properties depend on the differences in the solubility parameters. Unfortunately this fit is not guaranteed in all cases.

$$\Delta E = \Delta H_V - RT$$

$$\frac{\Delta E}{V} = \frac{\Delta H_V - RT}{V}$$

$$\sqrt{\frac{\Delta E}{V}} = \delta = \sqrt{\frac{\Delta H_V - RT}{V}}$$

ΔE = molar cohesion energy
ΔH_V = molar enthalpie of evaporation
$\frac{\Delta E}{V}$ = molar cohesive energy related to volume
δ = solubility parameter

Fig. 2.1.146
Definition and calculation of solubility parameters

Component 1	Component 2	Solubility	Δδ
n-hexane	methanol	bad	14,1
	polydimethylsiloxane	good	0,4
	polyisobutylene	good	1,4
n-heptane	diethylether	good	0,2
	benzol	good	3,5
	ethylene glycole	bad	13,2
	water	bad	30,6
n-octane	methylenchloride	good	4,7
toluene	polyvinylacetate	good	0,4
propanol	polydimethylsiloxane	bad	9,2
ethanol	polyvinylacetate	good	6,9
	polyisobutylene	bad	9,8
methanol	polyacrylic acid ester	medium	8,4
	polystyrene	bad	11,0
acetic acid ethylester	polystyrene	good	0,8
acetone	polymethacrylic acid methylester	good	0,6

Fig. 2.1.147
Solubility potential of two components according to the difference thesis $\Delta\delta < 6\ (J/cm^3)^{1/2}$

To eradicate this shortcoming, the δ-value is divided according to

$$\delta_{total} = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$$

δ_D = parameter for nonpolar contribution
δ_P = parameter for polar contribution
δ_H = parameter for hydrogen bridges contribution

into three individual components. The indices relate to the nonpolar dispersion forces, the dipole forces and the interactions caused by hydrogen bridges. The solubility related properties of the solvents are now expanded by three individual values to give a 3-dimensional solubility parameter, the so called *Hansen* parameter and recently to a proposed 4-dimensional parameter set [2.4.38].
Fig. 2.1.148 shows that it is quite possible for the same or similar δ_D values to have different δ_P and δ_H values.

	δ_{total}	δ_D	δ_P	δ_H
n-hexane	14,9	14,7	0	0
cyclohexane	16,8	16,8	0	0
toluene	18,2	18,0	1,4	2,0
xylene	18,0	17,8	1,0	3,1
ethylbenzol	18,0	17,8	0,6	1,4
styrene	19,0	18,6	1,0	4,1
n-propanol	24,3	15,1	6,1	17,6
isopropanol	23,5	15,3	6,1	17,2
n-butanol	23,3	16,0	6,1	15,8
isobutanol	21,9	15,3	5,7	15,8
2-ethylhexanol	19,4	16,0	3,3	11,9
cyclohexanol	23,3	17,4	4,1	13,5
diacetonealcohol	18,8	15,8	8,2	10,8
acetone	20,5	15,6	11,7	4,1
methylethylketone	19,0	16,0	9,0	5,1
methylisobutylketone	17,2	15,3	6,1	4,1
cyclohexanone	19,8	17,8	7,0	7,0
ethylacetate	18,6	15,1	5,3	9,2
butylacetate	17,4	15,1	3,7	7,6
butylcellosolve	18,2	16,0	6,3	12,1
ethyldiglycole	19,6	16,2	7,6	12,3
butyldiglycole	18,2	16,0	7,0	10,6
water	47,8	14,3	16,3	42,6
polystyrene	19,0	17,5	6,1	4,0
polyvinylacetate	23,0	18,9	10,1	8,1
polymethacrylacid methylester	22,0	18,7	10,1	8,5
polyvinylchlorid	22,4	19,1	9,1	7,1
epoxy resin	23,4	17,3	11,2	11,2

Fig. 2.1.148
Solubility parameter δ_{total} of different solvents and their disperse contribution δ_D, polar contribution δ_P and hydrogen bridging contribution δ_H

Despite this optimization in the calculation of solubility parameters there are still inconsistencies in some cases. Formulators will find this useful but should beware of uncritical acceptance.

2.1.2.2 Physical Properties

With regard to action on the various film forming agents, solvents or solvent groups can turn out to be genuine active solvents, latent solvents, but also nonsolvents. The genuine or active solvents dissolve a substance readily at room temperature. The latent solvents, which are not capable of dissolving a particular substance by themselves, can have their solvent power activated by addition of a genuine solvent, but also by addition of a nonsolvent. Supplementary solvents with a high activation effect are alcohols, ketones, highermolecular esters and sometimes even water. The activation is based on a shift in

Type of solvents	Mol. mass	Boiling-point/ region [°C]	Density at 20°C $[g/cm^2]$	Refraction index at 20°C	Evaporation number	Vapor pressure at 20°C [hPa]	Flash-point [°C]	Ignition temperature [°C]	Explosion limit [Vol%]
Aliphatic hydrocarbons and mixtures									
n-hexane	86,2	65 – 70	0,675	1,372	1,4	190	-22	240	1,2/7,4
Solvesso 100	123	155-181	0,877	1,502	40-45	3	41	>450	0,8/7,0
Solvesso 150	135	178-209	0,889	1,515	120	1	62	>450	0,6/7,0
Solventnaphta	123	150-195	0,870	1,500	40-45	3	41	>450	0,8/7,0
benzine 135/180	131	135-175	0,766	1,428	25-30	70	~22	210	0,6/7,0
cyclohexane	84,2	80,5-81,5	0,778	1,426	3,5	104	-17	260	1,2/8,3
Aromatic hydrocarbons									
xylene	106,2	137-142	0,874	1,498	17	90	25	562	1,0/7,6
toluene	92,1	110-111	0,873	1,499	6,1	290	6	569	1,2/7,0
styrene	104,2	145	0,907	1,547	16	60	31	490	1,0/6,3
Alkohols									
propanol	60,1	97,2	0,804	1,386	16	19	23	360	2,1/13,5
n-butanol	74,1	117,7	0,811	1,399	33	6,6	34	360	1,4/11,3
iso-butanol	74,1	107,7	0,802	1,396	25	12	28	410	1,5/12
ethylhexanol	130,2	183,5-185	0,833	1,432	600	0,5	76	250	1,1/12,7
isotridecylalkohol	200,2	242-262	0,845	1,448	>2000	<0,01	115	250	0,6/4,5
Gycol ether									
butylglycol	118,2	167-173	0,901	1,419	163	1	67	240	1,1/10,6
propylglycol	104,2	150,5	0,911	1,414	75	2	51	235	1,3/15,8
hexylglycol	146,2	208	0,887	1,429	ca.1200	0,08	91	220	1,2/8,4
methyldiglycol	120,2	194,2	1,021	1,424	576	0,3	90	215	1,6/16,1
butyldiglycol	162,2	224-234	0,956	1,431	>1200	0,1	98	225	0,7/5,3
methoxipropanol	90,1	122,8	0,934	1,403	25		38	270	1,7/11,5
ethoxipropanol	104,1	132	0,896		33	<10	40	255	1,3/12

Fig. 2.1.149
Physical and safety related data of important solvents (selection out of different resources without claiming to be complete and accurate) (to be continued)

the solubility parameters achieved by targeted mixing. Nonsolvents are incapable by themselves of dissolving the film forming agent in question. The definition of a solvent or a solvent mixture as a genuine solvent, a latent solvent or a nonsolvent refers in each case only to a particular film forming agent. With a different film forming agent conditions may be completely different and other solvents may act as a solvent or non-solvent.

As already mentioned above, the solvents in coating materials only have a temporary function, relating to the liquid coating material: it starts with its manufacture, accompanies the application and then finishes when it evaporates from the liquid film. The type and quantity of solvents or solvent mixtures depend particularly on the type of film forming agent and the application conditions. During their dwell time in the coating material the solvents fulfil a range of tasks and exert influences in a number of directions.

Type of solvents	Mol. mass	Boiling-point/ region [°C]	Density at 20°C [g/cm^2]	Refraction index at 20°C	Evaporation number	Vapor pressure at 20°C [hPa]	Flash-point [°C]	Ignition temperature [°C]	Explosion limit [Vol%]
Esters									
butylacetate	116,2	123-127	0,880	1,394	11	13	25	400	1,2/7,5
ethylethoxy-proprionate	146,2	170	0,943		96	2	59	327	1,05/
ethylacetate	88,1	76-78	0,900	1,372	2,9	97	-4	460	2,1/11,5
isobutylacetate	116,2	114-118	0,871	1,390	8	18	19	400	1,6/10,5
ethoxypropyl-acetate	146,2	158	0,941	1,405		2,27	54	325	1,0/9,8
methoxypropyl-acetate	132,2	143-149	0,965	1,402	33	4,2	45	315	1,5/10,8
pentylacetate	130,2	146	0,876	1,405	14	6	23	380	1,1/
butylglycolacetate	160,2	190-198	0,945	1,415	250	0,4	75	280	1,7/8,4
Ketones									
methyisobutyl-ketone	100,2	115,9	0,800	1,396	7	20	14	475	1,7/9,0
acetone	58,1	56,2	0,792	1,359	2	245	-19	540	2,1/13
cyclohexanone	98,2	155	0,945	1,451	40	3,5	44	455	1,1/7,9
methylethylketone	72,1	79,6	0,805	1,379	2,6	96	-14	514	1,8/11,5
methyl-n-amylketone	114,2	150,5	0,816	1,411	25	5	49	393	1,1/7,9
methyl-isoamylketone	114,2	141-148	0,813	1,407	55	6	41	425	1,1/8,2
isophorone	138,2	215	0,922	1,478	230	3	96	460	0,8/3,8
Others									
water	18	100	1,000				-	-	-
propylencarbonate	102,2	242	1,208		>1000		123		

Fig. 2.1.149
Physical and safety related data of important solvents (selection out of different resources without claiming to be complete and accurate) (continued from last page)

They dissolve solid or liquid film forming agents and also other components in the coating formulation and convert them into solutions with particular flow properties. With dispersion-based paints they are the liquid phase in which the solids are distributed. They assist in wetting the pigments and extenders via the dissolved binders during the dispersion process. In the case of dispersion-based paints the solvents or the liquid phase are generally the sole medium for the dispersion. They regulate the paint viscosity during both manufacture and processing.

Thanks to their selective evaporation properties they intervene to regulate the film forming process, they can improve flow, increase the gloss and prevent the formation of blisters, craters etc. by transporting volatile reaction products. They also aid in setting the conductivity for electrostatic spraying.

Important physical performance indicators of the solvents used for the coating materials are the density, refractive index, boiling temperature or boiling ranges and the vapour pressure or evaporation time. For safety reasons other values such as the flash point, ignition point and explosion limits must also be added (see chapter 5.2).

With reference to their boiling properties, solvents are divided into low boilers (boiling range < 100 °C), middle boilers (boiling range 100 – 150 °C) and high boilers (boiling range > 150 °C). Interestingly there are no real correlations between the boiling points or boiling ranges of the solvents and their evaporation time from the paint film as it forms. The evaporation time of a solvent is therefore expressed numerically in evaporation numbers by comparison with that of diethyl ether. Relative to diethyl ether (evaporation number = 1) numbers are obtained, on the basis of which the solvents can be subdivided into the following groups: high volatility (evaporation number < 10), medium volatility (evaporation number 10 – 35), low volatility (evaporation number 35 – 50) and very low volatility (evaporation number > 50).

If macromolecular film forming agents are dissolved in a solvent, the evaporation rate is reduced because of the interaction of the solvent molecules with the film forming agent. This effect is all the more pronounced, the better the solubility of the polymer in the relevant solvent. The actual conditions are more complicated, however, since paints always contain combinations of solvents whose solubility and evaporation properties have to be coordinated with each other.

Solvents with a low evaporation number cause rapid initial drying, while medium-volatile solvents ensure that the coating is kept open for a certain time so that any entrained air or gaseous reaction products can escape. High boilers leave the coating film only slowly and positively influence the flow, smoothness and gloss of the coating in the final phase of film forming. It is important for the most slowly evaporating element of the solvent combination to be a genuine solvent for the particular film forming agent combination. In this way many film faults will be avoided (see chapter 6.2).

In the case of solvent mixtures consisting of two or more components it is possible with certain mixing ratios for systems to be formed with a constant boiling point which is lower or even higher than that of the individual components. The occurrence of such azeotropic solvent mixtures is caused by intermolecular forces or molecular associations between the solvents themselves. As a consequence of the formation of an azeotrope, therefore, it is possible for a solvent mixture to exhibit different properties when evaporating from a liquid coating film from those that would be anticipated on the basis of the individual components' evaporation times. This can also affect the level of the flash point (see chapter 2.3.2).

2.1.2.3 Chemical and Physiological Properties

An important prerequisite for the technical usability of a solvent is its chemical stability. Almost all aliphatic and aromatic hydrocarbons meet this requirement. Alcohols also exhibit good stability. However, alcohols can be oxidized to aldehydes or ketones or even to carboxylic acid by strong oxidizers, though not by atmospheric oxygen. Because of their ready reaction with isocyanates alcohols (and glycols and glycol monoalkylether) must never be mixed with polyurethane hardeners. Ether and glycolether react with atmospheric oxygen to form peroxides which in turn can result in the formation of acids. Esters and ketones also display high resistance. Under unfavourable conditions, however, ketones can resinify, and esters can be split by saponification.

Solvents in liquid and particularly in gaseous form can be absorbed by human, animal and, should the situation arise, plant organisms and cause damage in the event of longterm action. The hazard and the degree of hazard depend on the nature of the particular solvent. An important measure of hazards for humans is the threshold concentration of a solvent in the air, below which, even with repeated and longterm exposure, no harm to health is to be expected. The figures for the maximum admissible concentration (MAC level; in German : MAK) in the workplace, otherwise known as the occupational exposure limit, are given in mg material per m^3 air (mg/m^3) and for solvents also in ml solvent vapour per m^3 air (ml/m^3) (see chapter 2.3.2). Comparison figures obtained from animal experiments are also often used as guidelines for evaluating the harmfulness or toxicity (see chapter 5.4). The usual method is to determine the concentration of the harmful substances which is lethal to a given proportion of the animal population studied, normally rats. The figure is quoted in the form of a solid concentration (LD = lethal dose) or gaseous phase concentration (LC = lethal concentration) with an additional index denoting the percentage of the animals which died after exposure.

The odour emitted by solvents is not directly linked to its harmfulness. Odours can cause significant annoyance in certain cases. The measure of odour intensity is the odour threshold. According to DIN EN 13725 this indicates the smallest concentration of the relevant solvent, expressed in mg/m^3, that can just be perceived in the air by people with an average sense of smell and without prior training. MAC (= MAK)-figures and other occupational health and safety information for the most important solvents are summarized in figure 2.1.150.

2.1.2.4 Important Solvents for Coatings

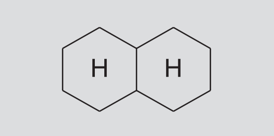
The many organic solvents which are important for coatings can be divided by their chemical character into groups with common features. The aliphatic, cycloaliphatic and aromatic hydrocarbons, esters, ethers, alcohols, glycol ethers and ketones are particularly common. The range of applications in which these solvents are used and their solvent power are evaluated below.

Type of solvent	MAK [ppm]	MAK [mg/m^3]	LD$_{50}$ rats, oral [mg/Kg]	LC$_{50}$ rats, inhalation [mg/l]	Class of danger to VbF	Class according to TA-Luft
Aliphatic Hydrocarbons and mixtures						
n-hexane	50	180	>2000	>5	AI	2
Solvesso 100	50	200	>2000	>5	AII	2
Solvesso 150	50	200	>2000	>5	AIII	2
Solventnaphta	50	200	>2000	>5	AII	2
Benzine 135/180	100	500	>2000	>5	AII	3
cyclohexane	200	700	>2000	1800 ppm	AI	3
Aromatic Hydrocarbons						
xylene	100	440	>2000	>5	AII	2
toluene	50	190	>2000	>5	AI	2
styrene	20	86	>2000	11,9	AII	2
Alcohols						
propanol			>2000	9,8	0	3
n-butanol	100	300	700	>17,7	AII	3
iso-butanol	100	310	>2000	>6,5	AII	3
methoxipropanol	100	370	>2000	>6	0	2
ethoxipropanol			>2000	>5	0	3
ethylhexanol			>2000		AIII	3
isotridecylalkohol			>2000		0	3
Gycols						
butylglycol	20	98	1480		0	2
propylglycol	20	86	>2000	2132 ppm	0	2
hexylglycol			1480		AIII	3
methyldiglycol			>2000		0	3
butyldiglycol		100	>2000		0	3
Ester						
butylacetate	100	480	>2000		AII	3
ethylethoxyproprionate			>2000		AIII	3
ethylacetate	400	1500			AI	3
isobutylacetate	100	480	>2000		AI	3
ethoxipropylacetate			>2000	7	AII	3
methoxipropylacetate	50	270	>2000	>23,8	AII	3
pentylacetate	50	270	>2000		AII	3
butylglycolacetate	20	130	>2000	2,7	AIII	2
Ketones						
Methyisobutylketone	20	83	>2000	8,3	AI	3
acetone	500	1200	>2000	>5	B	3
cyclohexanone	20	80	1900	10,2	AII	2
methylethylketone	200	600	>2000	12	AI	3
methyl-isoamylketone	50	230	>2000	3813 ppm	AII	
methyl-n-amylketone	50	238	1600	>2000 ppm	AII	3
isophorone	2	11	>2000	>7	AIII	2
Other						
water	-	-	-	-	-	-

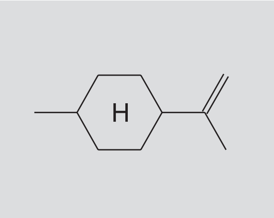
Fig. 2.1.150
Working place related physiological data of solvents (selection out of different sources without claiming to be complete and accurate)

$$H_3C-(CH_2)_x-CH_3$$

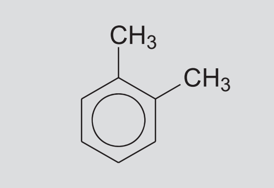
Aliphatic hydrocarbons, also termed gasolines, benzines or paraffin hydrocarbons, exhibit good stability with good solvent power for nonpolar to poor polar film forming agents. They are mixtures consisting of a large number of similar individual components. Mixtures are generally categorized by their boiling ranges into the light benzines (special benzine) and the significantly heavier mineral spirits (vernices). The special benzines, which are mainly used for rapidly drying coatings, have flash points below 21 °C to < 0 °C, which means that the coatings manufactured from them may only be processed under stringent safety precautions. Mineral spirits, all with flash points above 21 °C, are good solvents for chlorinated rubber, long-oiled alkyd resins, some vinyl chloride copolymers and polyvinyl ether. Polar film forming agents such as cellulose derivatives, epoxy, polyester, PUR, phenol, amino and amido resins are not dissolved.



The **cycloaliphatic hydrocarbons**, like the example of hydrated naphthalene shown, are between the aliphatic and the aromatic hydrocarbons in terms of solvent power. The range of resins soluble in cycloaliphatic hydrocarbons corresponds largely to that of the aliphatic hydrocarbons. The cycloaliphates are less common in the paint and coatings industry than the paraffin hydrocarbons. The main examples are hydrated naphthalene products such as tetrahydronaphthalene (Tetralin) and decahydronaphthalene (Dekalin), both high boilers with good solvent power. The hydrocarbons are exclusively of petrochemical origin nowadays.



The **terpene hydrocarbons**, headed by turpentine oil, are of plant origin. They are obtained by distilling the balsam of various pine species. They were mainly used in combination with mineral spirit in oxidatively crosslinking oil and alkyd resin coatings and are now largely replaced by aliphatic hydrocarbons (”turpentine substitute”).



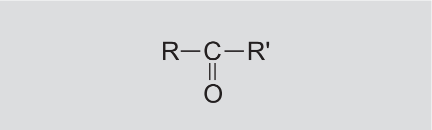
Compared with benzines, the **aromatic hydrocarbons** have a much broader solvent power for alkyd resins of all types, saturated polyesters, polystyrene, polyvinyl ether, polyacrylates and polymethacrylates, polyvinyl acetate, vinyl chloride and vinyl acetate copolymers. Aromatic hydrocarbons can be used as diluents for solutions of cellulose nitrate and other cellulose esters in ester and ketone mixtures. Apart from toluene and commercially available technical xylene, a mixture of changing quantities of o- (see above), m- and p-xylene, higher-substituted benzene derivatives designated solvent naphtha are in widespread use. These are primarily alkylbenzenes, including tri- and also tetramethylbenzene, isopropylbenzene (cumene), methyl ethyl benzene and diethylbenzene. These high-boiling aromatic mixtures, like toluene and xylene themselves, do not contain the potentially physiologically hazardous benzene which has not been used in the paint and coatings industry for quite some time because of its carcinogenic effect.
Styrene (vinyl benzene) and vinyl toluene, also aromatic hydrocarbons, act simultaneously as solvents and reactants for chemical crosslinking with unsaturated polyester resins and UV-coatings.

$$\mathrm{Cl_3C{-}CH_3}$$

Chlorinated hydrocarbons are now hardly used at all in paint formulations in Germany for environmental and physiological reasons, despite their excellent solvent power for a very broad range of film forming agents. However, they are still found in self-etch pretreatment primers for plastics coatings in North America and Asia.

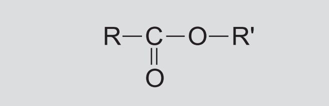
$$\mathrm{R{-}OH}$$

Because of their hydroxyl groups the **alcohols** and the gycols and glycol ethers differ from the hydrocarbons in having a high dipole moment and a marked tendency to form hydrogen bridging bonds. The alcohols' solvent power is influenced by the mass ratio between the polar hydroxyl groups and the nonpolar organic group. The lower alcohols with a pronounced polarity are good solvents for highly polar film forming agents such as phenolic resins, amino resins, cellulose nitrate, ethyl cellulose and polyvinyl acetate. As the carbon chain lengthens, the alcohols' solvent power for polar film forming agents decreases, as a result of which they can only be used as a diluent with them. Higher alcohols can also be used to improve the storage stability of baking enamels with etherified crosslinking resins. They prevent the removal of alcohols from the ether groups.



$$\mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R'}$$

Like the hydroxyl group, the carbonyl groups also introduce high dipole moments and a definite tendency towards hydrogen bridging bonds to the solvent molecules. The lower **ketones** are also excellent solvents for polar film forming agents such as cellulose ether, ketone resins, copolymers of vinyl chloride, for polystyrene, polyacrylates or chlorinated rubber, but also for the low molecular film forming agents of high solid paints. The higher ketones with their long carbon chains shift the solvent power towards less polar film forming agents.



$$R-\underset{\underset{O}{\|}}{C}-O-R'$$

The **esters** are similar to the ketones in the size of their dipole moments and the tendency to form hydrogen bridges and also have an excellent solvent power for most film forming agents. Acetic acid and propionic acid dominate as the acid component for the esters used in the paint and coatings industry. Esters based on butyric and carbonic acids, on the other hand, are of subsidiary importance. In this solvent class the chain length of the alcohol component influences the solvent power.

$$R-O-CH_2\text{-}CH_2\text{-}OH$$

Glycol ethers, particularly ethers of ethylene glycol, diethylene glycol and propylene glycol also feature high dipole moments and a marked tendency to form hydrogen bridges. They are excellent solvents for a broad range of polar and semi-polar film forming agents and have a stabilizing effect in alkyd resin paints because of their alcoholic hydroxyl group. They are gaining in significance as important cosolvents for waterbased paints. The ethers of propylene glycol are coming to the fore as more information is obtained about the possible harmfulness to human health of ethers of ethylene glycol.

Solvents from groups other than those listed are used only rarely and in very limited fashion in the paint and coatings industry. Cresols serve as special solvents for wire enamels. Methyl formamide is also occasionally used for wire enamels. The use of N-methylpyrrolidone is restricted to just a few special coatings based on physically drying, elasticizing polyurethanes. Propylene carbonate and members of this class of substances are gaining in importance.

2.1.3 Pigments and Extenders

The combination of film forming agents with solvents and possibly with additives results in transparent coating materials, the clearcoats. Despite the varied use of clearcoats to seal wood or plastics or to cover metallic coatings, the most frequently used coating materials are not transparent. The addition of color pigments, effect-inducing materials and extenders give them chroma, hiding power, special optical effects, but also functional properties such as sandability and hardness. The chroma is generated by selective absorption or interference, and the hiding power by light scattering. Color pigments have the ability to achieve hiding power and chroma at the same time. They are fine-

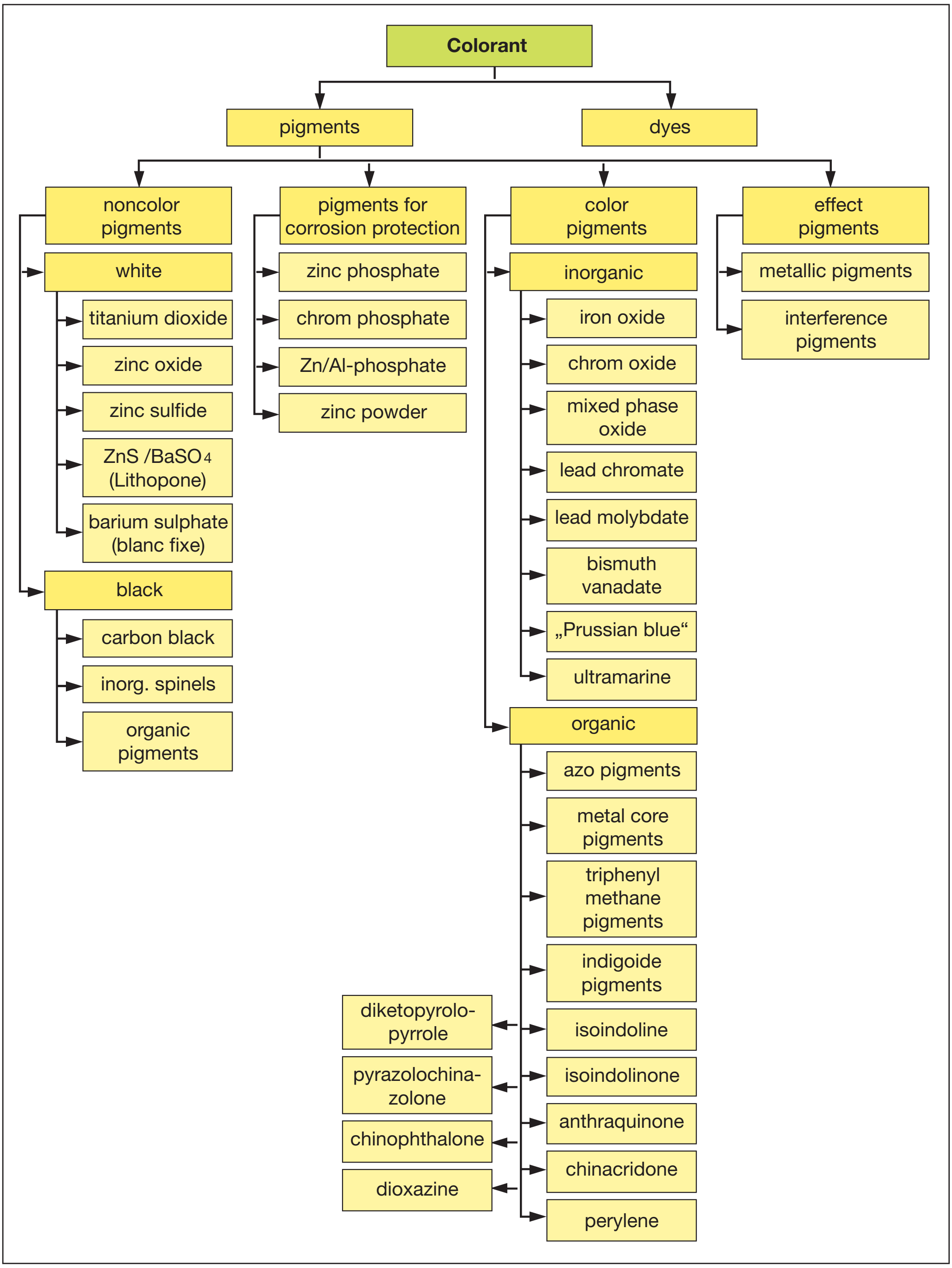


Fig. 2.1.151
Classification of pigments according to their function

particle substances which are insoluble in the film forming agent matrix. The term colorant is a generic term for all additives, including soluble dyes, which lend to color. Please see DIN 55943 for further details. Dyes play only a subordinate role in the coatings field compared with insoluble color pigments. Although soluble dyes have good coloring power and high color purity, they do not have any scattering or hiding power. Paints with soluble dyes are therefore only suitable for transparent coatings for paper or metal foils or for coating signal lamps made of transparent plastic. With a few exceptions, soluble dyes are inferior to pigments in terms of fastness to light.

Pigments are divided into organic and inorganic colorants depending on their chemical structure. In addition to the tasks already mentioned of giving color, forming effects and providing hiding power, pigments are also frequently expected to take on special tasks such as stabilizing coatings against the influence of UV light or even supplementary anticorrosive protection. Certain conditions must be met if such tasks are to be achieved. The pigment particles must be evenly distributed in the liquid environment, be well wetted by the film forming agent solution, permit troublefree coating with stabilizing resin molecules and enable rheological properties which are compatible with the processing method. Further demands that pigments have to meet include complete insolubility in the surrounding matrix, good fastness to light, longterm outdoor exposure and heat resistance, and lack of sensitivity to the effects of chemicals as well as physiological safety.

Tasks of pigments	Requirements for pigments and extenders	Special tasks of extenders
• selective absorption • light scattering • optical effects by oriented reflection or interference • UV-protection • corrosion protection	• dispersibility • unsoluble • lightfast and weather resistant • heat resistant • chemical resistant • physiological compatible	• ”filling” • sandability • improvement of mechanical-technological coating properties

Fig. 2.1.152
Tasks and performance requirements for pigments and extenders

Extenders’ tasks do not relate primarily to optical performance. Rather, they are aimed at raising the solid content of the paint and improving the mechanical/technological properties of the coating.

Economic importance

Because of the optical attractiveness which can be achieved by the use of pigments, coatings act as an enticement to buy consumer goods. The countless color nuances adapted to the designs of cars in conjunction with effects and high-gloss finishes are an example of this. Color-psychological studies provide an insight into the interactions of color and form and into the aesthetic perceptions of the observer which they generate. Newly created color schemes for model series issued at regular intervals by carmakers are intended to appeal to customers’ tastes and encourage them to buy. Whether changes in the buyer’s taste come from within or are attributable to the effects of advertising, it is an accepted fact that the percentage shares of car colors fluctuate greatly over time. Yellow cars were first a hit with buyers in the early 1970s, following years during which up to 40% of cars were white. At the end of that decade yellow was replaced by shades of blue. The era of the red car was ushered in during the mid-1990s before being replaced, with an interim revival for blue (22%), by the achromatic silver (40%) at the

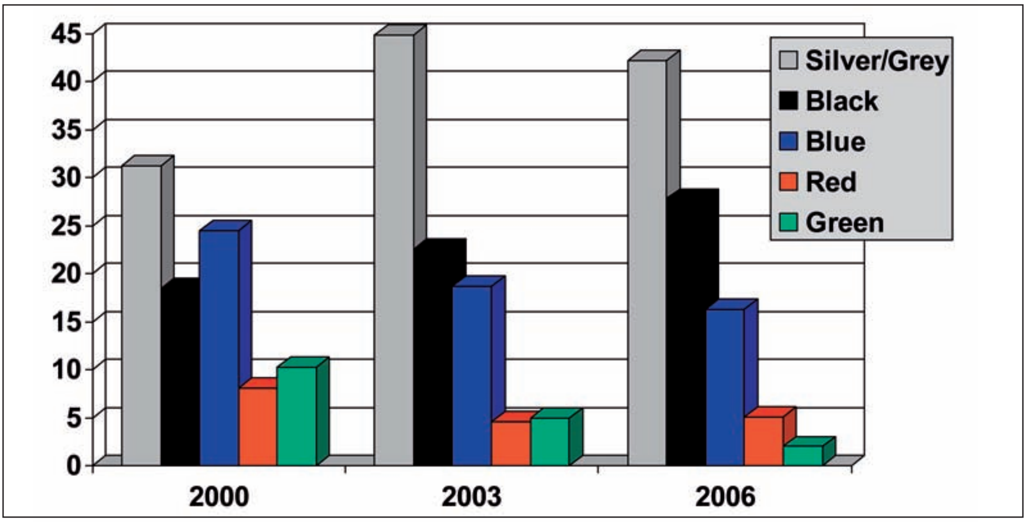


Fig. 2.1.153
Trends of automotive OEM colors in Germany (source: Farben und Leben)

end of the last decade. The latest trend is similar to be seen in North America in respect to silver and grey [2.4.39]

The pigments which are constantly being developed and produced by the pigment industry are not just used to color coating materials. Only half of the worldwide annual production volume of more than 6 million tonnes, including titanium dioxide, of inorganic colorants, almost exclusively in the form of pigments, is used for coating materials. Other materials also colored by pigments are plastics, construction materials, paper and ceramics. With organic colorants the situation is different. Only one quarter of the total of just 1 million tonnes is destined for the paint and coatings sector. By far the largest proportion is used as dyes, i.e. as soluble colorants for coloring textiles. The remainder, in the form of insoluble pigments, goes for printing inks, paints and plastics. Approximately half of all the pigments manufactured in the world each year are white pigments. The largest share by far is held by titanium dioxide. The next most important

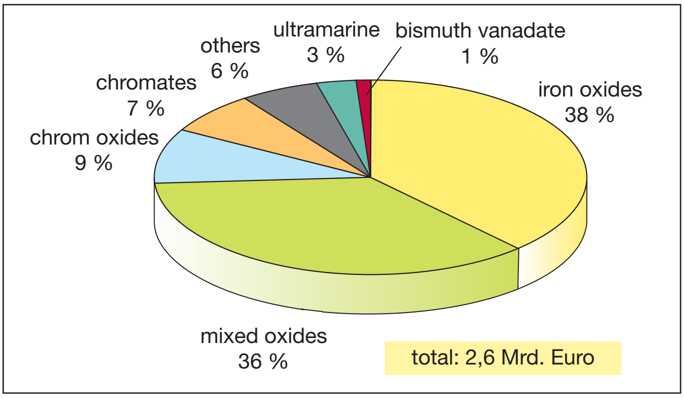


Fig. 2.1.154
Sales volume of inorganic color pigments in the European coatings industry

class of substances with a share of 25% of world production are iron oxides. Of all the pigments manufactured in the world, Germany produces about 15% of the inorganic materials but 25% of the organic.

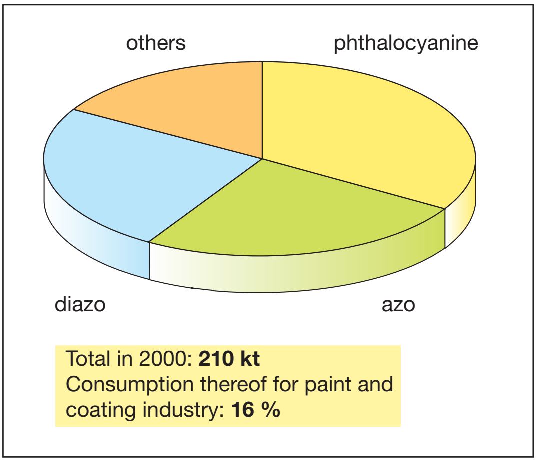


Fig. 2.1.155
Worldwide consumption of organic pigment groups

History

The use of colorants goes back over thousands of years. Natural iron oxides, carbon black and organic natural materials such as egg whites and tree resins form the basis for the materials used in the cave paintings at Lascaux and Altamira which are more than 40,000 years old.

Carbon black, copper-calcium silicate and ultramarine, the pigment from the purple snail, the plant-derived indigo plus kermes and crimson travelled along with age-old cultures from China via India to Egypt and finally also to Europe. In his book ”Germania” Tacitus reports in detail on dye works north of the Alps in which a colorless substance, extracted from a meadow plant, was transformed by atmospheric oxygen into a deep blue, insoluble pigment, indigo. The discovery of America enriched the color pallet with the addition of red cochineal, an extract from particular insects.

The following centuries were given over to chemical synthesis of nature’s color originals. For obvious reasons the first successes were with inorganic substances which were copied from nature or occurred as the byproducts of technical processes. Examples include zinc oxide, chrome yellow, cadmium sulphide, chromium oxide and the wide range of iron oxides. In the 19th century the more complicated structure of ultramarine was successfully synthesized.

The foundation stone for the successful synthesis of organic pigments was laid in the middle of the 19th century by the isolation of aniline from coal. *Perkin* achieved the breakthrough to synthetic dyestuffs in 1858 with the deliberate oxidation of aniline to a deep violet pigment, mauveine, also known as *Perkin*’s mauve.

Fig. 2.1.156
Cave paintings in Lasceaux

The availability of large quantities of organic dyestuffs which were also inexpensive made the world a more colorful place. Triphenylmethane dyes, azo dyes, synthetic indigo blue or red alizarin are just a few of the subsequent discoveries which revolutionized the world of colors. Today’s chemists are still developing attractive, new

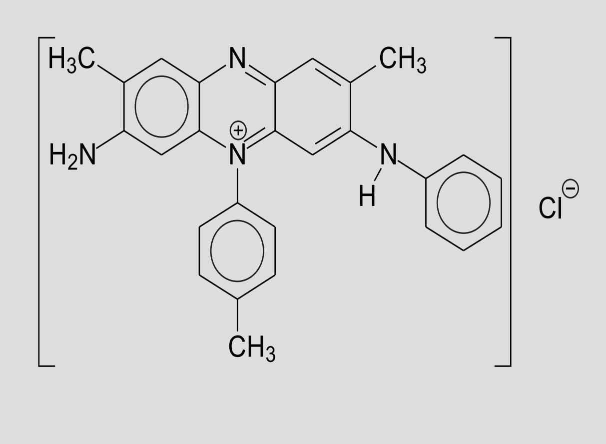


Fig. 2.1.157
Mauveine as the first completely synthesized organic color pigment

colorants and combining them with new optical effects. The metallic effect, caused by oriented reflections from mini aluminium mirrors or the enormous attraction of interference pigments whose color impressions vary with the angle of view are undoubtedly the most noteworthy inventions of recent decades in this field.

2.1.3.1
Physical Principles for Chroma and Hiding Power

Color as a sensory impression is generated by the interaction of light with the pigments because part of the spectrum is removed from the light by absorption or interference. People perceive color via the cones on the retina. These comprise three groups of sensory cells with different senstitivities to light. If part of the spectrum is removed from the white light by interaction with a selectively absorbent material, the individual sensors register changed intensities in the reflected light. These are transmitted to the brain where they are transformed into a color impression (see chapter 3.2.4).
The second visual requirement of coatings is their hiding power. Leaving aside black pigments which absorb light from the whole range of the visible spectrum, this effect is only achieved by pigments which are capable of scattering light. Since the scattering

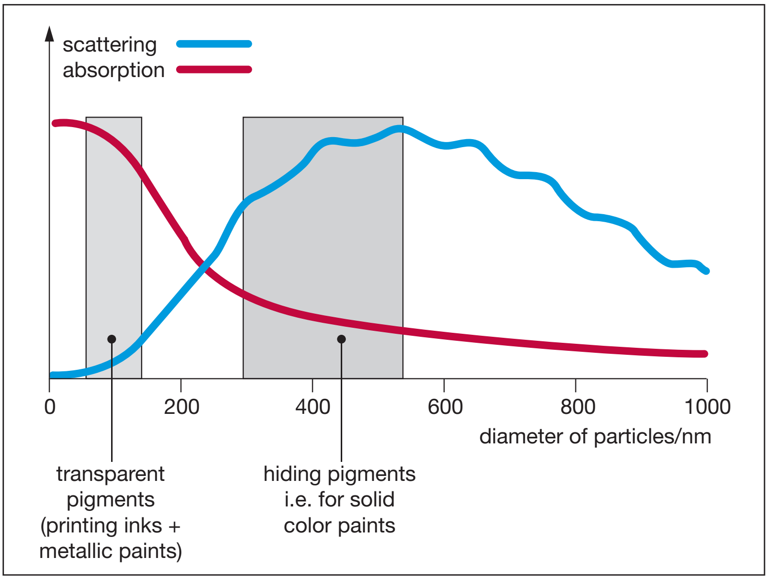


Fig. 2.1.158
Absorption and scattering of light depending on particle size of pigments

power, just like the tinting strength, depends on differences in the refractive indices of the pigment and binder and also on the particle size, pigment manufacturers make every effort to achieve the optimum particle size for tinting strength and hiding power in their commercial products to ensure economical use.

Because of the small particle size, the proximity that is possible as a result and the polarity of the pigments such strong attraction forces act that the pigment particles combine to form agglomerates or aggregates. Whereas in agglomerates the original particles (primary particles) are only loosely connected to each other with few points of contact, aggregates are particles which are rigidly joined together with large areas of contact. The coating manufacturer's aim of restoring agglomerates and aggregates to their primary particles to optimize tinting strength and hiding power is only achieved, however, with agglomerates. Aggregates in pigment powders are therefore a quality shortcoming.

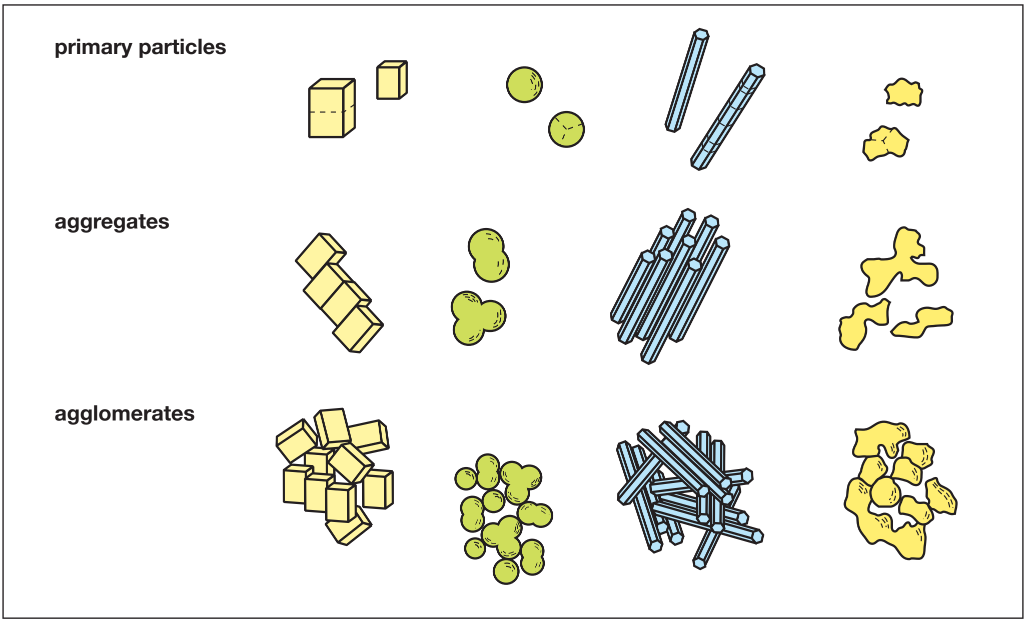


Fig. 2.1.159
Primary particles, agglomerates and aggregates of pigments

The separation of agglomerates into their primary particles must be accompanied by complete coating in suitable resin solutions to ensure lasting stabilization. Such stabilization prevents later reagglomeration and results in consistent quality even when the coating materials are stored for extended periods (see chapter 2.2.4).

Pigment performance indicators

The particle size and particle size distribution of pigments affect the color, tinting strength and hiding power to a large degree. They are therefore subjected to precise measurement.

Direct measurement using light-optical methods is not possible because of the small size of the particles. Proven methods include electron microscope images, measurements of accelerated sedimentation with disc centrifuges, determining the particle size with the *Coulter* counter and evaluating the bending or scattering of a laser light (see chapter 2.3.3). The particle size distribution curves which can be recorded by means of these measuring methods determine the color and coating-specific properties, depending on the position of the maximum and the width of distribution.

A proven practical method of mathematical processing and designation of particle size distribution was developed empirically by *Rosin*, *Remmler*, *Sperling* and *Bennet* [2.4.40] (see chapter 2.3.3).

A figure which is functionally linked to the particle size and is also important for pigment dispersion is the relation of mass or volume to the pigment surface area. The mathematical processing of vapour pressure measurements after *Brunauer*, *Emmet* and *Teller* (BET method) permits the specific surface area of the pigments under test to be determined from the pressure drop caused by the adsorption of nitrogen (see chapter 2.3.3).

Apart from the particle size and the specific surface area, the volume-related mass, i.e. the density, is a figure which is of interest both technically and economically. This determines paint consumption with specified film thicknesses. Likewise the pigment's apparent or bulk density is a figure which indicates the amount of cavities in the pigment powder. It also provides information about the cavities to be filled when dispersing the pigments.

In solventborne paints the oil absorption value and in waterbased paints the water absorption value give supplementary information on the need for binders to ensure thorough wetting (see chapter 2.3.3).

A particularly important means of evaluating the color of dyestuffs is the Color Index, which documents all standard colorants in a multivolume publication. Each material is clearly characterized in it by two or three letters and a combination of numbers. The letters come first, followed by a sequential number. The first letter indicates the type of colorant, the second and third letter, if any, indicate the color together with the sequential number. The description of the composition and chemical structure then follows in the second part of the Color Index. The Color Index supplements the manufacturers' information on tradenames, fastnesses and application fields [2.4.41].

Designation of colorant groups in the Color Index (selection)

1. letter	**2. letter**
A = Acid Dye	B = blue
B = Basic Dye	G = green
P = Pigment	BK = black
	R = red
	V = violett
	W = white
	Y = yellow

Characterisation or chemical structure

11000 – 36999	azopigments
41000 – 41999	diphenylmethane pigments
58000 – 72980	anthraquinone pigments
74000 – 74999	phthalocyanine pigments
77000 – 77999	inorganic colorants

Fig. 2.1.160
Keys to the Color Index

During the manufacture of pigmented paints, the change in particle size and tinting strength over time describes the progress of the dispersion process. The stability of the pigment dispersion can be seen in the tendency towards settling and the results of the rub-out test on freshly applied coatings (see chapter 2.3.3). Changes in tinting strength under specifically applied shear indicate enlargement of the particles and thus poor stabilization of the pigment dispersion.

2.1.3.2 The Most Important Pigments for Coating Materials

The large class of insoluble colorants which are important to coating technology can be divided into achromatic pigments, anticorrosive pigments and colored pigments by analogy with DIN 53944. The first group contains the ”white” scattering pigments and the black pigments which absorb light from the entire visible spectrum, the second contains special inorganic pigments, and the third consists of the organic and inorganic colored pigments and the interference pigment class of substances.

Achromatic pigments
Among the scattering pigments or **white pigments** titanium dioxide has successfully won by far the lion’s share of the market because of its high refractive index and its extraordinary chemical resistance. Of the three known crystal forms brookite is unimportant, and anatase is only of subordinate importance. With a share of about 90% of all coating pigments rutile plays by far the most important role. It is extracted from ilmenite, a naturally occurring iron titanate, using the sulphate process, or from natural rutile using the chloride process. After the introduction of the recycling process for the dilute acid produced during manufacture, the sulphate process has regained its share, with the result that the two processes now stand alongside each other with equal importance. Irrespective of the production process, however, the raw products do not meet the in part rigorous requirements for pigment dispersion and outdoor exposure without chemical modification and additional secondary treatment of the pigment surface.

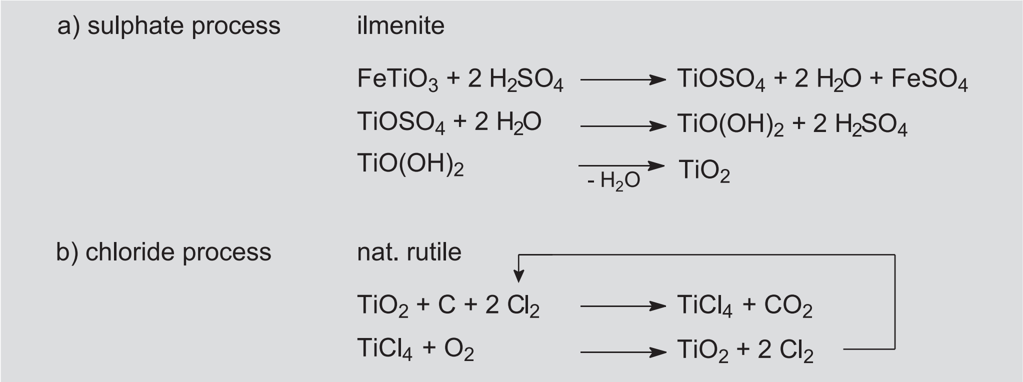


Fig. 2.1.161
Manufacturing steps of titanium dioxide

The thus necessary stabilization against the influence of UV light is achieved by doping the rutile crystal with aluminium or zinc, and the dispersion properties are achieved by coating the pigment surface with oxides of aluminium and silicon. Organic adsorption films have even proved successful for particularly easily dispersed types. Titanium dioxide in the modification described has incomparable longterm outdoor exposure properties and fastness to light while exhibiting excellent hiding power at the same time. Its resistance to chemical action and its insolubility in acids and alkalis mean that it can also be regarded as a safe product from a physiological perspective. Formerly important white pigments such as white lead (basic lead carbonate), zinc white (zinc oxide), zinc sulphide and lithopone (zinc sulphide with barium sulphate) have either been substituted for occupational health reasons or have largely been moved to use in primer coats or ground coats because of their inferior properties in topcoats by comparison with titanium dioxide.

Black pigments are mainly derived from carbon blacks. Depending on the production process and aftertreatment, the pigment particles vary in their fineness and consequently in their dispersion properties. it is now possible to produce extremely fine particles, in the nanometre range, by means of the incomplete combustion of natural gas mixed with oil. They have specific surface areas of up to 1000 m^2/g and thus an extremely high tinting strength and achieve a high hiding power even at low concentrations [2.4.42]. Of less importance are the carbon blacks from the incomplete combustion of plant or animal materials. They are coarser and are sometimes contaminated with quality-impairing mineral materials. Another pigment, which is substantially easier to disperse than carbon black, is black iron oxide, a magnetite modified with copper and chromium. Black iron oxide is inferior to carbon back in terms of tinting strength and chemical resistance.

Apart from the pigments which give the coatings hiding power and chroma and therefore primarily serve aesthetic purposes, the purely functional **anticorrosive pigments** have extraordinary economic importance for very different reasons. The active anticorrosive pigments intervene with chemical reactions in the corrosion processes at the interface between the metallic substrate and the coating. Their corrosion-inhibiting effect is based on valency changes in the soluble pigment components. In the past red lead and chromium-containing pigments were by far the most effective and therefore also the most used anticorrosive pigments. Proven physiological hazards of these pigments, the necessary labelling and the restrictions imposed on processing them mean that they have been almost completely superseded in Europe and North America by zinc phosphates and zinc-aluminium phosphates. These substitute products are also among the important active anticorrosive pigments. To optimize their effectiveness, zinc phosphates are crystallized such that they are particularly fine with a correspondingly large surface area. Since only a low pH value guarantees the effectiveness of the zinc phosphate pigment, the use of acid film forming agents and extenders is necessary.

Zinc dust occupies a special position as an anticorrosive pigment. The protective effect of zinc dust primers, always formulated with high pigment volume concentrations (PVC), can be explained electrochemically by the large difference between zinc and iron in the electrochemical series of the elements. Zinc dust is used both in organic and also in aqueous film forming agents. Zinc dust primers are weldable because of their PVC, i.e. high electrical conductivity.

Anticorrosive protection is also possible without chemical intervention. Such anticorrosive protection is achieved if the diffusibility and permeability of corrosive agents such as oxygen, water and salts are significantly reduced by appropriate formulation. Lamellar pigments such aluminium silicates, lamellar iron oxide or mica are best suited to influence this property positively.

Colored pigments

Among the **inorganic colored pigments** there are major applications for numerous variants of iron oxide, apart from the already mentioned black iron oxide, in yellow, red and brown tones. The most important basic types are red iron oxide (α-Fe_2O_3 as haematite), yellow iron oxide (α-FeOOH as goethite) and brown iron oxide which is a mixed pigment consisting of red, yellow and black iron oxides. Over the course of time the natural pigments have been replaced more and more by synthetic products, the mineral pigments, because of quality-impairing impurities. These are manufactured either by oxidation of scrap iron with nitrobenzene (aniline process) or by oxidizing hydrolysis of iron (II) sulphate (*Penniman* process).

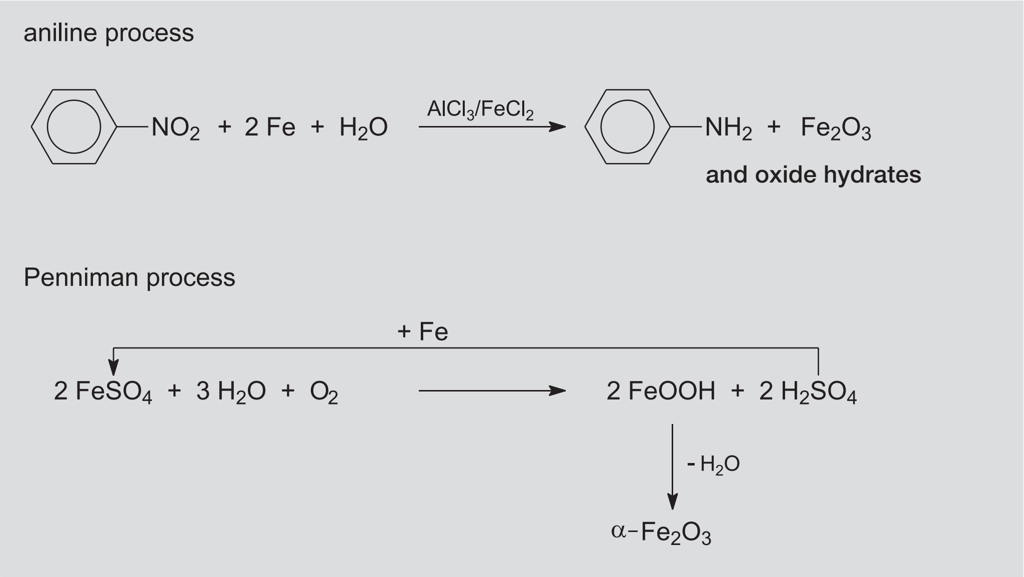


Fig. 2.1.162
Manufacturing steps for iron oxide pigments

Iron oxide pigments have excellent hiding power and longterm outdoor exposure properties, are lightfast and have excellent chemical resistance. By contrast with red iron oxide, which is stable up to 1000 °C, the yellow iron oxide pigments and their brown mixtures have only poor heat resistance. The hydrated oxides dehydrate above temperatures of as low as 160 °C and are then converted into the red form, haematite.

A large proportion of iron oxide pigments is used in primers. In topcoats iron oxide pigments are frequently covered on their surfaces with organic pigments to increase the brilliance. Iron oxide pigments with extremely small particle diameters are used as colorants in metallic effect coatings and transparent paints.

Chromium oxide pigments are used far less commonly. Chrome oxide (Cr_2O_3) and hydrated chromium sesquioxide ($Cr_2O_3 \cdot 3H_2O$) are limited in color terms to greens. Their fastness properties and the thermal instability of the hydrated form match those of iron oxide pigments. They are manufactured by reduction of the hexavalent chromate to the trivalent chromium oxide. It crystallizes like α-Fe_2O_3 in the corundum matrix and therefore has a high hardness. Because of its good chemical and thermal resistances chrome oxide green's main application fields are chemically resistant coatings for

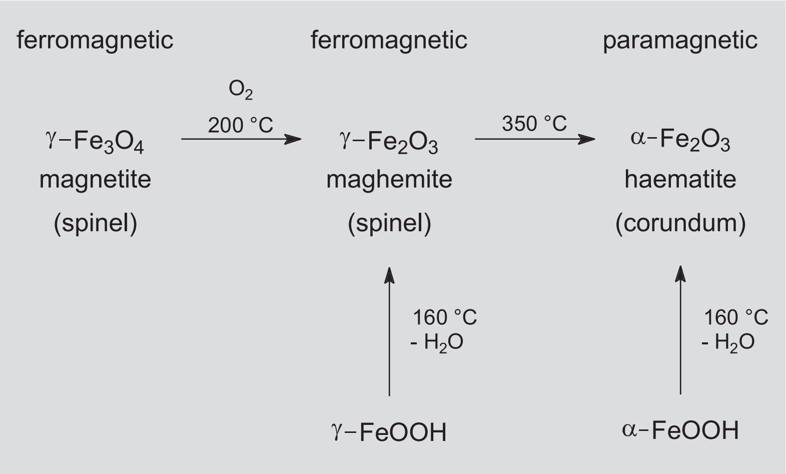


Fig. 2.1.163
Important iron oxide pigments

concrete and cement, dispersion paints and a few industrial coatings. Chrome oxide green is used in conjunction with micaceous iron ore for heavy-duty anticorrosive protection. Its characteristic reflection properties in the infrared range have also made it well-known as a pigment for camouflage coatings.

Other metal oxides which are technically important for yellows include the mixed phase pigments. These consist of antimony-containing titanium dioxide of the rutile type which is doped with small quantities of nickel during manufacture to produce the green-tinged nickel titanium yellow, and with chromium to produce the red-tinged chromium titanium yellow.

Rutile grid with hosts	Spinels
• Nickeltitan yellow $(Ti,Ni,Sb)O_2$ • Chromtitan yellow $(Ti,Cr,Sb)O_2$	• Spinel blue $(CoAl_2O_4)$ • Cobalt blue $(Co(Al,Cr)_2O_4$ • **Spinel black $Cu(Cr,Fe)_2O_4$** • Zinc iron brown $(Zn(Fe))Fe_2O_4$
	Inverse Spinels
	• Cobaltgreen $(Co,Ni,Zn)_2TiAlO_4$

Fig. 2.1.164
List of mixed phase pigments

This group of pigments provides a suitable replacement for lead chromate because of its good heat and chemical resistance while also being regarded as physiologically safe. The mixed-phase pigment group also contains a number of spinels such as cobalt blue, cobalt green as an inverse spinel and the already mentioned black spinel.

Although containing both hexavalent chromium and lead, lead chromate pigments are still of technical importance as mixed pigments of chromate and sulphate. Their toxicity is low because of the extremely poor solubility of the lead chromate and the resulting lack of biological availability. Their brilliant colors are limited to yellow. Partial replacement of the lead by molybdenum results in molybdate orange and molybdate red. All lead chromate-containing pigments are naturally sensitive to acids, reducing chemicals and the effect of sunlight. However, suitable stabilization processes permit the manufacture of chromate pigments with increased resistance. Each grain of the lead chromate pigment is coated with a protective layer of a chemically resistant material.

Lead- and chromium free, brilliant and, at the same time, highly opaque inorganic yellow pigments, consisting of bismuth vanadate and bismuth molybdate, have gained in importance.

$BiVO_4 \cdot x\,Bi_2MO_6$ $x = 0{,}2 - 2$
common: 0,75

Fig. 2.1.165
Bismuth vanadate as a multi phase oxidic pigment

As oxidic 2-phase pigments they are generally green-tinged with particularly high color purity and also a good gloss finish.

The pigments which were discovered by chance include Prussian blue or mineral blue. While attempting to obtain crimson red by lacquering, *Diesbach* was surprised to isolate a blue substance. As a result of the cyanide content in the potash which was needed to adjust the pH value, a deep blue iron-cyanide complex formed in the presence of iron ions and overdyed the crimson paint. Industrial production nowadays involves the incomplete oxidation of the colorless, iron (II)-containing intermediate stage. The presence of both iron (II) and iron (III) in conjunction with the crystal water gives the cyanide complex the required pigment properties [2.4.43]. The crystal water is particularly important with regard to the color. Prussian blue pigments are pyrophoric, i.e. they can spontaneously combust in the presence of oxidizing agents. This fact must, therefore, be borne in mind as special fire protection precautions have to be put in place because of the simultaneous grinding of Prussian blue with lead chromate, which acts as an oxidation agent, to produce the chrome green mixed pigment. Prussian blue as an extremely light inorganic pigment, which has an unusually low density of 1.75 g/cm^3, has poor acid resistance and only limited stability when exposed to alkalis despite supplementary stabilization. The tinting strength is high, as a result of which it is possible to use it for industrial paints with particularly deep blue tones because of the very good light fastness. One disadvantage is its metallic, copper colored shimmer after lengthy exposure to the weather. This bronzing effect can be reduced by subsequent treatment.

$Fe^{(III)}\,R\,Fe^{(II)}\,(CN)_6 \cdot x\,H_2O$ $R = Na, K$ or NH_4

Fig. 2.1.166
Chemical composition of Prussion blue

Ultramarine occupies a special place among inorganic pigments. This semiprecious stone, which was used back in Ancient Egypt to decorate the burial sites of the pharaohs, even fascinated *Goethe*. It is no surprise, therefore, that successful attempts at synthesizing this natural product were reported as long ago as the beginning of the 19th century. The first factory for the manufacture of artificial ultramarine was built in 1830 by *Leverkus* in a town which was then named after him and is thus known today as Leverkusen [2.4.44].

$Na_6Al_6Si_6O_{24} \cdot Na_2S_x$

Fig. 2.1.167
Chemical formula of ultramarine

Ultramarine is an aluminium silicate with a zeolite-like crystal matrix; the unusually warm blue tone comes from the incorporation of sodium and sulphur. Because of its poor hiding power and its sensitivity to acids ultramarine has proved more suitable for artists' paints and translucent painting on porcelain than for coating consumer goods. Violet and red ultramarines can also be manufactured by varying the proportion of sulphur and incorporating amines.

In addition to the pigments already mentioned, there are numerous other inorganic oxides which are used for coloring glass or ceramics because of their high thermal resistance. Blue Wo_3O_8 or yellow WoO_3, MnO_2, mixed oxides of silicon with calcium, magnesium and iron in the form of hornblende or green earth may be mentioned in particular.

Azo-pigments

- monoazopigments
- diazopigments
- (azokondensation pigments)
- BONS-pigments

Non-azo-pigments

- metal care pigments
- indigoide pigments
- triphenylmethane pigments
- isoindolinone, isoindoline
- anthraquinones
- chinacridone
- perylene, perinone
- dioxazine
- chinaphthalone, pyrazolochinazolone
- diketo pyrrolopyrrole (DPP)

Fig. 2.1.168
Classification of organic color pigments by chemical nature

Organic colored pigments feature strong and selective light absorption and therefore high color purity, cover very wide color ranges, yet are so close meshed in their color range that they are available in a wide variety of color nuances. With a high absorption capacity the scatter and hiding powers are lower than in most inorganic color pigments. To achieve satisfactory cover of the substrate, the organic pigments are often combined with opaque inorganic white or colored pigments. Longterm outdoor exposure and fastness to light are often less good. Weaknesses in fastness to light occur in particular where there is a high degree of brightening, i.e. with increasing levels of added white pigment. Another disadvantage which can affect certain organic pigments despite their other benefits is an inadequate heat resistance. Their use in baking enamels is therefore limited. As developments have advanced, however, organic pigments have come onto the market which are significantly better at meeting the requirements relating to this resistance. These are frequently associated with high manufacturing costs and high expenditure for the dispersion process.

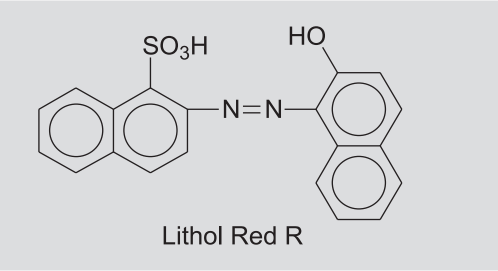


Fig. 2.1.169
"Litholrot" : the first important azo pigment

All organic pigments have chromophore structures, which cause a color impression by absorption in the visible light spectrum (see above). Chromophore groups generally comprise a number of conjugate

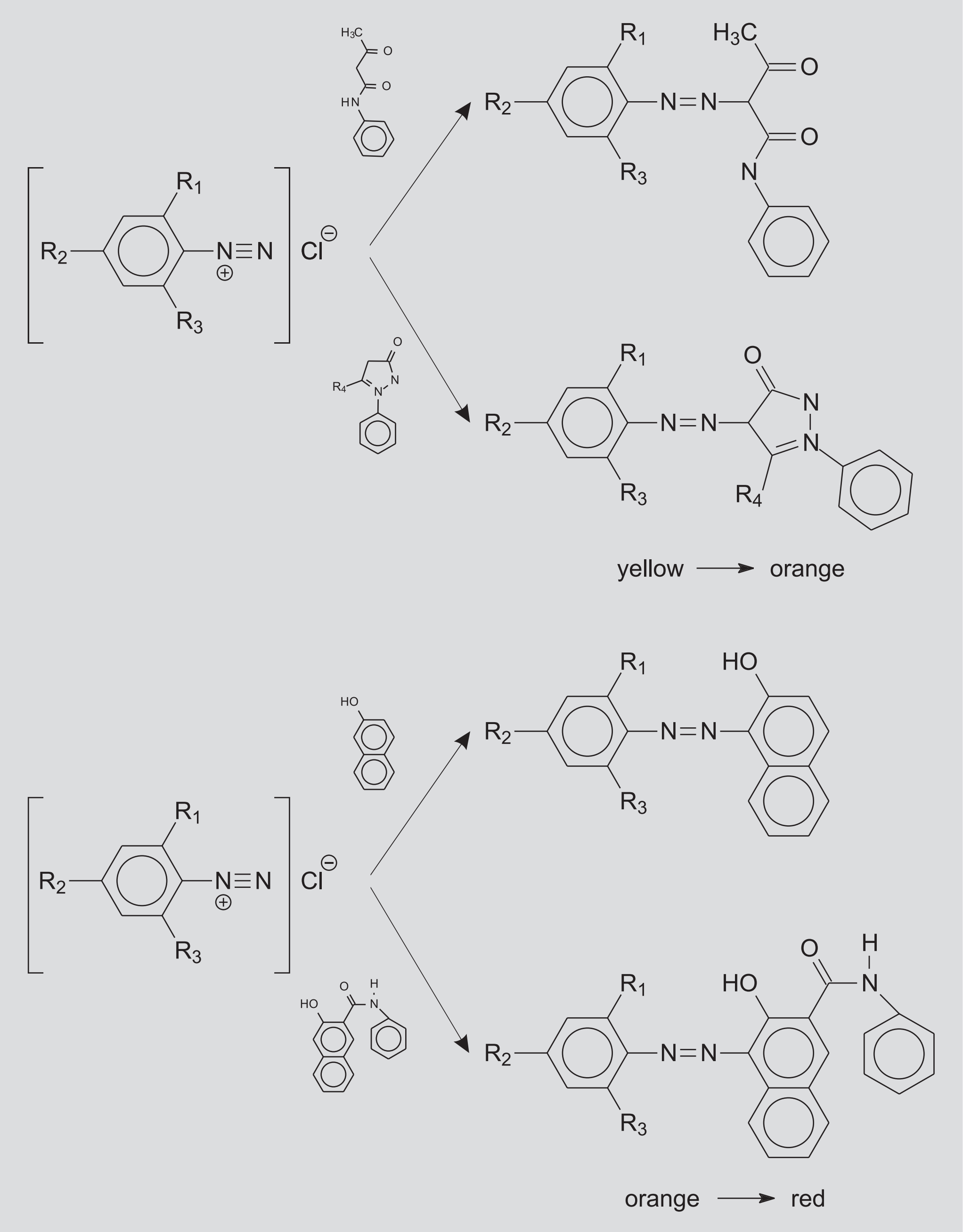


Fig. 2.1.170
Chemical formula of monoazo pigments (yellow, orange, red)

double bonds. These need not necessarily be carbon-carbon double bonds. Nitrogen-nitrogen double bonds, the azo groups or double bonds between carbon and nitrogen or oxygen are also very effective. The chromophore structures are generally also supplemented by auxochrome groups which result in color intensification and color shifts by inductive effects. Depending on electronegativity, shifts in absorption towards

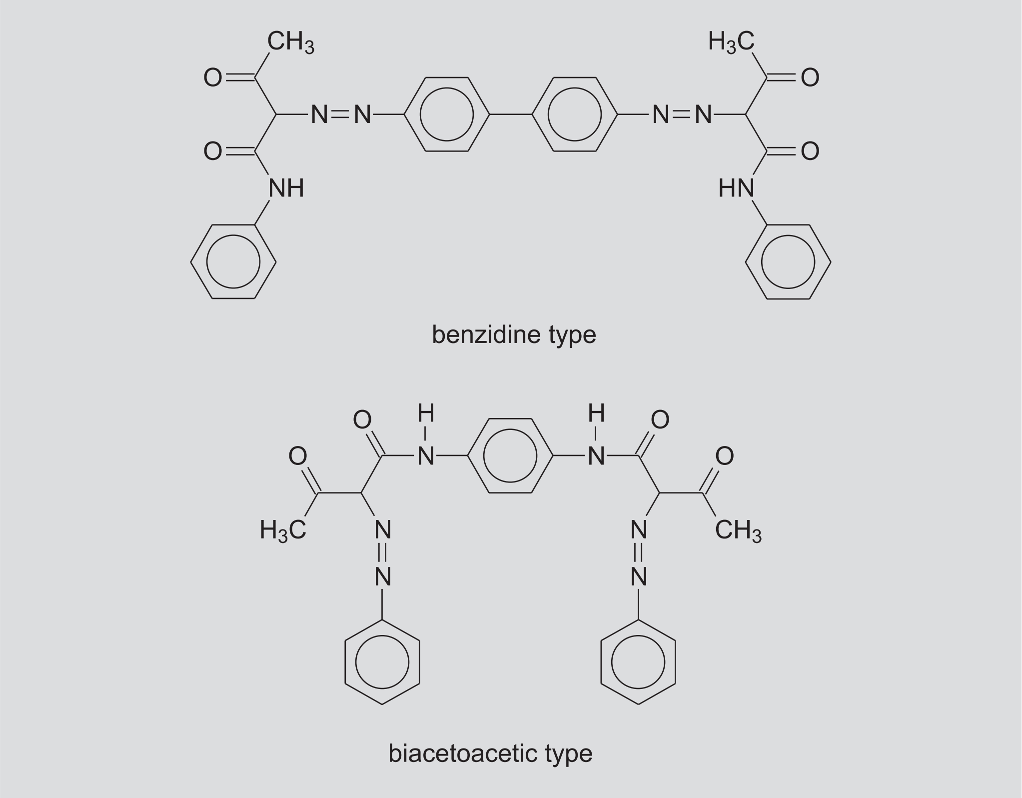


Fig. 2.1.171
Chemical structure of the diazo pigments

the longer (bathochrome effect) or the shorter wavelengths (hypsochrome effect) are achieved.
At 0.01 – 0.1 µm the particle size of the organic pigments is smaller than that of the inorganic pigments by about one power of 10. The smaller particle sizes of the organic pigments require particularly effective dispersion processes to ensure complete and even distribution within the coating material.
The preferred classification of the many organic pigments follows the typical structures of their chemical construction.

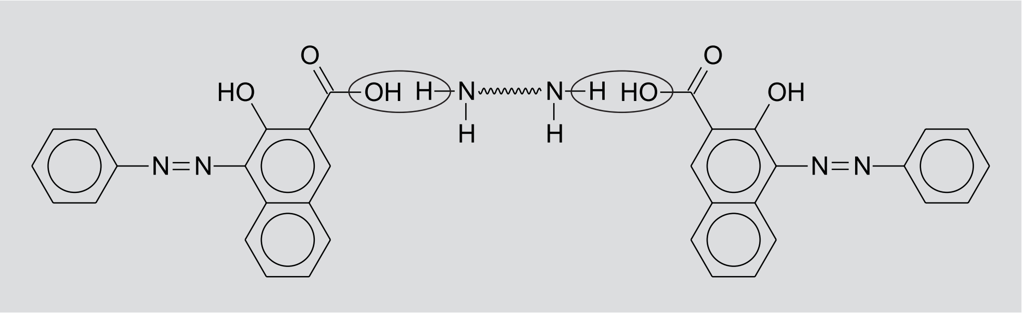


Fig. 2.1.172
Synthesis of azo condensation pigments

Azo pigments are the most important group among the organic pigments in terms of quantity (see figure 2.1.155). The azo group, which acts a link between the individual parts of the molecule, gives this class of substances its name.

The construction and chemical structure of the ligands which are linked by azo groups determine the performance profile of the pigments. A distinction is drawn between monoazo and diazo pigments depending on the number of azo groups in the molecule. The first synthetic product manufactured commercially was BASF's "Litholrot". They are now manufactured in an extremely large variety. Despite weaknesses when subjected to thermal stresses above approx. 140 °C, their merely mediocre fastness to light and only limited solvent resistance, the standard products in this class of substances represent by far the largest proportion of the organic pigments used in the paint and coatings industry.

Synthesis of the azo pigments requires a primary aromatic amine component which is diazotized with nitrous acid. This is usually aniline with a very wide range of possible substituents. The coupling of the diazotated amine with acetoacetanilide and phenylmethylpyrazolone results in yellow to yellow-orange pigments, and with β-naphthol and naphthol AS in orange to red pigments (see figure 2.1.170).

The weaknesses in the heat resistance, fastness to light and solubility of the monoazo pigments can be reduced by molecular enlargement. Either a diazotated diamine is bound to two conventional couplers or a 2-functional coupler is used with two diazotated amines. The first case yields the diaryl pigment class (benzidine type), and the second that of the bis-acetoacetic arylides (see figure 2.1.171).

Other proven methods of stabilizing azo pigments consist of bonding carboxyl group-containing monoazo pigments with diamines to the azo condensation pigments, forming acidamide groups.

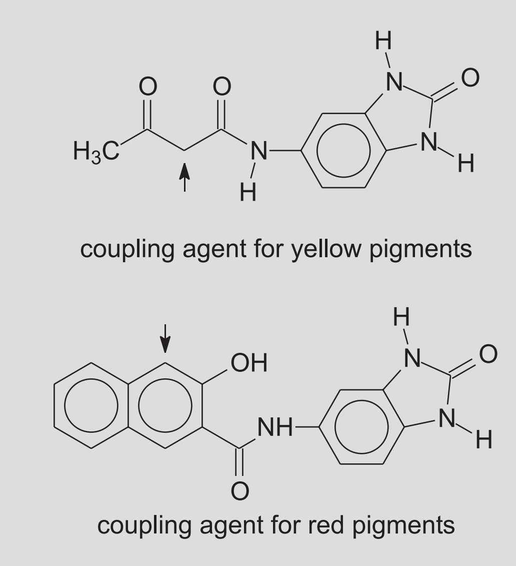


Fig. 2.1.173
Benzimidazolon containing coupling agents for azo pigments

A further reduction of the solubility associated with an improvement in the fastness to light can be achieved by strong intermolecular interactions via additional acidamid groups in the coupling components. The variants of the classic azo pigments containing benzimidazolone groups represent successful modifications.

Strong intermolecular interactions via numerous hydrogen bridges result in heat resistances of up to 220 °C with good fastness to light and excellent solvent resistance. Similar improvements can be achieved with coupling components synthesized from cyanuric chloride and acetoacetic anilide. The molecules in this pigment class are planar and therefore permit the formation of a large number of hydrogen bridging bonds.

Another method, known as lacquering, of manufacturing azo pigments which are insoluble in organic media involves forming salts and a complex with metal cations.

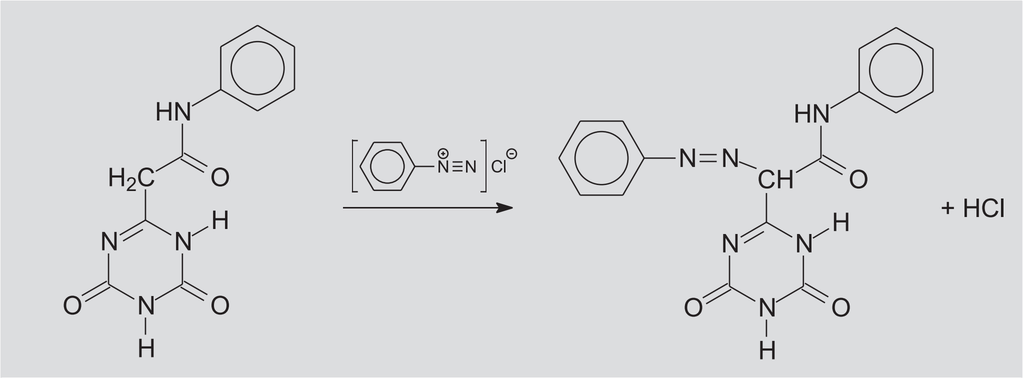


Fig. 2.1.174
Synthesis of azo pigments with cyanuric chloride containing coupling agent

This is only possible if there are acid groups in the molecule. If β-oxi-naphthoic acid (German acronym: BONS) is used as the coupler, the carboxyl group can be converted to almost insoluble metal salts using aluminium, iron or manganese ions. The insolubility of this group, known as BONS pigments, should be checked when pigmenting water-based paints.

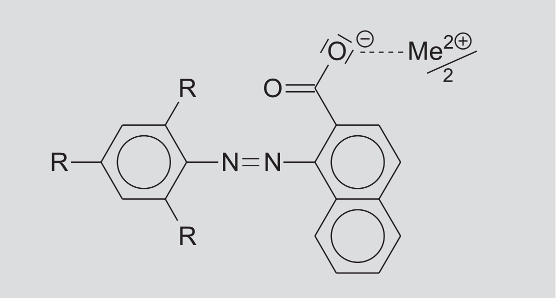


Fig. 2.1.175
Azo pigments on the basis of β-oxi-naphthoic acid

The **metal complex pigments** which are of most interest because of their enormous resistance to the effects of chemicals, acids, alkalis, light and longterm outdoor exposure cover the blue and green ranges of the color spectrum. The most important representative is related to the blood pigment and leaf green in terms of chemical composition and consists of a polycyclic, continuously conjugate ring system, in which the magnesium of chlorophyll or the iron of haemin has been replaced by copper. This class of substances therefore has the name copper phthalocyanines. They resist concentrated sulphuric acid and remain unchanged even at temperatures of up to 500 °C. Copper phthalocyanine pigments exist in several crystal forms, of which the red-hued α-form is less resistant than the green-hued β-form.

The incorporation of halogen in the basic skeleton of the copper phthalocyanines enables green pigments to be obtained which also have a high resistance.

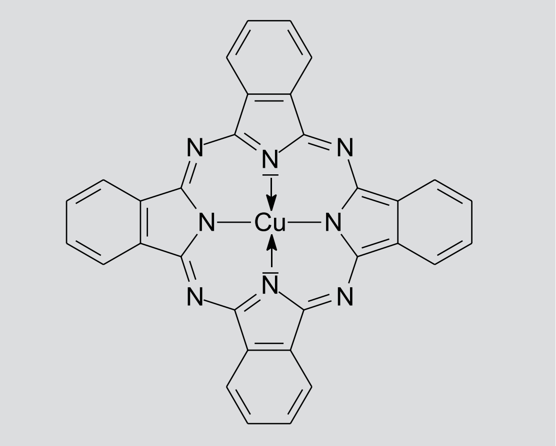


Fig. 2.1.176
Chemical formula of copper phtalocyanine

Other far less important metal complex pigments are the nickel complexes of certain hydroxyl-functional azo pigments and the iron complex of 1-nitroso-2-naphthol.

The alkyl substituted amine derivatives of triphenylmethane, the **triphenylmethane pigments**, are of almost unparalleled brilliance and color purity. They are transformed into the insoluble form by salt formation with complex polyacids. Triphenylmethane pigments are mainly used in the printing inks sector. Their fastness properties are inadequate for use in external coatings subjected to longterm outdoor exposure.

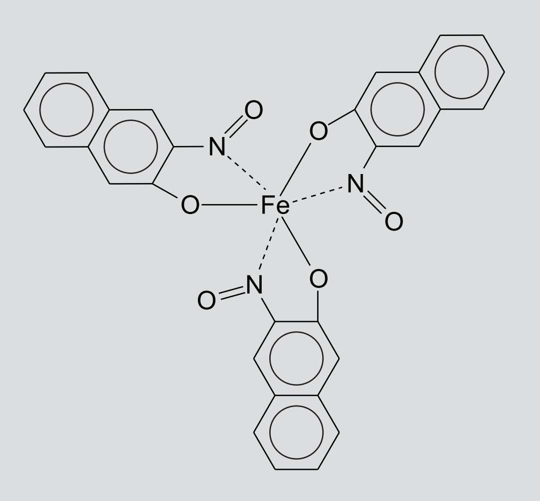


Fig. 2.1.177
Chemical structure of the iron complex of 1-nitroso-2-naphthol

The **carbonyl pigments** group is a technically important and varied group of pigments, in terms of the number of variants. The group takes its name from the presence of at least 2 carbonyl groups which are in a conjugate configuration to each other or to other double bonds. Compared with the azo and phthalocyanine pigments the quantity, though not the number, of carbonyl pigments used in the paint and coatings industry is comparatively low. The reasons for this are the sometimes very intricate and thus expensive synthesis processes. However, these pigments are particularly valuable with regard to the manufacture of yellow, red or violet colors with the highest standards of fastness and resistance. The indigo pigments may be cited as first among the carbonyl pigments with their often complicated structure. However, only derivatives of thioindigo

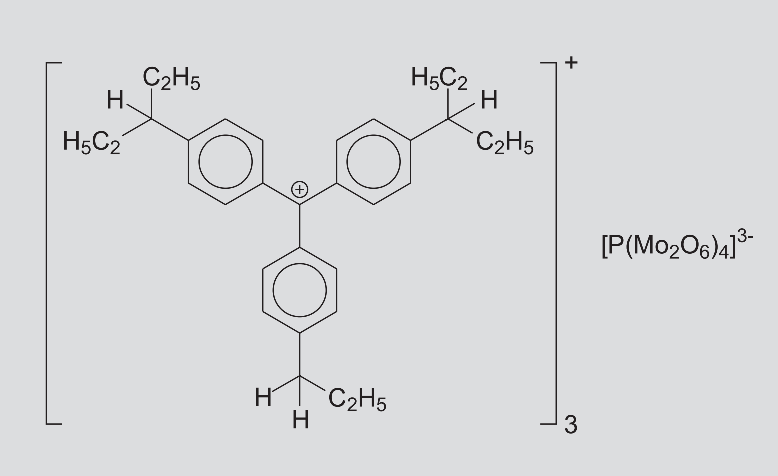


Fig. 2.1.178
Example of a triphenylmethane pigment

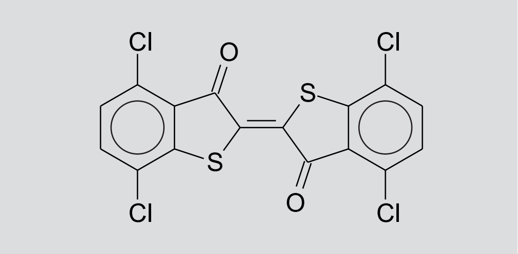


Fig. 2.1.179
Chemical structure of tetrachlorthioindigo

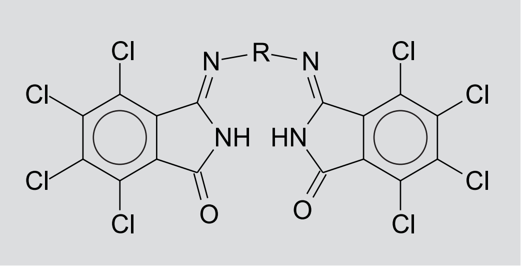


Fig. 2.1.180
Chemical structure of isoindolinone pigments

have limited practical importance for the paint and coatings industry today. One concrete example to mention is **tetrachloro-thioindigo**. This is resistant to solvents, temperature resistant up to 200 °C, light-fast and stable in longterm outdoor exposure even when blended with white pigments.

The carbonyl pigments also include the **isoindolinones** which are used for plastics and high-grade industrial coatings because of their good fastness to light and longterm outdoor exposure properties. They span the yellow, orange and red range and are formally accessible by condensation of phthalimides with diamines. Color shifts from green to red via yellow and orange are achieved merely by varying the diamine component.

By contrast with the isoindolinones, which have been known for some time, the **isoindolines**, i.e. compounds in which both carbonyl groups of the phthalimides have been replaced by double bonds with suitable substituents, have even better longterm outdoor exposure properties and excellent hiding power.

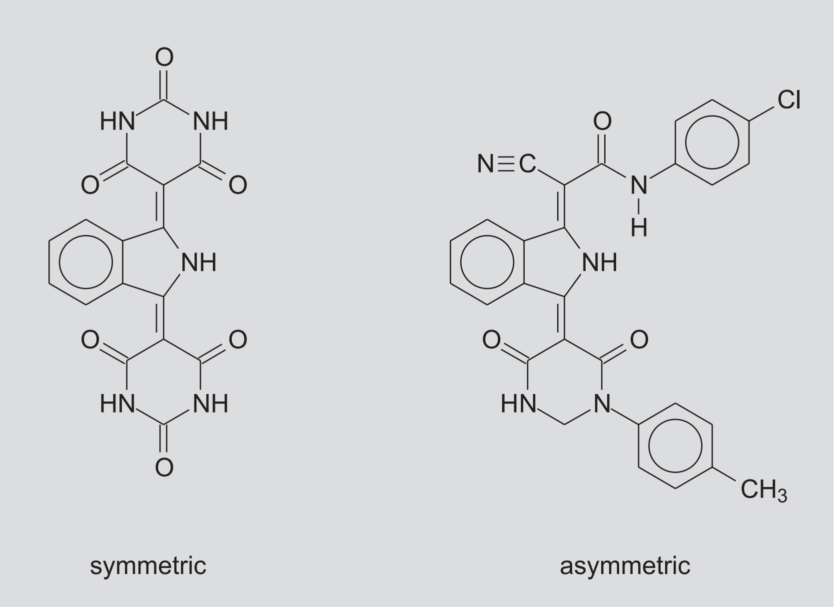


Fig. 2.1.181
Examples of chemical structures of isoindoline pigments

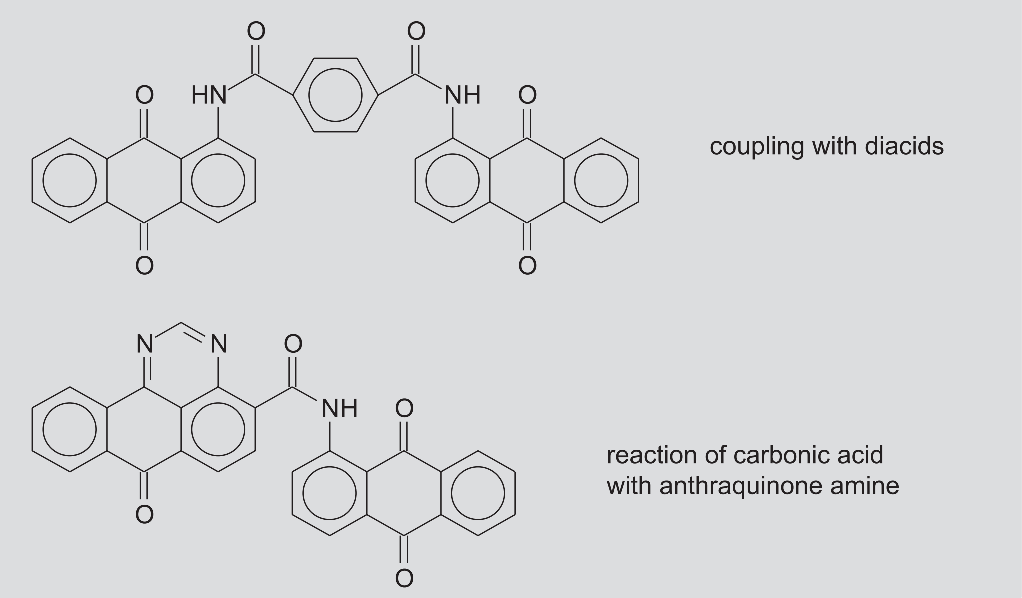


Fig. 2.1.182
Anthraquinone pigments by condensation with different compounds

Natural pigments which have been known for centuries, such as madder lake, kermes or cochineal, provided the blueprint according to which the **anthraquinone pigment** group was constructed.

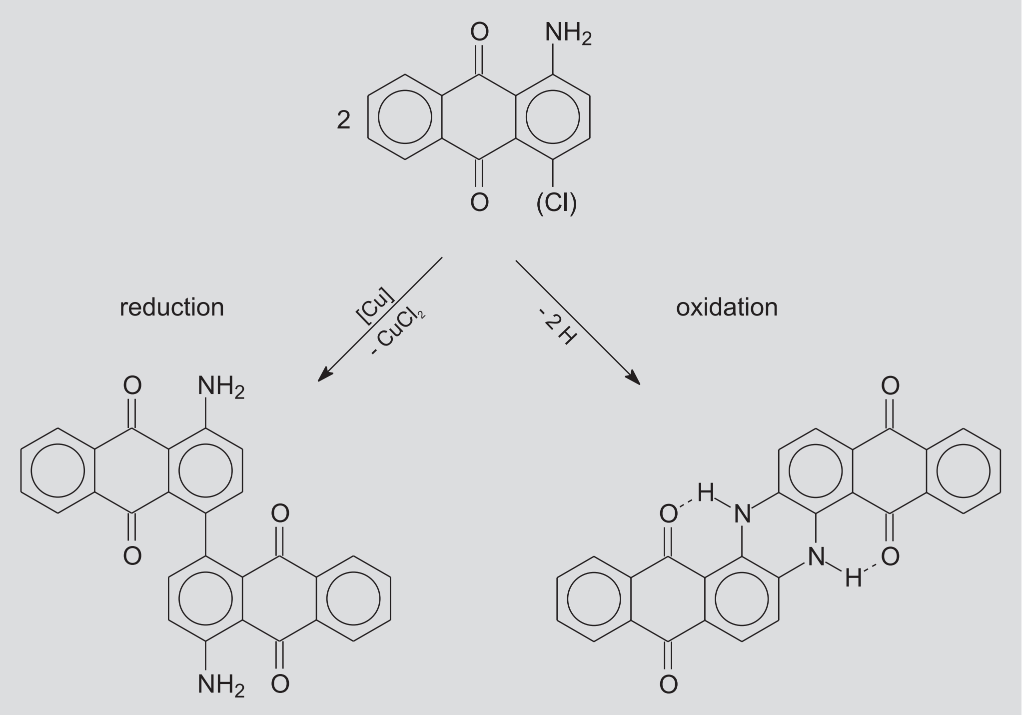


Fig. 2.1.183
Synthesis of dimerized anthraquinone pigments by oxidizing and reducing coupling reaction

The basic product, previously manufactured by oxidation of anthracene and more recently by *Friedel* and *Craft*'s acylation of substituted aromatics by phthalic anhydride, has no pigment properties itself, although it is inherently colored. The molecule is too small to meet the requirements on exposure to light, outdoor conditions and chemicals with heat resistance at the same time. Attempts at molecular enlargement were successful, and numerous high-grade products are available today as a result. The mere chemical bonding of two aminoanthraquinone molecules with a dicarboxylic acid results in excellent yellow pigments. Highly stable pigments are also obtained by condensing anthrapyrimidine carbonic acid with 1-aminoanthraquinone.

Molecular enlargement by linking two anthraquinone molecules is also achieved by reducing or oxidizing dimerization (see figure 2.1.183).

Superior pigment properties are obtained by the formation of further aromatic rings. The group of the highest-grade polycyclic anthraquinone pigments includes flavanthrone (red-tinged yellow), pyranthrone (red to orange) and anthanthrone (scarlet).

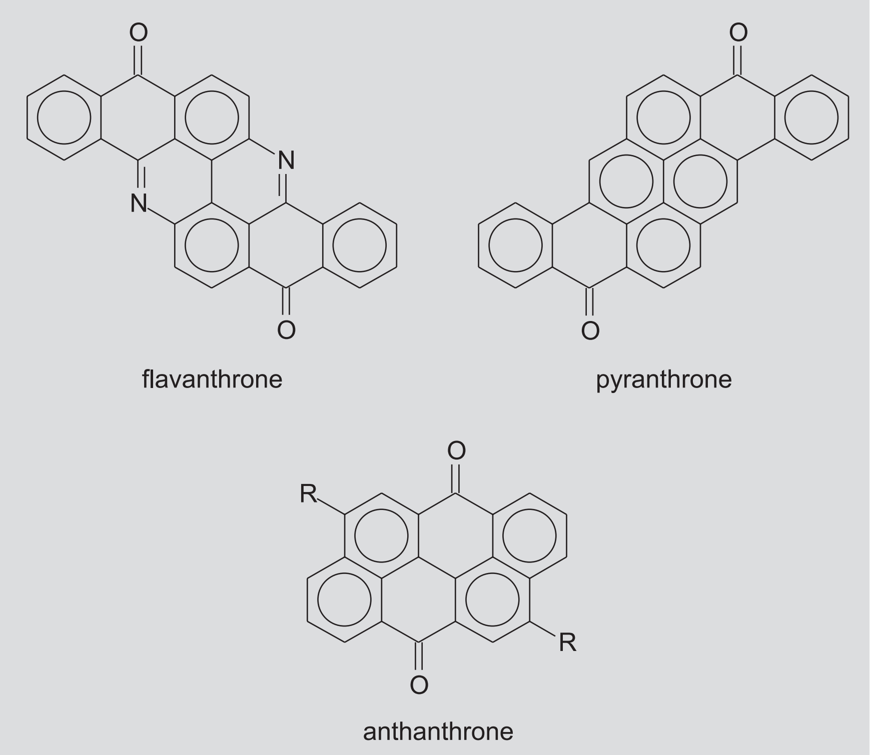


Fig. 2.1.184
Examples of condensated anthraquinone pigments

Although they are very expensive because of their multistage synthesis, they are among the most lightfast organic pigments of all at the same time.

Despite its excellent properties production of flavanthrone had to be halted for cost reasons.

The **quinacridones** are also high-performance red to violet pigments. The color of this pigment class is also determined by the crystal form. Of the five modifications now

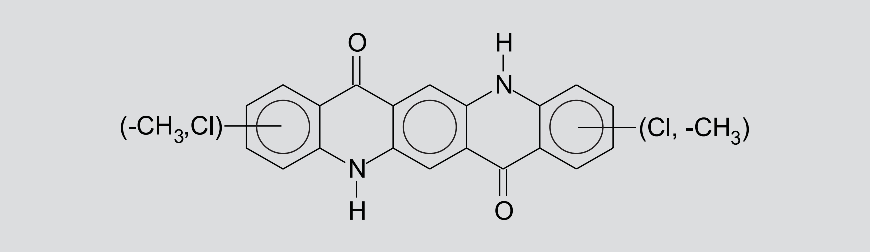


Fig. 2.1.185
Chemical structure element of quinacridones

known, the red γ- and the violet β-forms are the most important. They receive top marks for fastness to light and solvent resistance, but are sensitive to alkalis.

The **perylene** and **perinone** pigments are closely related to each other. Starting from aromatic, polynuclear tetracarboxylic acids, condensation with mono- or diamines is carried out during the synthesis process. The first case yields the perylene pigment group, while the second results in the perinones. Because of their symmetrical and asymmetrical forms (cis/trans) the latter have different color properties.

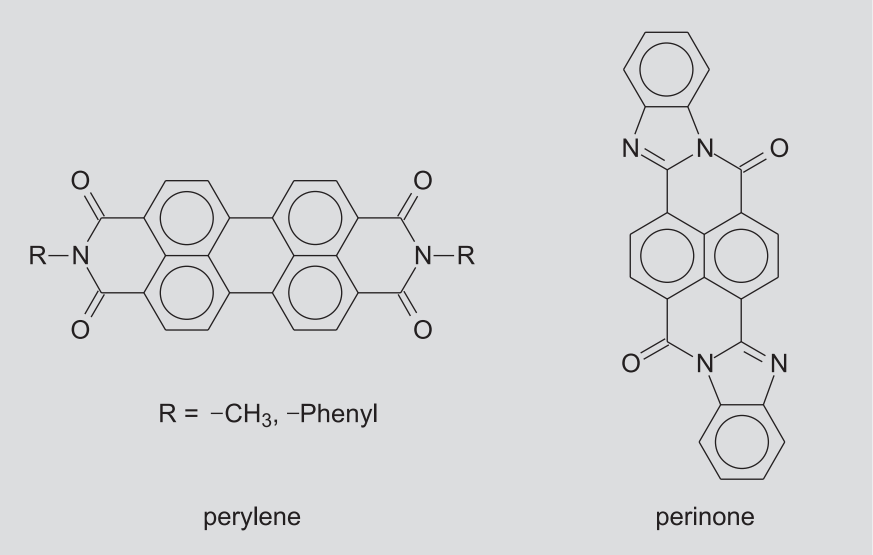


Fig. 2.1.186
Perylene and perinone pigments

Perylene pigments, though this also applies to perinones, exhibit excellent fastness to light and longterm outdoor exposure properties but also high heat resistance because of their chemical structure. Like the above mentioned anthraquinones and quinacridones, therefore, they are also used in high-grade industrial paints, particularly powder coatings. The fine-particle types are particularly suitable for metallic coatings because of the less pronounced scattering power, and the coarser types for opaque solid colors, i.e. without any added white pigments, generally combined with inorganic pigments.

The violet **dioxazine pigments** do not belong to the carbonyl pigment class, but they also deliver brilliant colors and are extremely lightfast in a suitable concentration.

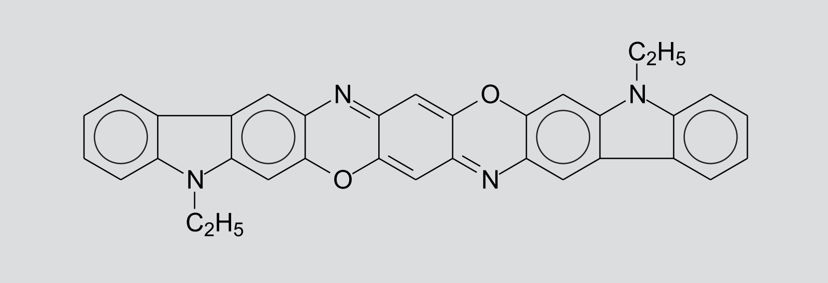


Fig. 2.1.187
Chemical structure of a dioxazine pigment

Because of the violet color and their high fastness to light even in tiny concentrations they are used, among other things, to ”clean up” the white tone of the slightly yellowish rutile form of titanium dioxide.

The dioxazine pigments have even better resistance properties if imidazolone groups are chemically incorporated [2.4.45].

Despite these numerous optically attractive pigment classes which are also suitable for paints in terms of application engineering and longterm outdoor exposure properties, researchers have continued their attempts to develop new knowledge based on the dependencies of structure and properties of familiar pigments. **Quinophthalones, diketopyrrolopyrrole (DPP)** and **pyrazoloquinazolone pigments** are without doubt the most important technically used results of pigment research in recent decades. Of these, the red DPP has gained an important place in automotive paints because of its high color purity.

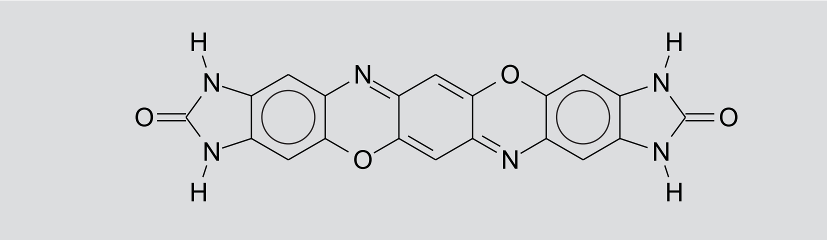


Fig. 2.1.188
Structure of an imidazolon modified dioxazin pigment

The example of the pyrazoloquinazolone pigments shows that rigorous implementation of the theoretical and practical knowledge of structure/property correlations can result in further improvements, even though quality standards are already high. Planar molecules with as many carbonyl and NH groups as possible in the right configuration result in good crystallization and strong intermolecular interaction, which are both important prerequisites for fastness to light and resistance to heat and solvents. The knowledge gained among the azopigments with acetanilide, pyrazolones and benzimidazolones resurfaces in optimized form in the pyrazolone matrix of quinazolone.

To this must be added the fact that the properties of pyrazoloquinazolone can be further improved by azo coupling with anthraquinone. They currently represent the leading

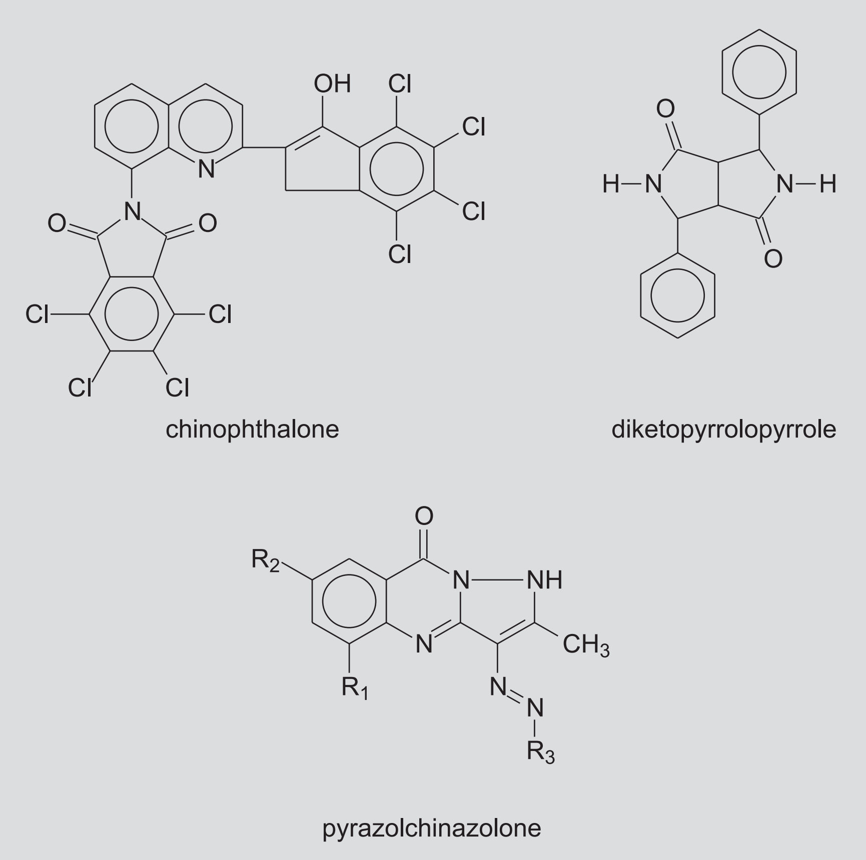


Fig. 2.1.189
Structure elements of newly developed pigments

edge in pigment development with a range of brilliant and, at the same time, highly opaque products.

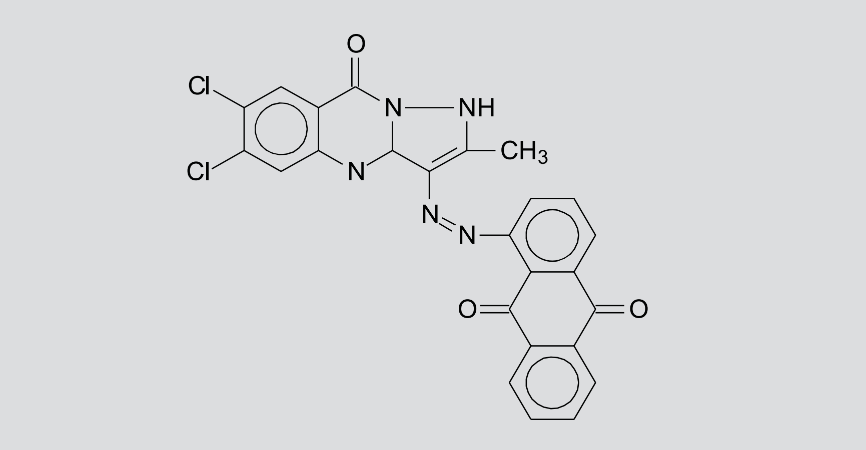


Fig. 2.1.190
Chemical formula of a pigment made of azo and anthraquinone structures

Effect pigments

Metal pigments, also termed ”bronzes”, are platelet-like metal particles, generally made of aluminium, which are up to 20 µm long and up to 1 µm thick. Their task is to settle in a plane-parallel configuration in the paint film in order to achieve a brightness of the reflected light which varies with the angle of view, also termed ”flip-flop”. The coatings thereby gain a metallic appearance which is particularly attractive optically. Depending on the previous surface treatment of the aluminium platelets, their properties will vary in the freshly applied, i.e. still liquid, film. The types modified with stearic acid float to the coating surface and form a glossy silver interface between the coating and its surroundings. The pigment scales are like leaves floating on the surface of water, and this phenomenon is therefore termed ”leafing”. They are in parallel alignment and are fixed in this position when the film hardens [2.4.46]. Use is made of the very high reflection by aluminium particles of IR and UV light to achieve longterm protection of topcoats for industrial steel structures, bridges, lighting masts, large containers, refineries or large chemical plants. This enables effective protection of the objects against the effects of light and thermal radiation.

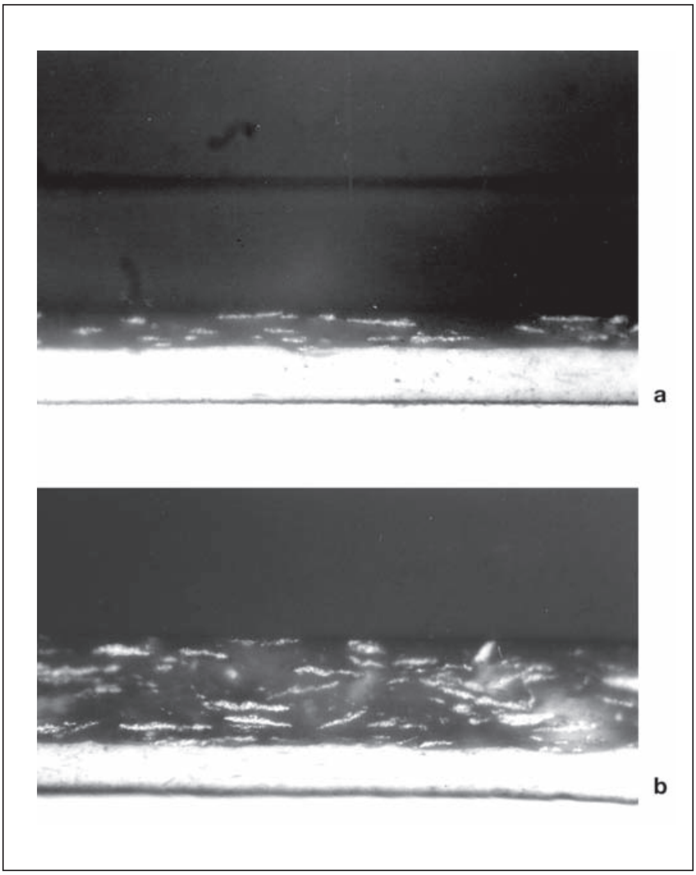


Fig. 2.1.191
Metal pigments in a cross section view of a coating with good (a) and bad (b) metallic effect (”flip flop”)

In the case of ”nonleafing” types stabilized by oleic acid this floating to the interface of the coating does not occur. If the tiny aluminium mirrors which are now evenly distributed in the film can also be aligned parallel to each other and to the substrate, the metallic finish which is so attractive as a paint finish for cars will have been successfully achieved, once sealed with a weatherproof clearcoat.

The **interference and pearlescent pigments** cause color shifts which depend on the angle of view. This effect, which is based on physical principles of light interference, is copied from pearls, fish scales, peacock feathers or beetle carapaces.

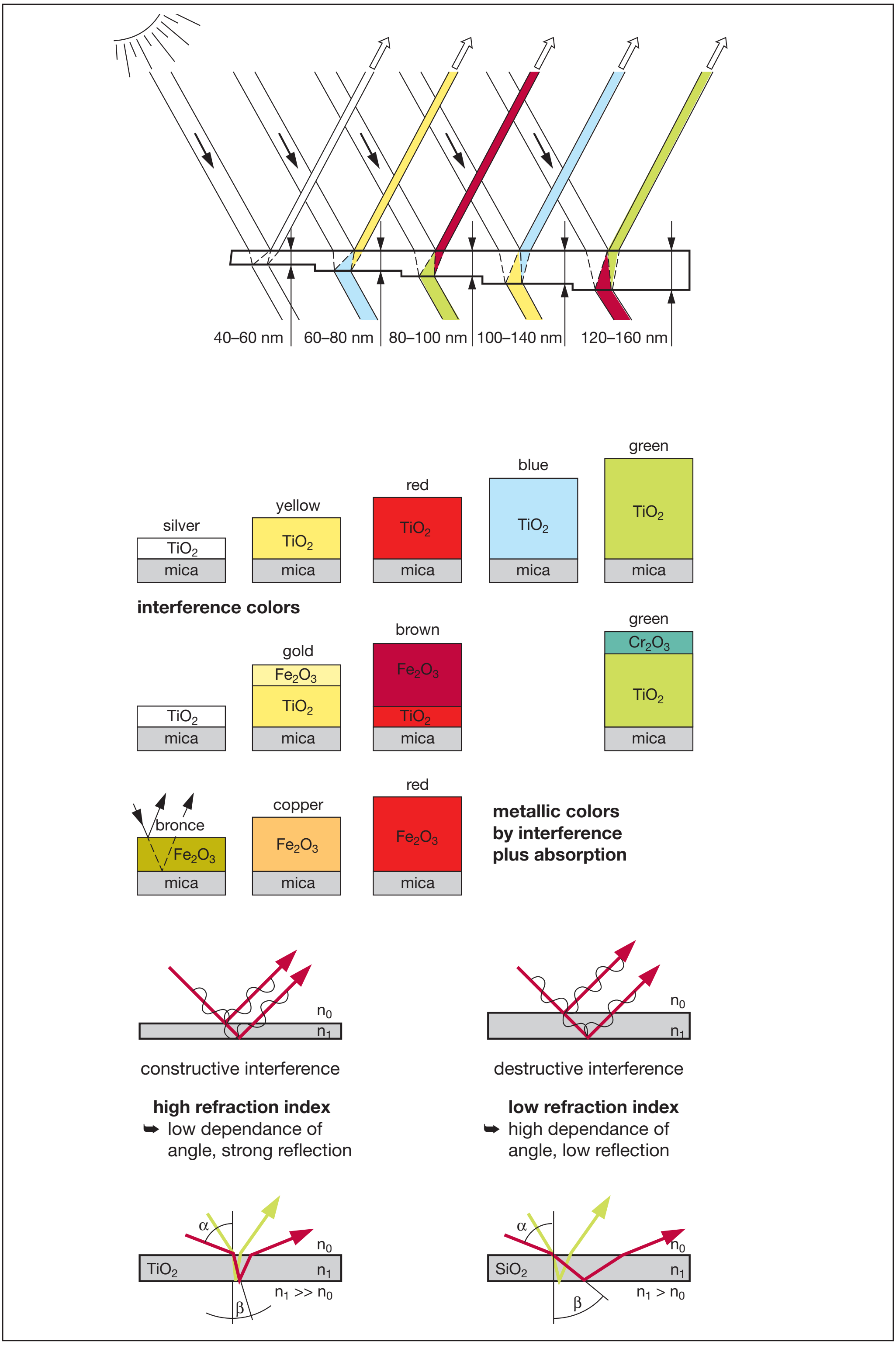


Fig. 2.1.192
Way of light rays through interference pigments

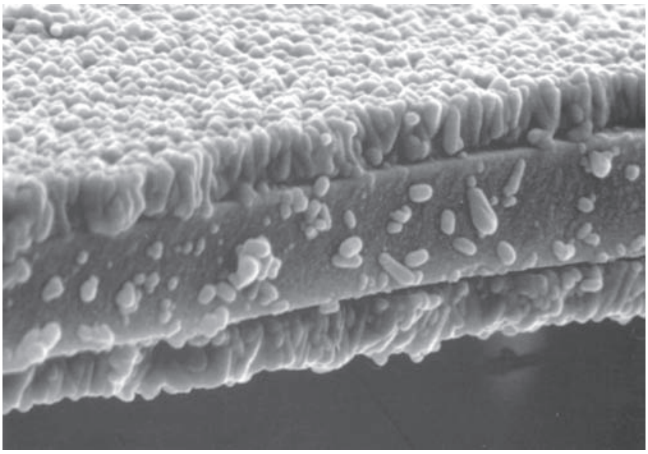


Fig. 2.1.193
SEM picture of a cross section of an interference pigment on a SiO_2 *carrier*

The cause of the selective cancelling of parts of the visible light lies in the double reflection at the surface and on the underside of the thin pigment platelets. The pigments are always structured in principle such that thin films of oxides with varying refractive indices are applied to a platelet like, reflective carrier. If the film is thin enough, the light rays which are offset by half a wavelength relative to each other are cancelled out, whereas those offset by a whole wavelength are amplified. The color of the reflected light is complementary to the transmitted light and is dependent on the angle of view with different angles of incidence because of the changing path differences of the divided rays (see chapter 3.2.4).

Because of the short wavelengths of visible light the film thicknesses of the interference pigments are correspondingly low. The pigments which were originally manufactured exclusively by the precipitation of titanium dioxide films onto mica platelets were then expanded by numerous modifications both to the color-providing component and also to the carrier.

The additional application of films with selective absorption properties means that interference coatings are being enhanced by new optically attractive colors by absorption coatings.

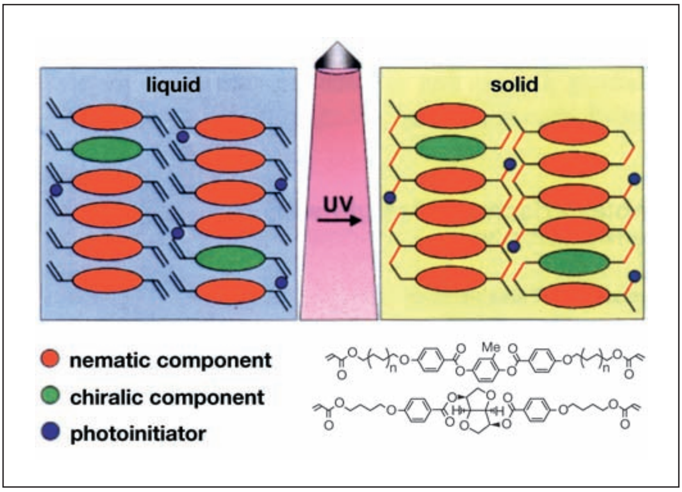


Fig. 2.1.194
Liquid crystal pigments by fixing into a polymer matrix via polymerization

In addition to mica as the carrier material, aluminium platelets, aluminium oxide, silicon dioxide, and even lamellar iron oxide are now also used for the later application of the λ/2 films. The latter can be applied using the CVD (chemical vapour deposition) process from the gaseous phase.

Another group of organically based interference pigments are the liquid crystal (LC) pigments. The liquid crystals which are oriented in a cholesteric phase in the form of helices and then fixed by copolymerization also cause interference effects with light because of their molecular order and thus represent an extension of the already wide range of interference pigments [2.4.47].

However, the high transparency of LC pigments demands that carbon black or opalescent pigments also be added. Only in this way is it possible to achieve both a good effect and hiding power at the same time.

Today's paint and coatings industry has a large range of organic and inorganic pigments with a broad spectrum of colors and effects. Suitable products are available for corresponding requirements relating to heat resistance, insolubility in an aqueous or organic environment, fastness to light, but also to hiding power and gloss. In practice mixtures of organic and inorganic pigments are frequently used in order to combine the strengths of the individual classes of substances with each other cost-effectively.

Modern pigment research uses not only the practical experience of structure/property correlations, but also the modern possibilities of molecular modelling to gain information on optically attractive pigments, without having to synthesize them first. It should be noted in this regard that the color properties depend not only on the structure of the individual pigment molecule, but also on its configuration within the crystal matrix. Predicting the right crystal packing out of the large number of possibles is a problem that has still not been fully resolved to this day, despite far-reaching understanding of the means of controlling crystal growth.

Whenever considering the selection of suitable colorants it is essential to bear in mind that the performance profile of a coating finish is not determined solely by the pigments. Their particle form, distribution, configuration and interaction with the polymer environment, on the one hand, but also the interaction with additives, on the other, ultimately determine the color, effect, hiding power and the longterm outdoor exposure properties. Pigments alone, therefore, though important, are but one of the elements which determine the quality of a coating finish.

2.1.3.3 Extenders

Extenders generally consist of inorganic substances of varying chemical composition and, consequently, different physical properties. Their task is to fill the coatings spatially with skeletal material and therefore to influence the mechanical properties in a particular direction, depending on the function of the relevant paint film. The refractive index is frequently used to demarcate them from pigments. With extenders this is less than 1.7 which is why this family of substances does not attain any noteworthy scattering and hiding powers. However, for coating formulation principles they must be taken into account together with the pigments when calculating the pigment volume concentration (PVC) (see chapter 2.3.3). The PVC is one of the principal factors in determining the mechanical/technological properties of coatings.

When extending the film volume by means of extenders their grain size distribution plays an important role. Correctly chosen combinations of small and larger particles result in the greatest possible packing density. The volume remaining for the binder in the cavities is then only small, and the PVC is correspondingly high numerically. Each coating system has a critical PVC (CPVC) which, if exceeded, means that the desired film properties will not be achieved since the binder no longer represents a continuum because of inadequate proportions.

Impact strength, swelling power and water vapour permeability are film properties which can be influenced by the addition of extenders. The effect of extenders is not limited merely to the interior of a coating; it also extends to their interfaces. In the film surface they can having a matting effect by enlarging the surface areas, thereby enhancing the adhesion of the following coating film. Wear resistance and sandability are further surface properties of films which are influenced by extenders.

In volume terms, extenders obtained from minerals and rocks lead the field in the product range. After large-scale extraction, the natural raw materials are comminuted in grinding processes. Depending on the degree of comminution and treatment, materials are classified as follows:

- Coarse powder with particle sizes over 250 µm
- Medium powder with particle sizes between 50 µm and 250 µm
- Fine powder with particle sizes between 10 µm and 50 µm and
- Pulverized powder with particle sizes < 10 µm.

Silicates	
• natural, platelike magnesiumsilicate hydrates	talc
• natural aluminiumsilicate hydrates	China clay
• natural potassium-aluminiumsilicate hydrates	mica
Carbonates	
• natural calciumcarbonates	chalk
• natural calciumcarbonates, crystalline	calcite
• precipitated calciumcarbonates	
• natural calcium-magnesiumcarbonates	dolomite
Sulphates	
• natural salts of barium	barite, spars
• synthetic salts of barium	”Blanc fixe”
Silicic acids	
• natural silicic acids (SiO_2)	quartz
• synthetic silicic acids	”aerosils”
Other extenders	
	graphite, micaceous ironoxide

Fig. 2.1.195
List of important extenders for coatings

In the case of synthetically manufactured extenders the materials are usually of the same chemical composition which are also used as natural extenders. They are purer, and their properties are more reliably reproducible.

Extenders are mainly used for primers, fillers and primer surfacers. Large quantities are also contained in dispersion paints. They are used only minimally, on the other hand, in solventborne topcoats.

The following extenders or groups of extenders are worthy of particular note:

Kaolin, also termed China clay, is a natural, very white aluminium silicate and is especially suitable for use in dispersion paints. Its lamellar structure gives coatings thixotropic properties. The hardened films are mechanically tough and exhibit good adhesion to the substrate.

Talc, a natural magnesium silicate, also has a lamellar structure. With a hardness of 1 on the *Mohs*' scale of hardness (see chapter 3.2.5) talc is extremely soft and promotes the sandability of fillers and primers by reducing the cohesive strength. **Chalk flint**, despite its misleading name, is not a type of chalk at all; instead, it is kaolin contaminated with quartz and dolomite.

Thanks to their hardness **silicon carbide** and **quartz powder** reduce abrasion of coatings, for example road markings and floor coverings.

Carbonates in the form of chalk and calcite powders are important extenders in the paint and coatings industry. The chalk comes from marine deposits of animal and plant skeletal substances. Microscopic examination of the initial material reveals residues of the shells of small marine creatures. Calcite, on the other hand, is crystalline calcium carbonate which contains no biogenic residues. Compared with chalk, calcite is finer and brighter. Calcite powders that have undergone secondary treatment and synthetically manufactured calcium carbonate, precipitated chalk, are also frequently used today. Extenders made of calcium carbonate allow fillers, primer coats and primer surfacers with high packing densities and excellent application properties to be produced. Another important application field for calcium carbonate is in dispersion paints. A disadvantage of this raw material, which excludes it from many application fields, is its sensitivity to acids. Dolomite, i.e. calcium magnesium carbonate, is demonstrably less acid-sensitive and harder at the same time.

By far the most important **sulphate extender** is barium sulphate. A major advantage of this extender is its high resistance to acids and other chemicals. The paint and coatings industry uses both naturally occurring and also synthetically manufactured (precipitated) barium sulphate. The former consists of ground heavy spar, barite, which is often contaminated by impurities because of its natural origin. It is not very bright and is characterized by different crystal forms and grain sizes in the individual particles. This promotes the formation of a high packing density for fillers and primer coats. Synthetically produced barium sulphate, under the tradename ”blanc fixe”, differs from ground heavy spar in its high degree of purity, its fineness and the uniformity of its grain size. Consequently it is also suitable for more demanding applications. Barium sulphate has the highest density of all extenders, at 4.5 g/cm^3. This must be borne in mind when used in waterbased paints.

Calcium sulphate is generally in the monohydrate form. Because of its sensitivity to water it is only used for less demanding coatings on wood, paper and plaster.

Textured, particularly **fibrous extenders**, such as fibreglass, make a significant contribution to increasing the tensile and tear strengths by forming a fine, matted network.

Other extenders with special roles include hydrous **aluminium oxide powders**, which have proved successful as flameretardant extenders in conjunction with other additives which release inert gas, such as urea or melamine.

Lamellar extenders are also worth noting. Micaceous iron ore in the form of lamellar haematite and mica itself merit mention. If such extenders are successfully aligned in a plane-parallel configuration to the substrate, this creates a barrier against the ingress of water vapour, thereby improving anticorrosive protection at the same time.

If there is a requirement for coatings to be electrically conductive, this can be met by the addition of graphite.

Synthetically produced **hollow microspheres** made of SiO_2 or organic material are particularly light and simultaneously bring about an increase in the scattering power and thus the hiding power also as a result of the air-filled cavities because of the increase in the relative refractive index. An improvement in the impact resilience is also achieved.

2.1.4 Plasticizers and Additives

While film forming agents as natural or synthetically produced resins are responsible for the protective effect, though it only becomes possible to process them because of solvents, and while pigments generate optical attractiveness through chroma and effect, it is the plasticizers and additives as coating auxiliaries which have the varied and important task of optimizing the paint and paint film properties. Plasticizers serve to reduce the film forming temperature and elasticize the coating. They are largely chemically inert and therefore mostly only function at a physical level.

Additives are generally added to the raw materials or the coating material in small or even minute quantities, but they affect coating manufacture, processing, film formation and ultimately also the optical and mechanical/technological properties of the film itself. Furthermore, they are able to improve the film resistance and thereby delay the ageing process.

Additives are often multifunctional and therefore influence several properties of paints and the finished coatings at the same time. Thus numerous wetting agents and auxiliary materials for the pigment dispersion process are exclusively substances with a tenside structure which can also be found in the same or only slightly modified form as defoamers or antisettling agents.

Silicone oils are also polyfunctional. They influence flow properties and the floating of pigments, they reduce the drag of coated surfaces and thus indirectly improve scratch resistance. They simultaneously optimize substrate wetting and make coatings water-repellent by reducing the surface tension.

Whether additives are always able to achieve their tasks of modifying and optimizing properties depends not least on their dose.

2.1.4.1 Plasticizers

As already mentioned a number of times, in addition to good adhesion to the substrate coatings are also expected to have a high level of hardness and good elasticity at the same time. Many film forming agents do not meet these requirements because their chain mobility is restricted by molecular interaction, i.e. by strong *van-der-Waals*' forces. The task of the plasticizer, therefore, is to reduce or entirely prevent the formation of such bridging bonds. This can be achieved, on the one hand, by having plasticizing carried out during manufacture of the film forming agents by incorporating elasticizing segments or monomers which sterically hinder such interaction. Such a system of

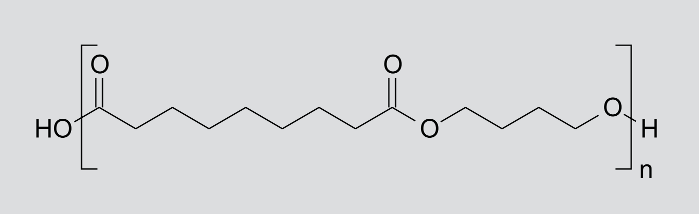


Fig. 2.1.196
Platicizer resin from azelaic acid and 1.4-butandiol

influencing the elasticity in advance, i.e. during the manufacture of resins, is termed inner plasticization. If inner plasticization of elasticized resins cannot be used for reasons of poor processibility or nonoptimum film properties, secondary elasticizing of ”hard” resins must be carried out. This can be achieved in two different ways. Either the hard film forming agent is ”diluted” with highly elastic resins, such as aliphatic polyesters, or classic plasticizers in the form of low molecular auxiliary materials such as phthalic ester are added to halt intermolecular interactions.

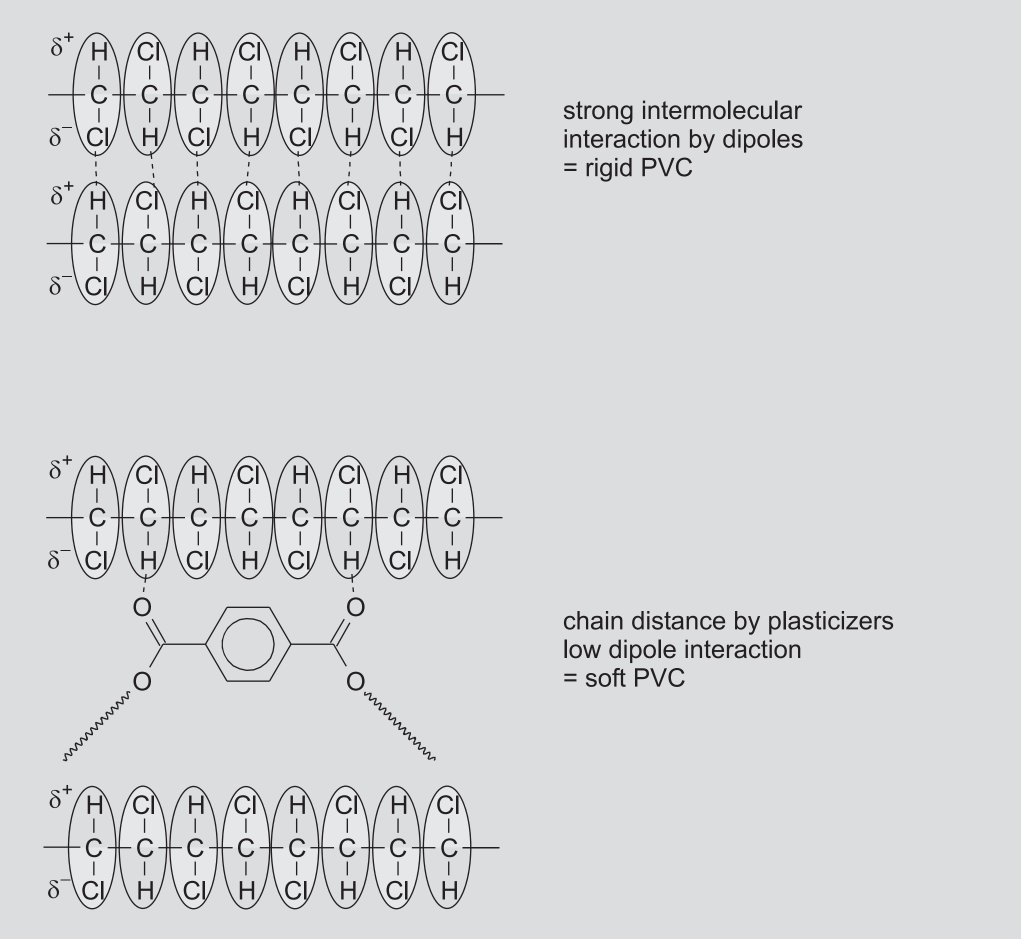


Fig. 2.1.197
Effect of classical plasticizer on polyvinylchloride (PVC)

The aliphatic polyesters mentioned first are nonvolatile and function more or less as oligomeric solvents. Because they do not migrate readily, they offer the advantage of good longterm effects. However, if such plasticizing resins or soft resins are added to excess, they result in a sticky surface to the coating. Important plasticizing resins are generally polyesters of adipic, azelaic or sebacic acids with aliphatic 1,2- or 1,4-diols. All plasticizing resins have good resistance to leaching and migration and only cause a minor reduction of the resistances of the coatings to petrol, oils, greases and soaps. They are resistant to UV light and are regarded as physiologically safe.

The disadvantage of the stickiness which occurs at high doses is avoided by using classic plasticizers. Classic plasticizers are, according to DIN EN 971-1 and DIN EN ISO 4617, liquid or solid, inert organic substances with low vapour pressure, particularly those of ester-like nature. They can interact physically with high-polymeric materials without a chemical reaction, preferably as a result of their swelling properties, and form a homogeneous system with them. This interaction is based on the special molecular structure. Plasticizers always contain polar and nonpolar molecular particles. The former enable them to interact with the polar groups of the film forming agents to be plasticized. With the nonpolar residue they prevent intermolecular interaction of the resin molecules by steric hindrance and thereby promote their mobility.

The outcome of this is that the glass temperature Tg (see chapter 3.2.5) is lowered. The reduction of the glass temperature in relation to the concentration is used as an important criterion for the effectiveness of plasticizers.

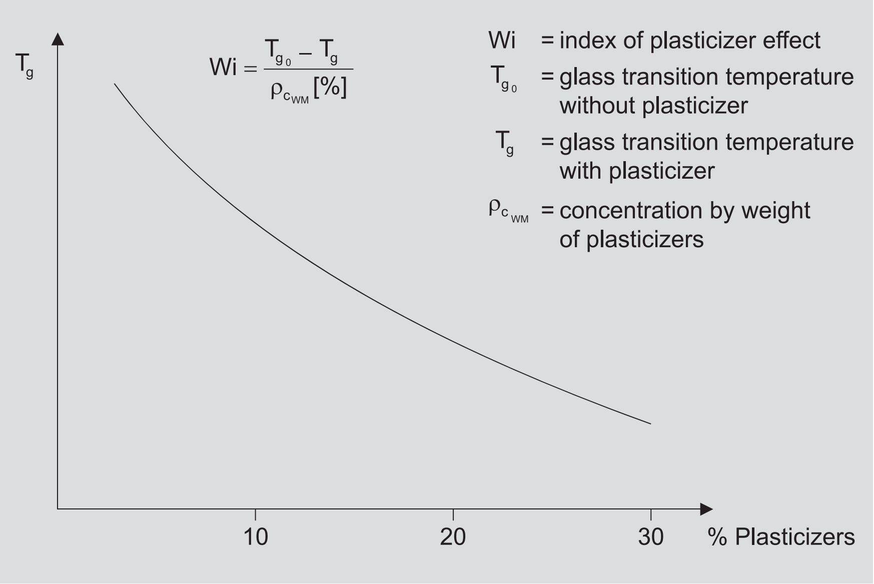
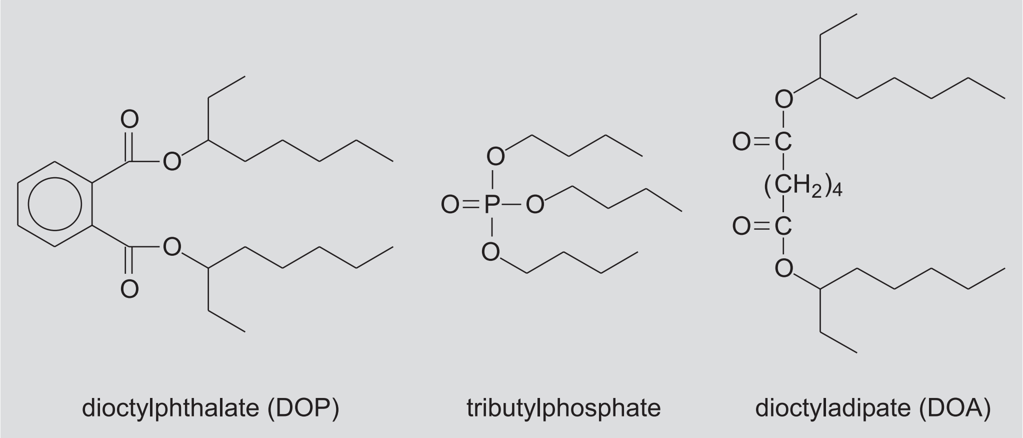


Fig. 2.1.198
Lowering the glass transition temperature (Tg) of a polymer by plasticizer

To ensure effective plasticization, therefore, substances should be used which can penetrate the resin to be plasticized when heated. Because of their low molecular weight classic plasticizers have a certain degree of volatility. They are inferior to plasticizing resins in the duration of their effectiveness.

Other demands placed on plasticizers include physiological safety, effectiveness at low temperatures and when exposed to heat and light, and also resistance to extraction and saponification. Materials which meet most demands include esters of phthalic acid, phosphoric acid, adipic acid and sebacic acid with aliphatic alcohols of varying chain length.

Epoxidized oils and various fatty acid esters increase the elasticizing effect as secondary plasticizers in conjunction with classic plasticizers.



dioctylphthalate (DOP) tributylphosphate dioctyladipate (DOA)

Fig. 2.1.199
Chemical structure of classical plasticizer

The widely used phthalate plasticizers, usually esters of α-ethyl hexanol are colorless and odourless, lightfast all-round plasticizers with only moderate cold resistance. Although phosphoric esters are inferior to phthalic esters in their fastness to light, they gel rapidly and have better extraction resistance. By comparison with the types mentioned, the acyclic esters of aliphatic dicarboxylic acids, generally adipic and sebacic acids, result in excellent elasticity in the coatings, even at low temperatures. They are often mixed with phthalate plasticizers because of their high price.

	Phosphoric acid ester	Adipic and sebacic acid ester	Phthalic acid ester	Ricinene oil acid ester
1. drying oils	–	–	–	+
2. asphaltes	–	–	–	–
3. bitumen	–	–	–	–
4. maleic resins	+	+	+	+
5. oilfree polyols	+	+	+	–
6. alkyd resins	+	+	+	+
7. phenolic resins				+
8. urea resins	+	+	+	+
9. melamine resins	+	+	+	+
10. polyvinyl acetales	+	+	+	+
11. polyvinyl chlorides	(+)	+	+	+
12. polyvinyl acetates	+	+	+	
13. dispersions of polyvinylether	+	+	+	

Fig. 2.1.200
Hints for use of plasticizer in film forming agents

Figure 2.1.200 shows a selection of resins which require plasticizing and gives information about their compatibility with the most important plasticizers or plasticizing resins.

2.1.4.2 Additives

When drawing up formulations it is often assumed that a system's target properties will be achieved by more suitable film forming agents or better pigments. If this approach does not succeed for qualitative and economic reasons, the next step is to resort to additives. It should be noted that determining the correct dosage of the correct additive requires very particular attention because of the tiny quantities added and their frequently physical interfacial effect. If, for example, a polar surface is to be made water-repellent by means of an additive, such an effect can only be achieved with a monomolecular tenside covering. If the dosage is too small, the goal will not be achieved. If the dosage is too high, double layers will be formed which will ultimately restore the status quo.

The coating additives usually employed to optimize and modify properties can be classified in accordance with various criteria. Despite the often multifunctional effect of various additives classification by the intended use has become accepted. For example, tensides of the same chemical nature can be encountered for dispersing pigments, defoaming, combating floating effects, but also for modifying the processing properties of waterbased paints.

The sections below deal first with additives for manufacturing, storage and processing and then discuss the additives used to form and stabilize the film properties.

Additives to optimize coating manufacture and storage stability

If the technical process of coating manufacture is examined to identify means of optimization via paint additives, the starting points concentrate on the rheological properties and the physical interfacial phenomena. The rheological properties determine, among other things, the penetration into the cavities of the pigment agglomerates and permit the modification of the shear forces which are transferred to the pigments in the dispersing machines (see chapter 2.1.3). The ability to influence flow properties is of critical importance during paint processing and the subsequent film formation (see chapter 3.1.1). To ensure more rapid pigment distribution and better pigment stabilization, additives which influence surface tension are of particular interest in coating manufacture and storage.

The forces of attraction between the molecules create cohesion and thus the attempt to present the smallest possible surface areas for a given volume. This material property, known as surface tension, can cause problems when different materials interact in the coating formulation. Thus the fine particle pigments agglomerate to form larger units and resist wetting by resin solutions if there is no coordination of the surface tensions of the substances at the interfaces (see chapter 2.3.3). Compatibility agents in the form of **tensides** are then needed to ensure that the pigment particles are completely coated in resin solutions and thus also to ensure the complete removal of the air from the agglomerates and the water adsorptively bound to the polar surfaces of many pigments. They promote wetting of the agglomerates.

Tenside molecules have a characteristic structure to fulfil their tasks. This consists of the chemical bonding of extremely hyrophilic and extremely hydrophobic molecule

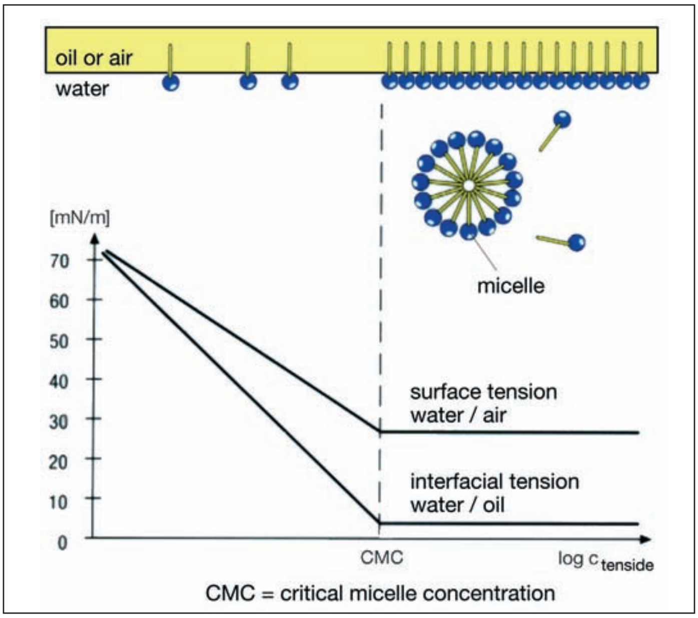


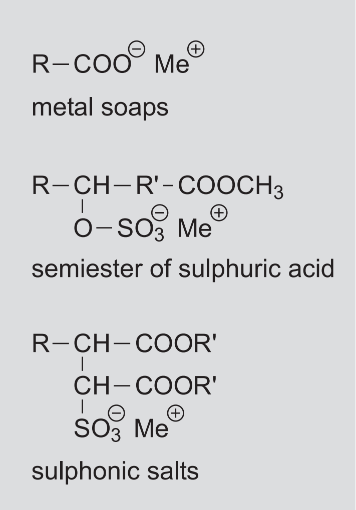
Fig. 2.1.201
Dependency of the surface and interfacial tension on concentration of tensides

segments. They therefore gravitate towards interfaces of differing polarity such that the polar group turns to the polar substance and the nonpolar to the less polar substance. For example, the carboxylate groups as salts of saturated fatty acids together with their nonpolar alkyl groups bring such opposed substances as oil and water together and permit the production of stable emulsions.

Since tensides accumulate in the interfaces, their effectiveness is only proportional to their concentration up to a certain threshold. With most tensides an excess results in the formation of tenside aggregates in the aqueous phase, the micelles, without further reducing the interfacial tension. The concentration at which the interfacial tension reaches its minimum is termed the critical micelle concentration (CMC). Theoretically the tensides reach their optimum performance from an application engineering viewpoint at this concentration.

Depending on their charge or charge distribution, the tensides are divided into ionic, nonionic and amphoteric types, while the ionic types are subdivided in turn into anionic and cationic types. Important representatives of the anionic tensides include the sulphuric acid-based semi-esters of longchain fatty alcohols or salts of alkylbenzenesulphonic acids.

Examples of commonly used cationic tensides are quaternary ammonium bases containing alkyl groups. The ionic tensides must be charged in the same way



$R{-}COO^{\ominus}\ Me^{\oplus}$

$R{-}\underset{\displaystyle O{-}SO_3^{\ominus}\ Me^{\oplus}}{\underset{|}{CH}}{-}R'{-}COOCH_3$

$R{-}\underset{\underset{\displaystyle SO_3^{\ominus}\ Me^{\oplus}}{\underset{|}{CH}{-}COOR'}}{\underset{|}{CH}}{-}COOR'$

Fig. 2.1.202
Chemical structures of anionic tensides

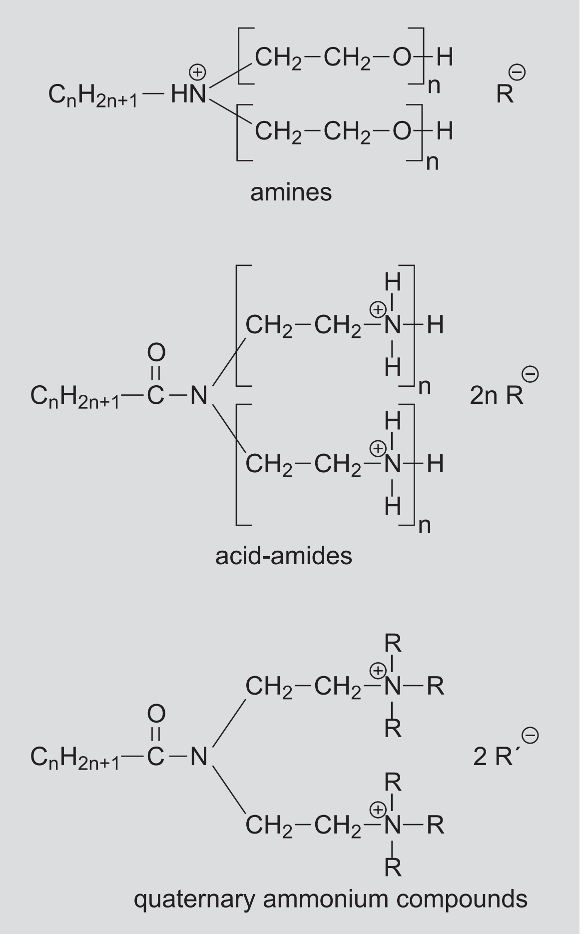


Fig. 2.1.203
Examples of chemical structures of cationic tensides

when formulating waterbased paints which are also ionically stabilized. Considerable stability problems otherwise occur.

As ampholytes, the amphoteric tensides contain both positive and negative charges in addition to a nonpolar group. Lecithin, a companion substance in vegetable oils, is important in coating technology. Lecithins should not be used in the formulation of ”air-drying” coatings because of their inhibiting effect on the oxidative curing of alkyd resins.

Nonionic tensides also have excellent interfacial properties. A distinction must be drawn between the alkylpolyalkylene glycol ethers or etheresters, on the one hand, and the butindiol derivatives, on the other. The latter orient themselves in the interface with their hydroxyl groups to the polar side and vary in their space requirements because of the special structure of the nonpolar alkyl groups. As a result there is also no clearly defined critical micelle concentration.

The HLB value (**h**ydrophilic **l**ipophilic **b**alance) is used to help in the correct selection of tensides. This is defined as the ratio of the polar groups relative to the molecular weight multiplied by 20.

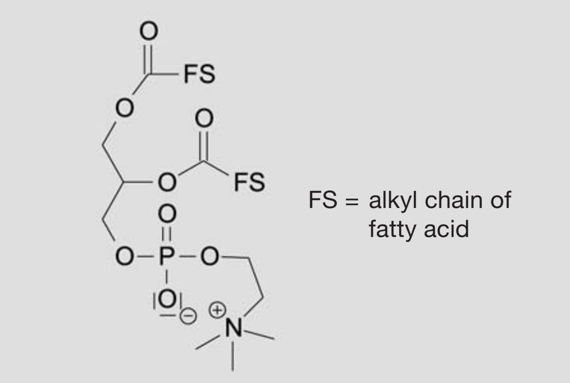


Fig. 2.1.204
Chemical structure of lecithine

The HLB value can lie between 0 and 20, depending on the ratio of the polar and nonpolar groups. Tensides with low HLB values are compatible with oils and become water-soluble with increasing values.

Wetting agents which act between pigment surfaces and resin solutions are in the range 7 to 9. Lower values are aimed at for defoaming agents, higher for washing-active substances and solubility promoters for waterbased systems.

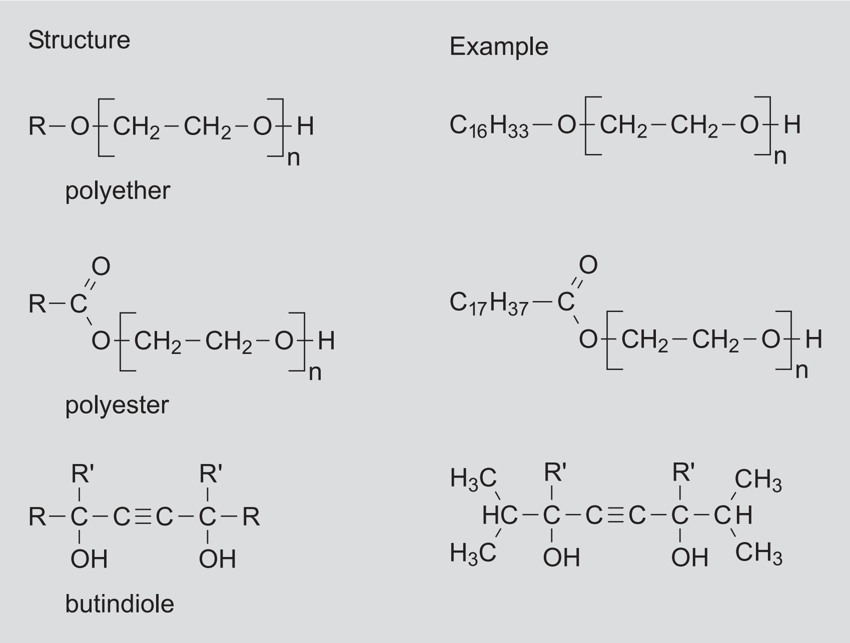


Fig. 2.1.205
Chemical structures of nonionic tensides

If the task is to combat foam effectively, the causes of the foaming must first be identified. Air bubbles trapped in liquid coating materials escape as a function of their size relatively quickly from tensidefree, low viscosity liquids and therefore are not a problem. In the event of higher viscosities and the presence of surfactant additives, however, two aspects of the deaeration process become more difficult. High viscosities slow the rise of gas bubbles, and tensides stabilize the foam bubbles. The first phenomenon results in trapped air in the liquid paint in the form of microfoam, while the second aspect manifests itself in large spherical or polyhedral bubbles at the surface. Both embodiments must be combated by various means.

$$\boxed{\mathrm{HLB} = \frac{\text{mass of polar groups}}{\text{molecular mass}} \cdot 20}$$

Fig. 2.1.206
HLB value to characterize tensides

If gas bubbles from a tensidefree liquid rise to the interface, the liquid lamella enclosing the gas ruptures as it becomes ever thinner and because of the effects of surface tension, and the gas escapes.

However, the physicochemical processes are more complicated when a tenside-stabilized gas bubble rises. Once this reaches the interface, a membrane stabilized on both sides by tensides forms at the surface of the liquid. Liquid no longer drains quickly from the membrane, and the subsequent rupturing of the lamella, which now contains tenside, no longer takes place.

Because of the mutual repulsion of the tenside molecules on the lower and upper sides of the thin membrane this remains around the gas bubble with a finite film thickness. A supplementary stabilization is achieved in that, if the lamella is stretched, this causes a shortage of tenside molecules which results in an increase in the surface tension, and

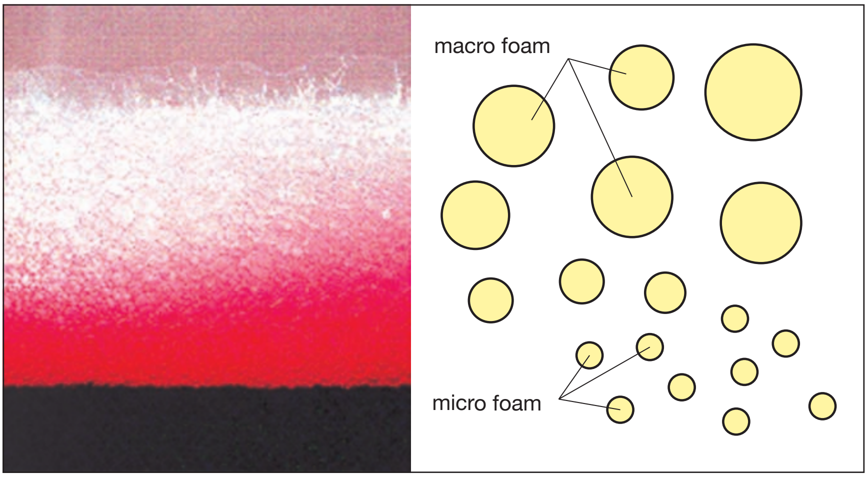


Fig. 2.1.207
Surface defects by micro and macro foaming

this is equivalent to an increase in the restoring force. The lamella becomes elastic and stable as a result of this *Gibbs-Marangoni* effect [2.4.48]. To combat foaming effectively, therefore it is necessary to create inhomogeneities in the surface tension of the foam lamella and thus instigate instability and rupturing by the use of additives. However, such an effect can only be achieved if the defoaming additives are almost insoluble in the foaming substance.

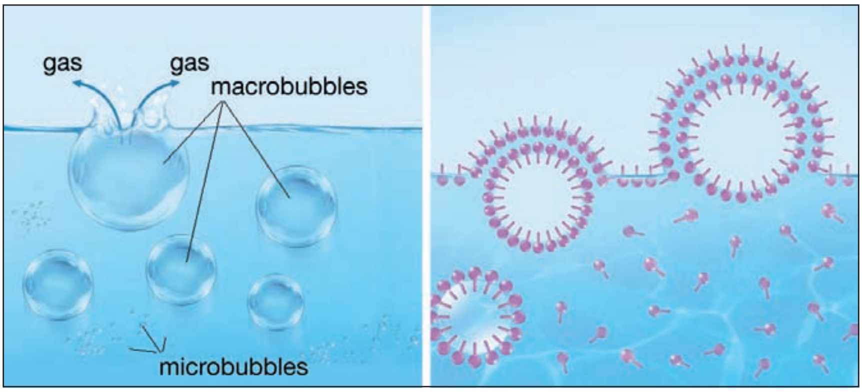


Fig. 2.1.208
Foam in tensidefree and tenside containing fluids

The **defoaming agent**, which is in the form of tiny droplets or solid particles, must therefore enter the foam lamella, penetrate the tenside film and destabilize it at the same time.

Mineral oils or polyether modified polysiloxanes initiate the spreading effect necessary for destabilization of the foam lamella if they are inhomogeneously distributed in the interface. Their heterogeneous distribution is frequently further promoted if they are adsorptively attached to extremely finely distributed SiO_2 particles.

Forecasts of the defoaming effect of additives can be made by calculating the spreading coefficient S and the penetration coefficient E. Both variables must be positive to create a defoaming effect.

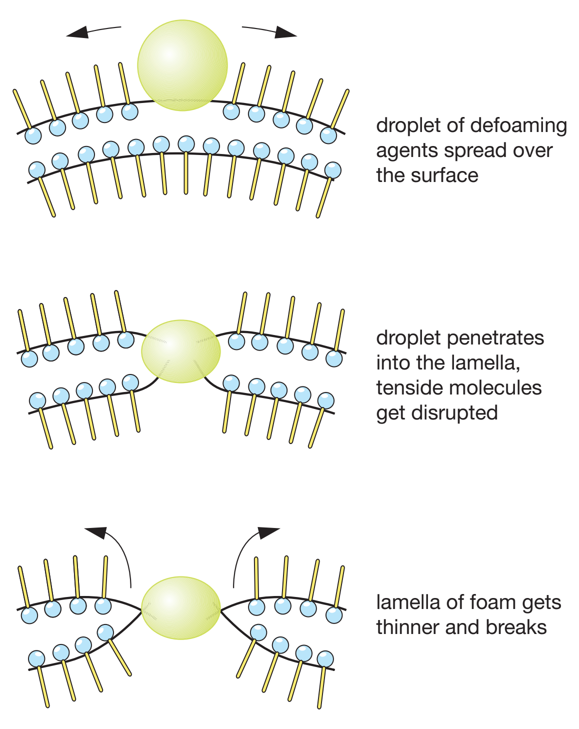


Fig. 2.1.209
Mechanism of defoaming

Extremely fine inclusions can occur during the manufacture and processing of coating materials by stirring air in, by the release of air inclusions from the pigment agglomerates, by trapping air during application or by bubble formation during curing of the coating. In the case of small bubbles and the resulting low rise rate, complete escape from the liquid phase is not possible. The consequences are air inclusions remaining in the coating of fine craters in the surface. In order to eradicate such film faults, steps should be taken to increase the rate of rise of the gaseous inclusions by the addition of **deaerators**. Sensitive variables for this include the viscosity, bubble size and the stabilization of the bubble in the surrounding resin solution caused by tensides. Since the viscosity has a specified magnitude in many cases, the remedial action must concentrate on destabilization and joining, and thus on increasing the size of the bubbles. As doubling the bubble size causes the rate of rise, and thus the deaeration process, to be squared, those additives which, when approached by individual bubbles, cause them to join and thus to become larger, are particularly effective. Deaerators, therefore, are additives which, because of their deliberately chosen incompatibility, accumulate in the interfaces of the air bubbles so that they can destabilize the bubbles there. A corresponding effect lies in the eradication of the flow-inhibiting tenside molecules [2.4.49].

$$S = \sigma_F - \sigma_{EF} - \sigma_F$$
$$E = \sigma_F + \sigma_{EF} - \sigma_E$$

σ_F = surface tension of liquid
σ_{EF} = surface tension of defoaming agent
σ_E = interfacial tension between defoaming agent and liquid

Fig. 2.1.210
Formula for calculating the spreading and the penetration coefficient S and E

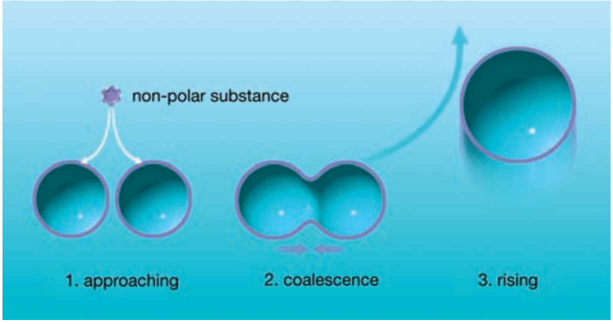


Fig. 2.1.211
Mechanism of deaereting

The use of **inhibitors** is necessary in many cases to improve the storage stability of coatings. Their role is to prevent premature crosslinking of the film forming agent combination. For example, the unsaturated polyesters dissolved in styrene are hindered from crosslinking before it is required by hydroquinone or quinone in just the same way as oxidatively curing alkyd resins by phenol bodies or oxims. In the first case the hydroquinone or quinone molecules inactivate any unwanted starting radicals which have been generated, and in the second sterically hindered phenol bodies functioning as antioxidants slow down the formation of peroxides by atmospheric oxygen. The oxims' effect is based on inactivating the siccatives which promote crosslinking by formation of complexes and thus prevents the skinning of decorative paints in the can. Baking enamels crosslinking with melamine resin are inhibited with the aid of monoalcohols by shifting the reaction equilibrium towards the initial products.

There are two fundamentally different ways of reducing the tendency of pigments to settle. Since the sedimentation rate u of pigment particles in the earth's gravitational field is a function of the different densities Δρ, the acceleration due to gravity g, the viscosity at rest η and the particle size d, **sedimentation inhibitors** are additives which have a negative effect on the settling of pigments by stabilizing the pigments and increasing the viscosity η at rest.

$$u = k \cdot \frac{\Delta\rho \cdot g}{\eta} \cdot d^2$$

Fig. 2.1.212
Formula to calculate the sedimentation speed of pigments

If no reagglomerations occur after lengthy storage and the particle size is not set to change, the only approach for effective additives is the formation of intrinsic viscosity and thixotropy. The latter creates a yield point during storage without impairing flow properties under the shear conditions encountered during processing (see chapter 2.3.2).

Additives for optimizing processing properties

Porefree films with good adhesion are a necessary prerequisite for the protective function of coatings. Uniform and thorough wetting of all the parts of the substrate is absolutely essential for this. Even after thorough cleaning and pretreatment of the objects to be coated it is often still necessary to add **wetting agents** to the coating material to coordinate the interfacial energy between the substrate and the coating (see chapter 2.2.3 and chapter 3.1.1). These are usually tenside like substances in which the polar part consists of hydrophilic polyether groups, and the nonpolar part of hydrocarbon chains or methyl-substituted polysiloxanes. Low molecular silicone polyethers have proved useful in the effective adaptation of waterbased paints to the conditions of the substrates. They are more effective than comparable hydrocarbon based additives.

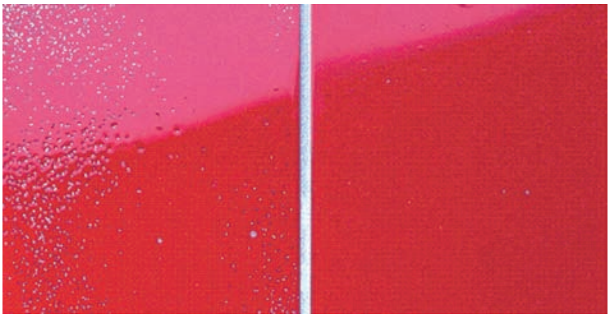


Fig. 2.1.213
Effect of wetting agents on coatings

As a result of the application fresh coating films exhibit a more or less pronounced texture. Wavy surface profiles therefore have to be equalized before physical or chemical hardening by lowering the peaks and raising the troughs (see chapter 3.1.1). At the same time action must be taken to prevent the still liquid paint from running off vertical surfaces or, because of its surface tension, withdrawing from the edges of the object to be coated. Runs impair the optical quality, and running from edges impairs the function of the coating. If no acceptable compromise can be found between flow and running, even after coordination of the solvent composition with the chemical reactivity of the developing film, the assistance of **flow control additives** must be sought. The cause of the flow problems must be considered if the right additives are to be selected.

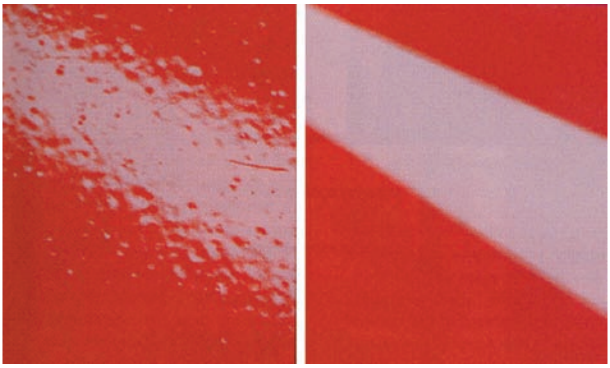


Fig. 2.1.214
Effect of flow control additives on the surface of coatings

On closer analysis of the film forming processes it becomes clear that the flow can be interfered with by levelling of the originally textured surface by currents in the film which counteract the equalization of the structures. Solvent evaporation causes inhomogeneities in the surface tension and density within the film. The generally lower surface tension and lower density of the evaporating solvents cause an increase in the surface tension and density in the surface of the film as it forms. If the viscosity is not yet high enough at this point, vertical currents ensue. The consequence is the formation of a texture in the surface which is opposed to the flow. These film faults, known as *Benard*'s cells, cause separation of the pigments and thus color shifts because of the varying

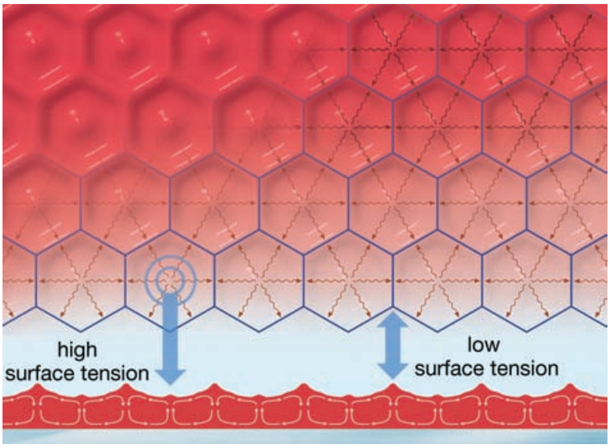


Fig. 2.1.215
Benard's cells : from top (on top), as cross section (below)

mobility of the pigments. Such effects can only be combated with means other than those used for the above described classic flow faults. The latter must be eliminated by means of viscosity-lowering additives. The formation of *Benard*'s cells, on the other hand, is countered by means of additives to increase the viscosity and reduce the surface tension.

Since both phenomena occur together in practice, a targeted and effective optimization of the flow properties requires the use of the correct dose of additives. Suitable flow-control agents are high-boiling solvents (high boilers) for the classic flow faults, or silicone oils which have been rendered compatible with the coating by means of side chains to avoid *Benard*'s cells. The latter are similar in their chemical composition and effect to the substrate-wetting agents. Consequently, they also promote wetting, improve the surface smoothness in addition and thus reduce the drag of coatings. This is also expressed in improved scratch resistance despite the physical hardness remaining unchanged.

Modern additives to increase the structural viscosity of the film as it forms and thus to avoid the fault arising from *Benard*'s cells include linear oligomeric polyurethanes, polyacrylates, cellulose ethers, polyvinyl pyrrolidones and special polyethers. Pyrogenic silicic acids (Aerosils) or montmorillonites (bentonites) have also proved effective.

Other film faults include cavities in the form of **craters** (see chapter 6.2). These are punctual cavities in coatings which can sometimes reach as far as the substrate. The reasons for such film faults always lie in a local inhomogeneity in the surface tension of the coating.

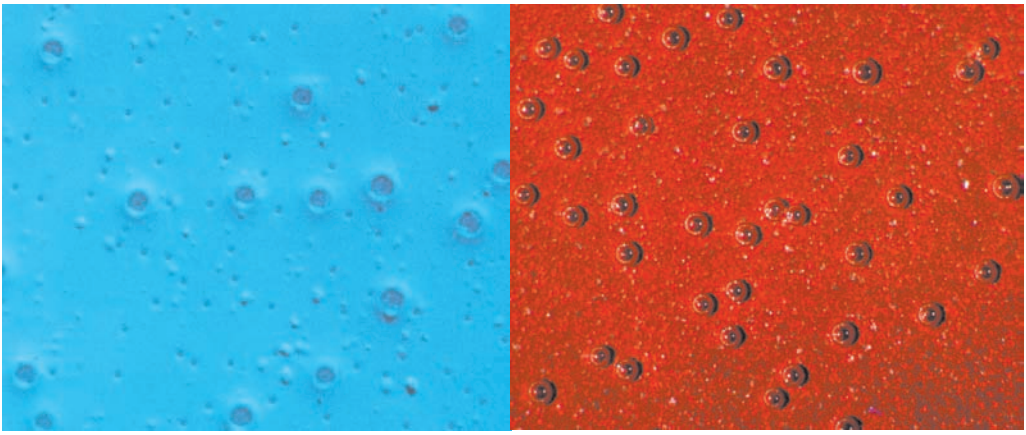


Fig. 2.1.216
Example of typical craters and pinholes in a coating film

Incompatible impurities on the substrate, in the applied coating material or in the form of oversprays, dust particles or oil droplets are the commonest causes of craters. Other causes of unwanted craters are gel particles from the film forming agents. These are high molecular portions of the film forming agent which are at the limit of compatibility and which can cause craters because of their lower polarity and the associated varying surface tension. The negative effect of the surface is frequently amplified by the accumulation of nonpolar additives in the gel particles.

In all cases the effect is the same. The paint which is still liquid after application cannot flow evenly. It is drawn away from the areas of low surface tension and accumulates around it. The result is a cavity which can be either just a cosmetic fault or a weakness in the protection afforded to the substrate.

Before combating craters with additives it is essential to attempt to identify the cause of the craters and, if possible, eliminate it (see chapter 6.2). Gel particles, for example, should be removed from the film forming agent by filtration or centrifuging. If straying overspray is causing craters in the fresh coating, the causes should be eliminated by modifying the surface tensions of the interacting paints. Fluorine-containing tensides or low molecular silicone oils are the most effective additives because of their low surface tension.

Pinholes are similar in appearance to the film faults caused by escaping air bubbles or craters (see figure 2.1.216). These are still intact or already ruptured bubbles caused by the excessively fast evaporation of solvents or cleavage products of chemical crosslinking. If the resin combinations have been set such that they are too reactive, the viscosity of the coating increases at an early stage when heated such that solvents still contained in the film solvent become congested at the polymer skin after evaporation, as a result of which intact or ruptured bubbles form.

The aim of combating pinholes with additives is always to retain the solvents' capability to diffuse throughout the entire film forming process. This can be achieved by adding low volatility solvents or by reducing the reactivity of the film forming agents. Longchain alcohols such as dodecylalcohol have proved successful for most baking enamels. In industrial coating processes pinholes can also be avoided through process-engineering measures when specifying the heating gradients.

Protection of the coated substrate is definitely guaranteed if the coating keeps all harmful agents away from the substrate. Water plays a special role in many chemical reactions at the interface to the substrate. Additives which reduce the influence of water are therefore helpful in many cases. Additives which accumulate on the surface of the coating because of their chemical structure and attach themselves there to their polar molecule groups have proved particularly successful. The nonpolar groups then result in a **water repellent state.** Polyolefin waxes, salts of stearic acid or polysiloxanes are suitable as additives.

Apart from modifying wetting properties, flow and running, preventing surface faults or adjusting the water-repellent finish of organic protective films, additives also perform tasks to **adapt the material for processing**. Adjusting the electrical conductivity and the pH values are two noteworthy examples for material adjustment with coating additives. The paints' electrical conductivity influences

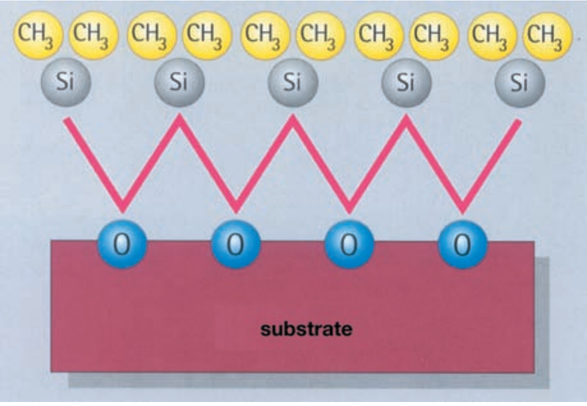


Fig. 2.1.217
Scheme of water repellancy of polymeric surfaces achievable by silicone oil

their processing with electrostatic methods. To achieve the maximum coating yield electrical resistances of 10^5 bis 10^8 Ωcm must be set for solventborne paints. Such ranges can be set without difficulty, for baking enamels dissolved in xylene and butanol for example, by varying the mixing ratio of the two solvents. If benzine-containing non-polar coatings are being processed, the resistance cannot be adapted via the solvent compositions alone. In such cases ionic additives which are compatible with the system are used. Materials such as tetraalkyl ammonium sulphate, ethoxilated ammonium sulphate and monobutylphosphate have proved successful.

The stability of aqueous polymer solutions or dispersions is influenced by the pH value. It is adjusted by means of acid or alkali **neutralizing agents.**

Amines such as dimethylamine, diethanolamine and 2-methyl-2-amino-propanol are the best known pH value regulators for anionic paints. The latter is a proven neutralizing agent because of its mild odour and high basicity (see chapter 5.6.2).

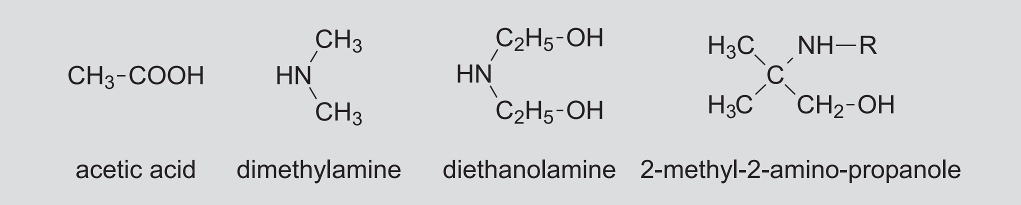


Fig. 2.1.218
Important neutralization agents

To adjust the rheological profile for the processing method of coating materials, cellulose ether or urea crystals in a specific precipitated form are added, in addition to the selected solvents [2.4.50]. A far more important role is played by such additives for waterbased paints which influence the rheological properties of the coating material. Such products, which are grouped under the popular terms **”thixotroping agents ”** or ”thickeners”, vary very greatly in their nature. The bentonites, i.e. inorganic compounds based on lamellar silicates, are important representatives of this group (see chapter 2.1.3). Their effect is based on the creation of tertiary structures by means of dipoles and electrostatic effects. The platelets are negative on the flat side and positive on the edge. This means that it is possible to build structures which are similar to a house of cards under no-load conditions which are then destroyed by shear. Construction proceeds slowly so that thixotropy is the outcome (see chapter 2.3.2). The bentonites show their effect in the formulations for waterbased coating materials at proportions by weight of approx. 0.2% to 5%.

A further class of thickeners is represented by the polyacrylic acids. Their effect is based on expanding the molecular coil by electrostatic repulsion of the carboxylate ions. They are effective in the alkali range and, at similar concentrations to the bentonites, result in pseudoplastic formulations at corresponding pH values. The high carboxyl group concentration has an impact on the film properties in that the resistance to water is reduced.

Specifically developed high molecular tensides, e.g. on the basis of polyethylene oxide and terminal polyurethane groups, are being used with increasing success as associative thickeners for aqueous dispersions. They generally feature a very low critical micelle concentration and result in inherently viscous properties at concentrations usually in the range from 0.05% to 0.5%. Their rheological effectiveness can be controlled very well at a molecular level throughout the polyethylene and polyurethane group [2.4.51].

Additives to influence crosslinking and film properties

The mechanical-technological properties of coatings are influenced by physical drying and, in the case of industrial coatings, also by chemical curing. When coating thermally unstable substrates and in order to save process energy **catalysts** are frequently used to lower the crosslink temperature. Organic acids such as p-toluene sulphonic acid have proved their value for polycondensation reactions.

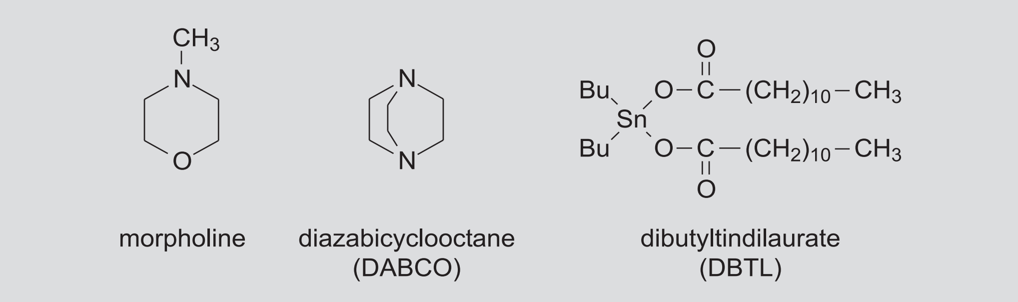


Fig. 2.1.219
Catalysts for hardening of coatings with polyisocyanates

For crosslinking isocyanates reactivity can be increased by the addition of tertiary amines, metallic soaps and metalloorganic compounds. N-methyl-morpholine, diazabicyclooctane (DABCO) or dibutyl tin dilaurate may be mentioned in this context.

In epoxy resins *Mannich* bases accelerate curing with amines, and boron fluoride activates the ring-opening polymerization of the epoxy groups to polyethers. In order to damp the very strong reactivity of boron fluoride, its amine adducts are often used which are then split again by heating, thereby reactivating the boron fluoride (see chapter 2.1.1).

The catalysts for initiating and accelerating polymerization reactions, termed **initiators**, form a large number of subgroups. First among these are the peroxides and hydroperoxides with their proven role in the radical curing of unsaturated polyesters. Dibenzoyl peroxide, cumene hydroperoxide and tertiary butyl perbenzoate are but a few examples from the large group of peroxide catalysts. They can be separated into radicals using heat or accelerators. The latter are metallic soaps which, when interacting with the peroxides, transform them at room temperature by means of a reversible valency change into radicals capable of polymerization (see chapter 2.1.1).

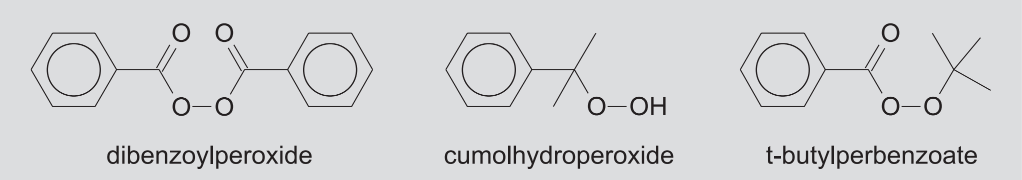


Fig. 2.1.220
Peroxides and hydroperoxides as starters for the radical polymerization reaction

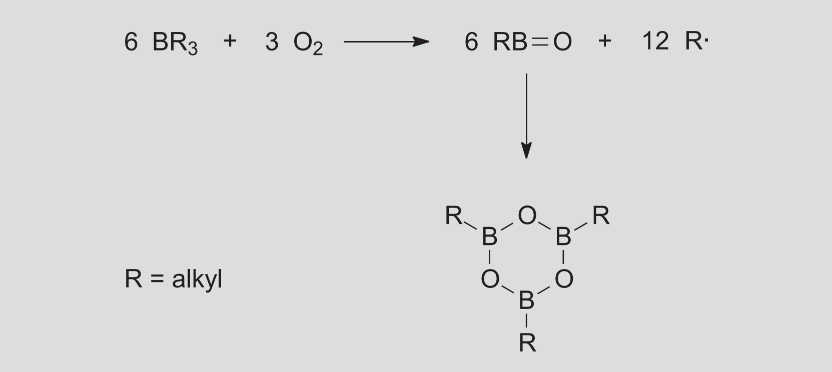


Fig. 2.1.221
Decomposition of boron trialkys in the presence of oxygen

Other radical formers include boron trialkyls. They decompose into radicals in the presence of atmospheric oxygen and form trialkylboroxine.

Examples of modern coating materials with extremely short crosslink times are the UV-curable or electron-beam-curable coating systems. Whereas electron-beam-curable coatings crosslink under the influence of electron beams without additives, film forming agents activated by UV radiation require **sensitizers** or **photoinitiators** (see chapter 4.3.2 and 5.6.5). These are additives which are split into radicals either homolytically by the high-energy UV radiation or by hydrogen abstraction. The latter require synergists to form radicals. These are amines which provide a hydrogen atom from their alkyl

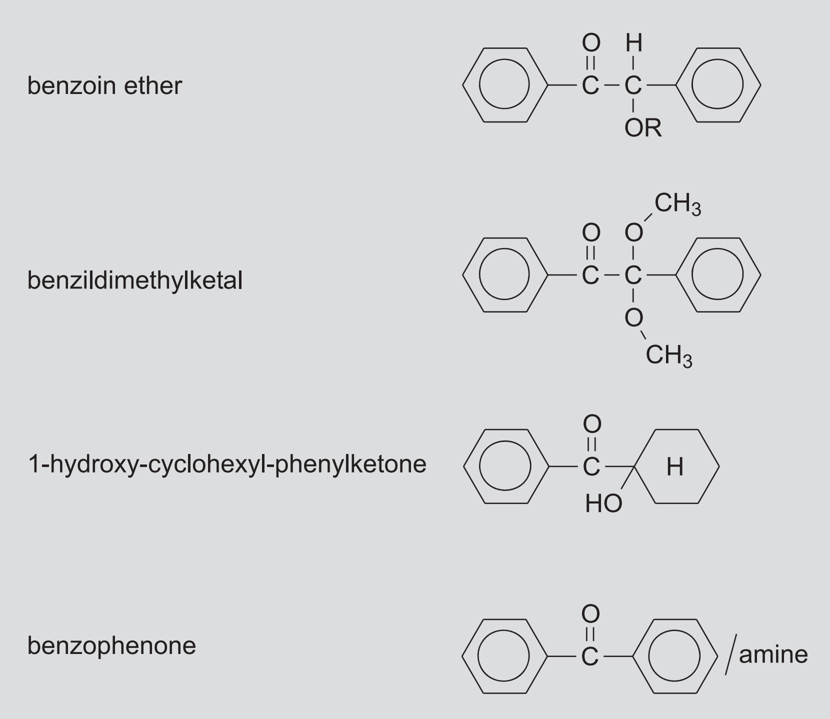


Fig. 2.1.222
Photoinitiators for activation of crosslinking of UV curable coatings

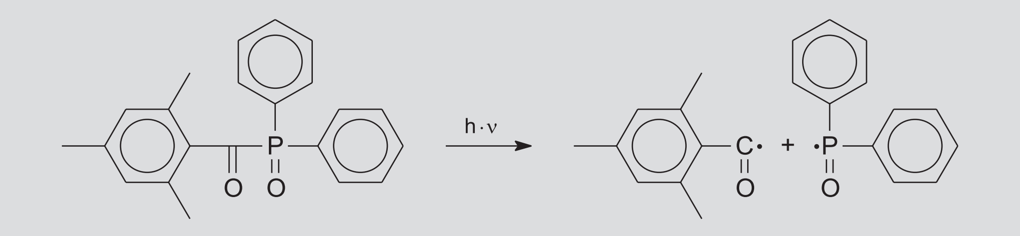


Fig. 2.1.223
Splitting of 2,4,6-trimethylbenzoyl phosphine oxide into radicals

group for abstraction and radical formation. The first group contains benzoin derivatives, benzil ketals and hydroxy-cyclohexyl-phenylketone, and the second benzophenone (see chapter 2.1.1).

2,4,6-trimethylbenzoyl phosphine oxide (TPO) is of particular technical interest because it acts in the longwave UV range. TPO enables even coatings opaquely pigmented with titanium dioxide to be cured by UV radiation. However, appropriate longwave radiating elements must be used for this (see chapter 4.3.2).

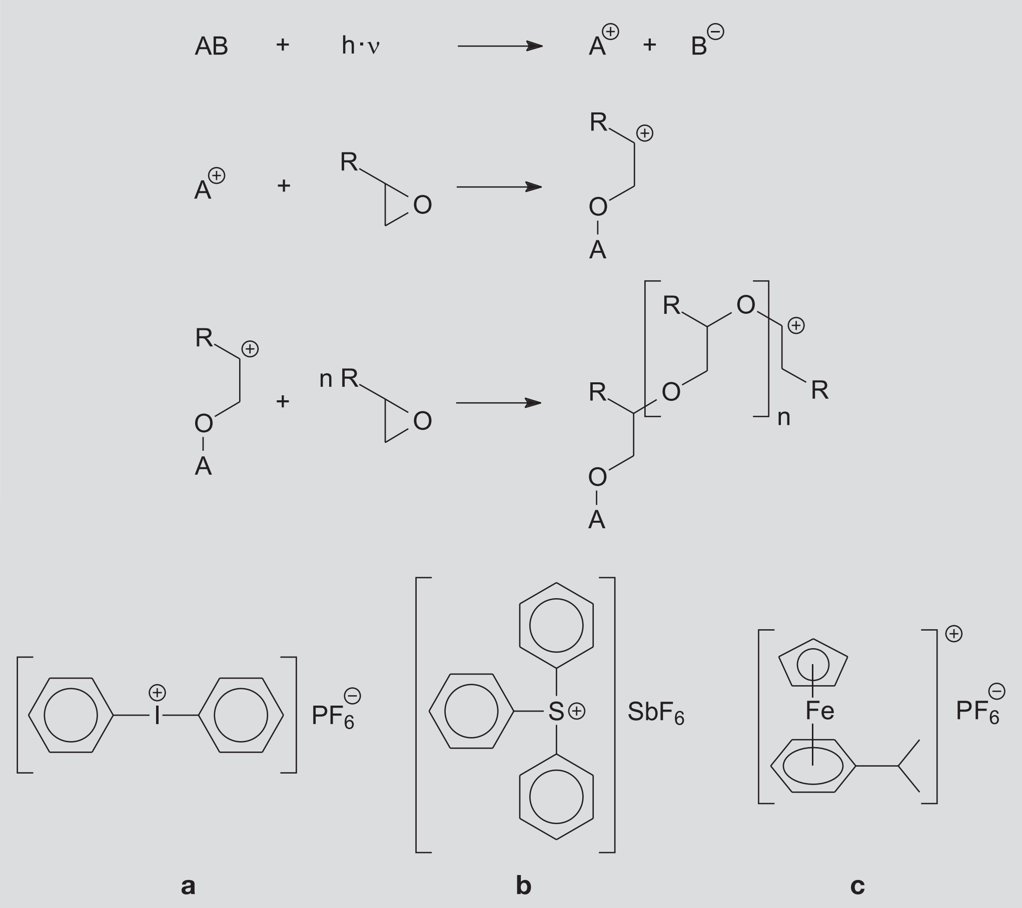


Fig. 2.1.224
Mechanism of UV curing of epoxy resins and examples of initiators therefore on the basis of iodonium(a), sulphonium (b) and ferrocenium (c) salts

Examples of chemical crosslinking by ionic polymerization are rare in coating technology. The ring-opening polymerization of oxazolines to polyamides by means of methyl tosylate and the UV-initiated polymerization of epoxy resins by catalysis with ferrocene-complexes or sulphonium salts (AB) are the most important reactions to mention in this context (see figure 2.1.224).

A further group of crosslinking catalysts for accelerated curing are the **siccatives** which are used for the oxidative curing of alkyd resins. They are chemically identical to the accelerators for unsaturated polyesters. It is possible to dispense with the peroxides required for crosslinking the unsaturated polyesters when curing alkyd resins because these are formed in the unsaturated side chains of the alkyd resins by the atmospheric oxygen during film formation (see chapter 2.1.1).

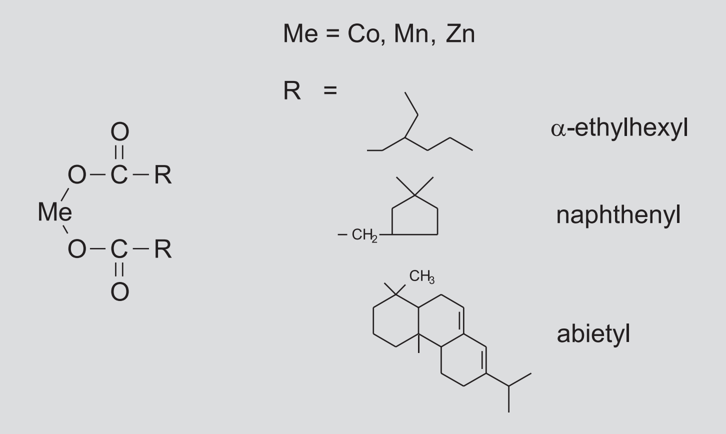


Fig. 2.1.225
Siccatives for hardening alkyd resins

The most important siccatives are cobalt, manganese, zinc and zircon soaps. The more hydrophobic anions which therefore promote solubility for the siccative are octoates and naphthenates, or more rarely abietates.

Additives also help to improve **film properties** such as the visual and mechanical/technological properties, thermal resistance and longterm outdoor exposure.

Visual properties are those which cause a sensory stimulus in the viewer after the interaction of light with a coating. The physical effects responsible for this can be divided into two categories. The first is **gloss** caused by the reflection of light on the surface, and the second is the **color**, caused by absorption, scatter or interference after interaction of the light with the colored pigments and **effect** materials inside the coating (see chapter 3.2.4). The task of gloss-influencing additives is either to smooth the film surface in order to increase the gloss or to create microstructures to reduce the gloss. Increasing the gloss by means of additives with a specified film forming agent and pigment mixture is only possible via the degree of dispersion and by means of flow-control agents. A reduction in gloss is achieved by means of micronized extenders, such as pyrogenic sicilic acids, floating wax dispersions, micronized polyethylene, natural waxes and aluminium or zinc soaps.

Other additives improve the alignment of the platelet-like effect substances either, for example, directly by means of polyethylene wax dispersions or indirectly by influencing the flow properties during formation of the effect. The viscosity, which is still low when alignment of the platelet like pigments starts, must subsequently be raised as quickly as possible by means of thixotroping additives. Additives already mentioned above in connection with combating floating effects in the form of Benard's cells can also be used successfully in this context.

The role of **optical brighteners** is to transform UV light which is invisible because of fluorescence into longer wavelengths and thus visible light. The reduction of yellowing by increased reflection in the blue range and the high conspicuity of pigmentations for emergency service vehicles are attributable to fluorescence effects. Depending on the task in hand, either stilbene derivatives, benzimidazoles or pyrazoline derivatives are mixed with the coating material as additives or special fluorescent and thus optically brightening pigments.

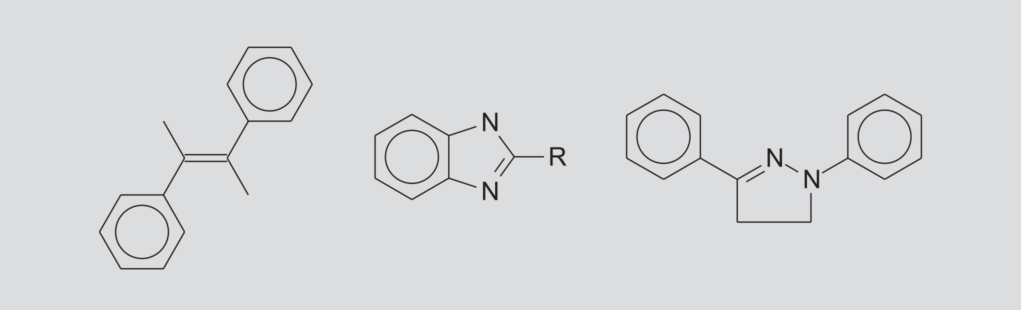


Fig. 2.1.226
Derivatives of stilbene, benzimidazol and pyrazol as optical brighteners

Manufacturers wishing to achieve very special film properties cannot do without additives. Flammable objects made of plastic and wood are coated with a flameretardant material for some applications. Although chlorine-containing film forming agents are flameretardant, they form toxic products at high temperatures by chemical decomposition. **Flameproofing agents** in the form of bromine-containing additives are in use today whose task is to react and combine with the radicals released during combustion in order to halt the exothermic chain reaction of combustion. Brominated cycloaliphatic and aromatic hydrocarbons are flame retardants which work synergistically with borates or phosphites. The dense smoke generated by the volatile reaction products cuts off the supply of oxygen to the fire. Another effective flameproofing method is achieved by the corresponding effect of organic and inorganic extenders. Hydrated aluminium oxides in conjunction with compounds forming nitrogen and carbon dioxide have proved particularly effective when residual carbon remains in the form of expanded crusts under the thermal load. These effective compounds include urea, methylol urea, melamine and ammonium hydrogencarbonate which decomposes entirely to gases.

A particularly important task of coatings is to protect the substrate against the harmful influence of UV radiation. The latter is available in the spectrum of sunlight with wavelengths of 295 – 400 nm. Because of its high energy content it is capable of degrading macromolecular materials such as wood, textiles, plastic and also coatings by radical formation. Some of the radicals form new bonds. In conjunction with the shortened chains this means a loss of mechanical strength and a reduction in elasticity at the same time. Poor cohesion and brittleness are the consequences. Supplementary changes in the color of the substrate, such as in wood, are also attributable to photochemical reactions (see chapter 3.3.1). Such damage only occurs in the substrate if the high energy radiation is able to penetrate through the coating as far as the substrate. This is only the case, however, if the pigments or film forming agents are incapable of UV absorption. For this reason the use of **UV absorbers** even for clearcoats is sensible and necessary [2.4.52].

Although their protective effect increases with the depth of penetration of the UV radiation into the coating because of the increasing probability of interaction, there is no such protection on the surface. Effective protection against light is therefore only possible if the UV absorbers are also supplemented by radical scavangers to protect the surface. These transform the radicals formed by the influence of light into stable products. High quality clearcoats therefore always contain combinations of radical scavangers and UV absorbers to ensure longterm protection.

A few inorganic substances, such as micronized iron oxides, ferrocene derivatives and organic nickel complexes are effective and, at the same time, chemically stable UV

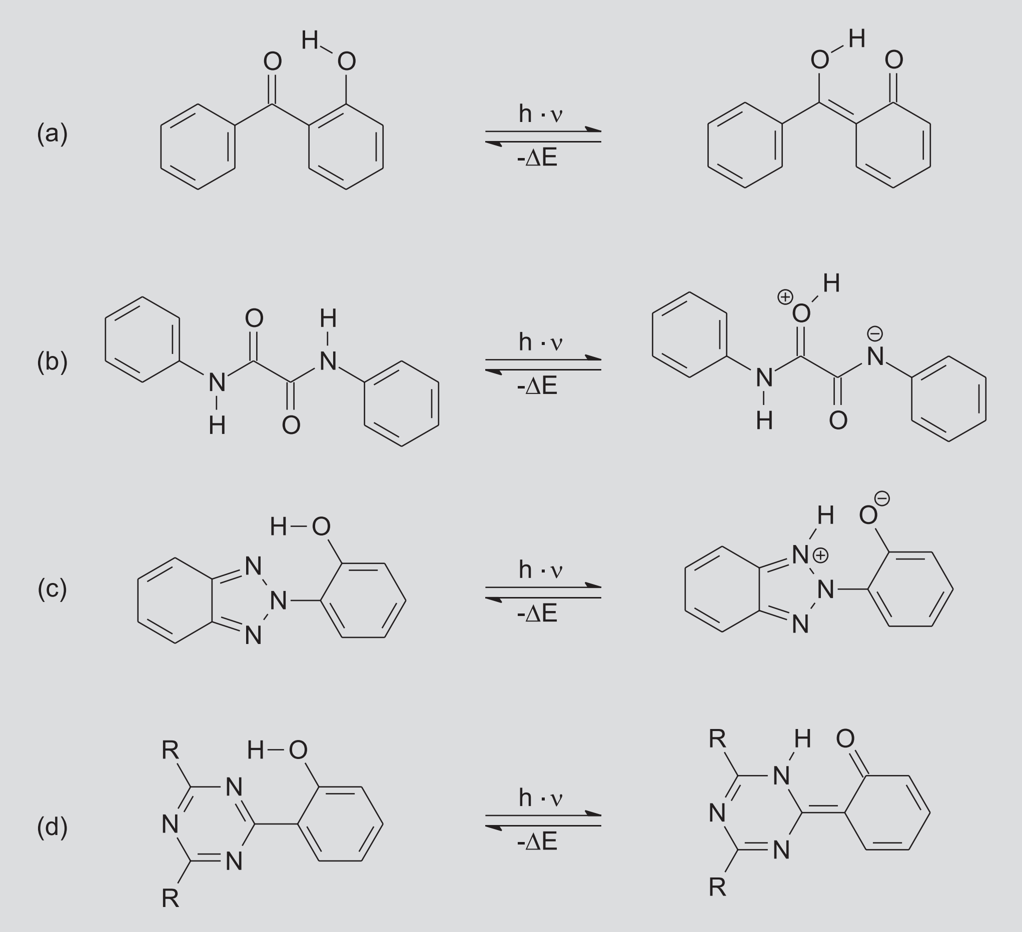


Fig. 2.1.227
Absorption of UV-light by mesomeric structures of the important light stabilizers

absorbers. However, all these active substances cannot be used in most cases because of their inherent color.

If colorless and, at the same time, color stable light stabilizers are demanded, hydroxybenzophenone (a), oxalanilides (b), benztriazoles (c) and triazines (d) are proven substances (see figure 2.1.227).

Their effect is based on the ability to set mesomeric structural changes which are reversible by UV light. The different energy levels of the interface structures result in selective absorption of UV light with simultaneous transformation of the absorbed energy into heat and restoration of the UV absorber to its default state.

The UV absorbers presented in figure 2.1.227 are merely basic substances. To reduce their volatility they must be provided with larger functional groups or be chemically bound to the molecules of the polymer matrix. Particularly with 2-coat effect paints the addition of UV absorbers even to the base coat is recommended, because of the tendency to migrate throughout the layers.

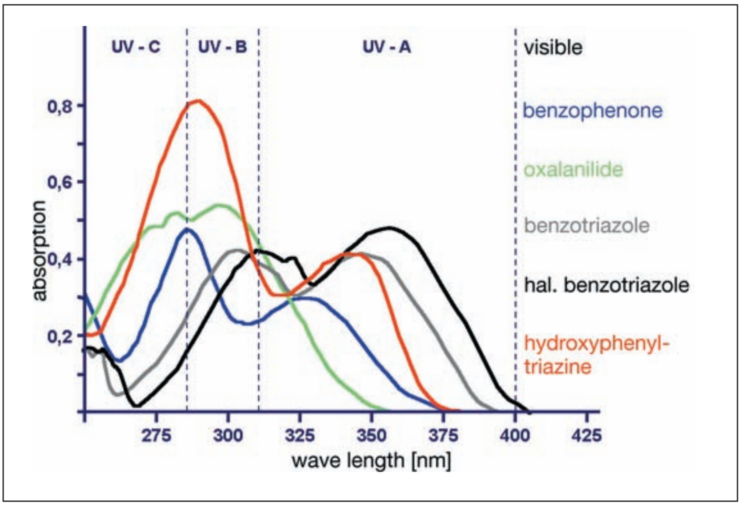


Fig. 2.1.228
Absorption spectra of the common UV absorbers

Hindered amine light stabilizers (HALS) are used as radical scavangers. They are transformed into stable nitrosyl radicals in the presence of atmospheric oxygen by high-energy radiation. These are capable after *Denisov* of trapping the radicals which destroy the film and permanently inactivating them by later combining them with other radicals [2.4.52].

Coordinated combinations of anti-UV agents enable 2-coat metallic paints to achieve color stability, gloss retention and crack resistance of more than 10 years.

Micro-organisms can attack paints and coatings as organic substances in an appropriate environment (warmth, moisture) and sometimes completely degrade them. **Preservatives** are intended to help prevent the destructive actions of bacteria, moulds or algae. Bactericidal, fungicidal or algicidal additives serve not only to protect the paint and the coating, but also to protect the substrate in the case of biodegradable substrates, such as wood. When selecting biocidal additives, therefore, it is important to distinguish between preservation during storage, protection of the coating itself and

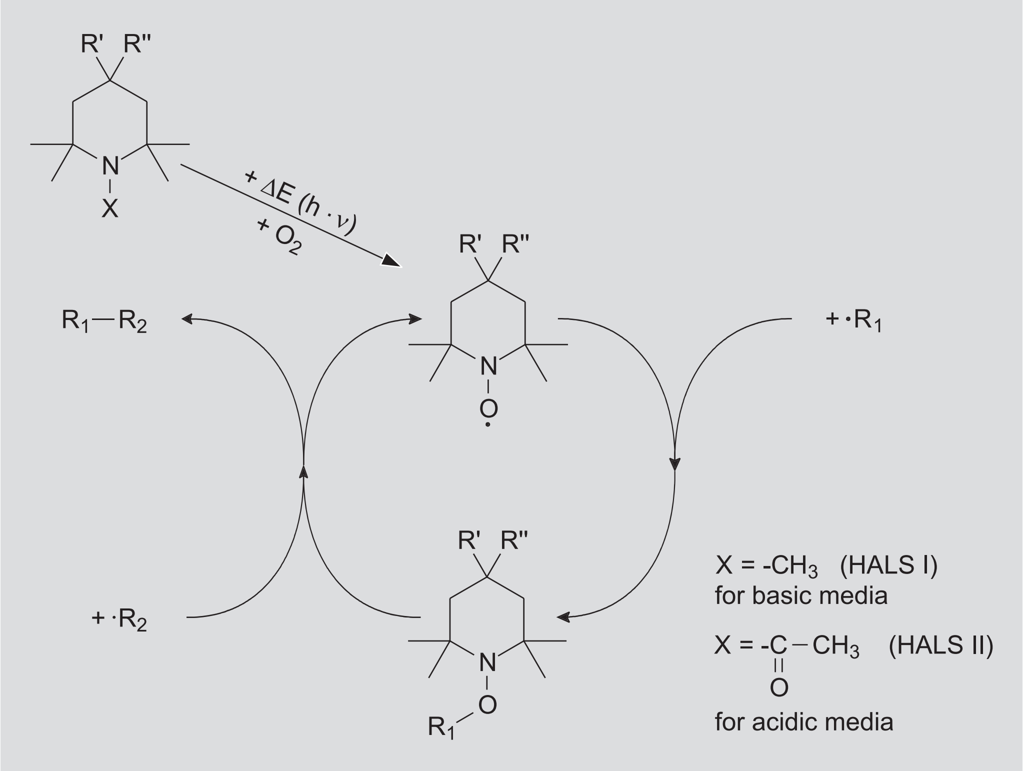


Fig. 2.1.229
Mechanism of radical scavanging by hindered amine light stabilizers (HALS) according to Denisov

protection of the substrate. Depending on the task in hand protective agents which are appropriate to the relevant application and in the correct dosage should be used. Low solvent waterbased paints pose particular problems in this context. They offer the microorganisms the best growth conditions of all coating materials. Plant and containers for the manufacture and storage of aqueous dispersions are sterilized by regular flushing with 0.5% formalin solution or the addition of barium metaborate as a preservative. A 10% butyl glycol solution in water is frequently used for cleaning and sterilizing.
An excellent longterm effect with a balanced influence on moulds and bacteria at the same time is achieved by adding chloromethyl isothiazolinone (CMI), methylisothiazolinone, loosely bound formaldehyde in the form of N-methylolchloroacetamide, tetramethylolacetylene diurea (tetramethylolglycoluril) and nano-scaled silver, as depot substances for the coating materials [2.4.53].
Coatings manufacturers have removed the highly effective organic mercury compounds and chlorophenols from their range of raw materials because of their potential physiological harmfulness. Organic tin compounds will also diminish in importance in future because of such labelling and the associated restrictions (see chapter 7.11.7).
Recent developments are following two lines, with regard to the toxicological aspects. Biocidal metal ions are being inserted into crystalline carriers. In this way their effect, in a quasi ion-exchange process, can be so precisely dosed that there are no hazards to human health. Silver ions inserted into zeolite, for example, have proved successful. A completely different means of achieving effective preservation which is also safe for

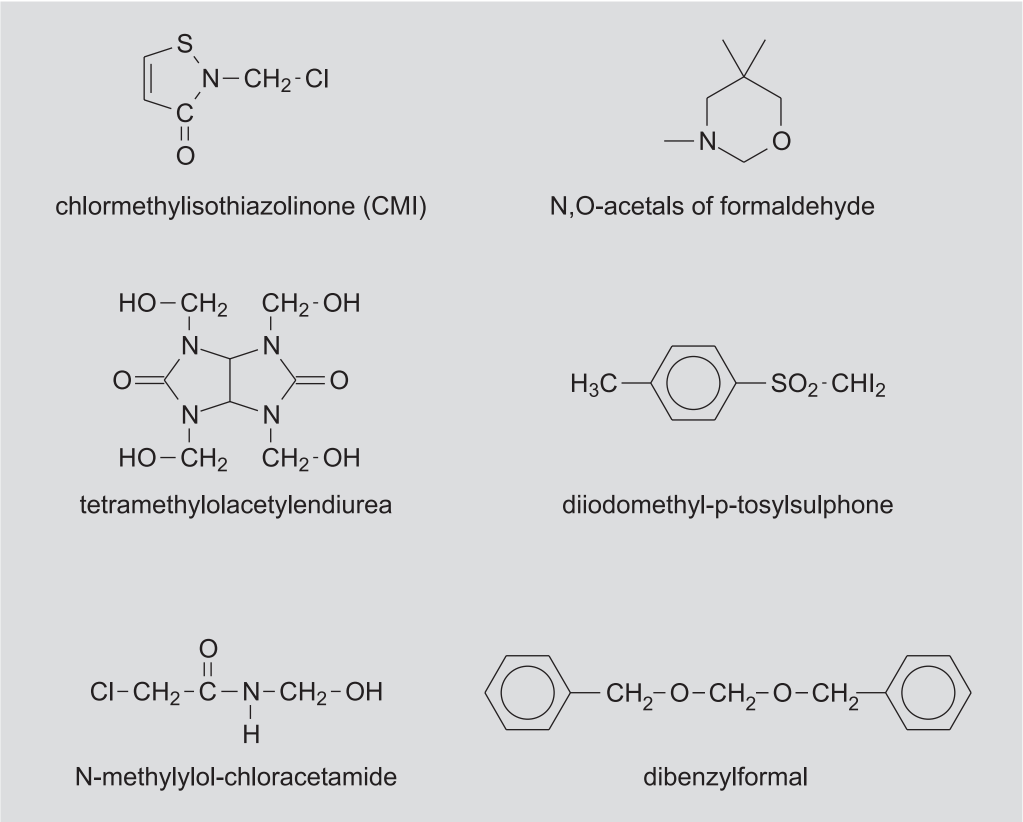


Fig. 2.1.230
Biocides for increasing shelf life of paints

humans is opening up in the development of biocidal substances which target their action on the micro-organisms' specific metabolism. The thiocarbamates and compounds with halogenated methylthioether groups (R-S-CX_3) also merit note. The latter work by opening the R-S bond and creating new bonds with the micro-organisms' protein molecules.

Despite the development of biocides which act directly and specifically on the metabolism of micro-organisms, further work will also be needed in future because the astonishing adaptability of microbes to new conditions means that proven materials can

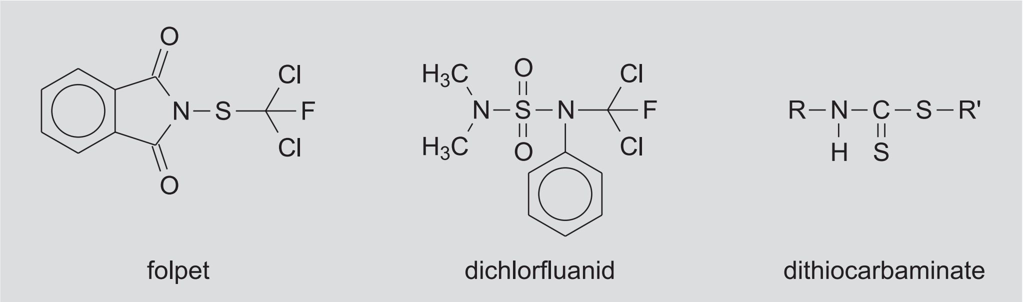


Fig. 2.1.231
Biocides with specific effect on metabolism of microorganism

lose their effectiveness. A completely new approach towards physiologically safe and, at the same time, longterm protection of coatings and substrates against attack by microorganisms is of interest and is worthy of note. SAM polymers (sustainable active microbiocidal polymers) are based on functionalized water-insoluble polymers which are intended to offer longterm protection, because of their special physical properties, without representing a danger to their environment. Current understanding indicates that the effect of the polymer biocides lies in the specifically set electrostatic surface interaction with the micro-organisms. This ensures lasting interference with the metabolism of the microbes' cells. Thus it is a contact biocide which acts without penetrating the cells. However, SAM polymers are only in the early stage of a market launch. It is not yet possible, therefore, to give a binding evaluation of this new class of substances [2.4.54].

2.1.5 Summary

On closer inspection the group of basic raw materials is transformed into a large quantity of individual substances. Only the film forming agents use a large and constantly growing number of synthetic products in addition to the natural products which are still important for coating technology in some sectors. Particular mention has to be made of the new film forming agents for emission- and waste free powder coatings which cure by polyaddition and polymerization and of the radiation curable systems. Nor may the trend towards water-dilutable coating materials be forgotten which are proving their value for both conventional processing and in the field of electrocoating.

The situation is similar with color and effect pigments and extenders, with the trend away from natural raw materials and towards defined synthetic products. The market offers a large and yet still increasing variety of organic and inorganic pigments of known chemical structure which can be reproducibly manufactured. Particular focuses of development work include the synthesis of new effect substances and, at the same time, the penetration of new areas of the coatings world in strict compliance with all technical and occupational health information for handling these materials in the production plant, during processing and later reprocessing and recycling.

Physiological issues relating to humans and the environment are of very particular interest in the field of additives, plasticizers and solvents. Whereas in the 1920s solvents for coatings were regarded as an indicator of technical and economic progress, the perspective changed fundamentally at the latest with the passing of many laws in North America and Europe. The reduction or substitution of solvents by physiologically safe water or demonstrably safer solvents is the watchword for current and future activities. Solvent which can be incorporated in the film like the reactive thinners in radiation curable coatings are another focus of future developments in coatings.

High quality in compliance with all occupational health and safety and environment-related requirements underpins raw materials development. Lasting success can only be anticipated if the costs in a global economy also show a positive bottom line in an environmental balance sheet.

2.2 From Raw Material to Coating Material

The paint and coating raw materials described in chapter 2.1 form the individual modules which are assembled such that the coating materials manufactured out of them meet the varied requirements of practical applications. The formulations which have to be developed for this contain not only detailed information on the raw materials to be used, but also provide precise details on the quantitative proportions, the sequence in which the formulation ingredients are to be combined and the settings for the machines to be used in production.

The correct selection of the raw materials must be based on accurate knowledge of the interaction in the product used for its later purpose, knowledge of the processing methods and the available plant and machinery at the paint manufacturer.

The varying requirements of the processor or end user relating to final product quality, in conjunction with the environmental demands, the application processes and the prices to be achieved in the market place are variables which have to be covered by a diverse range of raw materials.

The composition to be selected for a coating material is therefore subject to preconditions, requirements and external influences. It is thus obvious that universal solutions to problems cannot exist in the field of paints and coatings. The formulator or paint manufacturer is forced to find the optimum solution under the given outline conditions. Bearing in mind, furthermore, that in the automotive sector alone the number of producible formulations together with the necessary raw materials is hugely increased as a result of the desired variety of colors and effects, it is no wonder that major paint factories have to have many thousands of formulations on hand. Factors influencing the formulation will therefore be discussed below.

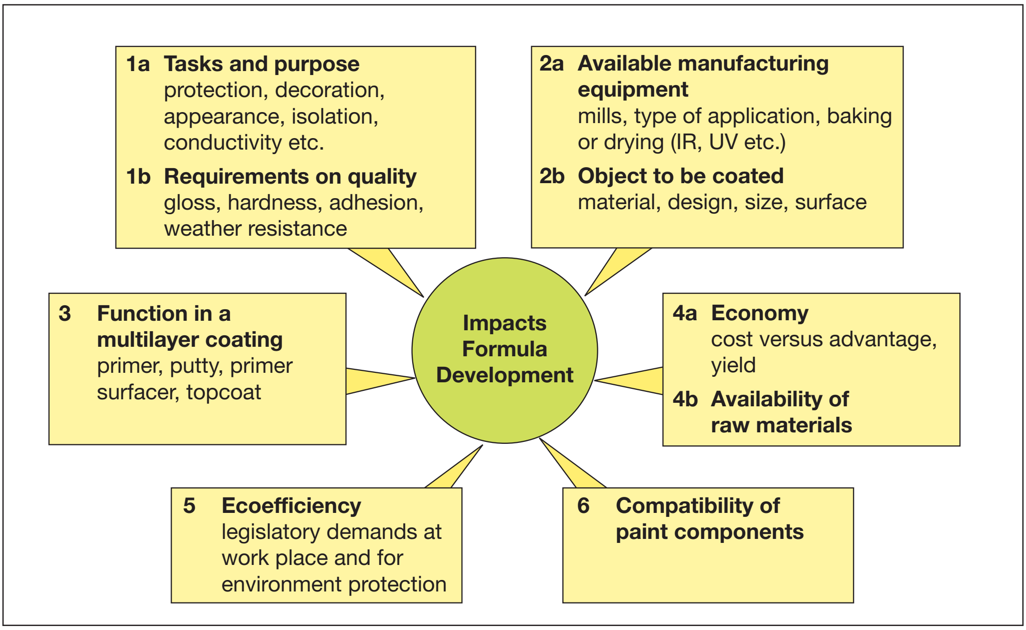


Fig. 2.2.1
Factors influencing the paint formula

2.2.1 General Rules on Drawing up Formulations

2.2.1.1 Purpose and Quality

If the customer merely wishes decorative goals to be met, more attention will have to be paid to the pigmentation and the selection of the effect materials than to the other raw materials. With many pigments a high gloss requires a low pigment level, which results in an inadequate hiding power. In order to achieve a large amount of room for manoeuvre in terms of color and gloss a certain separation of functions in the form of two coats has become accepted, as is standard practice in automotive paints. The hiding power is provided by a base coat, irrespective of gloss requirements, while the gloss itself is delivered by an additional clearcoat on top of the base coat.

If the purpose of the paint or coating is the protection of commodities, the selection criteria are aimed initially at the film forming agent. Special demands are made on low water vapor and ion permeability for coatings subject to long term outdoor exposure for the protection of metal objects. Further selection criteria include excellent adhesion under extreme climatic conditions combined with the physical and chemical effect of anticorrosive pigments. If, for example, zinc dust is used for active corrosion control, the pigmentation level is a decisive factor. Only at weight concentrations of more than 90% do the metal particles touch each other, thereby permitting their protective effect to develop.

However, the functional tasks of coating materials go far beyond corrosion control. Antichipping materials for cars, removable paints with a defined poor adhesion and coatings to increase or reduce electrical conductivity require significantly different raw material compositions. For sound insulation purposes high build coatings are used which have a high degree of solvent retention because of the thickness of their coat and thus require new formulation principles. Sound insulating coating materials are therefore solely aqueous dispersions (hydrosols) or dispersions which are distributed in plasticizers (plastisols).

2.2.1.2 Production Resources, Application Systems and Object to be Painted

When drawing up the formulation or assembling the raw materials the technical resources for the manufacture of the paints, the customer’s processing systems and the particular features of the object to be painted must also be addressed.

When it comes to pigment dispersion formulations for the manufacture of colored coating materials where dissolvers are used differ considerably from those produced in agitator mills. The pigment-binder ratio and the rheological properties have to be adapted to the particular machines by use of appropriate solvents and additives.

The processing systems in operation at the paint customer also have a significant impact on the formulation. It is obvious that a DIYer’s brush or roller requires different material properties from the spray guns or dip baths of industrial scale paint processors. Influencing flow properties during film formation by means of solvents and additives such that the painter can produce run free coatings which nonetheless are still fluid enough permit a smooth finish to be achieved with a brush requires a different product composition from those designed for quick drying spray paints without any postfinishing treatment.

Event paint films applied using the same processing method can differ significantly in the selection of the film forming agents and solvents, depending on whether the subsequent curing is instigated by tempered air (convection drying) or infrared (IR) radiation. Where curing is solely by means of IR radiation, the solvent composition depends on the radiation's wavelength. If the electromagnetic waves are not absorbed by the paint and if the film therefore heats up from below, different solvents have to be used because of the lower tendency towards pinholing than in the case of radiation absorption in the upper sections of the setting coating (see chapter 4.3).

If the high energy IR rays are replaced by ”cold” UV or electron rays, completely different film forming agent types have to be used. The main constituents of the formulation then include resins which cure solely by polymerization without any heat action and which may be combined with reactive diluents. It may be noted in passing that UV-absorbing pigments inhibit curing during UV curing and therefore must not be used.

In many cases the object to be coated is also the determining factor in the choice of raw materials. An already installed wooden window frame is difficult to heat up in a drier after coating. The same applies to thermally unstable plastics. The paint manufacturer cannot therefore rely on using baking enamels based on alkyd or acrylic resins which have proven their value for metal coatings. Oxidatively curing alkyd resins or, where there are particularly high quality demands, 2-component paints are then the appropriate base materials.

If more complex objects incorporating cavities with difficult access have to be coated, dip-coating processes are the only alternative to the standard spray application. If the latest electrocoating process is chosen, all the formulation ingredients have to be matched to the electrochemical precipitation process. Watersoluble resins can be made to coagulate on the objects to be painted, which are connected to form electrodes, by means of changes in the pH value, and these determine the formulation.

If flat items such as endless metal sheets are to be coated, coil coating methods can be used. Although higher viscosities and the associated higher solid contents mean lower solvent contents, they also mean completely different solvents because of the high coil speed and the associated high temperature during drying. Long alkyl ether esters as solvents and silicone modified polyesters as resins are the raw materials of choice here.

2.2.1.3 Function in Paint System

In many cases the demands made of the coating cannot be met with a single paint film. Multiple layers with discrete, clearly defined tasks then replace the single film coating (see chapter 7.1 and 7.2). In order to meet particularly stringent demands on the quality of coatings, where protective and decorative functions are of equal priority, three- and four-coat systems have proven their worth. This is the only way in the automotive sector, for example, in which the demanding requirements made of the paint finish can be met.

Primers, whose main task is corrosion control, are provided with resins from the raw material side which feature excellent adhesion even under extreme climatic conditions. Aromatic epoxy resins, aromatic polyurethanes or modifications of these can therefore be used because of their good adhesion, despite the lack of light fastness, as no account needs to be taken of the lack of light fastness in the aromatic structural elements. These are always optically covered by a further functional layer, the primer surfacer. This second layer provides everything needed to make the topcoat optically attractive while at the same time meeting all the demands on mechanical-technological properties. As indicated by the name, primer surfacers therefore have to prime the surface, i.e. even out any unevenness and be well sandable so that its surface can be smoothed, if required. Primer surfacers also take on the function of protection against stone chipping as an intermediate coat in conjunction with the topcoat. With this purpose in mind, resins have to be selected whose glass temperature is in the operating temperature range. Furthermore, extenders have to be used which create predetermined breaking points under extreme impact loads. This prevents the coating from separating from the substrate. The lightfastness requirements on the primer surfacer coat are not as rigorous as those on topcoats. As with the primer coat, epoxy ester resin and polyurethanes are the standard film forming agents for the functional intermediate coating.

The tasks of the last coat, the topcoat, are quite different. The emphasis here is on the visual properties, provided that the mechanical-technological properties have been addressed. A high level of gloss and pronounced optical color effects are the usual requirements for the topcoat. The functionability of the coating depends also on good adhesion to the primer surfacer and a high degree of hardness with good wear and scratch resistance at the same time. When it comes to selecting the raw materials for topcoats, resistance to sunlight and outdoor exposure, but also to chemicals from industrial emissions and natural atmospheric effects such as tree resins and bird droppings, are the primary considerations, in addition to the abovementioned factors. Topcoat formulations differ significantly, therefore, from the abovementioned items. Weather resistant alkyd-melamine resin or acrylic-melamine resin paints or polyurethanes based on polyester or acrylic resins are the standard film forming agents. By contrast with primer surfacers, the principle with single film topcoats is to use the minimum necessary amount of pigment.

As already mentioned, two layer coatings have become the accepted standard in many applications as a result of the greater demands on the durability of topcoats. Formulations for two layer topcoats differ significantly from the single film solid color coats which used to be standard. The base coat contains quick drying film forming agents which are frequently water soluble or dispersible. The solid content of metallic and pearlescent effect paints is set particularly low in order to achieve a good effect. For environmental reasons, therefore, the conventional solventborne base coats are currently being replaced by water soluble alternatives. The last coat, which provides the overall seal, is pigment free. Film forming agents such as alkyd resins and polyesters, which are standard for pigmented paints, last only a few years as clearcoats with outdoor exposure. Loss of gloss and crazing are the usual signs of degradation. Today’s clearcoats are usually acrylic resin combinations. They attain their high resistance of more than 10 years by the addition of UV absorbers and stabilizers.

2.2.1.4 Cost Effectiveness and Availability

The demands for cost effective production have a particular impact on formulation design. In the manufacture of pigmented paints the incorporation of pigments in the

paint formulation causes the greatest production input. The goal, therefore, is to identify the combination of pigments, film forming agents, additives and solvents which permits rapid dispersion of the pigments with the highest possible pigment component and thus the smallest possible volume. The resulting concentrates of each individual pigment are generally termed pastes or ”dispersions“ and are used for manufacturing paint formulations by simply mixing the necessary components. Such pastes are initially only designed for cost effective dispersion with a particularly high efficiency in dispersers. The high pigment content of the mill base means that it is essential to apply a subsequent clearcoat which is appropriate to the requirements. Consequently, formulations for the manufacture of coating materials using color concentrates are in two parts. First a paste formulation with the highest possible pigment component has to be found, so that in the second stage instructions can be given on processing the color concentrates. The completion stage ensures that the demands on the coating and on processibility are met.
In addition to manufacturers' demands relating to cost effective production the processor also requires coating materials which enable large areas to be covered at a low consumption rate. Paints always have a high yield if a high hiding power with a low dry film density at the same time makes it possible to apply thin film thicknesses (see chapter 5.7).

2.2.1.5 Occupational Health, Safety and Environmental Protection Regulations

Paint raw materials are regularly replaced by others for occupational health, safety and environmental protection reasons as new knowledge becomes available. However, great efforts are still required to achieve emission free, physiologically harmless paint technology which is reflected in the paint types and their formulations.
The replacement of volatile organic solvents by water, the reduction of solvents by increasing the solid content, or the replacement of volatile solvents by reactive diluents, but also the complete omission of solvents in the use of powder coatings have brought new formulation principles to the process of developing paints. Novel film forming agents, new additives and physiologically less harmful pigments are superseding the existing range of raw materials continuously. Environmentally polluting emissions of organic solvents and additives containing heavy metals are being avoided by means of new environmentally compatible painting technologies (see chapter 5.6).

2.2.2 Material Flow in a Paint Factory

The stages from raw material supply via production of the semifinished and finished products up to supply of the final product are accompanied by numerous organizational units providing control and assistance. These units include the laboratories of Research & Development and the Application Centre, Quality Testing, Production Planning and Order Processing.
In addition to the production runs to restock its inventory which a company can plan and control itself, particularly for branded materials, there is a high proportion of runs in response to customers' orders, especially for paint processing under series conditions in general industry. The first point of contact when customers have such wishes are the

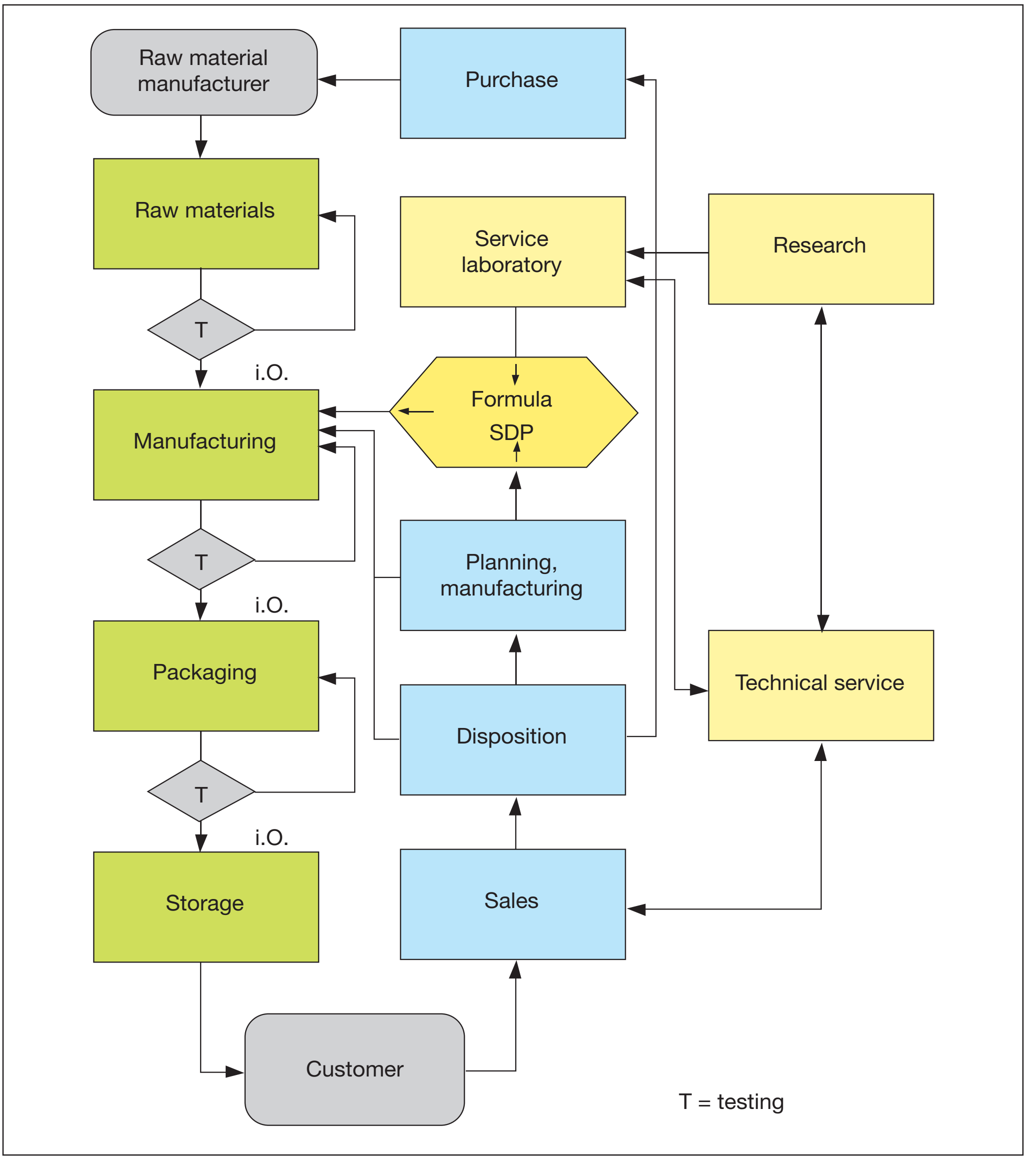


Fig. 2.2.2
Organization, processes and supporting functiones for paint manufacturing

sales departments in order that, in the event of a production run having to be instigated, the order can be given for the various steps necessary, viz. scheduling and the production planning responsible for the issuing of production orders, right up to the technical facilities for the development and maintenance of the formulations.
Since large paint plants with an extensive product range hold up to 20,000 ”live”, i.e. continually updated formulations, they are compelled to run comprehensive service and product development laboratories. They need to have excellent market knowledge and present their systems to consumers with good technical backup. The plants have to be fast and flexible to cope with the production demands arising from an extremely large number of raw materials and formulations. Unlike plants operating continuous

production processes the paint and coatings industry has to operate in batch production mode as this is the only way of handling the production demands of the abovementioned variety of products. Since customer orders differ in terms not only of the formulation itself but also of the order quantity, the plants must have an appropriate range of production systems. Production in response to customer orders results in a huge variety of batch sizes, ranging from just a few kilograms to more than 30 tonnes.

Two fundamental strategies are possible when manufacturing the batch before the dispersing process with the production of factory packed paints or color concentrates with subsequent completion. Production from scratch starts with the total quantity of all raw materials. Pigment mixtures are also frequently dispersed in a batch. Manufacturing by mixing paints, on the other hand, is based on premixed pigment pastes which are merged in paste series. Generally there is only a single pigment in each paste. The paste series differ from one another in the type of film forming agent used in each particular case.

In a prior stage to the actual paint production, the major companies in the paint and coatings industry manufacture significant volumes of the film forming agents for their key products in their own resin factories using formulations developed inhouse. Unlike smaller paint plants which mainly buy in their film forming agents and then convert them into other types of solution if necessary, they have the capability to develop and manufacture customized film forming agents. These are optimally adapted to the formulations, the production conditions, the coating system and the intended use of the particular coating material.

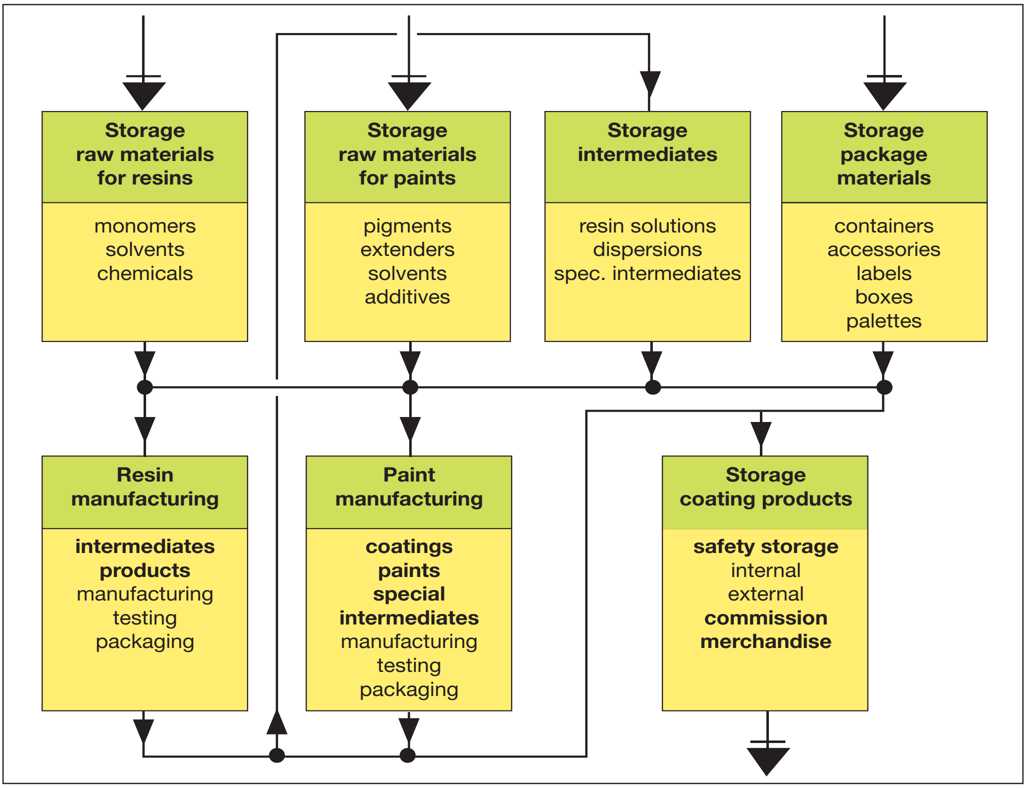


Fig. 2.2.3
Scheme of material flow during manufacturing of paint

A very complex logistical system operates in paint plants because of the various production modes already mentioned and as a result of the differing consistency of the raw materials, intermediate products, final products and packaging materials used.

Fig. 2.2.3 shows a simplified block diagram of the material flow in the production of paints and coatings. The material flow ranges from the stocking-in of the raw materials to the provision of the finished products which are ready for dispatch. The deciding factors in terms of material flow and feed are the raw material type, its consistency, the consumption quantities and the packaging form for the product when it leaves the plant. Large plants have to install large tank storage facilities for resin solutions and solvents which are equipped in accordance with the latest safety regulations. The preferred delivery method here is by road tanker. In addition to the liquid raw materials which are conveyed in large quantities to the locations where they are processed by pipe bridges there is a large number of raw materials in paste, solid and powder form which are delivered and made ready for use in containers, drums or bags, which may or may not be palletized. Depending on the specified storage conditions, indoor and outdoor storage and stacking facilities are provided for this. Modern, computer-controlled high bay warehouses are commonly used for large unit quantities and transfer volumes. Material movement is handled using a wide variety of different concepts, depending on the paint plant's structure and facilities.

The system outlined is much more complex if a company has several sites, and each site in turn has several production units. This calls for a highly sophisticated data and information flow system which can only be achieved by means of appropriate computer centres.

Logistical and quality decisions are constantly required during the flow of material and information. This requires an integrated organization pulling together sales, logistics, purchasing, production, quality related test units and application centres.

2.2.3 Theory of Dispersion

2.2.3.1 Pigment Specific Properties for Dispersion Processes

Whereas the manufacture of clearcoats is limited to the mixing of various film forming agents with solvents and additives, the production process of pigmented systems is based on complex wetting and stabilization processes. To ensure better understanding of the physicochemical background, it is worth recalling the specific properties of the pigments and their interaction with the film forming agent solutions (see chapter 2.1.3).

The interaction of the pigments with the incident light results in selective shares being removed from the white light and the remaining being scattered as widely as possible. The first property results in chroma, while the second is the prerequisite for good hiding power. The ability to produce chroma is proportional to the pigment surface area which can interact with the light.

This means that for a specified pigment quantity the degree of selective absorption increases with decreasing particle size up to a discrete stage. This stage is reached when the particles are completely penetrated by light.

The scattering power increases with the number of dipoles in the pigments which can be excited by light. For this reason the scattering power increases initially with increasing particle size.

$$I = I_0 \cdot k \cdot \left[\frac{n_{Pi}^2 - n_{Bi}^2}{n_{Pi}^2 - 2 \cdot n_{Bi}^2}\right]^2 \cdot \frac{V^2}{\lambda^4}$$

valid, if $\frac{d}{\lambda} << 1$

I = intensity of scattered light
I_0 = intensity of incoming light
k = constant
n_{Pi} = refraction index of pigment
n_{Bi} = refraction index of binder
V = volume of pigment particles
λ = wavelength of incoming light

Fig. 2.2.4
Formula of light scattering

However, this increase only continues as long as all the dipoles can interact in each pigment particle with the incident light. But this is only possible up to a specific particle size for each pigment. Above this critical size the dipoles inside the pigment become optically inactive. Furthermore, interference occurs, resulting ultimately in a decrease in scattering power. There is, therefore, an optimum particle size or particle diameter for the scattering power.

With titanium dioxide, the most important diffusion pigment, this optimum size is a particle size of about 0.25 µm. Experience shows us that this is generally around the wavelength of the part of the light spectrum absorbed. According to *Weber* [2.4.55] the following applies empirically:

$$D \approx \frac{\lambda_{max}}{(n_{Pi} - n_{Bi}) \cdot 2{,}1}$$

D = ideal diameter of particles for diffusion
λ_{max} = max. wavelength of absorbed light
n_{Pi} = refraction index of pigment
n_{Bi} = refraction index of binder

Such small particles tend to combine to form larger units as a function of their shape and polarity. If the primary particles are in contact with each other along edges and at corners, the conglomerations with diameters of more than 100 µm can become very large, though the forces of attraction remain relatively low. Such particles are termed agglomerates (see chapter 2.3.1).

If the primary particles are connected via common surfaces, the forces of attraction increase to such an extent that separation via mechanical means is only possible with difficulty. However, the volume of such aggregates is much lower.

The cavities in the agglomerates and the cavities in the pigment powder in the delivery form can represent up to 75% of the overall volume, depending on the pigment form and size. The pigment volume concentration (PVC) is then only 25%.

$$PVC = \frac{V_{Pi}}{V_{Pi} + V_{Bi}} \cdot 100$$

V_{Pi} = volume of pigment
V_{Bi} = volume of binder

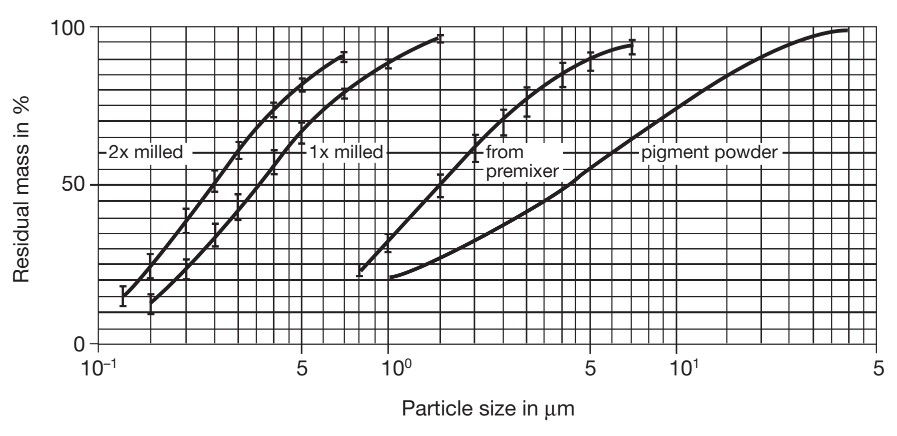


Fig. 2.2.5
Pigment particles size distributions depending on stirring and dispersing

The forces of attraction among the pigments themselves are an addition of *Coulomb* forces, *van-der-Waals*' forces and hydrogen bridge bonds, depending on the chemical structure. The range and strength of the forces of attraction are very greatly influenced by the type of interaction. Whereas the electrostatic forces decrease with the square of the distance d in accordance with *Coulomb*'s law, the range falls to d^{-4} in the presence of

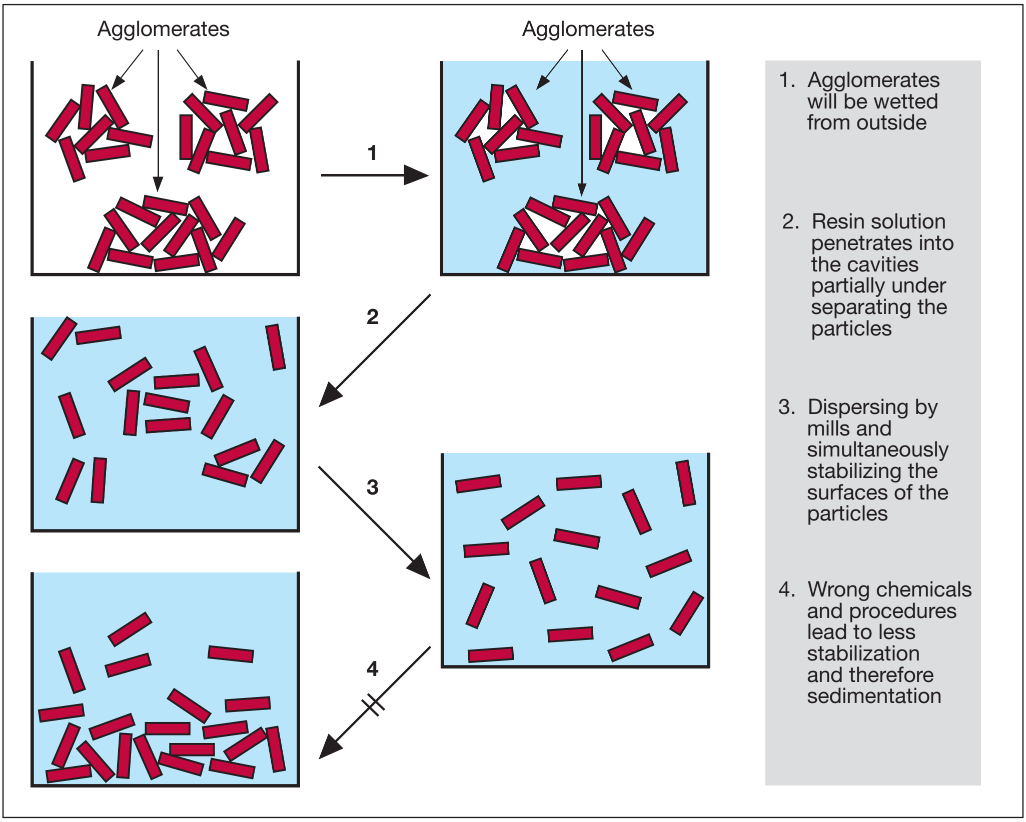


Fig. 2.2.6
Scheme of dispersing and stabilizing of pigments

permanent dipoles and to d^{-7} with induced dipoles (see below). The degree of agglomeration and the strength of the agglomerates are therefore defined by the size, form and type of pigment.

The greater or lesser degree of pigment agglomeration means that the incorporation, i.e. the uniform decomposition into the primary particle, and its thorough wetting are only possible with special techniques. Simply stirring materials in does not yield technically usable products in the majority of cases. Smooth coating surfaces are just as difficult to achieve as a closed, pore free coating. The optical properties, such as gloss and build, and the protective effect are completely inadequate with such coatings because of the high gas and water vapour permeability. Dispersion techniques then have to be used. Chroma and hiding power would also only partially develop because of the pigment surfaces which are not completely available to the light. An incomplete development of the optical pigment properties is also an economic shortcoming because of the sometimes high price of pigments.

To eliminate these technical and economic inadequacies, therefore, specific expertise is necessary for resin and solvent selection, for the right ratio of raw materials (formulation) and for the supplementary mechanical separation of the agglomerates.

Once dispersion has taken place collisions occur because of Brownian movement. Reagglomeration occurs because of the forces of attraction which are still active. Stabilization of the dispersed pigments is, therefore, absolutely essential.

The manufacture of pigmented coating materials thus concentrates on separating agglomerates while retaining the primary particles but also on completely covering the entire pigment surface with a stabilising skin which is intended to prevent reagglomeration during storage, processing or film formation. This phenomenon, which is also termed flocculation, results in color shifts and a more pronounced tendency to sedimentation.

The dispersion process is therefore divided into the individual stages of: wetting the pigment powder which consists of agglomerates, aggregates and primary particles with the resin solution; penetrating the cavities of the agglomerates; their subsequent transfer to the primary particle by means of mechanical decomposition; stabilization of the primary particle; and completion by means of lacquering with resin solutions for the manufacture of saleable products.

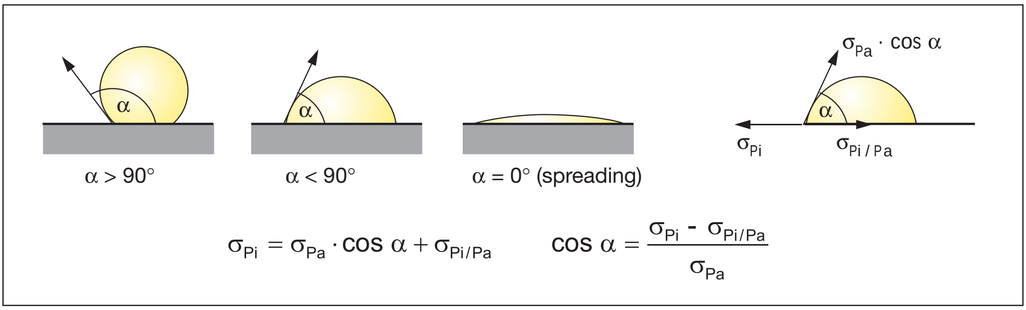
The process of dispersion is thus determined by the wetting capabilities of the surfaces, the size of the cavities in the agglomerates, and the penetration depth of the resin solution.

2.2.3.2 Wetting and Decomposition of Agglomerates

Wetting of the pigments is a surface energy process. The matching of the surface tension of the pigment to be dispersed with the interacting binder solution is thus the decisive fundamental prerequisite for successful pigment processing. The surface tension is the surface related work which has to be performed to form the surface which is newly created by the wetting of the pigments.

Thorough wetting of the pigment surfaces by resin solutions is only possible if the energy gain resulting from the interaction of fluid and pigment is greater than the work which has to be performed to increase the surface area of the liquid. The ratios are described quantitatively by *Young*'s equation [2.4.56].

The result of a good wetting of solid surfaces is demonstrated in that the wetting liquid can be seen to spread. The wetting properties can be measured by determining the wetting angle α of various liquid droplets applied to the surface of the solid. Wetting is at its optimum when the cosine of the wetting angle approaches 1. At the same time the interfacial tension $\sigma_{Pi/Pa}$ converges on zero. This state is reached if the surface tension of the wetting paint σ_{Pa} is equal to or lower than that of the solid pigment surface σ_{Pi} to be wetted (see chapter 2.3.2).



$$\sigma_{Pi} = \sigma_{Pa} \cdot \cos\alpha + \sigma_{Pi/Pa} \qquad \cos\alpha = \frac{\sigma_{Pi} - \sigma_{Pi/Pa}}{\sigma_{Pa}}$$

Fig. 2.2.7
Wetting of surfaces depending of the interfacial tension

The surface tension of solvents is generally lower than that of film forming agents. Polymer solutions therefore also show a decrease in surface tension with decreasing solid content. This means that the wettability of pigments can also be influenced by the resin-solvent ratio.

The wetting of the outer agglomerate is therefore followed by the **penetration of the resin solution into the cavities of the agglomerates**. Although the resulting wetting of the pigment powder is easier with a lower solid content, i.e. also at a lower viscosity, it is also slowed down at the same time because of the lower surface tension. The *Washburn* equation, which is derived from the *Hagen-Poiseuille*'s equation, states that the penetration rate $\dot{V}$ of resin solutions into the agglomerate cavities depends very clearly on the radius of the cavities r (see chapter 2.3.2). Surface tensions σ_{Pa} which are as high as possible promote wetting of the cavity walls provided they are still smaller than those of the pigment. High viscosities slow down the penetration rate.

Aiming for lower surface tensions in the resin solution for wetting and a high surface tension for rapid penetration into the cavities in the same way means that the optimum

$$\dot{V} = \frac{\pi \cdot r^3 \cdot \sigma_{Pa} \cdot \cos\alpha}{k \cdot \eta \cdot l}$$

$\dot{V}$ = penetration rate
r = average radius of capillary tube
σ_{La} = surface tension of paint
α = wetting angel
η = viscosity
l = length of capillary tubes

Fig. 2.2.8
Washburn equation for the calculation of penetration into pigment agglomerates

resin solid content and thus the most dispersion friendly mixture has to be found for each pigment.

The pigment absorbability of polymer solutions and the wetting speed are thus variables which are a function of solid content. The ideal ratios exist whenever the wetting and thorough moistening are matched by appropriate adjustment of the viscosity and surface tension to the specific conditions. Mixtures with a minimum interfacial tension therefore enable pigments to be changed into a flowable and thus dispersible state with relatively little resin solution. The achievable pigment volume concentration of the resin solution and pigment mixture is then at a maximum. The composition of the raw materials at the maximum pigment volume concentration for a flowable dispersion mixture is therefore termed an optimum mill base formulation, though optimum only inasmuch as surface features were addressed, without taking account of the material specific and mechanical influences which will be described later.

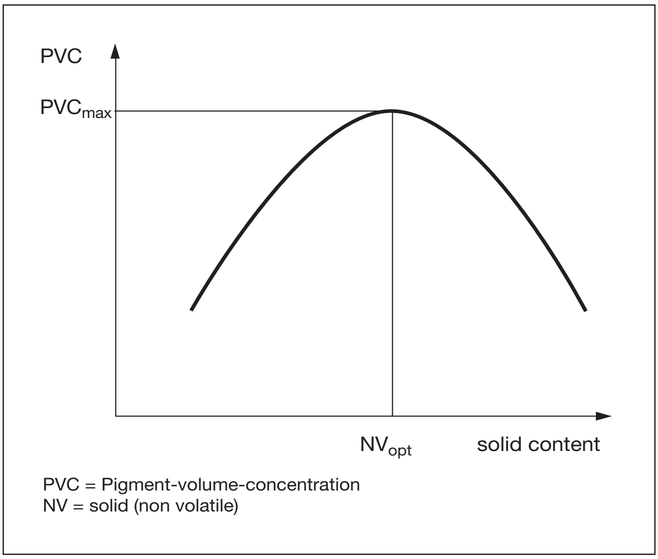


Fig. 2.2.9
Dependance of the optimum of the solid content of dispersions for the dispersing process

Various features are used to describe the **material specific dispersion properties** of pigments. These include the oil absorption value and the wetting volume (see chapter 2.3.3). For a known pigment surface area, the oil absorption value enables certain predictions to be made about the pigments' wetting properties. If a resin solution is used instead of linseed oil, the oil absorption value becomes the wetting point. Determining the wetting points with different binder-solvent mixtures determines the PVC of the optimum mill base composition [2.4.57].

Apart from the particle shape and size of the pigments the particle size distribution also has a particular bearing on the dispersion rate. Large particles with a narrow distribution band have better dispersion properties than smaller ones with a broader distribution band.

When it comes to fully describing the dispersal process, the chemical character of the pigment surface must also be taken into account. Although polar surfaces are better for wetting than nonpolar ones, the forces of attraction among the primary particles themselves are higher. The pigment agglomerates are more solid and therefore more difficult to separate.

It has already been mentioned that the dispersion rate is also a function of the resin-solvent ratio. The dispersion rate falls with increasing solid content, i.e. with increasing viscosity. Although high viscosities are desirable for transmitting shear forces to the material to be dispersed in dispersers, they are not beneficial because of the resulting poorer wetting and slower cavity penetration.

Apart from the viscosity and surface tension of the film forming agent solution already mentioned, the size of the film forming agent molecules influences the dispersion properties. Resins can be particularly well dispersed if they have a high solid content with a relatively low viscosity. Small resin molecules are more polar and can also penetrate the cavities better. Because of their high solid content they also offer a large number of film forming agent molecules to cover the pigment surfaces completely.

Both the molecule size and the molecule shape have an impact on the depth of penetration into the agglomerate cavities. Rigid and long molecule chains such as those of cellulose nitrate are less capable of instigating thorough wetting simply for steric reasons, despite their good affinity for the pigment surface.

Of the many resin types (see chapter 2.1.1) low molecular alkyd resins have proved to be particularly suitable as film forming agents to ensure the optimum dispersion of pigments. They have polar groups, yet nevertheless good wetting properties and a high solid content.

The type and quantity of solvents and solvent combinations also have a bearing on viscosity and surface tension, while also determining the configuration of the resin molecules which are in the form of coils. Since the low molecular solvent molecules have much greater mobility than the film forming agents, they also penetrate the agglomerate cavities more quickly. They generate a preliminary wetting of the pigment surfaces, termed pseudowetting, during dispersion. The solvent type and the film forming agent polarity must therefore be matched to each other such that the

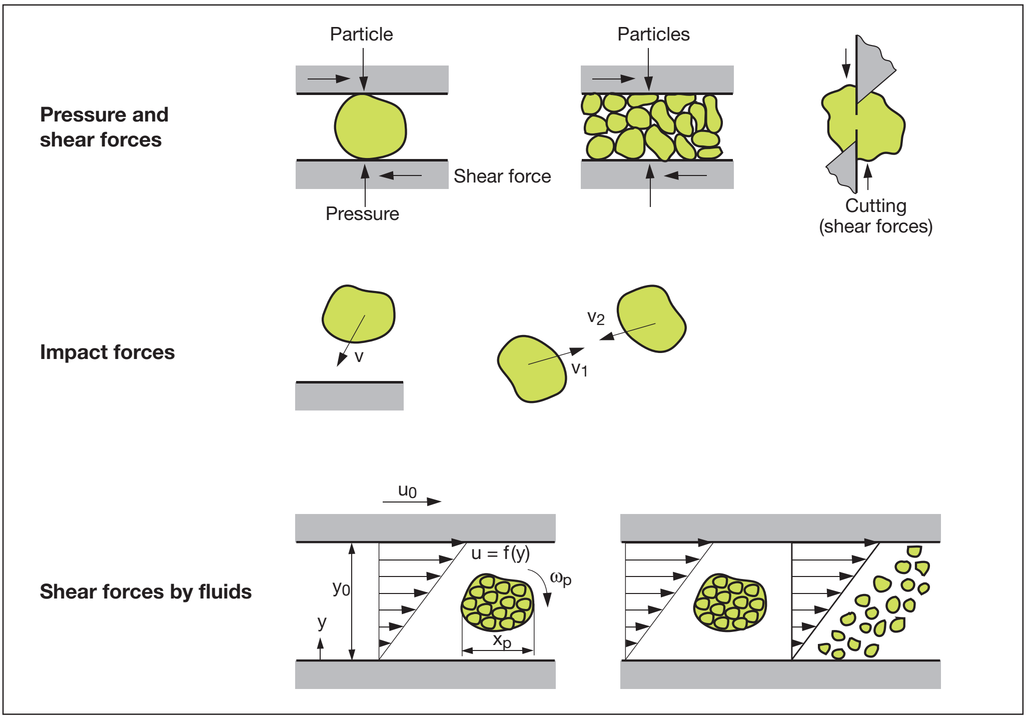


Fig. 2.2.10
Principles of methods for milling to get small particles

pseudowetting by solvents is then converted to real stabilization by replacing them with film forming agent molecules.

Only part of the agglomerates can be destroyed by the physicochemical interactions of the pigments with the resin solution. Complete conversion to the primary particle with the best possible pigment wetting at the same time can only be achieved by the additional **transmission of mechanical forces to the pigments**. Of the usual methods (see Fig. 2.2.10), only the gentle method involving the transmission of shear forces in laminar flows of viscous media can be used where it is also specified that the primary particle must be retained. Viscosity in this context does not refer to the measurable viscosity of the ternary binder/pigment/solvent mixture. The significantly lower viscosity of the pigment free resin solution is the sole determining factor in the transmission of shear forces [2.4.58].

It has also already been mentioned that although higher shear forces can be transmitted by increasing the viscosity, the overall dispersion rate can fall on the other hand because of the slower penetration of the agglomerate capillaries (see above). Care should therefore be taken to ensure a balanced match of viscosity and shear gradient when drawing up formulations and standards of operation.

Numerous dispersers have been developed to transmit shear forces to pigment agglomerates by laminar flows of viscous fluids. The most important are **dissolvers**, which are suitable for easily dispersible pigments, **three roll mills** for highly viscous pastes and the very effective **agitator mills** for universal use. A small number of **ball mills** are also in use, though these are uneconomic by comparison with agitator mills and dissolvers.

Even though the design of these units differs greatly, they all share the same operating principle. They permit the transmission of shear forces in laminar flow gradients with tensile-compressive loads at the same time which promote dispersion (see chapter 2.3.3). With the dissolvers a toothed disc moves at high speed in a matching smooth walled container. This disc transmits such large quantities of energy to the radially spun mill base by centrifugal force that decomposition of the agglomerate is assured. Another type of dissolver is the rotor-stator unit which is capable of dispersing in a small area by means of centrifugal and shear forces.

Ball mills are hollow cylinders which rotate about a horizontal axis when operating. They are filled to a particular level with grinding media, generally steatite or steel balls. As a result of movement of the grinding media relative to each other and the drum wall friction surfaces are generated which slide over each other and in which dispersion takes place.

The wide variety of agitator mills uses moving grinding media as in ball mills. However, the grinding media in this case are substantially smaller than the balls in ball mills which measure a few centimetres in size. The balls in agitator mills are only a few millimetres in size and have to be artificially moved to create a high degree of relative motion.

Three-roll mills have a central roll in fixed bearings, against which a roll which can move in the appropriate plane is pressed with great pressure from both sides. The three rolls are driven in counter-rotating directions at different speeds, with the speed increasing from the delivery, via the central to the discharge roll. The mill base is fed

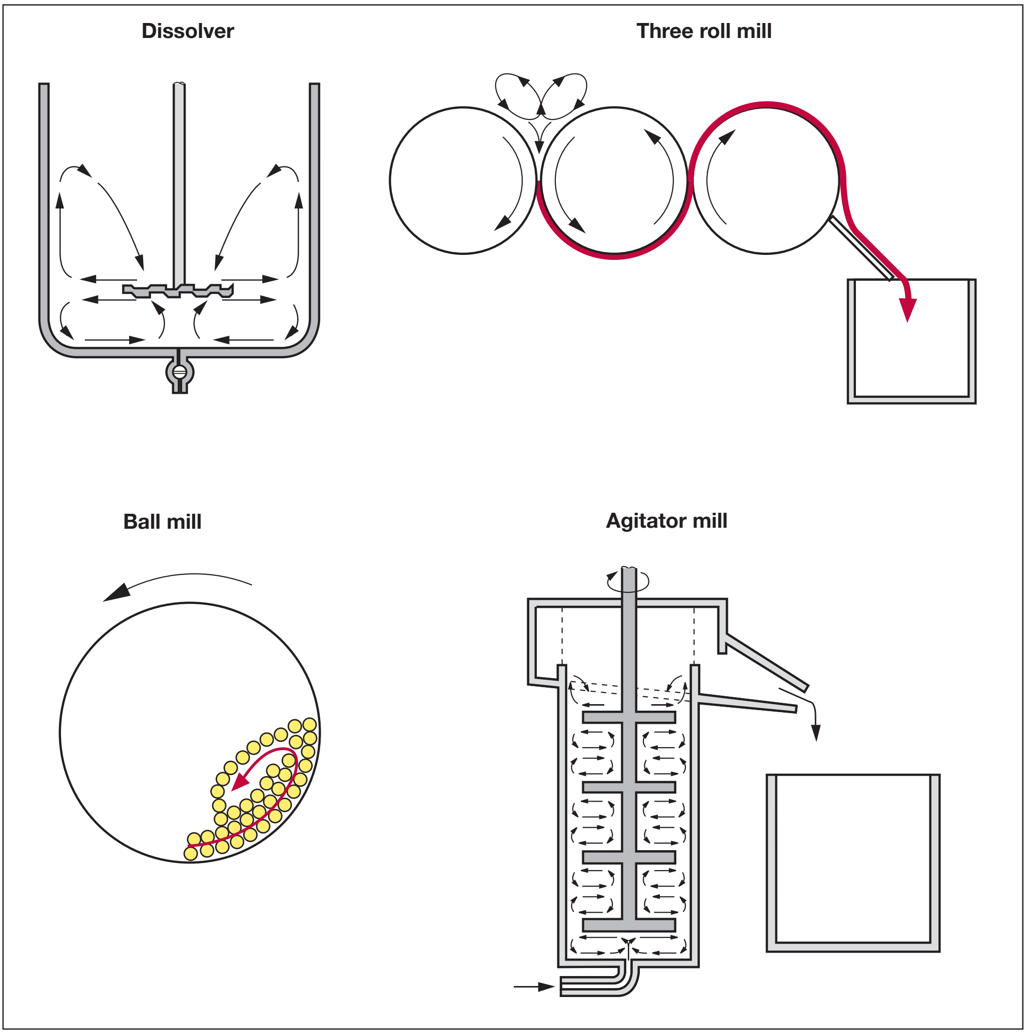


Fig. 2.2.11
Schemes of the most important dispersing eqipments

into the wedge shaped area formed by the feed and the central rolls. It then passes through the roll gaps, before being conveyed via the central roll to the discharge roll. Here there is a doctor blade which transfers the dispersed material to a separate container.

2.2.3.3 Stabilization of Pigment Dispersions

The uniform distribution of the pigments brought about by the dispersion process is only a feasible technical solution if the distribution state is also retained during formulation, storage, processing and the subsequent film formation. The reagglomeration of the primary particles would result in a reduction in gloss and a change in the tinting strength. Other side effects would include color shifts in pigment mixtures, specks and sedimentation.

If the surfaces of the pigments are changed by the dispersion process to such an extent that, in the event of a collision, no adhesion and thus no agglomeration takes place, the necessary stabilization has been attained. In the manufacture of pigmented coating materials any consideration of the pigment wetting and homogenization process must therefore also address the stability of the resulting product. For technical and economic reasons the dispersion cost and method must always be related to the covering of the pigment surface with substances which contribute to stabilization of the product. This can be achieved in two ways in principle. Whereas in polar media the formation of electrical double layers predominates with regard to stabilization, in a nonpolar environment steric, osmotic and entropic phenomena are the main types encountered. All mechanisms can work in isolation or jointly.

From a **thermodynamic perspective** the change in the free energy ΔG must be positive in accordance with the *Gibbs-Helmholtz* equation

$$\Delta G = \Delta H - T\Delta S$$

where there is stabilization of the approaching pigments. Such a case occurs where the entropy ΔS diminishes on approach or the enthalpy ΔH increases. If one of the two variables has a different sign from the other, stabilization still exists if the difference between the two is positive. If the entropy changes positively and at the same time the enthalpy negatively, no stabilization can be achieved.

Stabilization by means of electrical double layers

One of the first – still current – theories on the interpretation of the stability of dispersions, be they resin particles or pigments, was developed by the Russians *Deryaguin* and *Landau* [2.4.59] and, independently, also by *Verwey* and *Overbeek* [2.4.60] in the Netherlands. This is a relatively simple method of describing surface energies when there is a polar, i.e. ion forming environment, which makes it a useful method for practical operations. The mathematical correlations which are known by the term DLVO theory show that a pigment dispersion is stable if the repulsive forces acting on the surface as a result of ion adsorption exceed the *van-der-Waals*' forces of attraction.

$$V_T = V_A + V_R$$

The total potential surface energy V_T is composed of the attraction V_A and the electrically induced repulsion V_R energy levels.

Electrical double layers are formed by the adsorption of charge carriers at the pigment surface which attract the moving countercharges in the environment overproportionally in the form of an ion cloud. The repulsive forces are activated when ion clouds of two particles with the same charge approach and mingle. The models proposed by *Helmholtz*, *Gouy* and *Stern* provide a precise description of the conditions in the vicinity of stabilized pigment surfaces [2.4.61]. All the authors

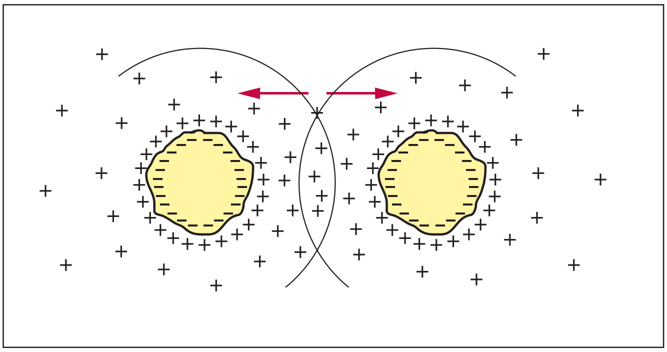


Fig. 2.2.12
Repulsion of particles with same electrical charging

agree that an electrical potential φ is generated from the pigment surface to the freely mobile counterions in the environment as a result of the adsorption of charge carriers. However, opinions diverge when it comes to the exact potential profile. Whereas *Helmholtz* assumes a linear fall in the potential to the gegenions which are a short distance from the environment, as in a bulb condenser, *Gouy* and *Stern* see the potential profile as being more complicated.

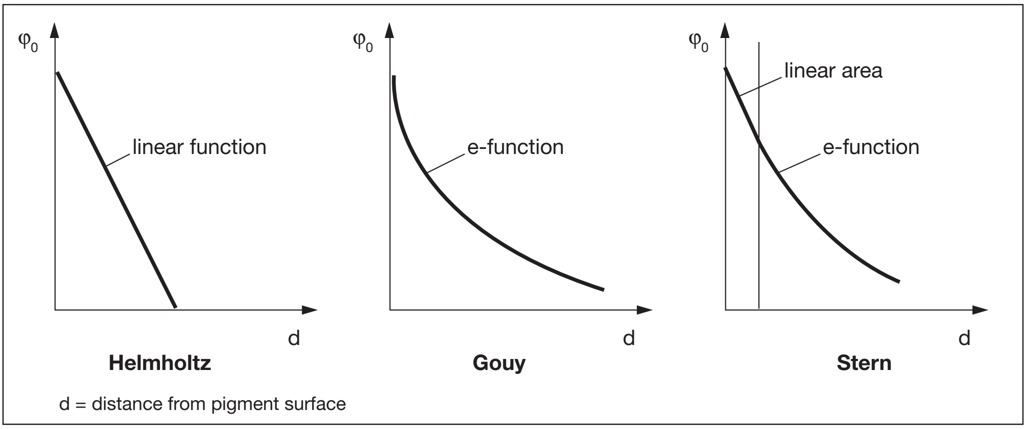


Fig. 2.2.13
Curve of electrical potential φ of electrostatically stabilized pigments

Gouy postulates a reduction in potential in the form of an e-function. *Stern*, on the other hand, combines *Helmholtz*'s model with *Gouy*'s. There is an initial potential drop in the vicinity of the pigment or dispersion particles, followed by a potential profile with an e-function. All three models can be applied in practice. While concentrated solutions are largely described by *Helmholtz*'s model, extremely dilute solutions follow *Gouy*'s model. *Stern*'s theory is consequently the most suitable for real solutions. Because of the easier applicability of *Gouy*'s model the comments below refer to this model only. If φ_0 is the potential at the interface to the pigment, the following applies for the potential φ at a distance d

$$\varphi = \varphi_0 \cdot e^{-\chi \cdot d}$$

The variable χ assumes a practical significance in that it gives an indirect indication of the thickness of the electrical double layer. 1/χ is the film thickness at which the potential φ has fallen to φ_0/e. According to *Debey* and *Hückel*'s theory the following applies for:

$$\chi = \sqrt{\frac{8 \cdot \pi \cdot e_0 \cdot 1000}{\varepsilon \cdot k \cdot T}} \cdot \sqrt{J}$$

where $J = \frac{1}{2}\sum_{i=1}^{n}(c_i \cdot z_i^2)$

c_i = concentration
z_i = valency
e_0 = elementary quantum of electricity
ε = dielectic constant
k = Boltzmann constant
T = absolute temperature

χ is proportional to the square root of the ionic strength J. J is composed of the product of the ion concentration c_i and the valency z_i^2 of all the ions. The thickness of the electrical double layer is therefore also determined by the electrolyte type and quantity. The stabilization of pigment dispersions is particularly good if the electrical double layer has a large range. As defined in the above formulae, however, this decreases with increasing electrolyte concentration. This enables the particles to come closer together and causes a decrease in pigment stabilization. If, on the other hand, the double layer consisting of freely mobile ions has a larger range at a low concentration, penetration of the double layers occurs as two pigment particles approach, even at an extended distance. A repulsive effect is therefore activated even at extended distances.

In accordance with the DLVO theory the following applies for the decrease in the *van-der-Waals*' forces of attraction V_A as a function of the distance from the surface:

$$V_A = \frac{A}{6} \cdot \left[\frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \left[\frac{s^2 - 4}{s^2} \right] \right]$$

with $s = \frac{R}{r}$

R = distance of particle clusters
r = radius of particles
A = Hamaker constant

for short distances applies:

$$V_A = -\frac{A}{12 \cdot \pi \cdot d^2} \qquad \text{where} \quad d = R - 2 \cdot r$$

The DLVO theory permits also the estimation of the repulsive forces

for large particles applies $(\chi \cdot r >> 1)$

$$V_R^{el} = \frac{\varepsilon \cdot r \cdot \varphi_0^2}{d + 2 \cdot r} \cdot \ln\left(1 + e^{-\chi \cdot d}\right)$$

for small particles applies $(\chi \cdot r << 1)$

$$V_R^{el} = \frac{\varepsilon \cdot r \cdot \varphi_0^2}{d + 2 \cdot r} \cdot e^{-\chi \cdot d}$$

and with infinite dilution $(\chi \rightarrow 0)$

$$V_R^{el} = \frac{\varepsilon \cdot r \cdot \varphi_0^2}{R}$$

If an overall balance for the potential energy as a function of distance from the pigment surface is drawn up with the aid of the equations for V_A and V^{el}_R, the result is curves as shown in Fig. 2.2.14.

The overall curve which is calculated by adding the individual potentials has three extreme values. The outer minimum V_{min1} is particularly flat and, although it results in the formation of flocculates in the event of pigment collisions, these are extremely soft and can be separated from each other again quantitatively during agitation processes by means of simple shear action. This minimum can be influenced by the concentration of the electrolyte. It can disappear completely with the correct stabilization (see red curve). Stabilization of the pigment dispersion is determined by V_{max}. Using the DLVO theory, energy barriers can be calculated which cannot be overcome even if the particles have a

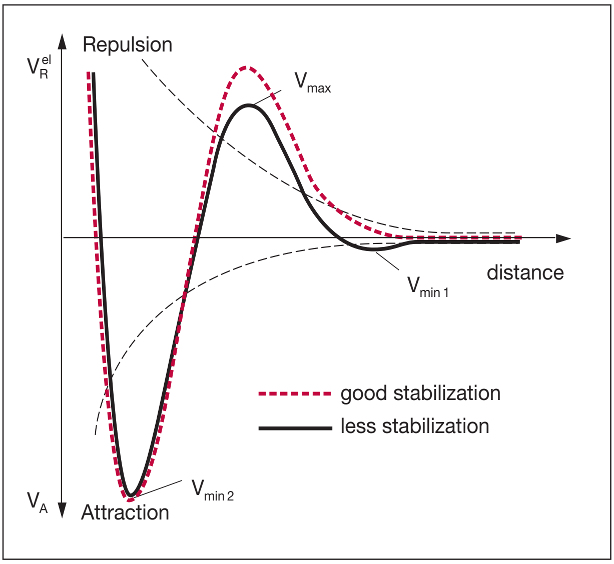


Fig. 2.2.14
Potential V of electrostatically stabilized pigments against distance of particle surfaces

relatively high kinetic energy. The distance and the level of V_{max} can also be influenced as described by the concentration and valency of the electrolytes and also by the pH value. A charge reversal occurs at the isoelectrical point as the pH value increases or decreases. This results in destabilization of the system in that $\varphi_0 = 0$. There is then no longer a repulsive barrier.

It is particularly important in practice to be able to measure the stability of a dispersion using simple means or record the influence of additives or formulation modifications [2.4.62]. The DLVO theory states that the electrical potential of the boundary surface between the pigment and the solution φ_0 results in the energy barrier being raised by the power of two. Knowing φ_0 or being able to influence it is therefore important for an objective evaluation of the stabilization of pigment dispersions. Unfortunately φ_0 cannot be measured because of the greater or lesser degree of sieveing by the electrical double layer. However, it is possible to comment indirectly on φ_0 by determining the migration rate of the stabilized pigment particles in an electrical field.

If dispersions of ionically stabilized pigments are introduced into an electrical field E, a force acts on the particles which causes them to move in the direction of the electrode with the opposite charge. As a counterforce is formed by the viscosity η during the flow which can be quantified using *Stokes*' law, a stationary state quickly occurs. The particles move in the dielectrical material with the dielectric constant ε in accordance with their charge at a uniform speed u. Since during transport of the charged particles these are partly sieved by counterions because of a firmly attached liquid sheath which moves with them, only the net charges of the pigment

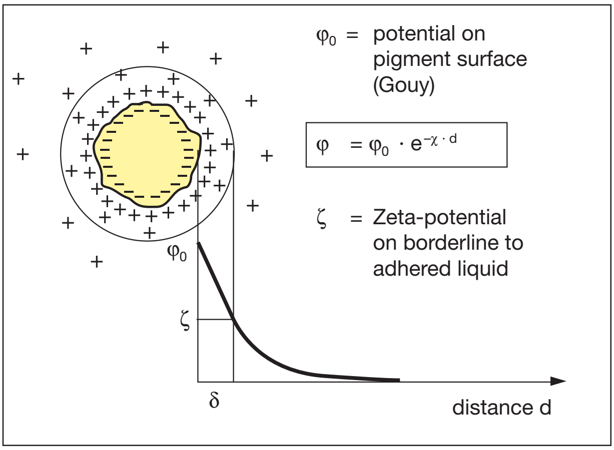


Fig. 2.2.15
Zeta-potential as a measure for stabilization of dispersed particles

particles which are behaving like a bulb condenser should be taken into account in calculating the electrokinetic processes. By measuring the migration rate of the pigment particles which are enveloped with charges in the electrical field it is possible to determine the so-called ζ-potential [2.4.63].

$$u = k \cdot \frac{\varepsilon \cdot \zeta \cdot E}{\eta} \qquad \zeta = \text{electrokinetic potential}$$

This has a functional correlation with the potential φ_0 and therefore enables the repulsion barrier V_{max} to be calculated.

The migration rate of the particles is measured using Laser-*Doppler* anemometry. Two coherent laser beams are passed through the sample. The particles in the measurement range cause fluctuating scatter of the laser light because of movement of the particles. The effect of this enables the migration rate and thus the ζ-potential to be calculated.

It may be noted in conclusion that the actual conditions are more complicated because, on the one hand, the thickness of the adhering and thus sieveing layer is a function of the speed of the pigments in the electrical field and, on the other hand, deformations associated with the removal and reestablishment of the double layer must be taken into account. It can be demonstrated, however, that such relaxation phenomena occur so quickly that they can be ignored in general.

Steric stabilization

While the DLVO theory allows calculations to describe conditions with a good fit when assessing pigment stabilization in aqueous media, this method is ineffective in a non-polar environment. It has been shown in practice, however, that pigment dispersions can also be transfered to a stable state without electrical charges.

The first noteworthy model for an entropic (steric) stabilization of pigments in a liquid, nonionic environment was proposed in 1950 by *Mackor* [2.4.64]. To permit stabilization, the pigment must be surrounded by polymer chains which are fixed punctually but which otherwise can move freely. When two particles stabilized in this way approach, the mobility of the polymer chains and thus the entropy are reduced. In accordance with the *Gibbs-Helmholtz* equation ΔS becomes negative and ΔG therefore positive. No further approach therefore occurs. Since this type of stabilization only refers to the entropic part, it is termed entropic stabilization. It is also termed steric stabilization.

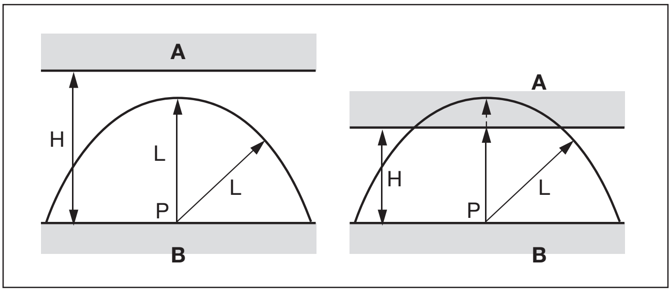


Fig. 2.2.16
Model to explain steric stabilization

Figure 2.2.16 shows a simple model to explain entropic stabilization. With a sufficiently large distance between the pigment surfaces A and B the polymer chain which is fixed at point P but can otherwise move freely and has a length L is capable of reaching all the positions within the semi circle of radius L. If the surfaces A and B approach to within a distance of

H < L, the free mobility of the chains is impaired. The probability W_∞ is reduced to W_H, and the change in entropy ΔS is then

$$\Delta S = S_H - S_\infty, \qquad \text{because of} \quad S = k \cdot \ln W \quad \text{follows}$$

$$\Delta S = k \cdot \ln \frac{W_H}{W_\infty}$$

ΔS = change of entropy during approaching of particles
W = probability of replacement

If it is assumed that the free mobility of the adsorbed polymer threads of length L decreases linearly with the approach of the two solid surfaces, the following therefore applies for the entropically induced repulsion energy V_R^S if n_S molecules are present per unit surface area:

$$V_R^S = n_S \cdot k \cdot T \cdot \Theta_\infty \cdot \left(1 - \frac{H}{L}\right)$$

H = distance of particles
L = length of chain
Θ = coverage of surface

Θ_∞ stands for a completely covered surface. This equation, which applies only to plane surfaces, was expanded by Sato to include spherical particles. It then permits the calculation of energy barriers for polymer chains of different mobility and of varying covering density and temperature [2.4.65].

A different approach is also available which attempts to interpret entropic stabilization by osmotic effects. These express themselves in an increased concentration of the adsorbed molecules and thus of the osmotic pressure in the overlapping area when the movable polymer sheaths approach and mingle with each other [2.4.66]. If the interpretation of stabilization by means of osmotic and steric effects is compared, it becomes evident that both models can be influenced in the same direction by the same variables. A high surface covering of freely movable polymer chains, uncoiled if at all possible, i.e. well solvated and of adequate chain length, yields the optimum pigment stabilization.

The selection of a suitable solvent is also important when stabilizing pigments. Because of the greater mobility of the solvent molecules the primary wetting of the pigment cavities is initially achieved by solvent molecules. A subsequent complete wetting conversion is only achieved if a gain in free enthalpy is identified through the wetting process of an adequate concentration of film forming agent molecules. The use of relatively nonpolar solvents enhances the immediate wetting process with polar binder molecules and at the same time the wetting conversion of the already adsorbed solvent components.

In practice reagglomerations are occasionally observed which are not in line with the theory. Even where there is adequate electrical or steric stabilization so-called bridging flocculations of pigment particles can occur. This effect is observed if resin molecules have several polar groups and are consequently capable of combining several pigment particles. Such destabilizations are also observed when either the chain length of the

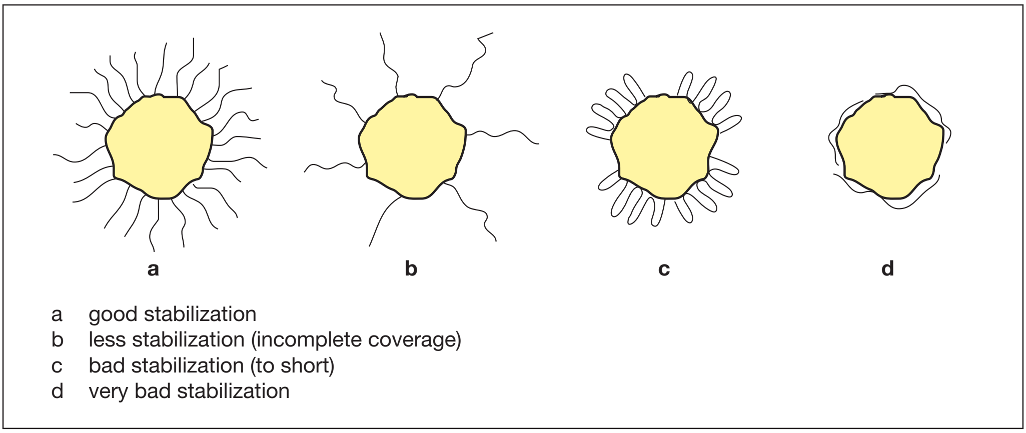


Fig. 2.2.17
Scheme of different types of entropic stabilization

protective polymer sheath goes beyond an optimum level or twisting or looping of the chains occur at a higher concentration and with very polar solvents at the same time, similar to the formation of micelles [2.4.67].

Mixed stabilization

The process of correlating theoretical considerations on the stabilization of pigment surfaces with practical operations is made more difficult by the fact that different stabilization mechanisms can overlap. Mixed forms of particle stabilization were discovered during the calculation of electrically stabilized gold sols after the addition of nonionic polyethylene glycol. *Heller* and *Pugh*, for example, discovered that the existing stabilization of electrically stabilized gold sols can be further improved by adding polyethylene glycol [2.4.68]. This stabilization can be further raised by increasing the concentration and chain length of the hydrophilic but nonionogenic polyether. This effect is attributable to the mobility of the macromolecular chains of the polyether absorbed on the gold surface and therefore represents a supplementary steric stabilization. Such combinations of steric and electrical stabilization are also frequently observed in pigmented coating materials.

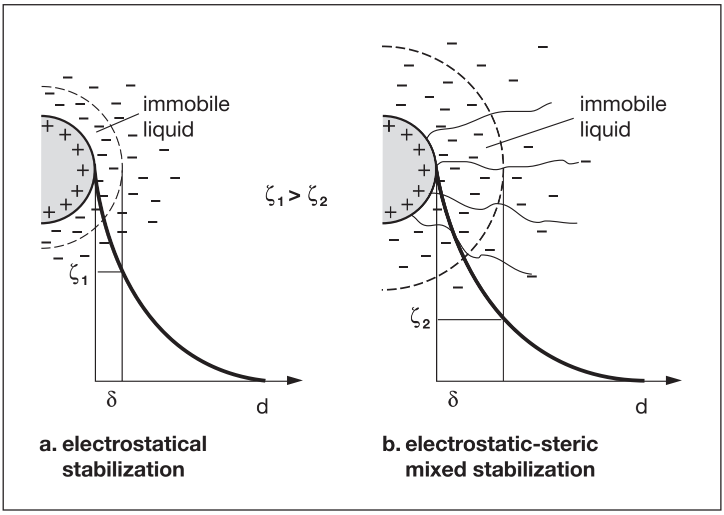


Fig. 2.2.18
Mixed stabilizations of pigments and their effect on the zeta-potential

The ζ-potential, which is an indicator of the stability of pigment distributions in the case of exclusively electrical stabilization, cannot be employed as a main stabilization criterion with combined stabilizations because of the thicker, immobile liquid sheath which can no longer be estimated. The ζ-potential is reduced without any consequential adverse effect on stabilization. On the contrary, the presence of freely mobile molecule chains results in a reduction in entropy and thus to additional stabilization when two pigment particles approach each other.

Stabilization limits

Despite the best possible stabilization the primary particles can approach the range of the forces of attraction if the kinetic energy is sufficiently high, for example at relatively high temperatures. This leads to pigment flocculation. However, the resulting flocculates can frequently be separated from each other again by relatively low shear forces. Under certain conditions, however, materials are forced together which entails irreversible material changes. Flocculation as a result of solvent loss and inadequate covering of the pigment surfaces can occur despite optimum dispersion and the best possible stabilization if the material to be dispersed is wrongly handled when lacquering pigment concentrates. **Pigment shock** and **solvent shock** in particular are commonly encountered in coating technology.

Since the mill base composition is determined as a result of the best conditions for dispersion (e.g. low solid content because of low viscosity and surface tension), but the binder, solvent and pigment components in the finished coating material have to meet the requirements of the coating to be produced, the mill base frequently has a different composition from the end product.

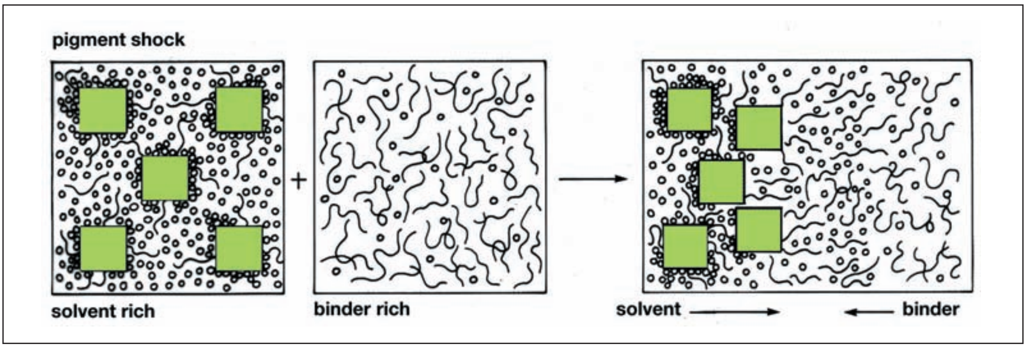


Fig. 2.2.19
Pigment shock by differences in solvent concentrations of dispersion and lacquer

Since film forming agents with a higher solid content than that of the mill base generally have to be added when lacquering the mill base, these can draw solvents from the paste and result in forced flocculation during the completing process as a result of a shift in the binder-solvent ratio. The major destruction of the pigment dispersion is caused by osmotic processes, as a result of differences in concentration with different mobility of solvent and film forming agent molecules at the same time.

Pigment shock can be avoided by setting merely small differences in the film forming agent solid content in the dispersion and the lacquer solution and by ensuring fast homogenization by means of intensive agitation.

The same problem can occur when operating with a lower rather than a higher binder concentration or, in an extreme case, only with solvents. This is a daily occurrence for

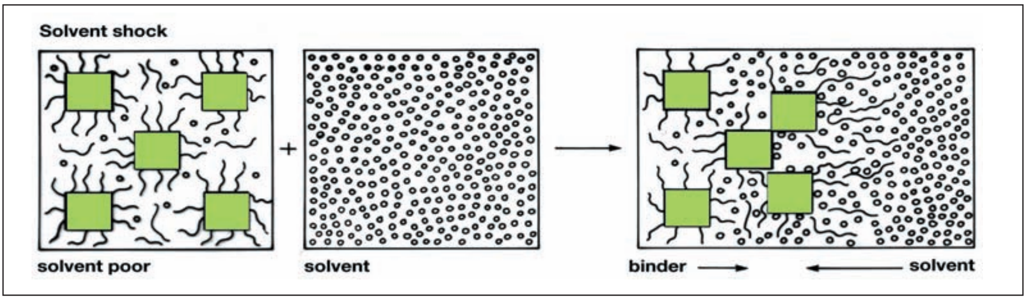


Fig. 2.2.20
Solvent shock by unprofessional addition of solvents to the dispersion

paint consumers when adjusting the coating material to spray viscosity. Because of the high mobility the solvent molecules penetrate the pigmented coating material quickly and in large quantities. In the process of this it is possible for the stabilizing film forming agent layer to be replaced locally by solvents to a greater or lesser degree. Solvent shocks should be anticipated whenever pigment dispersions are mixed with excessively polar solvents. Adjustment to processing viscosity should therefore only be carried out at the dilution specified by the paint manufacturer and with thorough agitation at the same time.

Reagglomeration which occurs during inexpert handling when lacquering, mixing or adjusting cannot always be recognized immediately, but results in an increase in the average particle size and thus a reduction in the tinting strength. Both phenomena are used to evaluate the degree of flocculation. The particle size which is increased by flocculation results in accelerated sedimentation, and this can be used as an indicator (see chapter 2.3.4). Another useful method of determining the degree of flocculation of colored coating materials is the rub-out test. This consists of nothing more than manually rubbing a freshly applied paint film and subsequently evaluating the color change caused by this rubbing (see chapter 2.3.4).

2.2.3.4 Optimum Mill Base Formulation

Since the paint manufacturer’s goal is to convert as much pigment powder into stabilized primary particles within a short period of time at the lowest possible cost, mill base formulations are sometimes significantly different from those of the saleable coating materials.

A proven method of determining the minimum quantity of resin solution for a given pigment and at the same time shortening the dispersion time for paints whose color can only be adjusted with a number of pigments is to disperse these individually. The pigment pastes produced in this way are mixed later in accordance with a specified formulation and adjusted to the required final composition.

Paint manufacturers therefore produce numerous pastes or paste series with a maximum pigment proportion. These are then adjusted to a standardized tinting strength and stocked. The handling of a customer order is thus limited to mixing and completion processes. The advantages are a major reduction in time input and a fast delivery capability, but these must be set against the costs of stocking sometimes more than 30 such pastes per quality series.

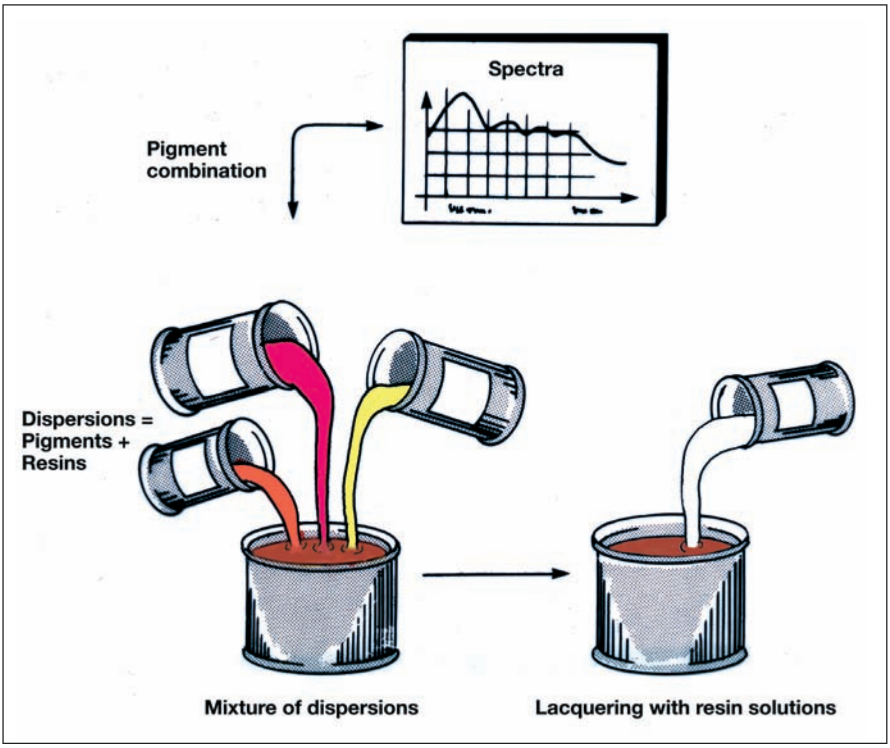


Fig. 2.2.21
Manufacturing of paints by dispersions

For the paint manufacturer it is particularly important for economic reasons and for the qualitative reasons described in the previous chapter to determine the optimum mill base composition and to use this when drawing up the formulation.

This is done by determining the solid content of a film forming agent solution at which a specified pigment quantity can be converted into a flowable mixture with the minimum amount of resin solution.

The pigment absorption capability is quantified using indicators for better evaluation. An important indicator for determining the optimum mill base composition is the yield value. This is defined as the volume of a film forming agent solution which is required to convert a specified pigment quantity into a flowable state. The characterizing feature of this property is that the mixture flows in a continuous thread from a glass rod.

If the compositions of the ternary mixtures of film forming agent, solvent and pigment determined from the individual yield points are plotted in a concentration triangle, the ranges of the flowable mixtures can be attractively presented in graphical form.

If the two ends of the yield point curve are extended to the triangle sides and the area of the supercritical pigmentation is hatched, the area enclosed by the curve with the exception of the hatched, supercritical area contains all the flowable binder/solvent/pigment mixtures. Supercritically pigmented mill base compositions lie above the critical pigment volume concentration (CPVC), at which the volume of the film forming agent is lower than that of the spaces between the pigments (see above). The CPVC can be calculated from the bulk volume of the pigments and must be converted into the critical pigment weight concentrations (CPWC) for entering in the concentration triangle.

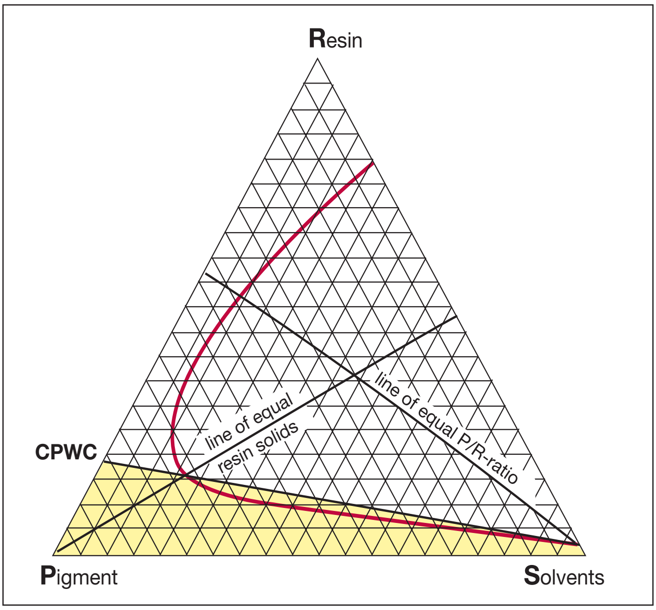


Fig. 2.2.22
Concentration triangle of film forming agent, solvent and pigment to demonstrate the flow curves

In most cases further corrections of the mill base formulation have to be made to achieve cost effective production. The reasons for this include the fact that the yield point determination method does not take account of the rheological properties of the paste after dispersion and the particular features of the disperser. It is, therefore, not possible to dispense with supplementary experiments with varying raw material mixtures when seeking to identify the optimum composition for cost effective production under realistic conditions. The rheological properties of the mill base change significantly with decreasing particle size. This frequently involves an increase in the viscosity and the degree of pseudoplasticity. However, the yield point method simplifies work in that a large proportion of the theoretically possible mill base mixtures can be excluded.

Because of the very different stresses on the mill base in the different dispersers the formulations must be adapted to the particular machines. Dissolver formulations differ substantially from those designed for agitator mills or three-roll mills. Dissolvers achieve only moderate shear gradients. To obtain optimum dispersion of pigments, therefore, particular attention must be paid to the

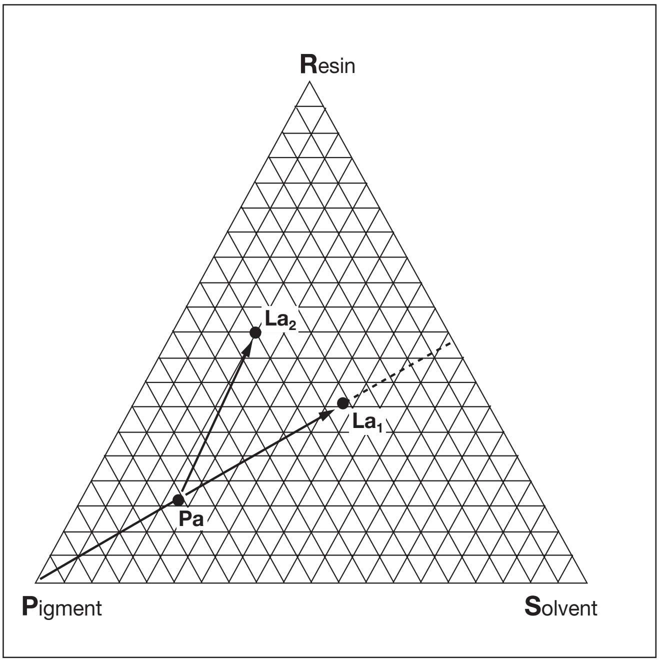


Fig. 2.2.23
Explanation of the pigment shock during lacquering by the concentration triangle

current viscosity occurring under shear. It is essential to prevent the mill base from developing thixotropic properties.

Roll mills feature a constant shear gradient because of the constant roll gap with a specified speed difference between the individual rolls. Because of the forced conveyance via the gap mill base mixtures can have a relatively high viscosity. The resin solid content and the binder proportion or pigmentation level of the mill base are correspondingly high in roll mill formulations.

The high rotational speed of agitator mills requires lower viscosities and frequently, therefore, higher solvent contents. The adaptation of the rheological properties often results in raw material mixtures with extremely low film forming agent levels in formulations for agitator mills. The latter should be borne in mind when lacquering pigment pastes in order to avoid pigment shocks. The danger of a pigment shock can be identified graphically in the concentration triangle of pigment, binder and solvent when the compositions of the pigment concentrate Pa and the saleable coating material La do not lie on the extension of the line formed by connecting the point of 100% pigment concentration with the point of position of the paste. For La_2 there is a serious danger of a shock whereas La_1 proves to be noncritical when lacquering (see figure 2.2.23).

2.2.4 Production of Coating Materials

The formulations drawn up by the laboratory must be supplemented by further detailed standards of operation and test specifications for large scale production. The latter refer equally to technical processing requirements and to quality. Manufacturing instructions contain information on the order in which raw materials are added, machine settings and temperatures for homogenization, dispersion and filtration systems, information on process monitoring and interim tests. Information on approval tests, instructions for filling methods, the container type and size to be chosen, together with safety information and labelling on the containers must be clearly specified in the manufacturing instructions.

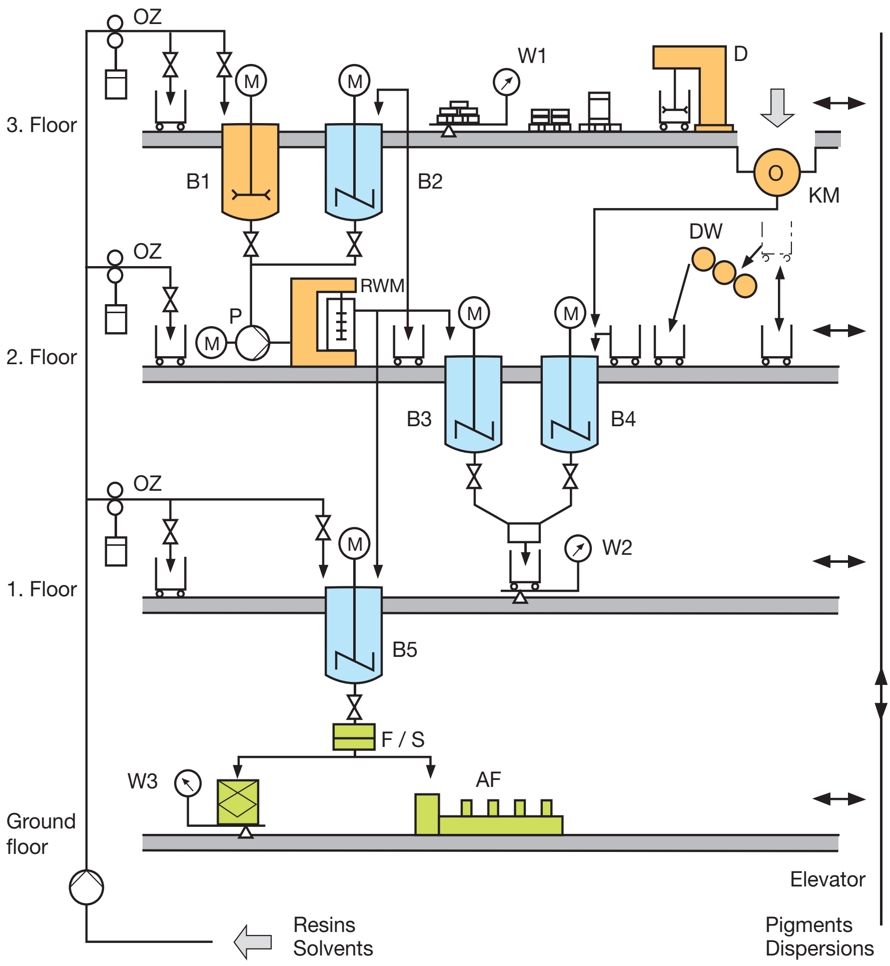
Modern make-to-order production can then use one of three methods: direct dispersion, production of pastes with later lacquering and the production of mixing paints. While the mixing paint principle has won through for the very varied color requirements of decorative and automotive refinishing paints, paste production and direct dispersion are commonly used for production for large scale users. Mixing paints are coating materials with a standardized color and tinting strength which mostly contain only one pigment and are turned into the final product by simply stirring together, without the addition of a binder. They are stored by paint users such as bodyshops and dealers in specially developed mixing machines and converted into the end products in accordance with given formulations. Direct dispersions and products made from pastes are manufactured by the paint manufacturer and sold as ready-to-use paint.

Paste production of individual pigments has proved its worth, despite the expense of storing the standardized pastes, because of the advantages of the more effective and thus more economical dispersion of batches for grinding. The individual pigment pastes are combined in particular mixing ratios as per the color requested by the processor, with completion to form the coating material as per the specification involving the addition of film forming agent solutions and additives.

2.2.4.1 *Processing Sequences in a Paint Plant*

A sample sequence of raw material supply, pigment dispersion and paste production, completion as paint and filling is shown in the overview plan in figure 2.2.24.

The material and production flow passes through four floors in a vertical direction. The top floor houses the interim storage and feed systems of the materials required for a batch before the dispersing process. Solid materials, such as pigments and extenders, are moved in bags, drums or cartons, while materials in liquid and paste form are transported in drums, cans or hobbocks. The film forming agent solutions and solvents,



OZ = Oval-wheel counter
W 1,2,3 = Balances
B 1–5 = Mixers
RWM = Agitator mills
D = Dissolver
KM = Ball mill
DW = Three-roll mill
P = Pumps

Fig. 2.2.24
Manfacturing process in a paint factory

which are often stored in tanks and transported via pipelines, are supplied to mobile containers, dissolvers or premixers via supplementary units fitted with flow meters.

The third floor is where fine dispersion in mill units takes place. The material to be dispersed is stored as a pigment paste in mixers, and its tinting strength is standardized and approved.

On the next floor down an appropriate number of completing mixers of different sizes corresponding to the range of formulations processed can be found. For manufacturing by mixing paints material is conveyed from the paste mixers via particular dispensing units into the completing mixers. For production from scratch the material to be dispersed is conveyed directly from the dispersers into the completing mixers. Samples are then taken from the completing mixers for testing and approval. On the ground floor the material is conveyed to the filling lines after cleaning processes involving sieveing and filtration, sometimes also including centrifuging and approval. The material is then transferred into tankers, containers, drums or small receptacles.

Various means of checking the material flow to achieve reproducible product quality are possible. On the one hand, the raw materials can be prebatched and supplied in this form to the relevant production facilities. On the other hand, the raw materials are weighed together with the individual production containers. This process involves placing these containers on pressure sensors.

Since the mixers and machines frequently have to be changed, depending on the product type and batch size, this results in a complex material flow system. A sensible approach is to assign machine and instrument groups to particular product groups by compatibility features with reference to color or chemical properties. This enables the cleaning input for the machines to be minimized. Quality tests are carried out in almost all functional areas with ongoing production. The correction strategy, particularly where color settings are concerned, is designed such that the target quality value is only achieved in small steps from one side. Correction here does not mean the elimination of faults but, in most cases, the addition of amounts of selected raw materials which were deliberately underdispensed initially.

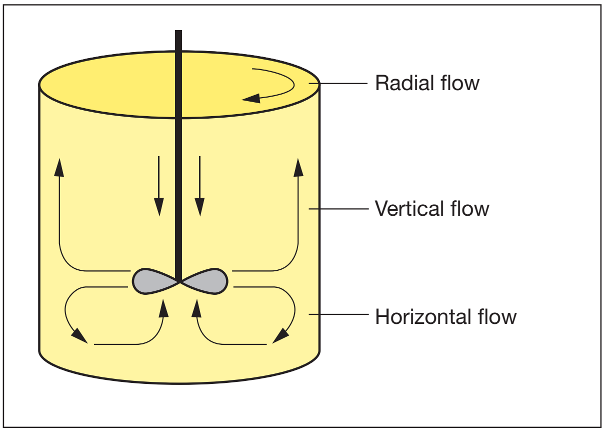
The essential basic process engineering operations in the manufacture of pigmented coating materials are the dispersion, dispensing (see chapter 4.2.1) and conveying of liquids and solids, homogenization generally by means of stirring and kneading and the subsequent sieveing, filtration or centrifuging stages. The theoretical principles and equipment for these basic process engineering operations are explained in greater detail below.

2.2.4.2 Agitation and Agitators

Visitors to a paint plant will see the basic mechanical process engineering operations to combine materials via agitation in the dissolving of resins, the mixing of liquids, the premixing of material to be dispersed or the tinting of color pastes, to mention just the most important process stages. In all cases the aim is to eliminate inhomogeneities in material mixtures. These can reveal themselves in differences in concentration, density or color. Temperature differentials or different refractive indices can also be used to characterize the mixing quality.

The indicators for the mixing quality are local deviations from the average in the abovementioned variables. If a sufficient number of individual readings are taken at various locations in the material to be homogenized, the degree of homogeneity can be quantified by determining the mean and the standard deviation. The standard deviation is indirectly proportional to the mixing quality and converges on zero where the individual components have achieved the optimum level of dispersion.

The homogenization of liquids or liquid-solid mixtures is carried out by generating flows which are as irregular as possible with the aim of achieving the desired degree of homogenization as quickly as possible with minimum energy input. If, because of excessively high viscosities, random shifts in position can no longer be achieved by free product flow but only by means of pressure or shear forces, this is termed kneading.



Frig. 2.2.25
Characteristic flow in a stirring vessel

The task of homogenizing free flowing material mixtures is achieved by agitation using vertical and horizontal flows. These are generated by rotating agitator blades. Numerous types of agitator have proved their practical value, depending on the type of material and the desired degree of homogenization.

Homogenization which has to be carried out under economic conditions is best achieved if horizontal and vertical circular motions are present in the mixing vessel at the same time. When homogenizing materials of different density it is recommended that vertical flow be used because of the tendency towards sedimentation of the heavier components. Wherever possible, movement of the entire amount of material together in the mixing vessel, which occurs frequently during the agitation process, should be avoided because of the unwanted separation caused by centrifugal forces.

The mixing time is short if the components to be mixed undergo a large number of changes of location. This can take the form of movement of the agitator itself or of material flows generated by the agitator. They can be achieved by impact, flow around obstacles, crossing directions of flow and speed differentials at the interfaces of parallel flows.

Two different agitator designs have become established. Either the entire contents of the vessel are circulated by means of a large agitator surface area and slow material motion or small partial quantities are transported at high speed by means of impact and mixing eddies with a small agitator surface area and a high rotational speed. The first concept is represented by blade agitators, and the second by propeller agitators.

At high agitation speeds the occurrence of conical eddies can be observed which entrain air into the mixture. To avoid this, baffles are fitted in the agitators or the agitator shafts are configured eccentrically.

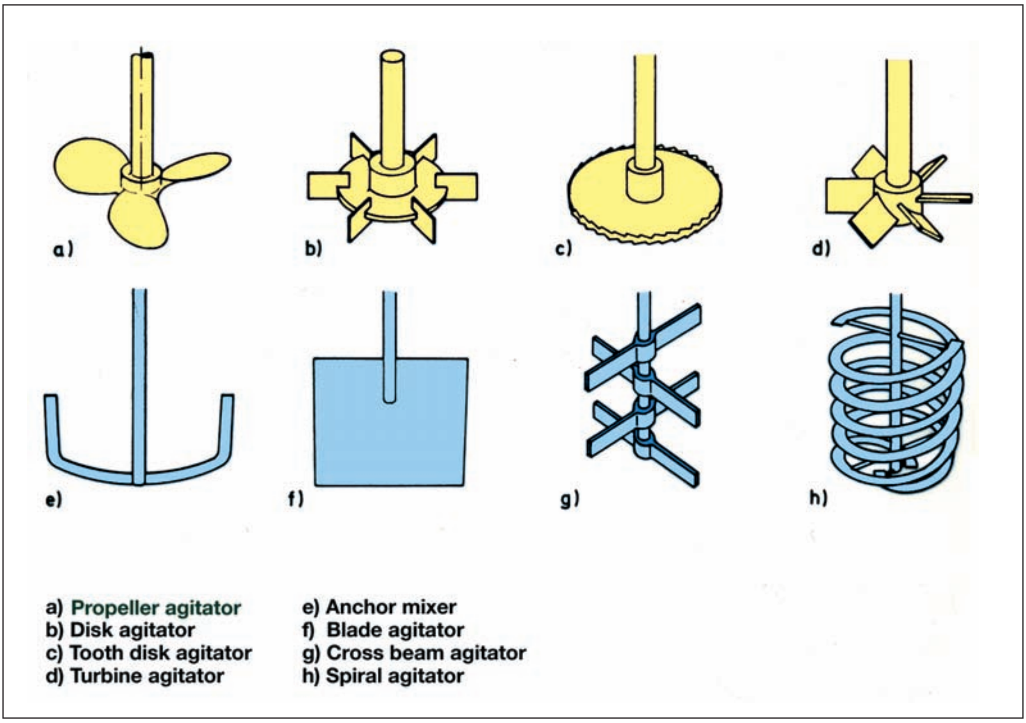


Fig. 2.2.26
Different agitator types

A broad range of different consistencies has to be covered in the paint and coatings industry when homogenising materials. The viscosity of the material to be agitated is therefore adjusted continually by altering the rotational speed or by means of gear mechanisms and interchangeable agitator blades.

Figure 2.2.26 shows a small selection of technically important agitator types. The anchor mixer is an old design which is unsuitable from an economic perspective. It rotates slowly and is now only still used in resin reactors for better heat transfer and to eliminate vapour bubbles. It is not suitable for homogenization tasks because of its lack of vertical flow.

The blade agitator is also a simple agitator design. It is mainly used to maintain already homogenized mixtures. Because of the size of the agitator blades there is the danger of radial motion being induced in the agitated material. Such motion can be prevented or reduced by means of baffles. Vertical flow is not very pronounced in blade agitators.

Flow is different in the beater or the modern variant, the multistage impulse agitator. Both achieve intensive vertical motion.

The propeller agitator moves part of the mill base at high speed. It entrains the material axially and discharges it in turn axially. This guarantees good vertical flow. The undesired circular motion can be prevented by rotating rings. The propeller agitator copes with a broad range of consistencies and has therefore become accepted in practical paint production operations as a universal machine. Its disadvantage is that the generated flow is often insufficiently turbulent, as a result of which long mixing times have to be accepted.

The agitator shaft and its seal are important when it comes to avoiding contamination of the paint material in all stationary open or closed agitators. The shaft seal can be of a noncontact design if no pressure differentials occur or are generated between the interior of the vessel and the atmosphere.

Shaft seals can be made of various materials. If the temperature remains below 100 °C when mixing the components, simple ring seals made of elastomeric plastics are used as standard. For overpressures of up to 2 bar or a vacuum of down to 0.1 bar moulded rings with lubricants are used to seal to temperatures of up to 130 °C. For extreme sealing requirements, high pressure differentials and relatively high thermal loads it makes sense to use mechanical seals with a supplementary sealing liquid and heat discharge via an air cooling system. It is essential to avoid the use of silicone containing sealing liquids and lubricants for the reasons mentioned previously.

Safety regulations must be observed when operating agitators and other mixing equipment. Explosion protection systems, rigorous earthing of all agitators and vessels, and the fitting of grilles in vessel openings are important measures to take to ensure accident free operation.

Useful data relating to the correct design of agitators and their adaptation to the material to be mixed can be obtained from mathematical equations from fluid mechanics. A number of preliminary considerations must be borne in mind.

Firstly the *Reynolds*' number Re, which is important in calculating flow processes in pipes, must be redefined for agitation processes. Büche replaced the flow rate u by the blade tip speed ω r and the pipe diameter d by the diameter of the agitator blade in Re [2.4.69]. Dividing by π yields the *Reynolds*' number for agitation processes Re_M.

$$Re = \frac{\rho \cdot d \cdot u}{\eta} \quad \text{because} \quad u = \omega \cdot r \quad \text{and} \quad \omega = 2 \cdot \pi \cdot n \quad \text{becomes} \quad Re' = \frac{\rho \cdot d^2 \cdot \pi \cdot n}{\eta}$$

$$Re_M = \frac{Re'}{\pi} = \frac{\rho \cdot d^2 \cdot n}{\eta}$$

Where $Re_M < 30$ there is laminar flow. A figure between 30 and 100,000 represents a transitional range leading to turbulence at $Re_M > 100{,}000$.

Important practical information on the power consumption and mixing time of agitator mills can be obtained from the generally applicable flow resistance law.

$$F_W = C_W(Re) \cdot \frac{\rho_L}{2} \cdot u^2 \cdot A$$

The resistance F_W acting on the agitator blade is composed of the drag coefficient C_W, the density of the liquid ρ_L, the surface area A subject to flow and the square of the path speed u. The value for u is the path speed at the outermost point of the agitator blade. Since the power L corresponds to the work per unit time, so that F_W s/t = F_W u the following results:

$$L = C_W(Re) \cdot \frac{\rho_L}{2} \cdot u^3 \cdot A$$

If the speed u is replaced by ωr = n π d where n = rotational speed, d = diameter and r = radius of the agitator, and if it is agreed that the height and diameter of an agitator are always in the same ratio to each other (h/d = k), irrespective of the total surface area and thus $A = k\,d^2$, because $A = h\,d$, it follows that

$$L = C_W(Re)\cdot\frac{\pi^3}{2}\cdot k\cdot\rho_L\cdot u^3\cdot d^5$$

If the constant values and the variables which are a function of Re are aggregated, the result is the *Newtonian* performance index $Ne(Re_M)$.

$$L = Ne(Re_M)\cdot\rho_L\cdot n^3\cdot d^5$$

Ne has to be established when the power consumption of model agitators is being determined as a function of the rotational speed. A geometrical similarity between the model and production system is an essential prerequisite to permit the results to be transferred to large scale production. In order to calculate the power consumption Re_M has to be determined for the relevant mixing process and Ne has to be located in tables or graphs so that the power consumption L can then be established.

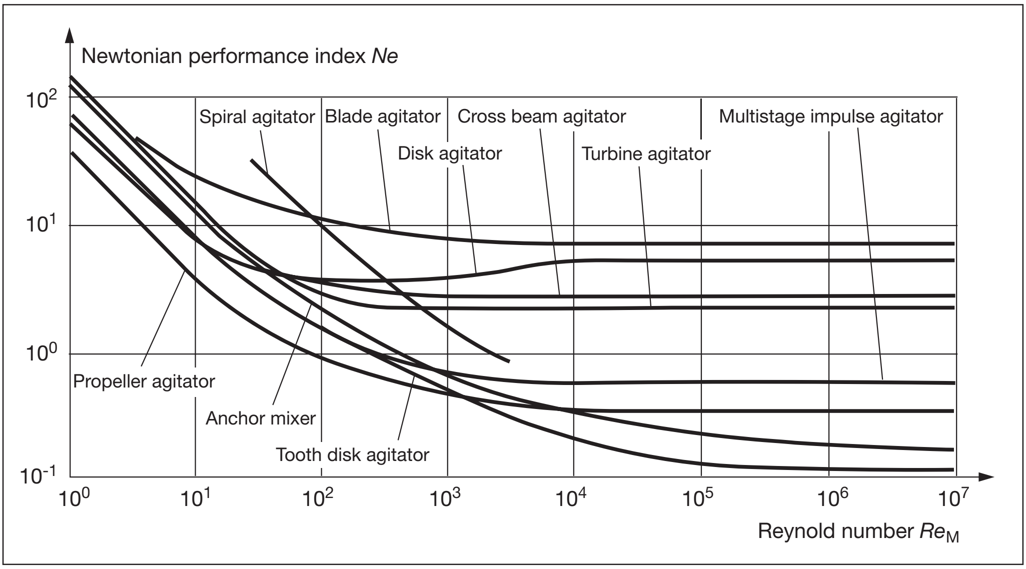


Fig. 2.2.27
Diagram for defining the performance index Ne of grinding mills

Cost effective operation of mixing systems requires low energy homogenization and also the shortest possible mixing time. The energy required for mixing is made up of the product of power and time. Since, however, the power consumption of an agitator mill increases to the power of three with the rotational speed, but the reduction in the agitation time only decreases by the power of one, agitation times can only be reduced with high energy input.

The mixing coefficient C, which is a function of the *Reynolds*' number, is used to calculate the mixing time required for complete homogenization. This has been determined experimentally for all the major agitator types and is transferable to larger agitators provided their geometry is similar. Fig. 2.2.29 shows the curve of the mixing coefficient as a function of the *Reynolds*' number for the relevant flow state. The mixing time t_M itself is defined as C(Re)/n.

As shown, an increase in the agitation speed causes an increase to the power of three in the power consumption in the energy calculation. Nonetheless, an almost negligibly shorter agitator utilization with a corresponding added value and order book situation can be more sensible than operating more slowly to save energy. The cost of the agitation energy relative to the total costs of the agitation process is also a decisive factor.

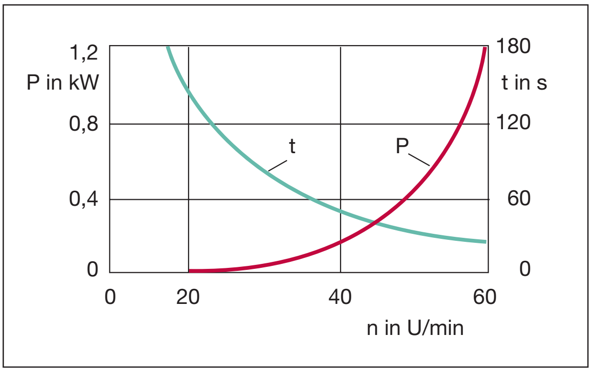


Fig. 2.2.28
Grinding power and time depending of rotational speed n of a stirrer

It may be stated in conclusion that mixing and agitation are the commonest process engineering operations in a paint plant. Numerous types of agitation equipment, operated either in stationary or mobile mode, are used for a huge range of homogenization types. Both the achievable mixing quality and the cost effectiveness of the process are of special interest.

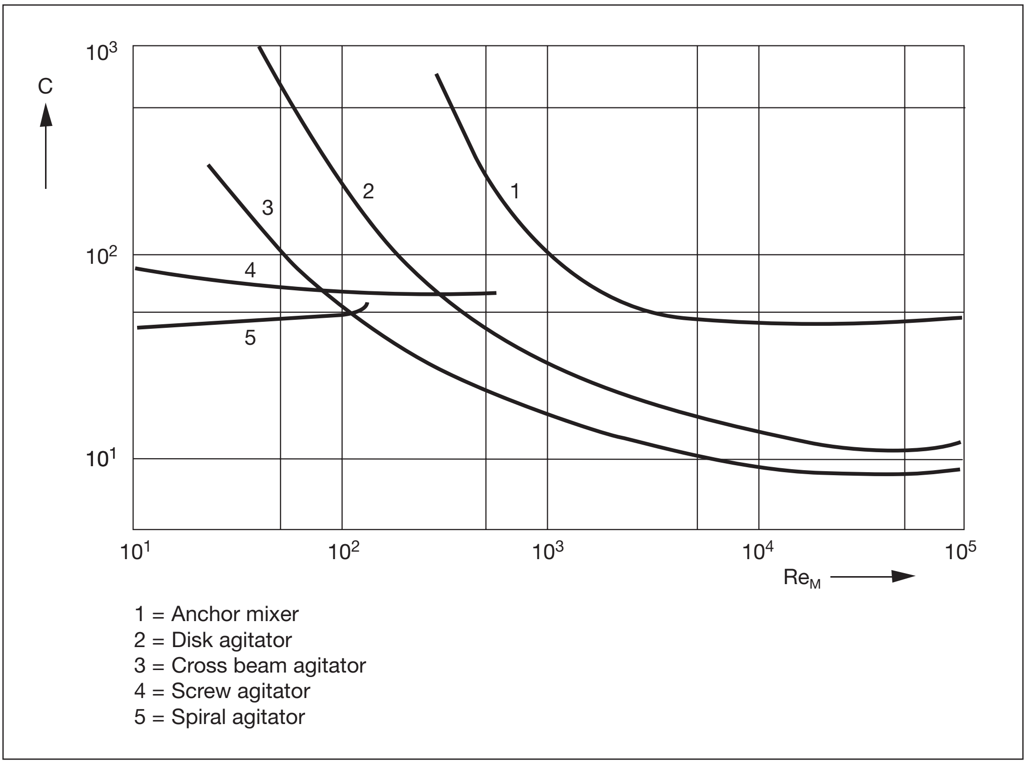


Fig. 2.2.29
Mixing coefficient C as a function of Re for different type of agitators

A problematic feature is that the theoretical considerations are limited in general to Newtonian flow properties. Changes in the rheological properties during the manufacturing process of coating materials with non-Newtonian mixtures cannot generally be fully calculated.

2.2.4.3 *Dispersersing and Dispersers*

Machines for wet paints

The task of dispersers is to separate pigment agglomerates in viscous fluids from each other by the transmission of shear forces. At the same time the conditions required for the stabilizing covering of the pigment surfaces which is also necessary are created by suitable raw material selection and formulation. The shear forces generated in the machines by flow are enhanced by supplementary rotation of the particles by centrifugal forces. In addition, there are also tensile and compressive loads at work which help in breaking down the agglomerates. Since the transmission of shear forces right to the level of the primary particle must be possible, flow states must be ensured which enable the transmission of forces irrespective of particle size.

The following relation shows that such a requirement cannot be met with turbulent flow. The transmissible separation forces τ in relation to the surface area are proportional to the particle size x_{Pi}, the power dissipation by volume N/V and also the density of the fluid phase ρ_{Fl} and inversely proportional to the pigment density ρ_{Pi}. Consequently the transmissible separation forces τ diminish with decreasing particle size during dispersion, with the result that it is not possible to go below a certain particle size.

$$\tau = 2 \cdot \rho_{Fl} \cdot \left(\frac{N}{V}\right)^{\frac{2}{3}} \cdot \left(\frac{x_{Pi}}{\rho_{Pi}}\right)^{\frac{2}{3}}$$

$\frac{N}{V}$ = power dissipation by volume

ρ_{Fl} = density of liquid

ρ_{Pi} = density of pigment

x_{Pi} = particle size of agglomerates

If the maximum technically applicable volume specific power of 10^3 to 10^4 kW/m^3 is used in this formula, the maximum decomposition achievable will deliver particle sizes ranging from 1 to 10 µm, as a function of the agglomerate strength. Consequently, primary particles with sizes of less than 1 µm can only be achieved with a power input of > 10^5 kW/m^3.

With laminar flow, on the other hand, the situation is different. In accordance with *Newton*'s equation $\tau = \eta$ D, the shear stress τ is not a function of particle size. The energy brought in by viscous resin solutions is then independent of particle size.

$$\tau = 2{,}5 \cdot \eta_{Fl} \cdot D$$

In this equation only the speed gradient D and the viscosity η_{Fl} are variables with an impact on the dispersion process.

Since the shear energy is transferred (dissipated) quantitatively in the form of heat, and this in turn rises by the power of two with increasing speed gradient D (see chapter 2.3.3), steps must be taken to ensure an effective means of cooling for high power dispersers.

The machines used for pigment dispersal are varied, and there is a wide range of designs. Nonetheless, all have the same operating principle. They transmit high shear forces in laminar flow gradients to separate the agglomerates. The most important machines used commonly in large scale production are dissolvers, agitator mills and roll mills.

Dissolvers are disc agitators which can transmit shear stresses to pigments under certain conditions which are sufficiently high to ensure dispersion. The necessary conditions for this are met if the agitator disc and the agitator vessel are matched in size and this is complemented by appropriate agitator disc sizes and shapes, an adequate rotational speed, an optimized fill level and adapted mill base formulations. Even when all the conditions are met, the shear forces transmitted by dissolvers are not high. Dissolvers are therefore only suitable for the dispersion of easily dispersed pigments, such as for dispersion paints and decorative paints. Different dispersion systems must be used if requirements are more demanding. Dissolvers are then only used for preliminary homogenization or preliminary dispersion. This enables the throughputs of the actual dispersion systems to be significantly increased (see below).

To generate the necessary laminar flow the sizes of the vessels

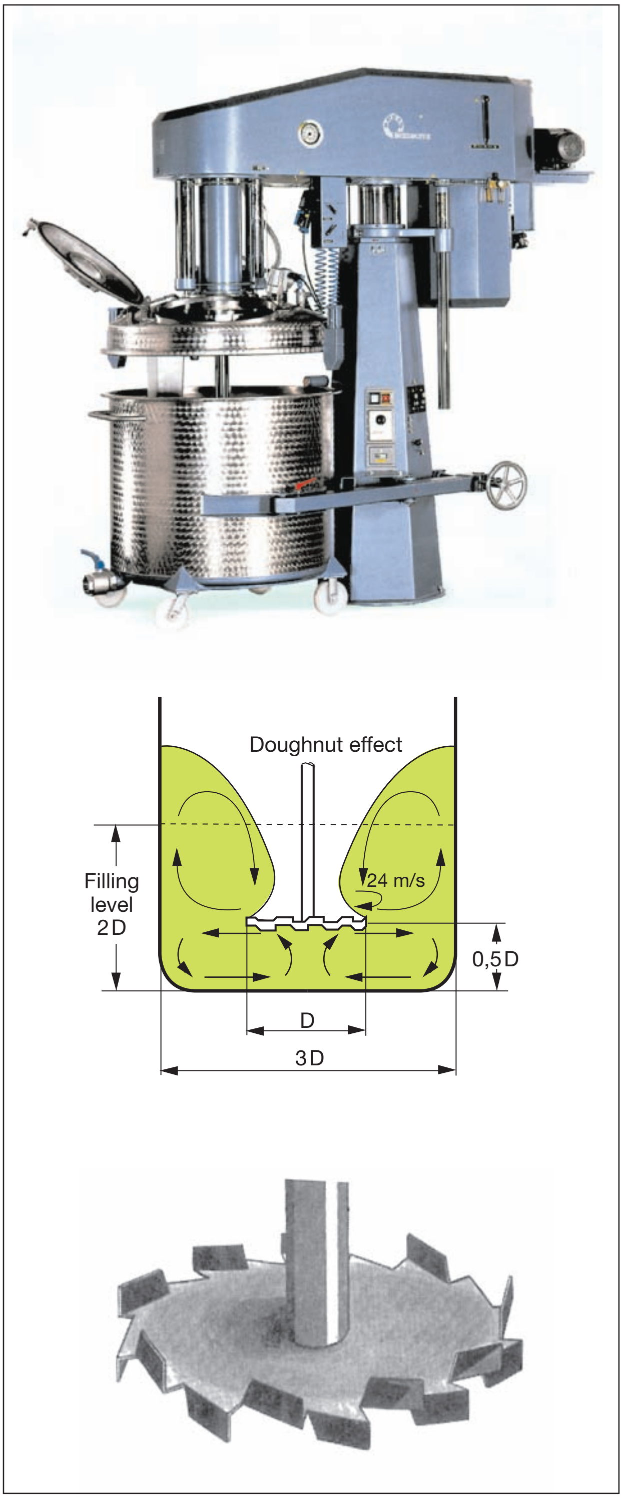


Fig. 2.2.30
Scheme of flow in dissolvers and pictures of a dissolver equipment and a dissolver disc

and agitator discs and the fill level and disc configuration must, as mentioned above, be matched to each other. Optimum dispersion results are achieved if the vessel diameter is 2.5 to 3 times the size of the disc diameter, and the distance from the agitator disc to the base corresponds to 0.5 and the fill level to 2 disc diameters. Under such conditions dispersions are possible once the tangential speed u_A at the periphery of the disc has reached 24 m/s. The limit speed is therefore a function of the disc size.

$$u_A = \omega \cdot r \geq 24 \text{ m/s} \quad \text{i.e.}$$

$$24 = 2 \cdot \pi \cdot n \cdot r \qquad \text{or} \qquad n \geq \frac{7{,}5}{D}\,\text{s}^{-1}$$

The design of the agitator disc (see figure 2.2.30) also has an impact on the dispersal effect. The agitator disc is similar to the blade of a circular saw and is fitted with teeth which are set at 90°. This toothing is only of minor importance for the dispersion process. It merely ensures better circulation of the mill base and an additional change between tensile and compressive loading of the material to be dispersed. For laminar flow gradients the disc must provide a horizontal discharge of the mill base. It is therefore essential to ensure that the agitator shaft is absolutely vertical.

The main part of the dispersal work is not performed, as might at first be thought, in the region of the disc but rather horizontally behind the disc. As a result of the varying lengths of the flow paths and the different braking forces in the upper and lower circulation ranges sufficiently high speed differentials are generated behind the disc to create dispersion. Furthermore, the rapid alternation of brief overpressure and underpressure zones promotes the thorough moistening, wetting and mechanical separation of the agglomerates.

The dispersal effect is also influenced by the mill base composition. At a binder solution viscosity of only 100 mPas the viscosity of the mill base increases, for example, to 3 – 4 Pas with the addition of the pigment. The dissolver reacts sensitively to the rheological properties of the mill base batches. While dilatancy is a desirable flow characteristic, there is the danger with thixotropic and very pseudoplastic mill base mixtures of incomplete circulation and thus incomplete dispersion of the pigments. With dilatant flow, however, the power consumption can rise dramatically when the rotational speed is increased, such that the possibility of the agitator shaft fracturing cannot be excluded.

If the shear forces are sufficient for pigment dispersion with appropriate rheological properties, dissolvers represent a rapid type of disperser. Generally the dispersion process is complete in less than 15 minutes. A further reduction in the fineness of the mill base will not take place, even if agitated for an extremely long period.

In operation, a dissolver is a stationary machine which can be loaded with mobile mill base containers. If the mixing vessel is also firmly installed, this is a dissolver with a volume generally of between 1,000 and 5,000 litres. Dissolvers with mobile mixing vessels can be moved hydraulically upwards and downwards for charging and to replace the agitator discs. The rotational speed is generally infinitely variable. The size and thus the power fluctuates with small, medium and large dissolvers from less than 25 kW right up to 200 kW.

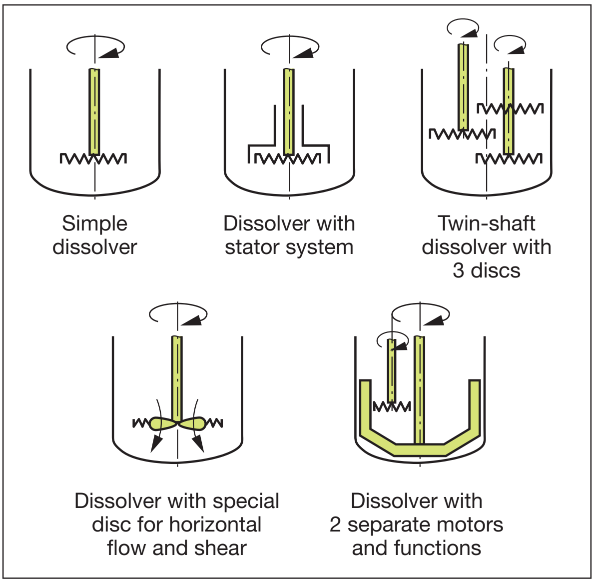


Fig. 2.2.31
Schemes of different dissolver types

Apart from conventional dissolvers numerous special designs will be found in paint plants. They differ in the type and number of agitator discs and in the configuration of the agitator vessels. Of the multishaft machines, the twin-shaft dissolver is the most commonly encountered disperser. It has agitator discs which are offset in height, mounted on two separate shafts, and thus better agitation properties (see figure 2.2.31).

Rotor-stator agitators (inline dissolvers) [2.4.70] have also proved successful for high speed homogenization, particularly for the manufacture of waterbased paints. Because of the high rotational speed of the rotor fast and effective distribution of the formulation ingredients is achieved with these, particularly when systems with a high pseudoplasticity have to be processed. They feature small dispersion chambers and are mainly used for continuous processes.

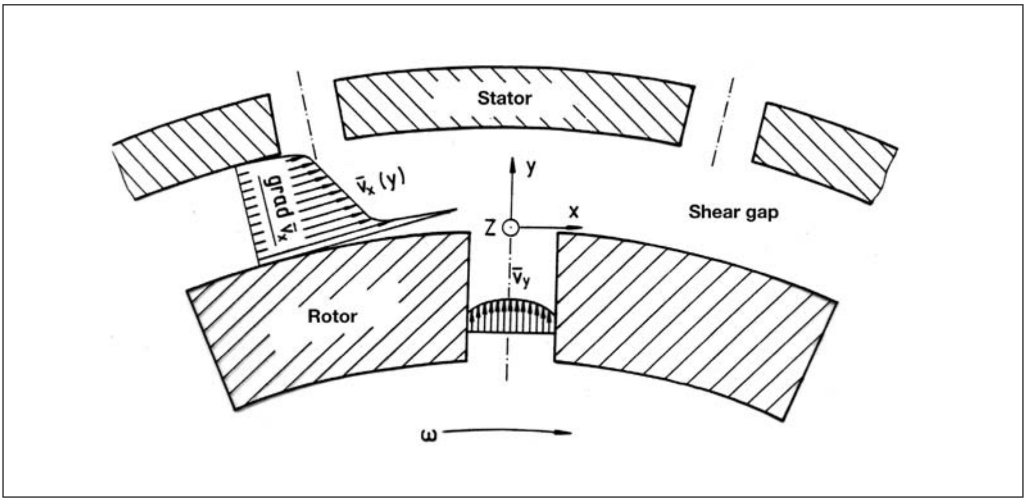


Fig. 2.2.32
Scheme and function of an inline dissolver

The principle of dispersion by means of **friction rolls** is implemented in single-roll, two-roll, three-roll and multiroll mills. The only one of any significance for the paint and coatings industry is the three-roll mill which has become less important because of its relatively low throughput by comparison with other types of dispersing systems. Its

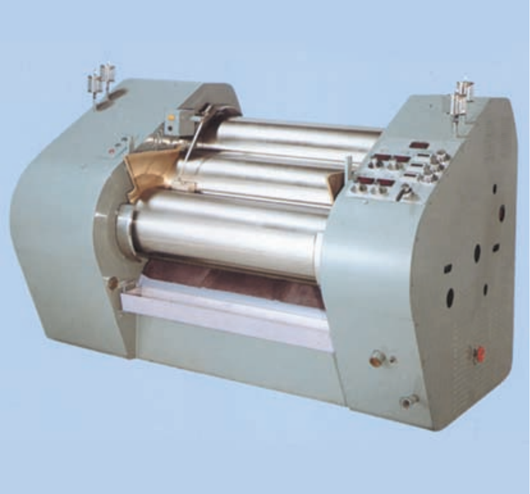


Fig. 2.2.33
Picture of a three-roll mill

use is now limited to the manufacture of fillers, highly viscous printing inks and, because of its gentle treatment of the pigment surfaces, to the dispersion of sensitive surface treated pigments and temperature sensitive pastes.

Three-roll mills consist in essence of three metal or plastic cylinders configured one after the other. The middle roll has a fixed mount, while the two outer ones are pressed against the middle one with pressures of up to 1,000 bar. High shear forces can be transmitted by viscous liquids in the narrow gaps between the rolls as a result of the different rotational speeds of the individual rolls. A speed ratio of 1:3:9 yields the best and most cost effective dispersing results, as has been repeatedly confirmed in numerous experiments.

In modern systems a gear mechanism can be used to set varying peripheral speeds. The mill base throughput $\dot{V}$ is determined by the roll width b, rotational speed u_m and gap width s.

$$\dot{V} = 1.225 \cdot u_m \cdot s \cdot b$$

where u_m is the arithmetic mean of the rotational speeds of the two rolls.

The rolls themselves generally have an extremely hard, 1 cm thick outer lining. Beneath this there are softer elements on the inside. These enable better heat transfer to the cooling hoses inside the rolls. The contact pressure for the rolls is provided via spindles or by motors with a corresponding hydraulic system. Under operating conditions a gap opening of approximately 100 µm is left which is many times larger than the diameter of the pigments to be dispersed.

Before a three-roll mill is used, the mill base should undergo preliminary dispersion in a dissolver or kneader, depending on its consistency. The mill base is then transferred to a feed device between the first two rolls. The mill base is drawn into the gap as it adheres to the wall of the rolls.

Because of the shear stress in the direction of flow and the diminishing gap opening a pressure is generated in addition to the shear load which promotes dispersion. This external pressure also causes pressure rises inside the agglomerates which may still contain air and promotes the decomposition processes. The width and height of the pressure profile depends on the diameter of the rolls and the viscosity of the mill base. It is all the narrower, the thinner the mill base and the smaller the roll diameter. The effect is enhanced by the shear of the material, caused by the differing roll speeds. The pressure is at its maximum shortly before the narrowest part of the gap. This is followed directly by a zone of underpressure, as a result of which a sudden pressure drop causes pigment wetting which is advantageous for the mill base. The mill base is then separated at the exit of the gap and distributed onto both rolls in a ratio corresponding to the rotational

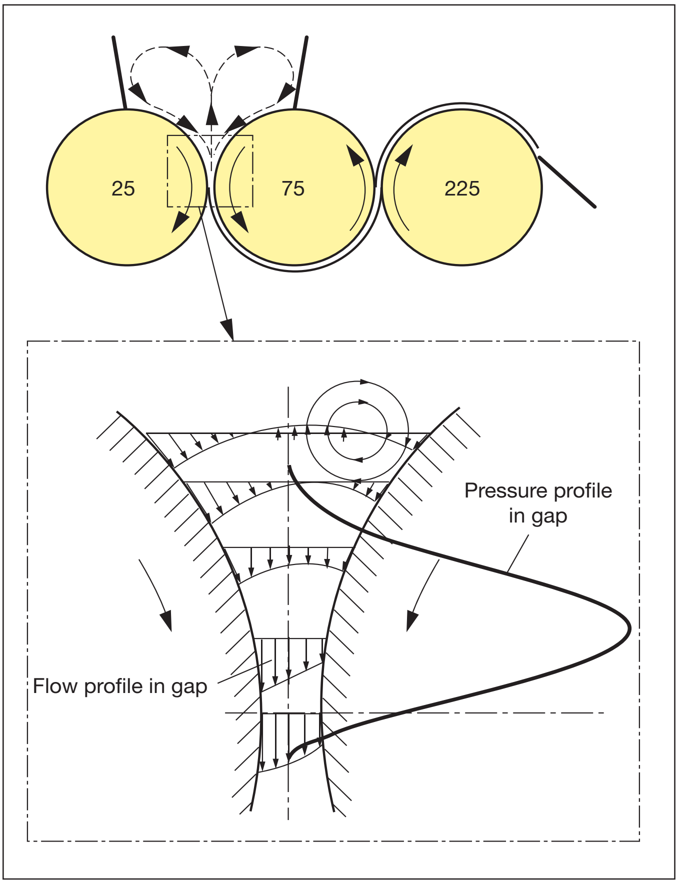


Fig. 2.2.34
Function of a three-roll mill and pressure profile in the milling gap

speed. With a speed ratio of 1:3 an appropriate amount of material is transferred to the second roll.

Corresponding processes also take place between the second and third rolls.

The dispersed mill base adhering to the third roll is then removed from the roll by a doctor blade and transferred to a storage container.

As with the other disperser types, the viscosity of the material to be dispersed must be adjusted to the three-roll process. If the viscosity is too low, this results in spraying in the filling gap and in inadequate shear forces; high viscosities, on the other hand, do not cause problems by comparison. However, because of the high energy dissipation and the corresponding heat build up, appropriate measures must be taken to ensure good cooling or supplementary high boiling liquids must be added to prevent the rolls from drying out. The latter would cause irrevocable damage in the form of grooves in the roll surface.

Another, though less important, application nowadays for the three-roll mill is the flushing of pigments. The pigment cake, which is generally aqueous, still wet and therefore not yet or only slightly agglomerated during pigment production, is not dried using the otherwise normal process during flushing, but is converted from the aqueous to the organic phase by treating it with organic binder solutions in kneaders. The intention of the subsequent roll dispersion is less to decompose the agglomerates but more to remove the residual water completely. Consequently, the rolls are not cooled, but are heated with steam to ensure faster removal of the water.

This method enables high tinting strengths and good fineness levels to be achieved with pigments that are hard to disperse. Carbon black pastes manufactured in this way, for example, are used to produce haze free, glossy, deep black topcoats.

Agitator mills are refinements of **ball mills** which used to be encountered relatively frequently. The latter have been displaced more and more by agitator mills because of their poor economy. Their use is now limited to just a few applications in dispersing.

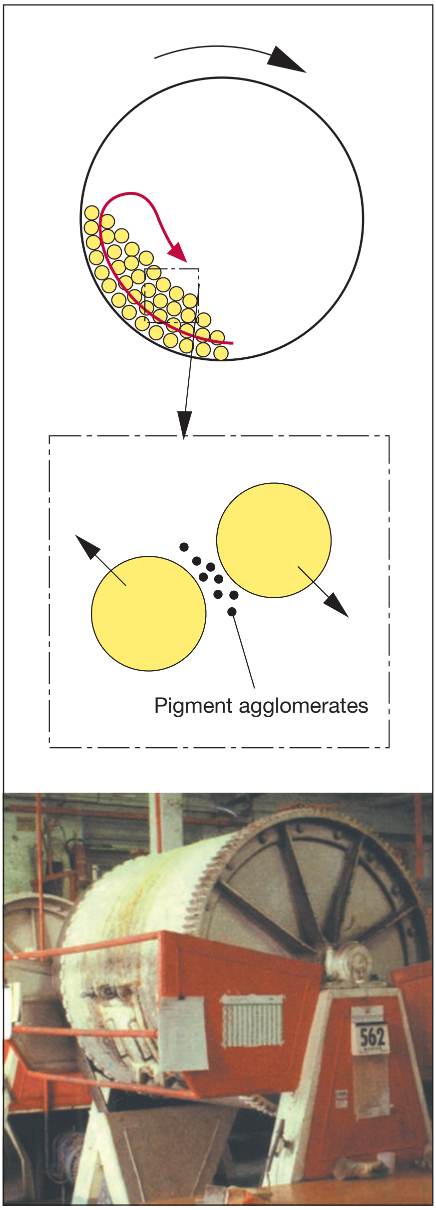


Fig. 2.2.35
Function and picture of a ball mill

Since agitator mills, which have now taken on such significance, were ultimately derived from them, the outmoded ball mills will also be discussed to enable better understanding of their mechanical development.

Ball mills are hollow cylinders which rotate about a horizontal axis in operation. They are filled to about 40% of their volume with mill base and grinding media, generally porcelain or steel balls with a diameter of 20 – 30 mm, in a given ratio. As a result of the relative motion of the grinding balls passing each other at different speeds, friction surfaces are generated which enable the dispersion of the pigments. Above a certain rotational speed the moving grinding media are lifted and cause an additional unwanted impact load on the pigment agglomerates as they fall back down. This results in decomposition of the primary particle, which is associated with a deterioration in the optical power of the pigments. The drum is therefore set to rotate more slowly for roll friction.

The actual dispersion process occurs whenever grinding media pass each other at different speeds and generate the shear stress necessary for dispersion at the point where they are closest together. Upper layers roll downwards, while lower layers are entrained upwards by the mill jacket. Since the movement of the grinding media is caused solely by gravity, but this is a mass dependent variable, grinding media in ball mills must have a certain minimum size. The consequence of this is that the ratio of the effective grinding volume to the total volume is extremely low in ball mills. Noteworthy disadvantages include the associated long dispersal times of up to 5 days, extensive cleaning work and a not inconsiderable noise level.

Because of their closed design, however, ball mills have the benefit of being able to use low boilers as solvents. A further advantage of ball mills worth mentioning is their low maintenance during the dispersion process.

In seeking to improve the unfavourable ratio of the dispersion volume to the total volume, the only variable is the size of the grinding media. However, as the grinding media volume decreases, so the their mass also decreases. The resulting lower gravitational force and, at the same time, the decreasing kinetic energy therefore have an adverse effect on the dispersion rate.

It was, therefore, an obvious step to generate the energy necessary for dispersion artificially by installing additional agitator mills when using relatively small grinding media. One of the first dispersers developed in accordance with this principle in the 1920s in the US was the **attritor**. This consists of an upright milling vessel in which 3 – 5 mm thick balls are artificially moved by means of an agitator.

The mill base is fed into the mill chamber at the bottom and drawn off again at the top. The cycle carries on continually until the required particle fineness or tinting strength has been achieved. The continuing shortcomings of a high level of wear and the high power consumption were largely eradicated by changing the shape and the type of the agitation tools and by making the grinding media even smaller. The attritor became slimmer and taller, with the outcome that it was possible to achieve adequate dispersion after one pass. In principle, therefore, the agitator mill had been invented.

The grinding media, consisting in the past solely of sand particles with diameters of approx. 1 mm, were moved artificially by adapted agitator units, thereby permitting the transmission of substantially higher shear stresses than was previously possible with conventional equipment. The separation of the grinding media from the mill base was and still is to some extent achieved by using wedge wire sieves at the open upper outlet.

However, a one-off pass through the disperser presupposes preliminary homogenization in a separate mixer or dissolver. Such refinements of the milling process brought about a considerable improvement in effectiveness and product quality.

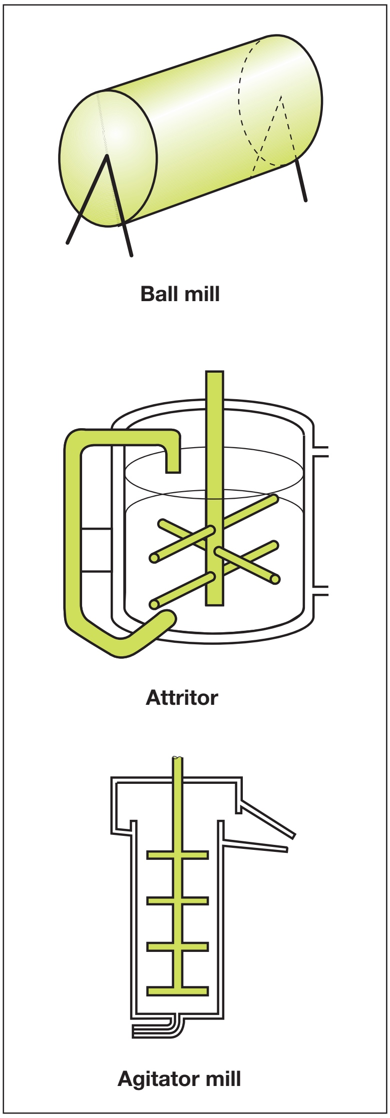


Fig. 2.2.36
From ball mills via attritors to agitator mills

Further optimizations were directed primarily towards the transmission of even higher shear forces and influencing the dwell time range of the pigments.

Agitator mills which were usually open and fitted with wedge wire sieves were increasingly replaced by closed systems. By a closed system we mean a disperser which enables the separation of the mill base from the grinding media by means of friction gaps. Such closed agitator mills bring numerous additional benefits. Dispersion can take place at increased pressure, thereby making higher throughputs possible. Material

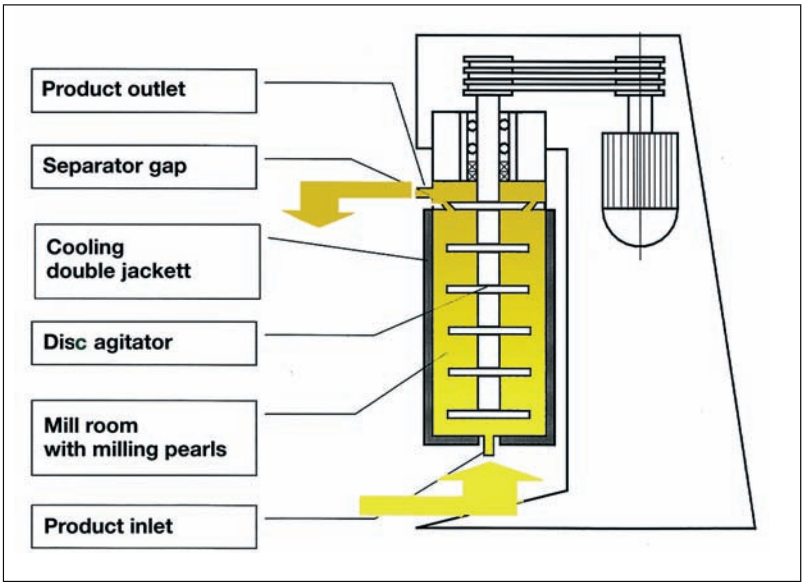


Fig. 2.2.37
Scheme of an agitator mill

feed or material throughput can be varied by means of infinitely adjustable pumps in order to achieve better adaptation of the disperser to material specific features in many areas. As with ball mills, steps must be taken to provide an effective cooling system in agitator mills too.

The grinding media and the mill base lie in the dispersing chamber of the agitator mill as a mixture which is then set in intensive, defined motion by the agitation tools. The grinding media take on varying levels of kinetic energy as a result of friction and impacts at the energy bearing surfaces. High shear forces can then be transmitted at the points where the grinding media interact in the presence of viscous fluids.

Larger grinding media are also suitable for larger pigments because of the better entrainment of the pigment agglomerates into the areas of high shear. With increasing breakdown, however, the number of smaller particles greatly increases. The number of effective dispersal areas is then no longer sufficient with larger grinding media for faster fine dispersion. Optimum conditions prevail, therefore, when larger grinding media with a larger entrainment area ensure preliminary dispersion in the first part of the agitator mill, while the small grinding balls, which have by far the larger total frictional surface area, handle the fine dispersion of the smaller agglomerates. Smaller beads are also generally used for the smaller organic pigments, while correspondingly larger ones are used for agglomerates of inorganic pigments which are sometimes rather large. For those involved in practical operations it is also important that the grinding media and the pigments are of sufficiently different sizes to enable them to be separated without difficulty.

The density of the grinding media also has a bearing on the dispersion effect. Zirconium oxide beads with a density of 5.6 g/cm^3 transmit higher shear stresses to the pigments than conventional sand or plastic particles with densities of only 2.6 g/cm^3 and less under otherwise identical conditions.

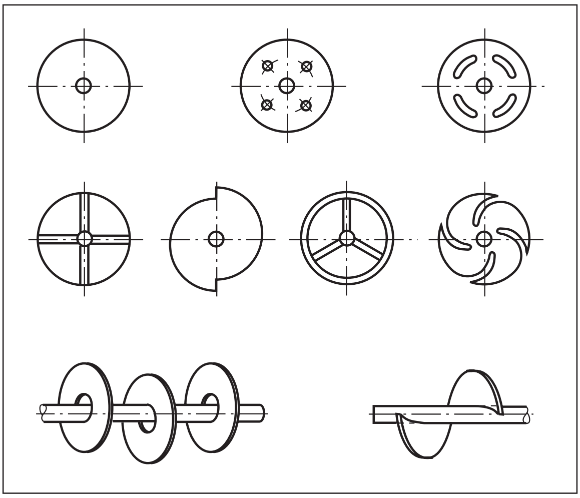


Fig. 2.2.38
Agitator discs for agitator mills

It has already been mentioned that the shear stresses can be increased still further by increasing the rotational speed of the agitator tools. However, the excessive wear of the agitator mills and the grinding media places limits on the increase in speed.

The desire to intensify the milling process therefore also resulted in the refinement of the agitator tools. Solid discs which used to be standard, where shear was caused solely by the adhesion of the mill base to the disc and the centrifugation of the layers lying above this, are being replaced by other designs including spoked ring discs or punched discs.

Punched discs have similar dispersion properties to solid discs. However, the apertures offer the advantage of better removal of the air released by the agglomerates and other materials and of better pressure equalization. Cam discs fitted with projecting impactors have a greater influence on the dispersion effect. Screw discs also deserve mention. They exert an additional pressure on the mill base against its direction of flow, thereby also enhancing the dispersion outcome. The negative aspect is the extension of the dwell time range associated with the return transport.

Since it is not only shear forces in laminar flow, but also tensile/compressive effects which promote the dispersion process, grinding trough shapes have been developed which permit an alternation between areas of underpressure and overpressure. The sectional drawing in figure 2.2.39 illustrates the regular passing of material through compression and decompression zones in a corresponding milling unit.

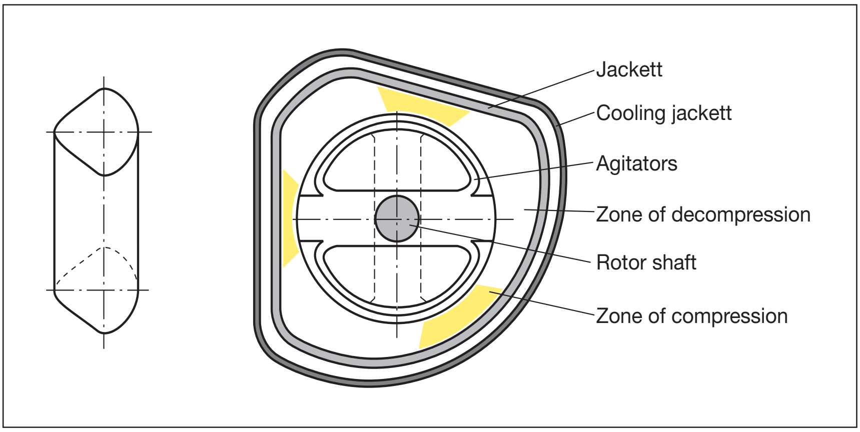


Fig. 2.2.39
Cross section of a chamber of an agitator mill with zones of under- and overpressure

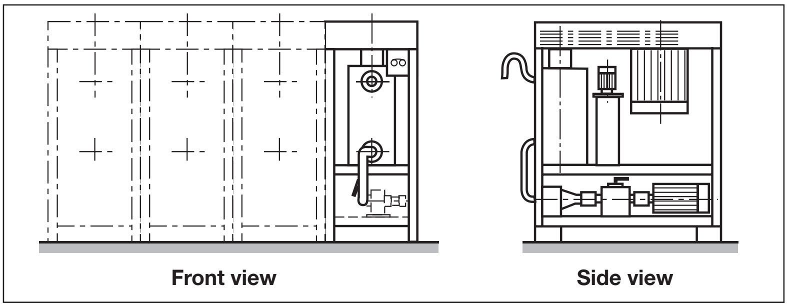


Fig.2.2.40
Scheme of a multi compartment mill

The grinding trough shape also affects the dwell time range of the mill base. High grinding troughs with only a small diameter result in closer dwell time ranges than short and correspondingly wider ones. Commercial mills, however, only show marginal differences.

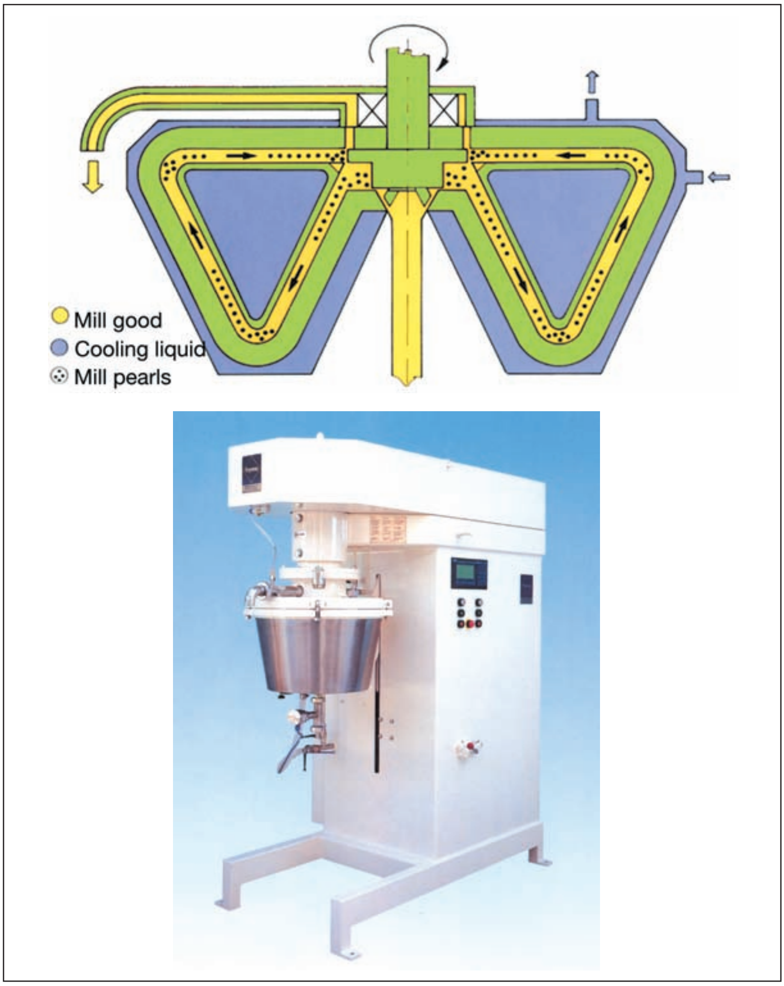


Fig. 2.2.41
Scheme and picture of a ring-gap mill

A different and better way to have a positive impact on the dwell time range is to use compartment mills.

Faster passes with short dwell times through several smaller mills configured in series result in closer dwell time ranges and thus a more uniform pigment loading.

Apart from the design and the rotational speed of the agitator mill the quantity of grinding media also has a decisive effect on the dispersion rate and quality. Open agitator mills have a grinding media volume of 40 – 70%, and closed types up to 90% relative to the volume of the trough. A fundamentally applicable principle is that a high grinding media quantity increases the power consumption and wear of the entire mill unit, while reducing the dispersion duration and generating a high level of heat at the same time. Ring-gap mills were developed to enable high cooling performance and a close dwell time range with a uniform grinding media loading at the same time (see figure 2.2.41). The milling chamber has the shape of an inverted conical envelope whose tip has been folded inwards. The outer wall of the cone is rigidly mounted, while the inner cone rotates. The relatively narrow gap between the rotor and the stator enables high shear forces to be transmitted. Since the flow rate falls with increasing cone diameter, but at the same time the shear stress rises because of high blade tip speeds, the dispersion process becomes more intensive with decreasing particle size. This effect is highly advantageous when decomposing smaller and thus more solid agglomerates. The mill base is then removed via a separation device on the shaft, and the grinding media are separated axially downwards via recirculation ducts.

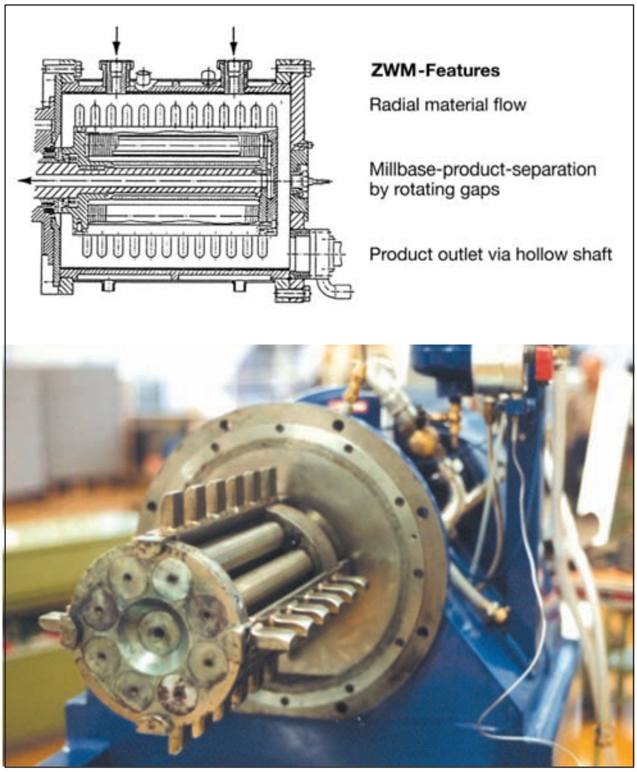


Fig. 2.2.42
Scheme and picture of a centrifugal fluidized bed mill (ZWM)

The centrifugal fluidized bed mill (see figure 2.2.42) uses a different geometrical configuration. This consists of a cylindrical, horizontally configured mill chamber and a rotor, fitted with 8 rows of blades and 8 wedge wire sieve tubes. The grinding media contained in the mill are moved by the blades. The material to be dispersed flows by means of three feed pipes from the outside to the inside radially through the rotating grinding media bed to the wedge wire sieve tubes which are also rotating. At this point the material passes through a relatively large separating plane and then exits the milling chamber via a hollow shaft. As a result of centrifugal forces the pressure of the grinding media is adjusted independently of the product throughput. High specific throughputs are possible as a result [2.4.71, 2.4.72].

Medium and small paint plants in particular use basket and immersion mills in addition to high performance agitator mills. Basket and immersion mills are vessels that permit flexible use, in which a mobile dispersion unit is immersed after filling with mill base. This unit consists of a sieve-like grinding trough holding the grinding media which are intensively agitated by appropriate equipment. At the same time the mill base is entrained into the dispersion chamber and discharged again after dispersion.

A combination of a basket mill with a dissolver represents an interesting variant. This enables the preliminary dispersion to be carried out in the dissolver and the subsequent fine dispersion in a agitator mill in a closed system.

In immersion mills the rotor is also responsible for circulating the liquid. Dispensing with a pump means that the viscosity spectrum of the mill base is limited. The mill base composition must be determined and assessed for this type of agitator mill in accordance with similar criteria to those used for other agitator mills (see above). The optimum energy input when operating agitator mills is achieved when the mill base has a relatively low viscosity. There are limits to the degree to which the viscosity can be reduced because of the increasing wear of the grinding media and the mill. Furthermore, it is worth noting, when using mixtures with high solvent levels, that problems should be anticipated because of pigment shocks when lacquering.

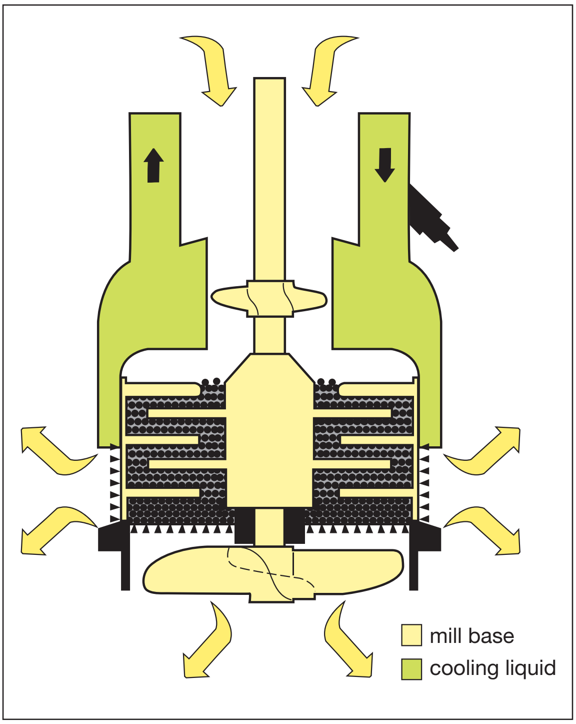


Fig. 2.2.43
Scheme of an immersion mill

Agitator mills are still the most economical and thus technically important type of disperser. The large variety of individual types is the result of the wide range of mill base formulations. The most important criterion for the technical evaluation of agitator mills is the ratio of throughput to power consumption with the closest possible dwell time range for the pigments.

In addition to the type of agitator mill the milling process sequence or operational method plays an important role in the production output and dispersion quality. For easily dispersible pigments one pass using the pass method is sufficient. In this the homogenized mill base as per (A) in figure 2.2.44 is conveyed from one vessel via the agitator mill into a second vessel. The milling process is repeated if the quality is below standard. Generally feed or receiving containers are swapped or, in the case of stationary vessels, the feed and discharge lines are changed over. Most pigments require 2 – 3 passes, though this swinging process may have to be repeated 5 – 10 times with pigments which are harder to disperse. The cascade method represents a continuously operating alternative in which the products pass through several mills in succession as in example (B).

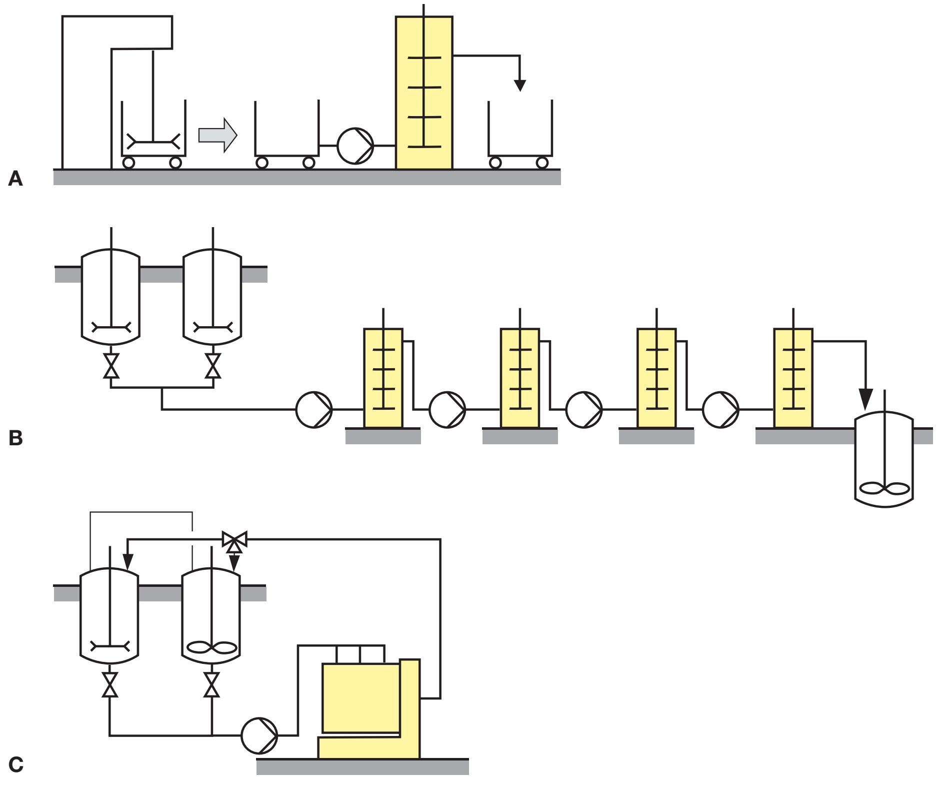


Fig. 2.2.44
Process flows of dispersing techniques by passages (A), cascades (B) and cycling (C)

This configuration can also be used for the cycle method (C) which requires only one vessel from which the mill base is continually charged and then returned via the agitator mill. To ensure that each volume element of the feed vessel has passed through the mill, a statistical approach would require that 5 – 10 times the vessel capacity be pumped through the system. The volumetric rate of flow should therefore be about 10 times higher than in the pass method. A critical point in the cycle method is the necessity for constant and thorough mixing of the material in the feed vessel. The possibility to use a process monitoring system is an advantage. Milling progress can, for example, be correlated with and checked by means of the energy consumption (see figure 2.2.44).

If dispersion with classic dispersing equipment is no longer possible because of excessively high viscosity of the mill base, **kneaders** must be used [2.4.73]. Their use is essential when fillers or flush pastes are to be manufactured. Kneaders must be designed such that they are particularly stable because of the high compressive and shear stresses to which they are subjected and are therefore generally closed systems.

Kneading systems are divided into **paddle and screw type kneaders**. The first group includes trough, double trough and planetary kneaders, while single and double screw kneaders are examples of the second. The first type, particularly double trough kneaders, transmits the shear forces necessary for dispersion of the highly viscous mill base with counter rotating scoops adapted to the housing. As a result of the special design, the material is regularly conveyed from one section of the kneader to the other. Planetary kneaders are similar to conventional mixers. Several kneading arms which project into the mixing vessel and are fitted with small but stable agitator blades describe a circular path while rotating themselves at the same time in a mixing trough which has a suitably stable design to withstand the high shear forces. The shear forces which can be transmitted in planetary kneaders are lower in general than those in double trough kneaders.

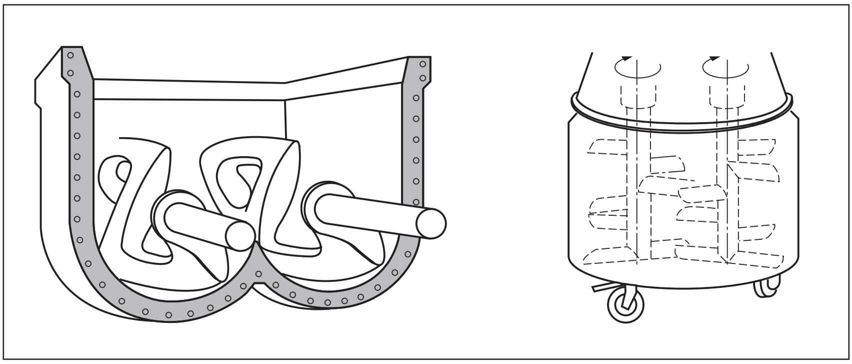


Fig. 2.2.45
Scheme of a paddle kneader and a planetary kneader

Screw type kneaders operate in accordance with a different principle. Simple types consist of a tube in which a cylindrical shaft with a screw shaped metal band rotates. This conveys the mill base to the kneader outlet under shear load. The height of the shear forces can be significantly increased by means of slots milled in the screw,

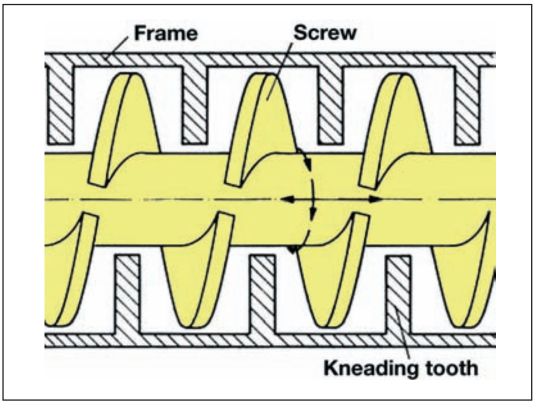


Fig. 2.2.46
Scheme of a screw type kneader

kneading teeth mounted on the housing and the oscillating motion of the agitator shaft.

Machines for manufacturing powder coatings

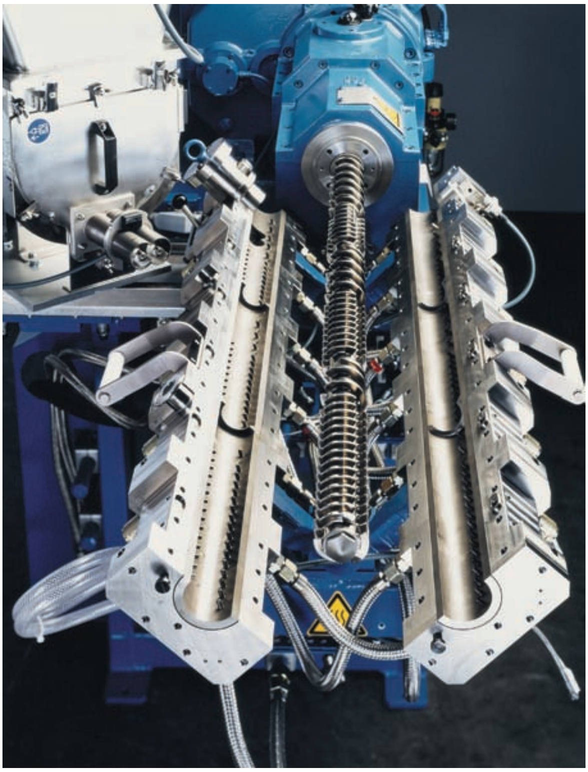


Fig. 2.2.47
Picture of a single screw extruder for manufacturing powder coatings

Heatable kneaders are used in the paint and coatings industry for dispersing powder coatings. The material to be dispersed, which is solid at normal temperatures, is melted and then used as a fluid to transmit the shear forces necessary to crush agglomerates.

Because of the lack of solvents and the associated high viscosity of powder coatings, conventional production techniques are not suitable for the homogenization of the resin components and the incorporation of pigments and extenders. The individual components are therefore homogenized or dispersed in the extruder after melting. In preparation for the melting process steps should be taken to premix the formulation ingredients as effectively as possible. This works especially well if the individual solid components are correspondingly well crushed in advance. Since the solid resins are supplied in coarse form by the manufacturer, homogenization should be preceded by decomposition of the brittle raw materials by crushing and milling to particle sizes of just a few millimetres. Once weighing and adding of all the formulation ingredients have been completed, mechanical premixing takes place in tumble or plough mixers. The actual dispersion of the pigments in the polymer matrix can be carried out without difficulty in a kneader after melting with thermoplastic nonreactive systems. For reactive systems, on the other hand, conventional kneaders operating in batch mode are unsuitable because of the excessive dwell time of the thermally stressed melt. Continuously operating extruders are used for this application. They are capable of homogenizing the melt just a few degrees above the melting point, i.e. when it still has a relatively high viscosity, with dwell times of only a few minutes. The shear forces are high enough to crush the pigment agglomerates and achieve uniform distribution in the continuous resin phase.

Action needs to be taken to ensure the best possible preliminary homogenization and cooling in the feed zone to prevent the raw materials from forming lumps. Precise control of the temperature curve over the entire extruder range is also important.

Oscillating single screw extruders, planetary roller extruders and double screw extruders have proved themselves suitable extruder types in practical operations.

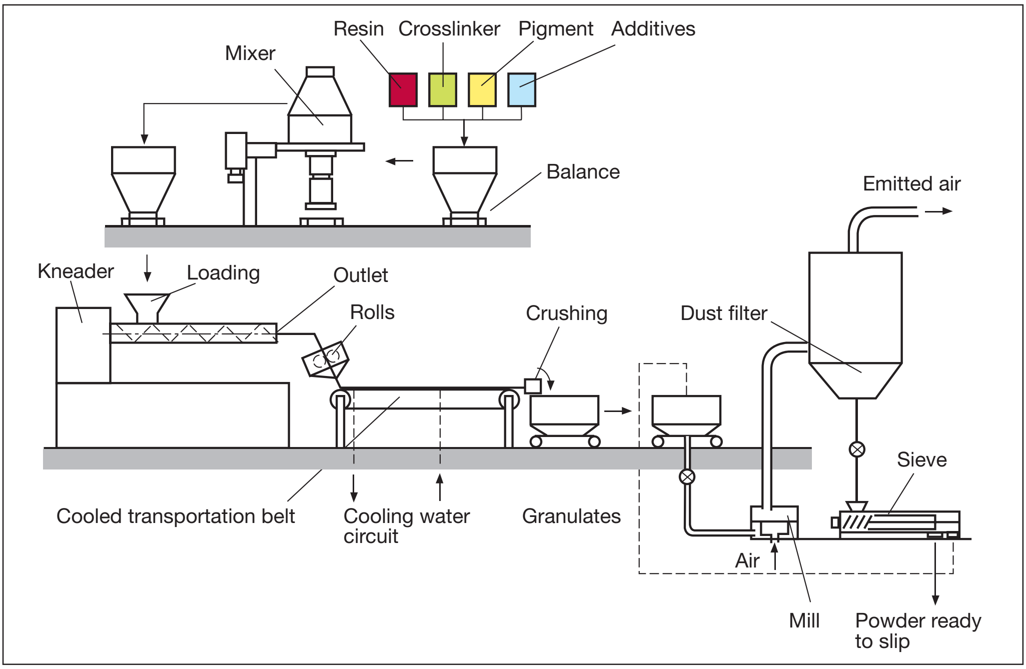


Fig. 2.2.48
Classical process flow for manufacturing powder coatings

The shear forces to be applied for dispersion are generated in the single screw extruder by a screw oscillating in the material flow direction. This enables extremely high shear forces to be transmitted between the screw and the matched screw liner. A similar effect can be observed when planetary rollers move about a central screw. High shear forces are also generated by permanently changing the gaps and by the rotary motion.

In double screw extruders the shear gradient required for homogenization and dispersion is generated by two meshed, counter rotating screws. An appropriate configuration of the shafts enables alternating compression and decompression to produce the required shear forces. Double screw extruders are especially suitable for reactive melts because they have a melt dwell time of less than 30 seconds.

A suitable system must be in place to ensure rapid cooling of the reactive melt immediately on exiting the extruder. The outcome of this is that the still liquid mill base is drawn by two cooled rolls into a wide sheet that is only a few millimetres thick.

Conveying the product on a conveyor belt which is also cooled further accelerates the temperature drop. On leaving the cooling section the extrudate is converted back to a granulate material in suitable crushing systems. In order to make a processible powder coating from the material manufactured in this way which is still relatively

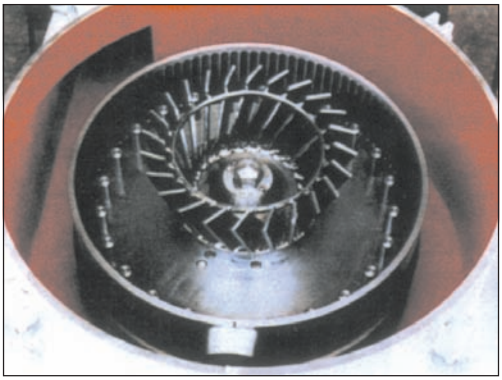


Fig. 2.2.49
Pin mill for grinding powder granulates

coarse, fine grinding and pulverizing stages must follow. The usual target particle sizes are < 100 µm for relatively thick and < 50 µm for relatively thin film layers. Grinding of the powder coating granulates is generally carried out in pin, impact disc or cone mills.

All the systems work in accordance with a similar principle. The particles to be grinded are accelerated to a great speed and then crushed by means of an impact or friction against the sides of the vessel. The air required for this acceleration is cooled to prevent the powder coating particles from sticking together.

When the powder articles exit the milling units they are separated according to their levels of fineness by means of cyclones, vibrating and rotary sieves or filter systems. Selection of the separating system is based on the desired particle size or particle size distribution (see chapter 4.2.2).

In the light of the large energy input for the homogenization and decomposition of the powder coating particles, there has been no shortage of attempts to develop alternative production processes. Of the possibilities investigated on a laboratory scale, spraying the polymer melts with supercritical carbon dioxide [2.4.74] or ultrasonic pulverization are undoubtedly the most interesting. To pulverize using ultrasound resin melts are introduced into the oscillation nodes of a standing sound wave.

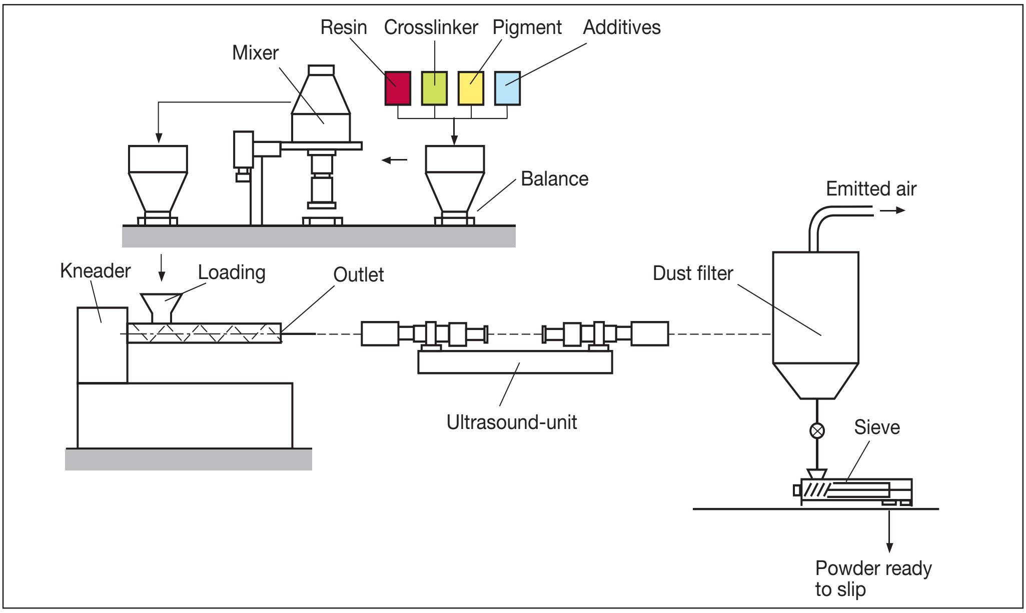


Fig. 2.2.50
Manufacturing of powder coatings via ultrasound technique

The resulting particles solidify on cooling down and, by contrast with the fantastically varied conventional powder coating particles, yield a spherical powder with a close particle size distribution.

The use of the ultrasonic standing wave pulverization method could simplify the conventional production process. The homogenized melt travels via a nozzle directly into the ultrasonic field where the decomposition into spherical particles takes place. The resulting powder is subsequently sieved and packaged. This production method enables the stages of rolling, cooling, primary crushing and the grinding and sieveing process with its high energy requirement to be dispensed with. The spherical particle shape also offers the advantages during processing of improved transport in pipelines and containers, a more uniform charging and therefore also a more even deposition on the substrate. All these advantages are attributable to the minimization of the contact surfaces of spherical particles. The process has been tested on a laboratory scale. Numerous preliminary investigations still have to be conducted, however, before large scale use can proceed [2.4.75].

2.2.4.4 Separation Processes in the Manufacture of Paint

In the paint manufacturing industry numerous separation processes also have to be carried out during the production of pigmented and nonpigmented coating materials. Examples include the partial or complete removal of solid particles from liquids, the separation of grinding media in the wedge wire sieves of agitator mills, the recovery of hard agglomerates or the removal of foreign matter before the coating materials which are ready for dispatch are transferred to their relevant containers. The separating operations are carried out in sieveing and filtration units or by accelerated sedimentation in centrifuges.

Sieving and filtration

Sieving or screening is a sizing process and is used for fractionating mixtures of solids. This can take place in the gaseous phase or in a liquid phase.

The principle of **separation by sieves** lies in offering up the solid particles to be separated as frequently as possible to the openings of the sieve surface. The aim is to permit smaller particles to pass through, while holding larger ones back. The sieves with their defined openings are made of metal, organic fibres or plastics. These are divided into perforated, woven or clamped sieve surfaces, depending on the design.

To ensure a consistent longterm separating effect it is important to ensure that the sieve design does not permit any shift, i.e. any enlargement of the openings. The necessary

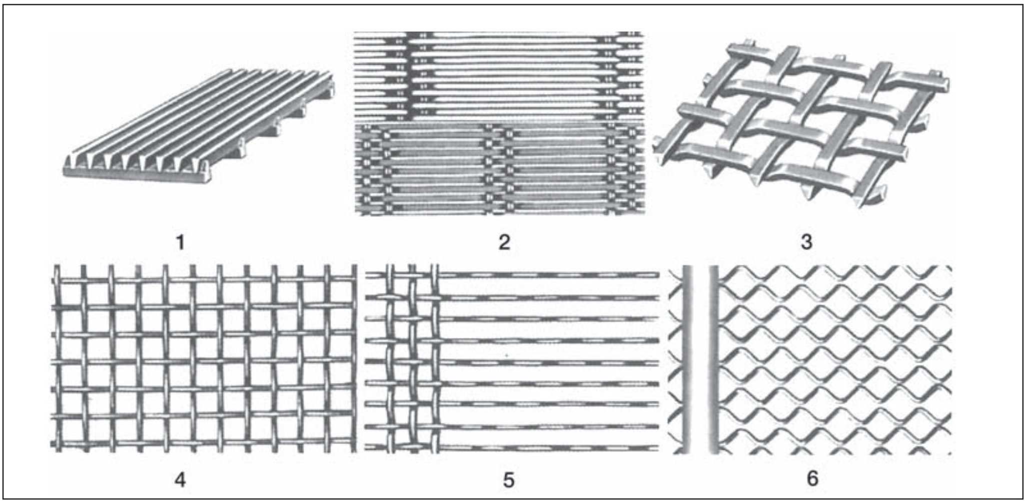


Fig. 2.2.51
Different forms of sieves

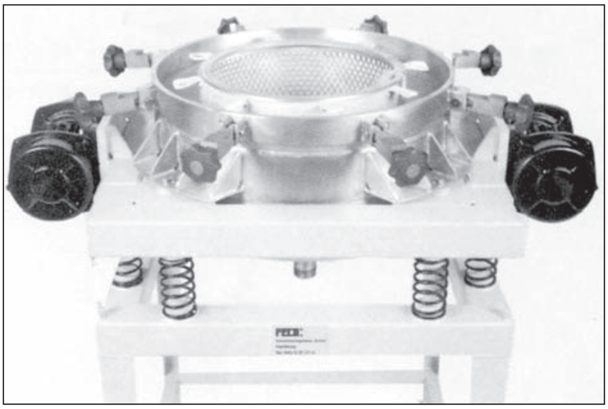


Fig. 2.2.52
Vibrating sieve

stability in the sieve surface is achieved by the use of monofilament yarn, a fixed weave in the fabric and nonswelling materials. It is also important in practice to use materials which are not attacked by the material being separated. Depending on the material to be separated, solvent, acid, alkali or bacteria resistant sieve fabrics should be used. When dealing with hot materials ensure that the heat resistance of the used materials is adequate.

High specific separation performance is achieved when all particles are offered up to the sieve openings as frequently as possible by inducing movement of the material to be separated. The frequency with which material is offered up can be increased by horizontal or vertical motion and by vibration.

One proven form of sieve system consists of a vertically configured sieve device through which the material to be cleaned is pressed. The sieveing residue is continuously released by vibrations and then removed via gravity sedimentation.

Rigidly fixed, nonmoving sieves can only be used where there are extremely large particle size differences, such as those that occur when separating the mill base from the grinding media. The separation of foreign matter when transferring coating materials to their storage containers by passing the materials through sieve bags is also impossible without the use of artificial sieve movements.

Filtration is the separation of solid particles from suspensions with the aid of porous filter media. Strictly speaking, therefore, the filtration process is the complete separation of solids (filter cake) from the liquid phase (filtrate). Depending on the purpose of the filtration process, the treatment of the liquid is termed clarification, and separation of the solids is termed cake filtration.

The treatment of pigmented coating materials to separate foreign matter and any agglomerates still present is a sieveing process, if the definition is accurately interpreted. Because of the small size of the pigments the term ”filtration” is applied when fine and extremely fine sieves are used although the dispersed pigment is still in the filtrate. Whether such processes are termed sieveing or filtration in the paint and coatings industry depends merely on the degree of fineness of the separation system.

Filtration processes are divided into surface filtration, cake filtration and deep bed filtration, depending on the separation method employed. Surface or sieve filtration is a method of solids separation which obeys the laws of sieveing. It is used when only small quantities of solids have to be separated by means of fine sieve bags with pore sizes of up to just a few micrometres (clarification).

Cake filtration is a separation process in which the solid cake accumulating on the partition also serves as a filter aid at the same time. It enables the isolation of large

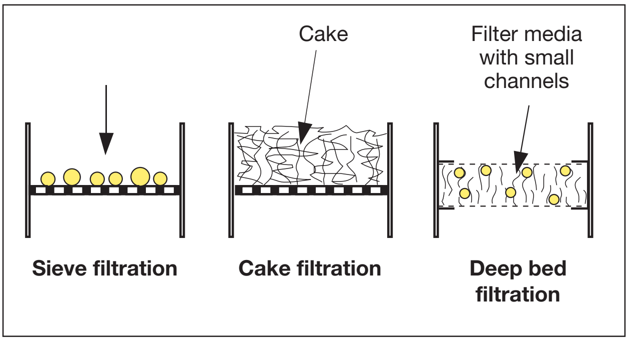


Fig. 2.2.53
Principles of filtration techniques

quantities of solids. With a pure surface filtration system all the solid particles are larger than the openings in the perforated plate. With cake filtration this is only partially true. In the course of the filtration process the solids form a cake which then enables the separation of finer particles. In both processes the solids are deposited above the filter medium.

The principle of deep bed filtration is quite different. This uses thicker filter media with larger pores than the diameter of the solids to be separated. As a result these penetrate the labyrinth of the channels in the filter medium where they are lodged either mechanically in relatively narrow side passages or adsorptively on the internal walls of the capillaries.

Because of the fineness of the pore labyrinth deep bed filtration is not generally carried out with pigmented paints. Deep bed filtration is mainly used for purifying clearcoats and binder solutions. The mechanical choking of the channels, by contrast with purely adsorptive separation, results in a decrease in filter performance. On the other hand, the adsorptively retained particles can be transported more or less quickly through the channels if filtered for long enough, depending on the size of the attractive forces, with the result that deep bed filters can ”blow” after excessively long use.

Deep bed filtration allows even relatively small gel particles, i.e. deformable particles, to be separated if their diameter is small enough. Larger gel particles, on the other hand, choke the pores of the filter medium and result in a rapid drop in filter performance.

To prevent blockages in the fine filter channels, supplementary filter aids are frequently used to clear critical suspensions. These include diatomaceous earth, fuller’s earth,

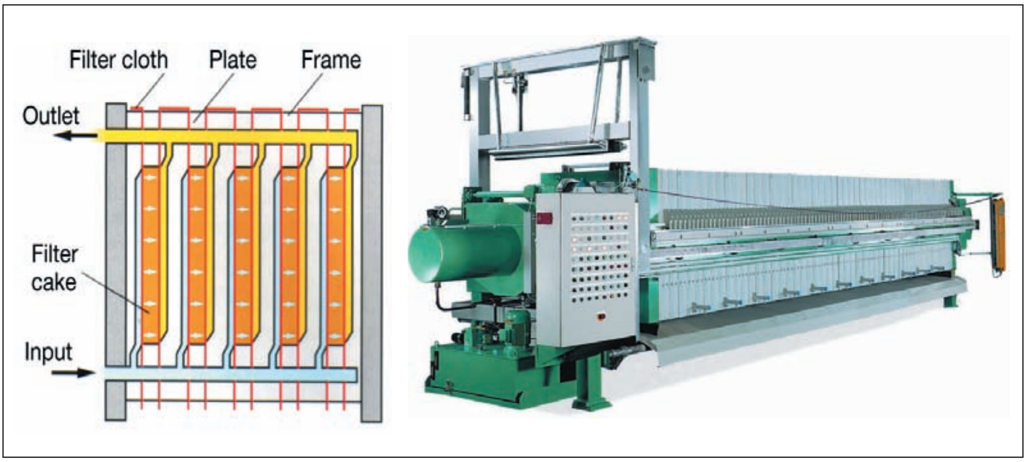


Fig. 2.2.54
Scheme and picture of a plate-and-frame filter press

activated carbon or fine plastic grains with particle sizes of 5 – 50 µm. These are either stirred into the suspension or are coated on the filter beforehand. As a result of adsorption by the filter aid the especially critical elements of the material being filtered are practically retained in the artificially created filter of the filter aid. Constant filtration entails only a small rise in pressure because fixation on the filter aid is overwhelmingly adsorptive. The advantages of filter aids can be increased still further if only part of the filter aid is added to the material being filtered after the rest has been used to form a coating on the filter medium. Filter aids ultimately transform deep bed filtration into cake filtration.

Filtration devices are important for the separation processes in the paint and coatings industry, and there is an enormous variety available. Particular mention may be made of plate-and-frame (see figure 2.2.54) and chamber filter presses for cake filtration, and bag and plate filters for the usual clearing processes during the manufacture and use of paints, because of their importance in these processes

The main differences between the plate-and-frame filter press and the chamber filter press are its larger chamber volume of the former and the option of carrying out flushing and washing operations. It is therefore used for filtering suspensions with a high solid content, such as in cake filtration for recovering pigment powder during the manufacture of pigments, for example.

Chamber filter presses are used for the clarification filtration of suspensions with lower solid contents (for example contaminated clearcoats or binder solutions). Both filter presses comprise numerous modules made of iron or aluminium, connected in parallel. The filter surface area can be varied at will by changing the number of plates.

Depending on the filter medium, the filter material consists of cotton or synthetic fabric. Gear pumps are preferred to piston pumps to achieve uniform filtration quality because of the pulsating pressure build up.

A variant which is of interest for paint and resin manufacturers is the plate filter. By contrast with plate-and-frame or chamber filter presses, these do not have a fabric pressed between the metal segments, but cellulose or plastic reinforced plates. The film thicknesses of these filter media lie between 2 and 6 mm, and the pore size is approx. 0.8 – 15 µm.

Particularly good filter performance is achieved by double filtration using different pore sizes.

Cartridge or tubular filters, which are relatively small and easy to install, are also used for cleaning a very wide variety of coating materials.

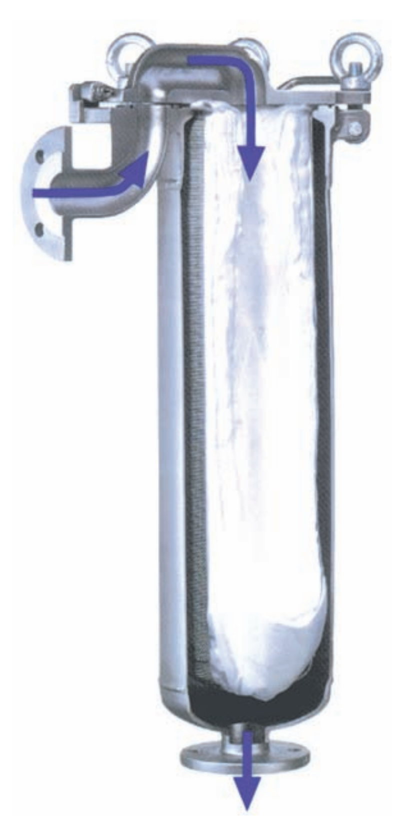


Fig. 2.2.55
Bag filter equipment

The filter elements are cylindrical cartridges made of paper, felt, synthetic fibres, porous clay or ceramic materials. The synthetic fibre cartridges have proved particularly successful because of their good depth effect.

In recent times the importance of filter cartridges has waned in favour of bag filters. While the first filter bags were practically nothing more than bag shaped sieves, there are now numerous different types that offer a level of depth action which can otherwise only be matched by plate filters. The reasons for the increasing importance of bag filters are essentially commercial. Higher throughputs, lower costs for rigging and derigging, lower material costs and less waste merit particular mention. Certain bag filter materials even allow the type of foreign matter which causes craters to be removed.

Sedimentation

Solid particles of different sizes can be separated from the liquid phase selectively or completely if there is a difference in density between the liquid and dispersed phases. With gravity sedimentation the acceleration due to gravity g and, in the opposite direction, the frictional forces of the fluids act on the solid particles. In the stationary state the following applies to the sedimentation rate u

$$u = \frac{\Delta\rho \cdot g \cdot d^2}{18 \cdot \eta}$$

The relation shows that high sedimentation rates and thus short separation times are only possible with high differences in density $\Delta\rho$ between the particles and the fluid phase, large particles and low viscosity η. The particle size d has a quadratic effect on the result. Because of the very low deposition rate of small particles and thus the long separation process, methods are used which achieve sedimentation via centrifugal acceleration $4\,\pi^2\,n^2\,R$, where R is the distance from the axis of rotation.

$$u = \frac{\Delta\rho \cdot 4\,\pi^2 \cdot n^2 \cdot R \cdot d^2}{18 \cdot \eta}$$

The acceleration forces are generated in rotating drums. In the course of this process the mixture to be separated is spun outwards, thereby forming a liquid ring on the drum wall. The relative speed of the liquid to the wall is zero when stationary. The centrifugal force acting during the accelerated separation of the solid particles is quantified by means of the relative centrifugal force C. This is defined as the ratio of the effective centrifugal acceleration to the acceleration due to gravity g.

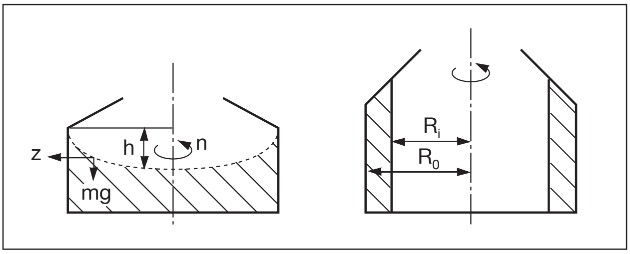


Fig. 2.2.56
Scheme of fluid distribution in a centrifuge

$$C = \frac{4 \cdot \pi^2 \cdot n^2 \cdot R}{g}$$

Depending on the drum diameter, sufficiently high migration rates are achieved at rotational speeds of 5,000 to 20,000 rpm.

The relative centrifugal force for normal centrifuges is around 200 to 4,000, and between 4,000 and 50,000 for super centrifuges. Thanks to the enormous increase in the migration rate of small particles (gel particles or agglomerates) in only averagely fast technical centrifuges, it is possible to separate hard residual agglomerates from already dispersed primary particles. The flow rate determines the critical particle diameter. Even gel particles can be separated completely in this way, provided the density differential to the polymer solution is large enough.

The centrifugal separation method has been implemented in various designs. Because of their different separation principles, a distinction is drawn between solid bowl and sieve centrifuges. Sieve centrifuges are ultimately merely an accelerated form of sieve filtration. Just like decanters as simple solid bowl centrifuges or the very high speed, yet very small tubular centrifuges, they are of virtually no importance for the paint and coatings industry.

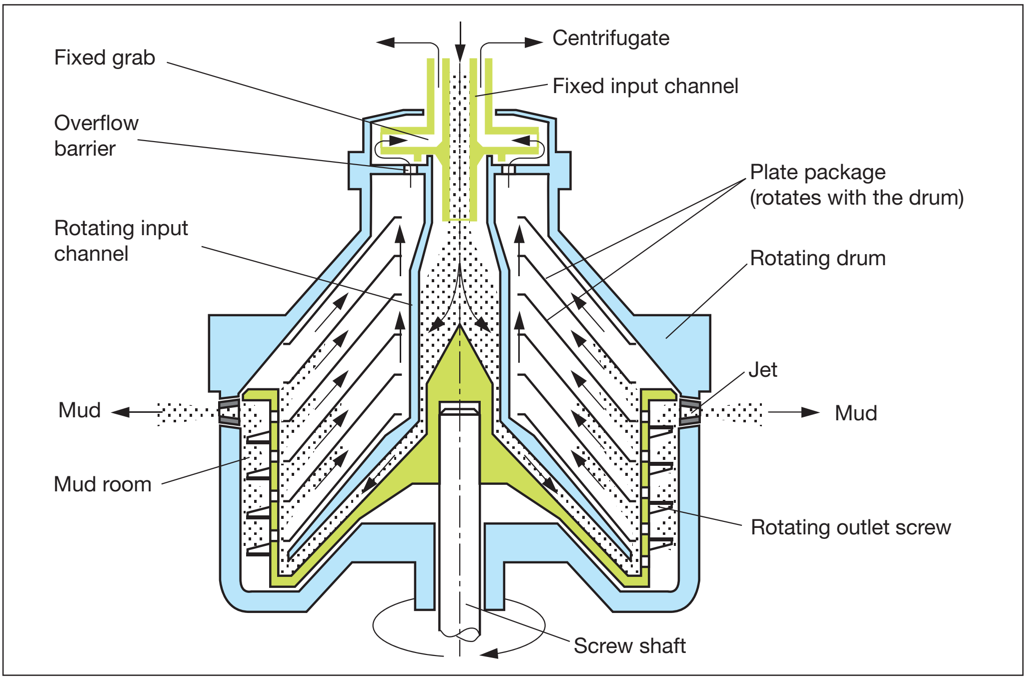


Fig. 2.2.57
Cross section of a disc centrifuge

By contrast, separators are important devices for the aftertreatment of resin solutions, clearcoats and pigmented coating materials. With a blade tip speed of 160 m/s they reach 6,000 to 8,000 times the acceleration due to gravity.

Nowadays, however, centrifuges are only used where other separation processes are unsuitable. The reasons for this are their lower power, the high operating input for a discontinuous process and safety aspects.

Separators or disc centrifuges in the form of solid bowl centrifuges have a large number of conical discs configured in parallel. The paths travelled by the materials to be separated are very short in such systems. The solid particles are pressed against the disc wall and, because of centrifugal force, are transported against the liquid flow to the

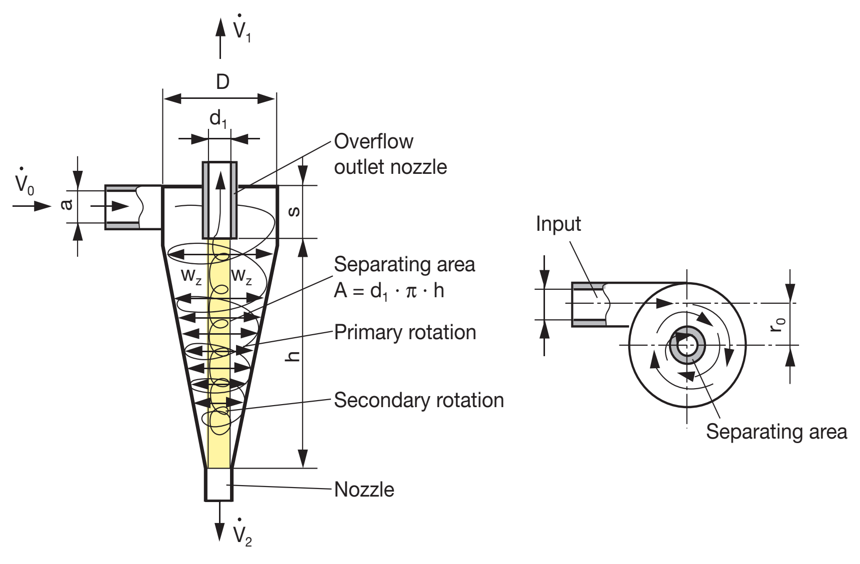


Fig. 2.2.58
Scheme of a hydrocyclone

solids discharge point. The flow rate of the suspension determines the critical particle diameter. Separators are therefore especially suitable for separating expensive, reusable pigment agglomerates.
Hydrocyclones are particularly simple, but not very effective separators for suspensions. By contrast with centrifuges it is not the housing but the liquid which rotates. The rotary flow is induced by the tangential feed of the suspension into a housing which is cylindrical at the top but tapers towards the bottom. Centrifugal forces are generated as a function of the feed rate and the diameter of the cyclone which cause the solid particles to move towards the side walls. This principle is of great technical importance in the form of the aerocyclone which uses air as the medium for the classification and recovery of powder coatings (see chapter 4.2.2).

Practical examples

Separation processes are useful for almost all stages throughout the manufacture of paints. Clearing operations are required right back at the manufacture of polymer solutions by chemical synthesis and the subsequent creation of solutions. In paint manufacture a distinction has to be drawn between the production of clearcoats and pigmented systems or effect paints. While the aftertreatment of clearcoats serves merely to eliminate foreign matter, the treatment of pigmented systems and effect paints is intended to achieve a partial separation of foreign matter and oversize material.
There are few cases where it is more sensible to separate hard agglomerates and reuse them as raw materials in other production stages than to damage the products by excessively frequent and aggressive dispersion. The separation processes therefore relate to formulation ingredients and foreign matter which is not part of the formulation. Since it is not possible to draw a hard and fast line between agglomerates, aggregates and primary particles, the separation measures change important paint properties. For example, the separation of pigments at critical particle diameters which are set too low

can alter the hiding power, color or effect to such an extent that material corrections are necessary.

Foreign matter or formulation ingredients which are to be separated can be rigid (agglomerates, aggregates) or have a changeable outer form. Because of their mobility, length and very small diameter, fibres and fluff must be separated using different methods from those used for gel particles which are deformable almost at will.

The process and filter medium to be used are essentially determined by the nature of the material to be separated. In the case of metal fabrics and filter cloths which act in two dimensions, mesh sizes of 10 – 60 µm are usual. The elimination of foreign matter from solid color paints is generally achieved by means of bag filters with mesh sizes of 5 – 50 µm. It is much more difficult to remove foreign matter from metallic paints since the materials creating the effect are particularly large, in one plane at least, because of their platelet shape. Vibrating sieves with slit type openings are generally used to enable the bronzes to pass without problem.

Three dimensional deep bed filters with their fibrous filter plates have far smaller pore diameters. However, it is not only the ratio between the particle diameter and the mesh size which is important for the ability to pass and the clarification effect; the rheological properties and the surface tension of the suspension are deciding factors in addition to the particle shape and structure. Further influences are exerted by the solvent and the charge of the dispersed particles.

A further important variable in optimizing filter performance is reducing the viscosity by increasing the temperature of the material being filtered. If, for example, the temperature of an alkyd resin solution is increased by 50 °C, the viscosity drops to such a level that the filter performance is increased 5-fold. Excessive heating can, however, also have a detrimental impact on the filtration effect, for example if foreign matter or dirt particles passes into solution when heated up and then precipitates again after filtration when it cools down.

In many cases it is expedient, if very fine foreign matter is present, to precipitate this material first by adding suitable flocculants so that this foreign material forms larger aggregates. This process is divided into bridging flocculation by bipolar resin molecule chains and coagulation by direct deposition on solid particles (see chapter 2.2.3). The phenomenon of flocculation, which is undesirable during paint manufacture, is deliberately induced in this particular case. Polymer compounds or metal salts are used as flocculants.

2.2.5 Summary

The manufacture of coating materials is a technical process which has been optimized from economic and environmental perspectives and which is composed of numerous basic operations. Transportation, metering, homogenization in agitators and dispersers with subsequent separation processes by sieveing, filtration and centrifugation are the most important processes during the journey from raw material to coating material. All the production stages are subject to scrutiny by relevant laboratories. Formulations developed by the labs address not only the economic aspects but also the quality standards and environmental regulations. The specific task for a paint manufacturer – manufacturing a semi finished product which will be converted into a coating at a later date by technical equipment or people – requires special coordination between technical practice in production and application and the theoretical background.

The central task of pigment dispersion forms part of the complex sequence of wetting, thorough moistening of the agglomerates with the film forming agent solution and the subsequent mechanical stress in viscous laminar flow gradients. When it comes to rapid and complete dispersion, the pigment type, size and form are variables in just the same way as the polarity, size and form of the polymer molecules. The latter play a fundamental role in shaping the rheological properties and the surface tension of the film forming agent solution.

The pigment stabilization necessary if pigmented coating materials are to be usable can be achieved by coating with ions and the associated formation of electrical double layers or with sufficiently long mobile and well solvated polymer chains with as complete a coating as possible.

Optimum conditions can only be identified to a limited extent by theoretical considerations. Experimentation is therefore still the indispensable way of determining the optimum grinding conditions.

2.3 Characterization of Coating Materials

Coating materials are semi finished products which have to meet a large number of requirements relating to storage stability, processing and properties. It is absolutely essential for the paint manufacturer to manufacture individual products with a consistent quality level which conforms to the agreements made between the manufacturer and consumer. Numerous tests have to be carried out so that the desired property profiles can also be guaranteed. The demand for consistency in processing conditions must always be linked to the requirement for consistent coating quality (see chapter 6.1 and 6.5).

It must be borne in mind that the term ”quality” is a variable which cannot necessarily be forecast on the basis of the composition of the coating materials. Although well defined physical indicators such as density, viscosity or surface tension, for example, are necessary in evaluating property profiles, they are far from enough to permit binding statements to be made about the processibility and final properties of a coating.

All attempts to control the raw material property fluctuations, which cannot be avoided completely, and the absolute reproducibility of the technical process of paint production, which is just as impossible to guarantee, have resulted in a position where the paint manufacturer’s task is seen as less about the identical combination of raw materials and more about the creation of an identical property profile. The term ”property” refers equally to processing and film properties. Fluctuating product quality is tolerated less and less with industrial scale painting processes because of increasing automation. Achieving identical properties in two batches therefore has priority to a certain extent over achieving an identical material composition. Processing performance on the paint processor’s individual coating lines cannot be forecast solely by reference to physical performance indicators. Only when processing has been carried out under the processor’s own conditions with all the tiny variations that this may include or when a comprehensive audit has been made of the application properties by statistical methods is it possible to make a binding assessment of the processing properties of coating materials.

An overview of the physical and processing properties of coating materials can best be drawn up if the requirements and demands are discussed in detail in advance. Issues to be addressed in particular should include storage stability, consistency of application properties with the various processes and, not least, the film properties. The permanent shear stress in the circulation systems or the circulation in dip tanks, for example, should not cause any changes in color, effect or rheological properties of the material. The latter is also a significant variable with regard to flow during the film forming process.

Because of the numerous requirements relating to properties and processing performance, the parties involved draw up agreements specifying every detail relating to the quality level and the permitted tolerances. Such specifications or technical terms and conditions of sale contain an exact description of properties but also information on relevant measurement and test methods (see chapter 8).

For the liquid coating material which is still to be processed the deciding criteria are the stability of the product, environment related aspects and suitability for application. A distinction must be drawn here between application properties which are determined directly and general physical indicators which can only provide indirect information on application properties.

The first group includes all the practical tests to determine the tendency to run, flow properties and the formation of film faults in the form of pinholes or craters. The indirect test group involving the measurement of physical indicators includes viscosity, surface tension, density and, with special reference to pigmented paints, hiding power, tinting strength and fineness of dispersion.

Quality assurance procedures are not limited, of course, to the use of measuring equipment. Only a comparison of measurement results with the agreed property and production tolerances provides the desired information on acceptance or rejection. So measuring becomes testing and thus an important element in quality assurance (see chapter 6).

Furthermore, not all test methods yield binding, precisely defined indicators. Many property profiles simply have to be assigned a rating. As specified in DIN 53230, ratings ranging from 0 as the best to 5 as the worst result should be awarded while this scale is from 10 – 1 in North America. Creating standardized images and using these as a guide during the evaluation process has proved a successful method of objectifying the test results in many cases.

Test methods and evaluation criteria originally drawn up by the individual paint users and specified in writing as in house standards cause paint processors a large amount of work because of the number of test instruments they have to use and test methods which have to be employed.

Attempts to bring about uniformity by the drafting of international standards were undoubtedly not without success. Unfortunately the welcome activities were carried out in the individual industrial countries independently of each other, as a result of which it is still necessary to refer to a variety of standards. Efforts to specify international standards as a binding requirement have certainly advanced matters, but the goal of binding global standards has not yet been met (see chapter 8).

2.3.1 Measurement Accuracy

As referred to above, the manufacturers and consumers of coating materials negotiate tolerances in the performance indicators for processing and final properties. Compliance with specification by the products must therefore be determined by testing to establish whether the performance indicator in question is within permissible tolerances of the ideal value or not.

In order to achieve binding declarations of acceptance or rejection of a product batch, the measurement accuracy of the test equipment itself must also be regularly checked when measurements are carried out. Measurement errors cause a loss of confidence in the evaluation of product quality. They are therefore a significant factor in quality assurance. Analyses of the measurement accuracy of all measuring instruments are thus necessary aids when processing measurement results.

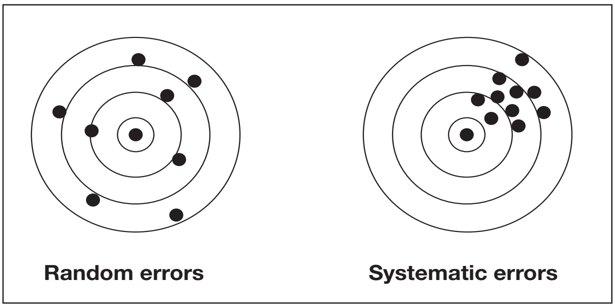


Fig. 2.3.1
Visualization of random and systematic measurement errors

In particular it is necessary to distinguish between systematic and random deviations from the correct reading.

Figure 2.3.1 shows two targets with numerous hits. In the second case the marksman has short with precision inaccuracy with a low rate of deviation. In the first the hits are scattered over the entire target. In case 2 there is a systematic error which can be eliminated via a correction factor. No system can be identified in the first case. These are random deviations.

Such coincidental measurement uncertainties can be analysed using mathematical methods. Appropriate processing of the results of multiple measurements enables the reliability of a statement to be significantly increased. In the case of random errors the calculation of the mean is a simple way to obtain a more precise statement. A definition which is meaningful in practice is the arithmetic mean $\bar{x}$, i.e. the sum of all the individual readings x_i divided by the number n of individual readings.

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Calculating the mean may be meaningful, but it does not permit any particular comment on the gap between the individual readings and the correct value. For this, the deviations of the individual readings from the mean must be included in these considerations.

Since the sum of the errors is zero where there are random errors because of the uniform distribution of positive and negative deviations from the correct value, the sum of the squares $(x_i - \bar{x})^2$ of the individual errors is calculated to determine a so called confidence range. The square root of the squared mean of the individual errors divided by the number of readings less 1 is termed the standard deviation S or mean error.

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n - 1}}$$

If the standard deviation is related to the arithmetic mean of the readings, this yields the coefficient of variation or relative error. The smaller the standard deviation, the more accurate the measurement process.

Experience shows us that the frequency of readings decreases with increasing deviation from the mean or from the unknown correct reading. With an increasing number of readings the frequency distribution comes ever closer to a curve which can be mathematically described by the *Gaussian* distribution curve J.

$$J = \frac{1}{\sqrt{2\pi} \cdot \sigma} \cdot e^{-\frac{(\bar{x} - \mu)^2}{2 \cdot \sigma^2}}$$

With an infinite number of individual readings the standard deviation s moves towards σ, and the value $\bar{x}$ approaches the theoretically correct value μ. The *Gaussian* curve is clearly defined by σ and μ and permits a distinct statement about the probability of errors in individual readings. If, therefore, a measurement process has been described in a one off action with reference to its standard deviation with a sufficiently high number of individual readings, quantitative statements can be made about the probability of individual errors. Thus 68.3% of all readings lie within ± 1 σ of the maximum of the *Gaussian* curve, as many as 95.4% within ± 2 σ and no fewer than 99.7% of all readings within ± 3 σ.

Agreements about the quality that can be achieved by painting can therefore only ever be related to a percentage certainty. The manufacturer and consumer are left with the residual risk, despite an extremely accurate testing regime, of mistakenly selling merchandize which does not conform to specification as ”OK” or rejecting products which do conform to specification, based on individual readings. Taking the example of tinting strength, figure 2.3.3 shows that a paste A with a tinting strength of 102 (and thus a product within the agreed tolerance of 100 ± 5) and a standard deviation of 2 σ has a 7% probability of being outside the permissible tolerance, whereas with product B with

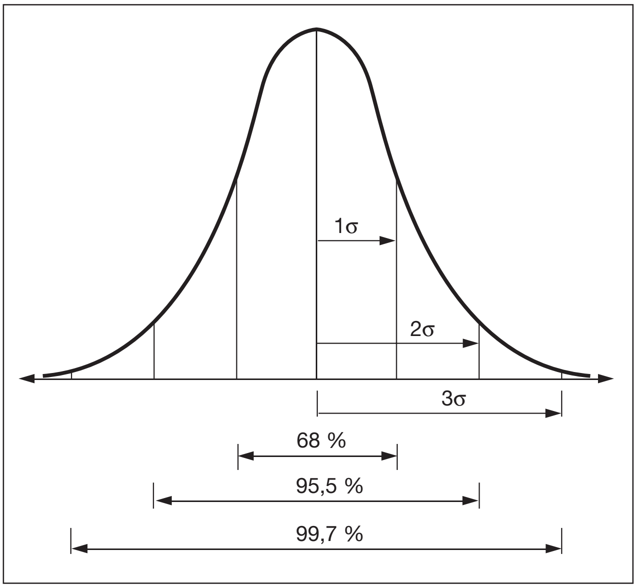


Fig. 2.3.2
Error distribution curve with statements for error probabilities

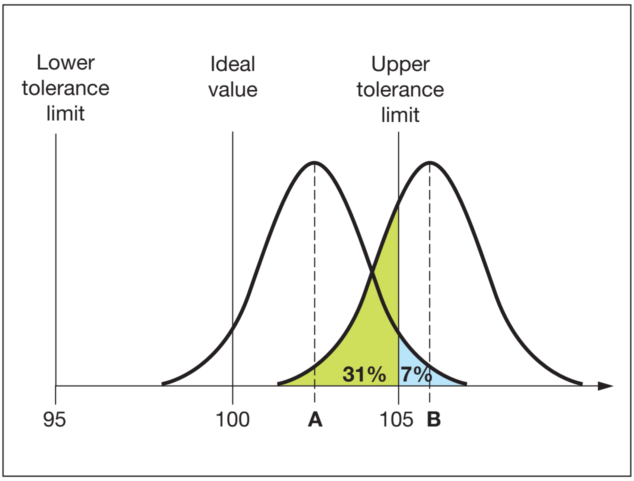


Fig. 2.3.3
Quality risks of specifications based on single measurements for manufacturer and customer

a value of 106, thus clearly outside the agreed limits, 31% of all readings would nevertheless be identified as being within the specification. The first case represents the manufacturer's risk, and the second case the consumer's risk.

The consequence of this is having to comply with supplementary safety margins for the agreed tolerances. These are calculated on the basis of the agreements on the reliability of the correctness of the readings. If the standard deviation of the test method is known, a reading is acceptable if it is within the agreed tolerances with the agreed level of confidence (for example 95%). In other words, the reading may not exceed a deviation of 1.96 s, which represents 95% of the area below the *Gauss*ian curve, from the agreed limit. The standard deviation s must be determined experimentally using an adequate number of individual readings for each measurement process. The threshold value or significance threshold is:

$$\frac{s \cdot t_{S,N}}{\sqrt{n}}$$

s = standard deviation
$t_{S,N}$ = Student factor
S = factor for relative accuracy
N = number of measurements to determine the standard deviation

The lower and upper limit y for a significant statement for rejection or acceptance is then:

$$y = \text{tolerance limit} \pm \frac{s \cdot t_{S,N}}{\sqrt{n}}$$

The margins to be met are reduced in the event of multiple readings in the form of $1/\sqrt{n}$, where n is the number of readings for the approval test.

These correlations are used when a significant statement has to be made about acceptance or rejection with a minimum number of readings. Tests are therefore not carried out until the "right" result is achieved, but until a decision is possible with a calculable risk [2.4.76].

This method of processing readings, termed a sequential test strategy, is based initially on determining one reading. The position of this value relative to the tolerance threshold is verified. If it lies significantly outside or within an agreed limit, a decision is possible.

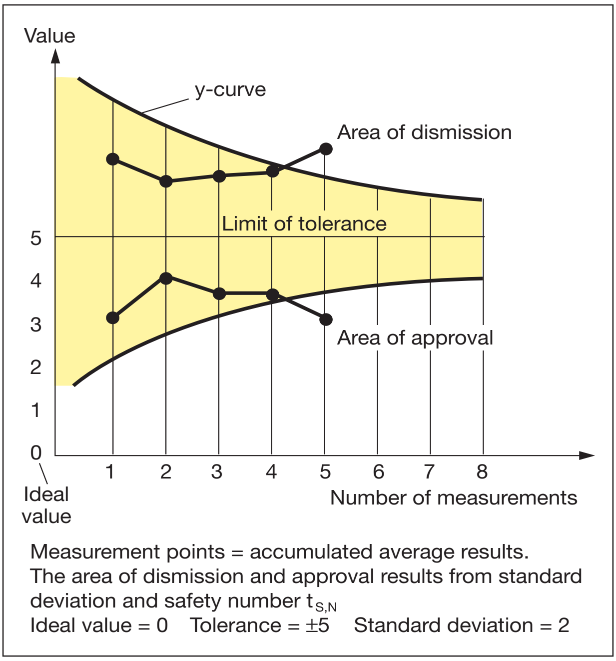


Fig. 2.3.4
Method of sequential test strategy

If it is in a range which does not permit a significant statement, a second reading must be taken, the arithmetic mean of the two calculated and its position relative to the significance with a now narrower range of uncertainty determined.

Testing continues until the result calculated in this way leaves the zone of uncertainty, either into the rejection range or the acceptance range.

It may be noted in conclusion that errors must be anticipated at every stage of the evaluation of process chains where tests are carried out. The consequence is error propagation over the individual stages of the production and testing sequence. The squares of the standard deviation are then added to the variation s_{tot}

$$S_{total} = \sum_{i=1}^{n} S_i^2$$

if only the results of individual readings are available. In the event of multiple readings the total variation is reduced to

$$S_{total} = \sum_{i=1}^{n} \frac{S_i^2}{n_i}$$

These explanations of calculating errors prove that readings can only be used with confidence for test purposes and thus evaluating quality if they have undergone appropriate mathematical processing.

2.3.2 Testing Raw Materials and Coating Materials

Numerous test methods have proved successful for the supply approval test of raw materials and final inspection of coating materials in paint plants. They can be divided into safety and environment related indicators, analytical chemistry data and physical material and application properties. Because of their special properties and the resulting specific nature of the tests the pigments and pigmented coating materials have been given their own section at the end of this chapter.

2.3.2.1 Safety and Environment Related Performance Indicators

Paints are complex mixtures of a range of raw materials which, if the chemical and physical properties are not known, represent a potential hazard to the people in the paint plant, but also to the environment. The governments have therefore passed a range of laws and directives to regulate the handling of such materials (see chapter 5.1 – 5.4).

The most important material properties are flammability, the formation of explosive mixtures and physiological hazards in the event of incorrect handling.

In order to assess the hazard, indicators are defined in the individual laws which are used to assign products to risk classifications or to specify limits. Safety variables such as the flash point, ignition temperature and the explosion limits provide information on the conditions to be met when handling flammable formulations. The maximum admissible concentration in the workplace (MAC values), biological threshold limit values and the lethal dose (LD) and lethal concentration of gaseous substances (LC values) give information on the physiological hazard to people and the maximum concentration of immission.

- **BGV:**
  - flash point, class of danger, ignition point, ignition limits, ignition classes, explosion limits
- **Ordinance on hazardous substances:**
  - MAC-, BTLV-, TDC-values, LD_{50}, LC_{50}
- **BImSchG (TA-Luft, VOC-Directive):**
  - VOC-limits
- **Waste water:**
  - BOD_5, COD

Fig. 2.3.5
List of safety and environment related criteria according to German law

The BOD_5 and COD figures, representing the biological and chemical oxygen demands in waste waters, are limits that have to be met to ensure the safe handling of paints and paint raw materials (see chapter 5).

Flash point

Above a certain temperature every flammable liquid develops so much vapour, quantifiable by its vapour pressure, that it ignites on approaching an ignition source. However, the initially flammable vapour/air mixture does not necessary continue to burn for any length of time. The temperature, above which the material is flammable, is termed the flash point. It is therefore the lowest temperature, expressed in °C, at which vapours build up under specified conditions from the liquid under test in such quantities that they form a flammable mixture in combination with the atmospheric air.

Statutory hazard categories have been defined with reference to the flash point. Formulations are classified according to the height of the flash point and miscibility with water. It should be noted that flash points of mixtures of substances cannot be calculated from the flash points of the individual components. Azeotropic mixtures of solvents or their interaction with the film forming agents sometimes have a significant impact on the level of the flash point.

Flash points are determined according to *Abel-Pensky* (DIN53213), *Pensky-Martens* or *Marcusson*.

$$t_{F_n} = t_{F_B} - \frac{(b - 1013)\,\text{mbar}}{40\,\text{mbar}/°\text{C}}$$

T_{F_n} = standardized flash point
T_{F_B} = measured flash point
b = air pressure in mbar

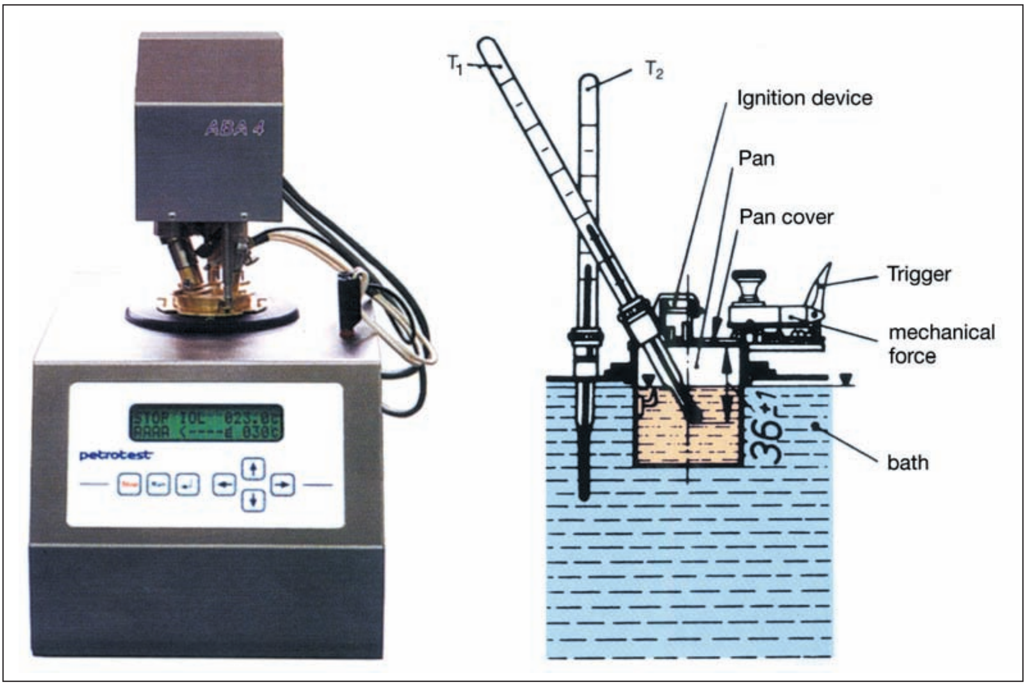


Fig. 2.3.6
Scheme and picture of a device for determination flash points according to Abel-Pensky

The main difference between the individual test systems is the heat transfer medium. Whereas *Abel-Pensky*’s apparatus is fitted with a water bath, *Pensky-Martens*’s apparatus has an air bath, and *Marcusson*’s has a sand bath. The actual test process is the same for all the systems. At regular intervals an ignition device carries out a 2-second check on the flammability of the liquid which is being heated. The temperature at which a burning liquid, following artificial ignition, is not extinguished after a certain time, is defined as the flash point after conversion to standard temperature and pressure.

Explosion limits

If solvents enter a vapour chamber by means of evaporation, they are capable, above a minimum concentration and after external ignition, of developing so much energy that the chemical reaction which proceeds extremely quickly, is perceived as an explosion. This occurs, therefore, whenever there is a sufficiently high sol-

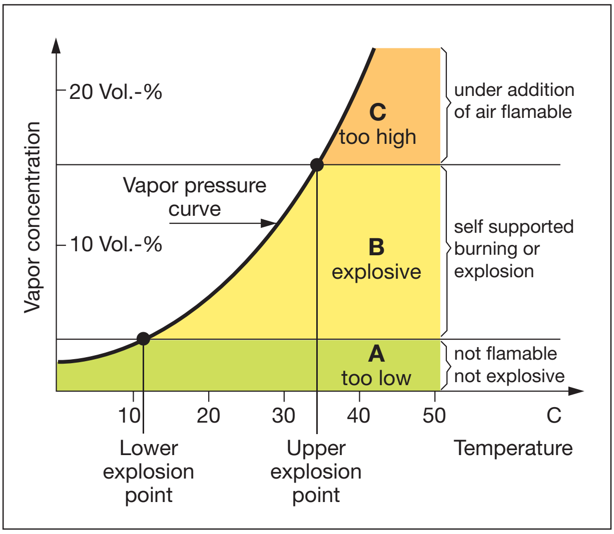


Fig. 2.3.7
Generalized vapor pressure curve of a liquid with lower and upper explosion limits

vent concentration in the vapour chamber at a correspondingly high temperature for propagation of the artificially initiated oxidation to occur automatically.

With increasing temperature the solvent concentration in the gaseous phase increases further and can become so high that the volume of atmospheric oxygen still available in the environment becomes too small to permit complete oxidation. The mixture then becomes too ”rich”. An explosion is also no longer possible after an upper explosion limit has been reached.

Explosive mixtures are thus present when the lower explosion limit has been exceeded, but at the same time the upper limit has not yet been reached. However, mixtures with such readiness to ignite must still be supplied with so much energy that the activation energy for the oxidation of the solvent molecules is exceeded. The lower and upper explosion limits are well defined values for most substances. In some materials, such as xylene, whose lower limit is 1% v/v and upper limit is 6% v/v, the explosion limits are very close together. Other materials on the other hand, such as hydrogen, have very widely spaced limits (4% v/v and 76% v/v in this case).

So if manufacturers or processors of coating materials release solvents in the form of vapours, these must be diluted to below the explosion limits by supplying pure air. Regulations issued by the appropriate German employers’ association and accident prevention regulations, therefore, require that solvent vapours be diluted to less than 0.8% v/v.

Ignition temperature

Above a certain temperature an external ignition is no longer required for an explosion to occur. If the activation energy of the reaction mixture is exceeded, exothermic chemical oxidation is spontaneously initiated. The temperature at which a mixture with readiness to ignite can explode without any external intervention is the ignition temperature.

Ignition temperatures play an important role in defining the hazard potential of explosive gas/air mixtures. The ignition temperatures, divided into temperature categories from T1 to T6, are in the range between 250 °C and 500 °C for standard paint solvents. To simplify the selection of the right electrical equipment from a safety perspective, binding statutory classifications for solvents have also been specified (see chapter 5.2).

Health and safety indicators

With regard to the protection of people handling hazardous materials in the workplace there is the danger from fire and explosion and also a potential hazard involved in handling toxic, corrosive or irritating formulations.

Germany’s Ordinance on Hazardous Substances (GefStV) regulates the handling and labelling of hazardous materials by means of hazard symbols. Supplementary indicators such as the maximum admissible concentration (MAC level), Technical Direction for Concentrations (TDC, Biological Threshold Limit Value (BTLV) and the toxicological terms) LD_{50} and LC_{50} are additional tools in evaluating hazards.

MAC levels correspond to the concentrations of materials which would not be injurious to health even with eight hours’ exposure daily. The figures are quoted in either mg/m^3 or ml/m^3 (ppm).

For some hazardous materials, e.g. carcinogenic substances, no limits which are backed up by toxicological tests can be cited. Instead, technical guideline concentrations are proposed which are intended to give an indication of the necessary protective measures. The specification of MAC levels and TDC values is carried out by evaluating toxicological experiments on laboratory animals. The toxicity of materials is quantified by the LD_{50} level. The LD_{50} (lethal dose 50%) is the quantity of a hazardous material (generally taken orally) at which 50% of the treated laboratory animals die. The LD_{50} is quoted in mg/kg body weight of the laboratory animal. If it is in the range 0 – 25 mg/kg, it is a very toxic material. Figures of 25 – 200 mg/kg indicate a toxic material, while LD_{50} values of 200 – 2000 mg/kg are defined as a chemical which is harmful to health. The LC_{50} values permit the inhalation toxicity to be assessed. They indicate the maximum concentration of solvent vapours or gases in the atmosphere at which 50% of the laboratory animals survive.

In Germany a list of scientific data for defining maximum admissible concentrations in the workplace published by the Federal Ministry of Labour and Social Affairs is revised each calendar year by the Senate Commission of the Deutsche Forschungsgemeinschaft [DFG – German Research Association] to test materials which are harmful to health. The European Commission then specifies the relevant figures which are subsequently implemented in national regulations or lists in the individual member states.

Apart from occupational health and safety regulations and the associated indicators, the environment related consequences of coating technology are also significant. Emissions in the form of solvents, noise or odor have to be discussed in this regard, as does the pollution of waste water. The chemical (COD) and the biological (BSB_5/BOD_5) oxygen demands are important indicators of waste water pollution. Both figures provide information on the level of oxidisable organic pollutants. In the case of the BSB_5 value samples of the waste water are mixed with bacterial strains. The biological oxygen demand is the volume of oxygen dissolved in 1 l water which the microorganisms consume to break down the pollutants. Since this breakdown is associated with a reduction in concentration analogous to an e-function and the breakdown rate falls, the test period is limited to 5 days. This time limit is indicated by the index 5. The analysis of the chemical oxygen demand COD is a supplementary method. Potassium dichromate solutions are used as the oxidising agent. The volume consumed is determined by titration and converted into oxygen equivalents. The result is quoted in mg O_2/l waste water. The COD method covers all materials, i.e. including inorganic materials, which are oxidizable with dichromates. These include iron (II) ions, sulphides and nitrites as the commonest pollutants in water. For this reason BOD and COD values are not identical. The two values are a rating basis for calculating discharges into public waste water treatment systems [2.4.77].

Various methods can be used to measure organic emissions, termed volatile organic compounds (VOC). Depending on their type and quantity, the volatile compounds are indicated as a mass concentration in mg/m^3 or a volume concentration in ml/m^3 or ppm. In the event of continuous emissions it is possible to use the mass flow in g/h. To enable comparative evaluations the measured values must be converted to standard temperature and pressure (air pressure of 1013 hPa and temperature of 0 °C). In cases involving low concentrations and known composition test tubes are used in which the material to be tested is determined quantitatively in a specific color reaction. In other measurement methods the test tubes are filled with carrier materials which adsorb the volatile compounds. They are desorbed and quantitatively determined, generally by means of gas chromatography. The adsorption stage can be dispensed with by sampling directly from the emissions in the air using so called gas collectors. This type of sample can then be measured directly using headspace gas chromatography.

If continuous measurement is necessary, for example in the waste air flows of coating systems, instruments are used which measure changes in the composition of the air flow by means of physical properties such as electrical conductivity in flame ionization detectors (FID) [2.4.78]. Another type of detector takes the form of a heated platinum wire in the waste air which is heated still further by the catalytic oxidation of the organic substances corresponding to the volume of emissions. The change in resistance is recorded. Once calibration curves have been recorded, the VOC values can be determined.

If the consumption quantities of coating materials and the air flows in a plant are known, and if the volatile portions of the coating materials used are known, the material flows and thus the VOC values of a system can be calculated. To determine the volatile components of the coating materials it is enough to base the calculation on the determination of the solid content and the solvent components with subsequent conversion into volumetric data. This calculation is handled differently in North America from Europe (see chapter 5.3.1).

2.3.2.2 Chemical Characterization

Chemical analysis as a means of characterising materials is mainly used for film forming agents, reactive diluents and additives as far as the paint and coatings industry is concerned.

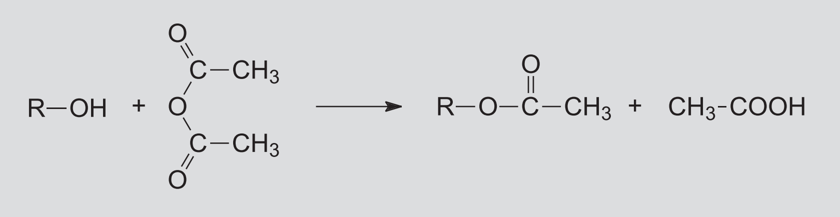
If film forming agents are to be developed and produced, and their identity is to be determined with a retained sample, resin specific indicators are mainly used. The saponification value, acid value, hydroxyl value, number of NCO groups, iodine value and the amine or acid equivalents (MEQ_B, MEQ_S) provide information on the composition of resins and resin solutions.

Polycondensation resins are identifiable by a finite saponification value SV. To determine this, the weighed object E of the sample under analysis is mixed with a large excess b of 0.1 n KOH solution. After heating and complete saponification the sample is back titrated with acid to determine the amount of alkaline a used. The saponification value is calculated from the difference between the acid consumption before and after the saponification of the resins.

$$SV = \frac{(b - a) \cdot 5{,}61}{E}$$

If resins contain carboxyl or hydroxyl groups, these are also easy to quantify. According to DIN EN ISO 3682 the acid value AV of a resin is the quantity of KOH in mg which is used to neutralize 1g substance under specified conditions (indicator: phenolphthalein). If, for example, a resin has an acid value of 56, it contains 1 mmol carboxyl groups per 1 g; or, to express it a different way: an acid value of 56 indicates that there is one carboxyl group in 1000 g substance.

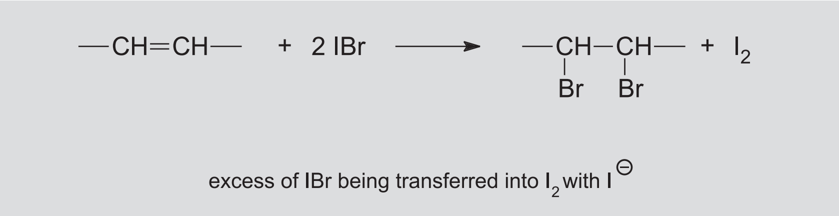
Determining the hydroxyl value OHV is a little more complex. DIN EN ISO 4629 specifies acetylating the hydroxyl groups with an excess of acetic anhydride before saponifying the excess acetic anhydride and, together with the resulting acetic acid, back titrating it with KOH.



If the resin under analysis also contains carboxyl groups, these are also determined during the back titration process. The reading is therefore too low. Consequently, the acid value must be added as a correction term.

$$\mathrm{OHV} = \frac{(b - a) \cdot 5{,}61}{E} + \mathrm{AV}$$

Other important functional groups such as isocyanates or double bonds can also be quantitatively analysed using simple chemical reactions. Thus the NCO group can be converted to urea with dibutyl amine. The excess dibutyl amine is back titrated with hydrochloric acid using bromophenol blue as an indicator. The process to determine the iodine value is equally straightforward. Halogen adding to double bonds is converted to the analogous quantity of iodine and, by contrast with all other tests specified so far, is related not to 1 g, but to 100 g test substance. Of the processes described in DIN 53241-1 among others, *Hanus*'s method may be cited as an example.



$$-\mathrm{CH{=}CH}- \; + \; 2\,\mathrm{IBr} \longrightarrow -\underset{\mathrm{Br}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{Br}}{\underset{|}{\mathrm{CH}}}- \; + \; \mathrm{I_2}$$

excess of IBr being transferred into I_2 with $I^{\ominus}$

Iodine bromide as the titrating solution b is reacted with the sample. Regardless of whether iodine or bromine is added, the remainder of the titrating solution is completely converted to iodine by the addition of iodide a. The iodine is then titrated with thiosulphate. The iodine value JV is calculated as follows:

$$\mathrm{JV} = \frac{(b - a) \cdot 1{,}26}{E} \qquad 1{,}26 = \frac{1}{100} \text{ atomic weight of iodine}$$

The straightforward indicators which apply particularly to watersoluble film forming agents, in addition to the OH and acid value, include the amine and acid value to DIN 53 176 which can be used together as a measure of the degree of neutralization of anionic or cationic resins or paints.

The amine value in the familiar form of the $\mathrm{MEQ_B}$ value (H^+ milliequivalents) indicates how much hydrochloric acid is equivalent to the amine component. To calculate this, the hydrochloric acid consumption is multiplied by the molecular weight of the amine, applied to 100 grams substance and converted to the solid content.

$$\mathrm{MEQ_B} = \frac{\text{ml 1 n HCl} \cdot \text{molecular mass of amine}}{\text{\%FK} \cdot \text{probe mass in grams}} \cdot 100$$

To calculate the $\mathrm{MEQ_S}$, the titration is carried out with potassium hydroxide solution in accordance with DIN EN ISO 3682. Mathematical processing involves replacing the molecular weight of the amine in the above formula by that of the acid used.

The MEQ value is an important complementary test to the pH value, since the latter often only shows an insignificant change when the concentration of the neutralising agent changes because of the buffering action of watersoluble paints.

The pH value can be measured quickly and simply using paper strips impregnated with indicators. However, this method is not very accurate. Glass electrodes are used to establish more precise figures.

Instrumentation based analysis

More and more, sometimes complex, techniques of instrumentation based analysis are gaining ground to complement the chemical identification methods introduced in the previous chapters.

Spectroscopic detection of molecular elements, for example by measuring characteristic vibrations, different levels of mobility or adsorptiveness, or determining caloric effects when heated under defined conditions may be cited as examples. On the other hand processes which take account of the influence of the molecular weight on the viscosity, vapour pressure, light scatter and migration rate under gravity have also proved valuable. The following deserve particular mention in this context:

The **spectroscopic methods** of instrumentation based analysis utilize the interaction of electromagnetic radiation with the molecules and deliver readings in response to the change recorded in the radiation on the structures.

UV rays, with wavelengths of between 200 and 400 nm, are capable of exciting electrons. The absorbed energy is used for electronic transition from the ground to the excited state. Molecular forms, molecular structures and chemical bonds can be identified from the spectra generated in this way. UV spectroscopy is also useful in analysing additives which are used for UV protection of coatings.

The rays with longer wavelengths of 1 – 20 µm, i.e. in the infrared range, are suitable for exciting molecular vibrations which can then be used to identify the chemical struc-

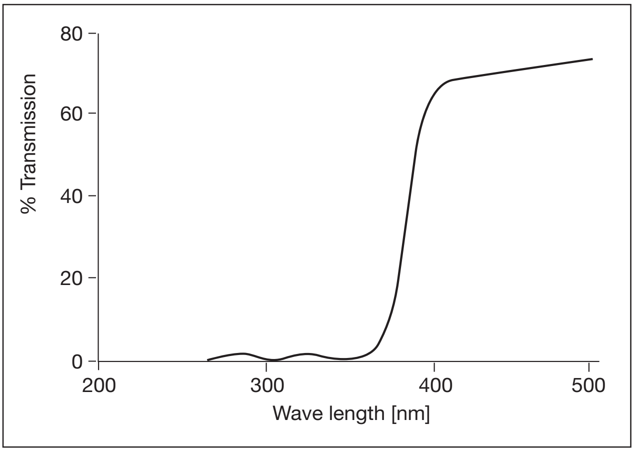


Fig. 2.3.8
UV-spectra of a clear coat based on acrylic resins

tures. Infrared spectroscopy is more universally applicable and in considerably more widespread use. Unlike UV spectroscopy, it is not electrons which are excited to rotational, horizontal and bending vibrations, but molecular elements because of their significantly longer wavelength, though only when the absorption of infrared rays is possible as a result of unequal charge distributions (= dipoles) of the vibrating mass. Strong dipoles are therefore particularly intense in the IR spectrum. The individual molecular elements yield absorption bands whose position and intensity allow conclusions to be drawn about the composition and configuration of the atoms in the molecule. Infrared spectra are therefore especially suitable for identifying substances by means of reference substances. OH groups, NH groups, carbonyl groups and CH groups exhibit characteristic bands whose exact position is again influenced by their link with their environment. This enables conclusions to be drawn about the functional groups, their molecular neighbors and the bond structure.

Modern instruments work extremely quickly and with excellent reproducibility. Using the transmitted light method, they are equally capable of recording spectra of film forming agents from solutions and from solids moulded with potassium bromide. IR radiation reflected on films also permits IR spectra to be recorded .

Infrared spectroscopy also enables mixtures of substances to be identified and the proportions within the mixture to be estimated by comparing the ratios of the characteristic absorption bands for the individual components.

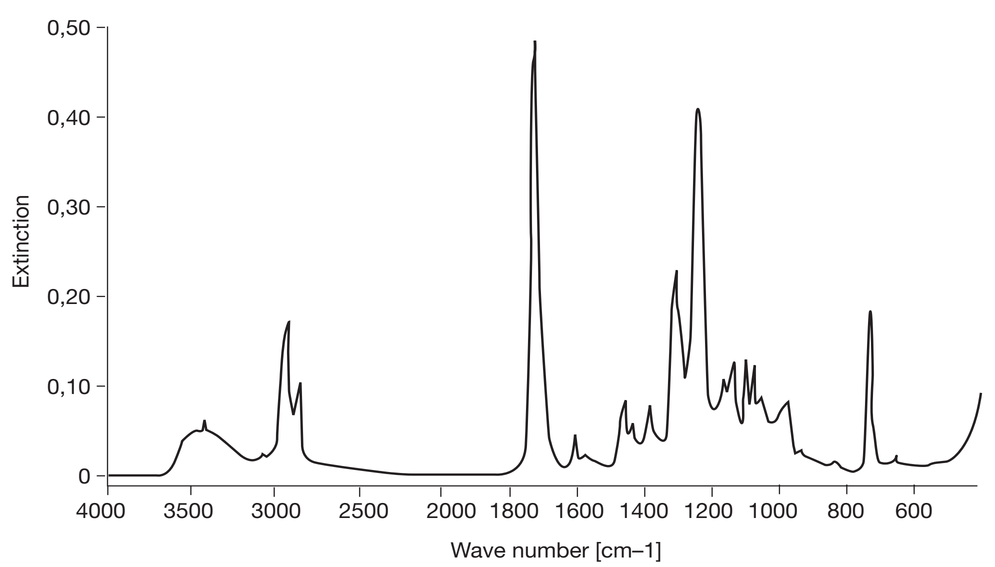


Fig. 2.3.9
IR-spectra of an alkyd resin

Infrared spectroscopy is particularly successful for analyzing PUR paints. The absorption band for NCO groups at approx. 2260 cm^{-1} (approx. 4 µm wavelength) is covered by only a few functional groups and is also extremely narrow and therefore suitable for kinetic analyses of crosslinking processes in association with isocyanate groups. Tracking the hardening of epoxy resins and the oxidative crosslinking of alkyd resins are further examples of the successful use of IR spectroscopy. Numerous standard spectra are now stored in digital form and can therefore be accessed without difficulty and evaluated electronically [2.4.79].

Instruments based on magnetic nuclear resonance (NMR) as the measured variable operate according to a completely different principle. The principle is based on the fact that nuclei with an odd number of protons (^{1}H, ^{13}C) in a homogenous magnetic field undergo a frequency dependent spin reversal in an irradiated magnetic field because of their magnetic moment and because of the nuclear spin resulting from the rotation of the nucleus. When nuclear magnetic resonance spectroscopy is used, the sample is first introduced into a strong, linear magnetic field to orient the rotating nuclei. The nuclei, which act as mini magnets, are aligned in parallel and antiparallel form in two different energy levels. If a second magnetic field with a variable frequency acts on the oriented mini magnets, for example of the hydrogen or ^{13}C nucleus, a spin reversal takes place in the nuclei at the lower level by absorption of energy at the nucleus's resonant frequency. The frequency of the spin reversal is bond specific insofar as the electrons shielding the nucleus result in a change in the resonant frequency and the chemical shift as a function of the chemical bond among the atoms and also of the spatial environment. The shift in the resonant frequencies is determined in relation to an internal standard. Tetramethylsilane is used as a standard particularly for proton resonance spectra. The intensities of the signals are used for quantitative evaluations. The use of ^{1}H-NMR, for example, makes it possible to determine whether protons are assigned to a carboxylic acid, a hydroxyl group or just to a CH bond. This enables the identification of molecular structures [2.4.80].

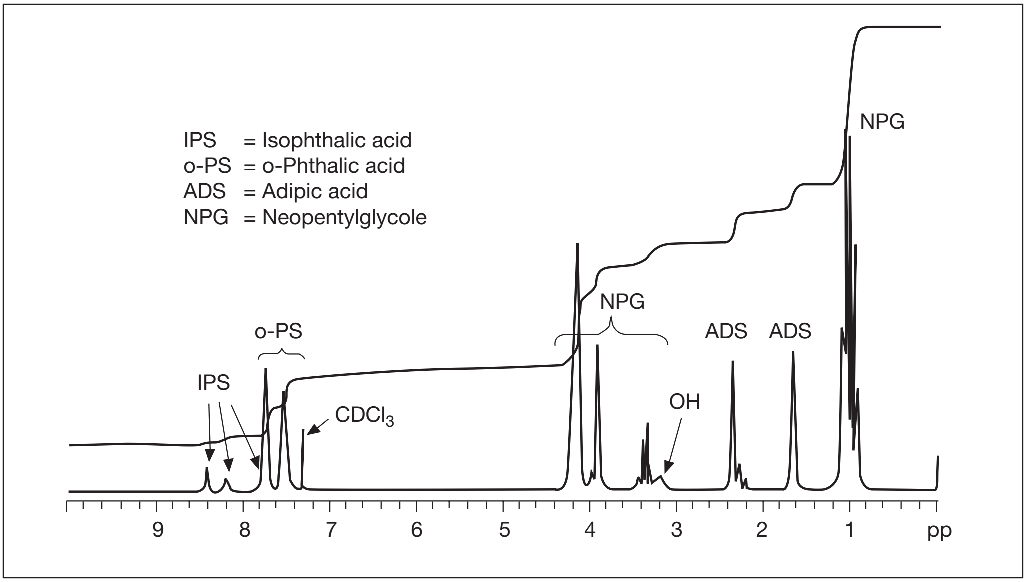


Fig. 2.3.10
^{1}H-NMR-spectra of a polyester resin

Intermolecular interactions or cis-trans-isomerization can be detected by nuclear magnetic resonance spectra, which means ultimately that secondary structures can also be identified.

A frequently used method of structural identification of molecules is mass spectrometry. It makes use of the mass dependent inertia of accelerated charge bearing during deflection in a magnetic field.

The design of a mass spectrometer consists in principle of a sample reservoir from which the sample is fed to an ionization chamber after being vaporized. Highly accelerated electrons in the chamber cause the ionization of the substances under analysis. Depending on the energy input, the molecule can be either left intact or fragmented. The resulting ions are accelerated by electrical fields, bundled and then deflected from their flight path by an electromagnetic field. The flight path is determined by the charge, particle speed and mass. Where the charge and the speed are the same, deflection is then only a function of mass, and this can therefore be used as a measurement variable for the molecules under analysis or their fragments.

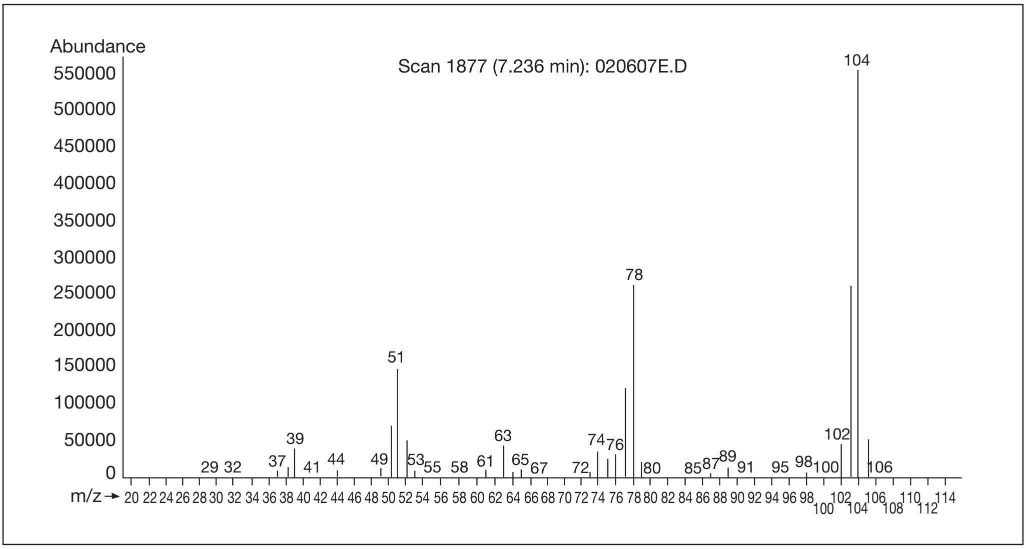


Fig. 2.3.11
Mass spectra of styrene

Because there is no guarantee of volatility, the analysis of macromolecular materials requires fragmentation of the original molecules. The imaginary recombination of the identified molecular elements into a meaningful form is thus a secondary task.

For quantitative analyses mass spectrometry has largely been replaced as the sole test method. On the other hand, it has proved useful as a complementary method for identifying mixtures of substances which have already been separated by gas chromatography or by chemical reactions, in a process termed GC/MS [2.4.81].

Chromatographic methods

A common feature of all chromatographic separation and identification methods is that the materials or material mixtures are routed as a mobile phase past a stationary phase so that material specific interactions occur. These influence the migration rate in the mobile phase. The retention times measured are then used to identify the material.

Since **gas chromatography** is a process for separating gaseous materials, only materials which can be vaporized are capable of being analyzed.

For macromolecular materials, therefore, it is sensible to produce volatile oligomeric or monomeric elements in advance using defined wet chemical degradation reactions. It is often possible to transform these products into nonpolar forms and thus into more volatile variants by means of subsequent esterification with methanol or by silylation with trimethylchlorosilane. A simple method of obtaining volatile substances consists of the advance pyrolysis of the test substances in the gas chromatograph itself.

The gaseous initial product in isolation or also as a mixture is passing a solid material with an inert carrier gas or passing a liquid absorbed in a carrier in capillaries. This interaction results in material mixtures being separated and therefore reaching the outlet of the separation unit at different times. The retention times, measured by means of material specific properties such as thermal conductivity, refractive index and similar, permit conclusions to be drawn about the individual components. A mass spectrometer system downstream enables identification of the materials. Quantitative analysis can then be achieved by comparing the signal intensity with reference substances (see below).

Compared with gas chromatography **high performance liquid chromatography** (HPLC) offers the advantage of being able to analyze solutions. The liquid sample in the mobile phase passes the solid carrier material in capillaries (columns) and is transported at varying speeds as a result of varying interactions before being sensed by detectors. Porous SiO_2 particles modified with amino, cyano or hydroxyl groups are used as the polar column material.

HPLC is primarily used for low volatility substances. Because of its high sensitivity it is a proven method for identifying traces, but it is also suitable for analyzing polymers. It permits, for example, the separation of acrylic resin mixtures, aliphatic and aromatic epoxy resins, but also various melamine resins, to mention just a few of the wealth of possibilities [2.4.82].

An even better method, because it can be used both for nonpolar polymers and also for determining polymer fractions, is **gel permeation chromatography** (GPC). GPC, by contrast with HPLC, does not use the different polar interaction of material and carrier in the stationary phase, but enables the separation and identification of polymer mixtures as a result of cavities of differing size in the particles of the stationary phase.

Styrene/divinyl benzene copolymers are generally used as gels with cavities of differing size. The pore diameters lie between 5 and 500 nm. As a result, large molecules penetrate the pores less deeply than the smaller ones and are therefore also transported more rapidly. Quantitative evaluation must be preceded by calibration with known substances. The concentration in the eluate, plotted against the process time, provides information on the molecules of differing size in the material mixtures. Since macro- and oligomeric materials, as present in film forming agents, are always mixtures of molecules of differing size, gel permeation chromatography is excellent at determining the molecular weight distribution of paint resins and also enables means to be indicated after mathematical processing [2.4.83]. GPC is superseding fractionated distillation or fractionated precipitation methods which were standard in the past but which are expensive to carry out and require particular experimental skills [2.4.84].

Special methods for determining molecular weights and their means

Analytical chemists use numerous methods particularly for characterizing the size of molecules and providing their mean values where molecules of differing size are present.

Either the numerical mean or the weight mean of the molecular weight is determined, depending on the measurement method used.

The numerical mean M_n is the sum of the molecular weight of the individual fractions, multiplied by the number of molecules contained in the fraction, divided by the total number of molecules. The weight mean M_w, on the other hand, relates the molecular weights of the individual fractions not to the number but to the mass components of the fraction.

$$M_n = \frac{\sum n_i \cdot M_i}{n_i} \qquad M_w = \frac{\sum w_i \cdot M_i}{w_i}$$

$$\text{where} \quad w_i = n_i \cdot M_i$$

Since M_w must always be greater than M_n in the presence of molecular weight distributions, the quotient of M_w/M_n is a measure of the distribution range. This can be given as the dispersity D or nonuniformity U:

$$D = \frac{M_w}{M_n} \quad \text{and} \quad U = \frac{M_w - M_n}{M_n} \quad \text{or} \quad U = D - 1$$

Membrane and **vapour pressure osmometry** are important measurement processes in determining the numerical mean. An osmotic pressure is created in a resin solution separated from the pure solvent by a semi permeable wall by the diffusion of the solvents into the resin solution. This pressure is determined by the molecular weight M_n and the concentration. The vapour pressure of the solvents, which has been reduced by comparison with the pure solvent by the presence of resins, is also used as a measurement variable. As above, the reduction is a function of the molecular weight M_n and the polymer concentration. **Light scattering** at the macromolecules in dilute solutions is used to calculate M_w [2.4.85].

M_w can be determined, approximately rather than exactly, by measuring the migration rates of the polymers in the centrifugal field of an **ultracentrifuge** or its viscosity in dilute polymer solutions. Because of their simple equipment requirements **viscosimetric methods** have largely superseded the ultracentrifuge. Correlations with the molecular weight are established by measuring the different concentrations of solutions and calculating the concentration dependent increase in viscosity relative to the viscosity of the solvents.

Thermal analysis

Thermal analysis covers analyses of temperature dependent conversions which can be detected via caloric effects. If, in addition, the thermal conversion is also associated with the formation of volatile cleavage products, the gravimetric effect can be used analytically in thermogravimetry (TG). Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are common methods of thermal analysis.

In DTA the samples are heated under defined conditions together with a reference material which is inert in the measurement range and compared with it. The difference in temperature between the two samples is equal to zero provided no material specific caloric effects occur. If, however, changes in the free energy relative to the reference sample occur because of changes in the degree of crystallinity, the intermolecular bridging bonds or even as a result of chemical reactions, a finite ΔT is measured. The size of the effect and its position on the temperature axis provide important information on the material under analysis. DSC instead does not use the temperature differential but the supplementary heat flow which is necessary to equalize the resulting temperature differential to obtain information.

The position of the glass transition temperature Tg, crystallinity and chemical reactivity are some of the material properties which can be identified. For those involved in the paint and coatings industry analyses of already cured coating materials are also of interest, firstly because the temperature resistance can be estimated, secondly because undercuring can be highlighted by identifying residual activities, and thirdly structural change can be determined, for example by means of the change in the position of Tg (see chapter 3.2.5).

Example of a full analysis of a coating material

Analysis of the paint begins by determining the nonvolatile components (solids). An exact analysis of the volatile components is not possible in every case. Particularly with amino resins there are fluid transitions since fragmentations of resin components can easily occur. The presence of plasticizers also blurs the dividing lines between volatile and nonvolatile components.

To separate the pigment and binder the ready-to-use paint is diluted with a solvent and centrifuged. Highly volatile solvents, such as ethyl acetate, acetone or tetrahydrofuran are preferred. In general centrifuges with speeds of 500 – 6000 rpm are adequate for separating pigments and extenders from the binder. If carbon black or finely distributed organic pigments are present, speeds of up to 20,000 rpm are required to ensure the complete separation. Once the pigments have been separated, the diluted binder is decanted, and the pigment is agitated again with a fresh solvent and then centrifuged again. After repetition of this process the pigment is finally dried, and its quantity is determined. The binder proportion is generally calculated from the difference between the solids and pigment components. However, it can also be determined directly by combining the decanted binder portions and distilling the solvent off. The sum of the directly determined binder and pigment components must be equal to the proportion of the nonvolatile components.

To determine the composition of the volatile components gas chromatographic analysis is carried out with solventbased systems. In the case of aqueous samples a supplementary determination of water content is also necessary which can be conducted titrimetrically using Karl *Fischer*'s method in the case of low concentrations, or by means of the calcium carbide method for higher concentrations.

Before using gas chromatography the volatile component can be separated by distillation using a micro rotary evaporator. The separation process can produce certain errors with both high boilers and low boilers. These errors can be avoided by direct injection into the gas chromatograph. The mass spectrum of the individual components can be used in addition to the retention time to identify the GC peaks.

Analysis of the separated pigment/extender mixture begins with classic preliminary tests. The substance under analysis is then treated with both acetic and hydrochloric acids. The proportions soluble in each case are determined, among other ways, polarographically and with the aid of complexometric titration. Infrared spectrometry is often an indispensable aid in analyzing pigments. It can enable various silicates such as kaolin, talcum, barium sulphate and the titanium dioxide modifications rutil and anatas to be distinguished and also organic pigments to be identified. It may be noted that IR spectrometry during pigment analysis can also provide information on film forming agents which have remained on the surface of the pigments.

Synthetic waxes, such as copolymers of ethylene and vinyl acetate, are separated together with the pigments and extenders. These waxes can be dissolved out of the centrifugate by reflux boiling in tetrahydrofuran and identified using IR spectrographic methods.

A large portion of the elements can also be analyzed qualitatively and quantitatively using atomic absorption spectrometry (AAS). This method is particularly useful when the elements under analysis are present only in low concentrations.

Apart from simple preliminary tests for nitrogen and chlorine, the binder analysis starts by recording the IR spectrum of the binder mixture in the solvent free state. This enables at least the principal components of the available mixture to be identified. If esters are present, saponification with ethanolic KOH is useful. When analyzing alkyd resins, for example, this results in four fractions, viz. the di- and oligocarbonic acids, nonsaponifiable components and the fatty acids and polyols. Among the di- and oligocarbonic acids the substances that can be analyzed polarographically include phthalic, maleic, fumaric and trimellitic acids. Conversion into methyl ester is necessary before gas chromatographic analysis can be conducted. The nonsaponifiable components are analyzed using IR spectroscopy. Among other things they contain fragments of amino resins and epoxy resins. HPLC is often an ideal chromatographic method to characterize this fraction more accurately.

The fatty acids and other higher monocarboxylic acids are available for gas chromatography after methylation. Suitable capillary columns enable the identification of linolenic acid, conjugate linoleic acids, ricinoleic acid, abietic acid etc. Since the fatty acid fraction can also contain modified fatty acids such as dimerized, maleinized, styrolized and epoxidized fatty acids, the use of HPLC is advised. It should be noted that escort substances, such as epoxy phenol resin components, can be present in the fatty acid fraction.

The polyols occur in free form and can be separated by means of gas chromatography after silylation.

However, saponification is not always a suitable means of characterizing a binder mixture completely. Apart from with melamine resins which can be analyzed by direct titration in an anhydrous medium or by means of UV spectroscopy after acid catalysed hydrolysis, there is inadequate information, especially where polyacrylics are present. In this case pyrolysis in association with gas chromatography is the most appropriate analytical method.

Also when urethane bonds are present, normal saponification is inadequate. In this case cleavage can be achieved via the KOH melt. The diisocyanates incorporated as urethanes are converted into the corresponding diamines and then identified by means of thin layer chromatography. Thin layer chromatography, a simple, fast and straightforward process, also permits the reference detection of organic peroxides, UV absorbers and plasticizers, but also, after appropriate material preparation, di- and oligocarboxylic acids, lower fatty and aromatic monocarboxylic acids, and finally also polyols which are commonly used in paints.

Another method which can be used to assist in analysis of binders is the extraction of the dried binder. The situation can occur where phthalic acid plasticizers are also present in addition to alkyd resins. While saponification provides a sum for the phthalic acid component, the phthalic acid plasticizers can also be quantitatively separated by prior extraction with pentane. Other plasticizers, for example soft resins, can be extracted with aliphatic hydrocarbons. Identification of the extract can be conducted using IR spectrometry. In the event of mixtures, gas chromatography or high performance liquid chromatography has to be used.

It is often advisable to continue the extraction process by gradually moving to polar solvents. The binder for a combination cellulose nitrate paint, for example, should initially be extracted with pentane to separate the monomeric plasticizers. The extraction should be continued using dichloromethane which permits all synthetic and natural resins with the exception of cellulose nitrate to be identified [2.4.86].

2.3.2.3 Physical Data

The most important physical data of coating materials relating to their processing include their solid content, viscosity, surface tension and density. Of these, the solid content and density are the most significant economic variables. They determine the yield (see chapter 5.7). They also impact on a range of application properties in the same way. Like the surface tension, the viscosity, which varies with the different loads to which coating materials are subjected, is of great relevance to the process engineering aspects of paint manufacture and processing. Since the kinetic energy of the viscous components is converted into heat when the material is flowing, whether during conveying in pipes or during homogenization in agitator vessels, the viscosity is also an economic variable. Atomization, wetting, flow, tendency to run, running away from edges and the adhesion of coatings are phenomena which are also affected by the surface tension.

The indicators described below and their measurement methods relate to liquid coating materials. The characteristic variables for powder coatings and the ways of determining them are described in chapter 4.2.2.

Solid content

DIN EN ISO 3251 defines the solid content as a nonvolatile mass component, determined in percent under clearly defined (i.e. agreed between the customer and the supplier) drying temperatures and times (generally 60 min at 130 °C). Other requirements which must be complied with are a test dish diameter of 75 mm and a weighed-in quantity of 2.00 g ± 0.02.

Since numerous paints and film forming agent solutions not only lose their solvents on heating, but can also undergo chemical reactions which are associated with the formation of volatile cleavage products, differences in the oven temperature and sample preparation can lead to significant differences in the results measured. Bearing in mind that the solid content, even leaving its economic importance aside, is also an important environmental variable for calculating environment related data, measurement errors can have serious consequences. Furthermore, many paint based indicators refer to the solid content.

Role of viscosity in evaluating the flow properties of coating materials

The flow properties of paints and solutions are of huge importance in evaluating the overall manufacturing process of coating materials, starting from the pumping of the raw materials into the storage vessels, via numerous interim stages, to the finished products. Moreover, the application properties of the coating materials such as brushability, flow and tendency to run are closely connected with the flow properties.

Extremely different demands are placed on the flow properties of paints as they progress from manufacture to the finished coating. During conveying in circulation systems paints should be as liquid as possible, whereas when it comes to the application of the coating materials on the object, a smooth film should be produced without running on vertical surfaces. These apparently contradictory demands can only be understood and implemented by those with the expertise to evaluate and influence the flow properties of polymers, polymer solutions and paints in detail.

In the explanations below, ”flow” is understood to mean the irreversible deformation of bodies in which the energy required for said deformation is converted into motion and into heat as a result of internal resistance (= viscosity). Another extreme is the automatic elastic recovery of the deformation to the initial state. Between the extremes of purely viscous liquids and elastic bodies which can store the free deformation energy quantitatively to ensure recovery lies the wide range of viscoelasticity. The components of viscous flow and the reversible storage of deformation energy are merged in such a material property profile [2.4.87].

To better understand the phenomenon of viscosity, consider the force which must be applied to stir a thin or a thick liquid. A thick paint poses a higher resistance for the agitator tool than a solvent and therefore requires more energy. The reason for this lies in the higher internal friction of the larger molecules of the film forming agents by comparison with the small structural elements of the solvent.

The physical measurement variable for the quantitative description of this internal friction is viscosity. The physical correlations can be illustrated by means of the *Newton*ian twin plate model.

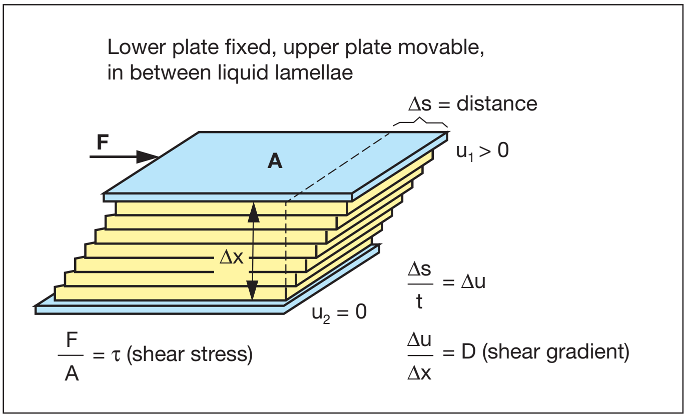


Fig. 2.3.12
Newtonian twin plate model

The gap Δx between two parallel plates of surface area A is filled with a liquid. One of the two plates is moved with a force F and a speed u_1 parallel to the stationary plate. The liquid, which can be imagined to consist of an infinitely large number of liquid lamellae overlying each other in a parallel configuration, adheres to the plates and is therefore also moved at its upper edge at a speed u_1, while remaining stationary at the lower, unmoved plate.

Because of the friction between the layers or lamellae a counterforce now acts on the imaginary liquid layers (laminar flow) which are moving parallel and opposed to each other in the time t in a direction along the path Δs.

The degree of displacement of the individual lamellae relative to each other depends on the distance between the plates, in addition to the resulting speed difference between the two cover plates. The shear force per unit area, the shear stress τ, is thus proportional to Δu/Δx. This variable is termed the speed or shear gradient D. In general there is a direct proportionality between τ and D for laminar flow in accordance with the *Newton*ian twin plate model, where the proportionality factor η is the viscosity.

$$F = \eta \cdot A \frac{\Delta u}{\Delta x}$$

because of $\frac{F}{A} = \tau$ and $\frac{\Delta u}{\Delta x} = D$ follows

$$\tau = \eta \cdot D$$

In accordance with the definition the viscosity η has the dimension Pa·s.

$$\eta = \frac{\tau}{D} \quad [Pa \cdot s]$$

A liquid consequently has a viscosity of 1 Pa · s if there is a speed gradient of 1 s^{-1} with a shear stress of 1 Pa.

Apart from the thus defined dynamic viscosity η it is it also usual to apply the kinematic viscosity ν per unit density to characterize liquids and paints.

$$\nu = \frac{\eta}{\rho} \left[\frac{m^2}{s}\right] \qquad \varphi = \frac{1}{\eta} \left[\frac{1}{Pa \cdot s}\right]$$

The reciprocal value of the dynamic viscosity is the fluidity φ.

The dynamic viscosity defined by *Newton* in the twin plate model can be quantified by measuring the resulting speed gradient with varying shear stress. As defined in $\tau = \eta \cdot D$ the viscosity then corresponds to the increase in the straight lines determined.

The examination of the flow properties of a range of liquids shows that not all obey *Newton*'s fundamental law. Water, mineral oils and also solvents, i.e. without exception low molecular substances, largely demonstrate the anticipated linear dependence in a τ/D graph. Viscosity measurements with liquid coating materials, i.e. solutions of higher molecular substances, only obey the linear correlations described at high dilution levels or in exceptional cases. The viscosity of paint preparations, by contrast with *Newton*ian liquids, is a function of the greater or lesser degree of shear. In many cases the viscosity decreases with increasing speed gradient. With such pseudoplastic

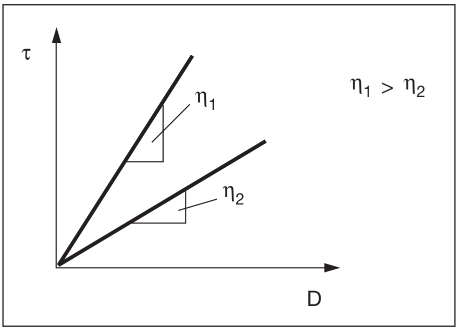


Fig. 2.3.13
Flow curves of Newtonian liquids

liquids the viscosity is in this case not a material constant. The τ/D graph is identical with increasing and decreasing shear stress. Relevant informations on the viscosity must therefore always refer to the shear set during measurement for those pseudoplastic materials.

The reduction in viscosity with increasing shear stress is a frequent, but also desirable property in paints and pigmented coating systems. It is based on the fact that the flow inhibiting interaction within the polymer solution decreases with increasing shear stress. This can occur by stretching macromolecules which are in the form of a coil at rest. Pigments and extenders can also be aligned during flow, thereby reducing internal friction. And finally, deformations of particles have a viscosity reducing effect. The pseudoplasticity is the basis for the low and high viscosity of one and the same coating system during processing and subsequent film formation.

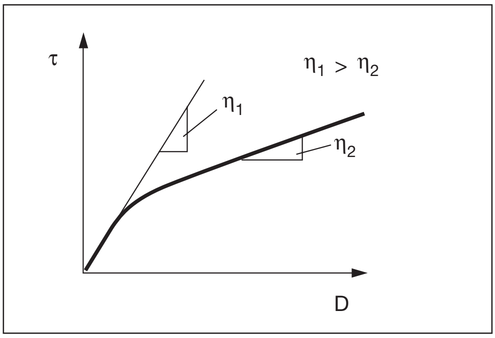


Fig. 2.3.14
Flow curve of a pseudoplastic liquid

Substances are also known in coating technology which generate a rise in viscosity with increasing shear. Sand/water mixtures, starch suspensions and certain types of dispersions and plastisols are examples of such liquids, which are termed dilatant liquids. The increase in frictional forces with increasing shear which underlies the phenomenon of dilatancy can be caused by an induced charge replacement at the friction surfaces and an increase in the electrical interaction.

Every coating material has the tendency to run on vertical surfaces, because of its own weight; this tendency is all the more pronounced, the thicker the freshly applied coat. The paint and coatings industry has succeeded in its endeavours to eradicate these unwanted concomitants by manufacturing corresponding coating materials with a flow point. The weight of the coating material per unit area must then be less than the force which could cause it to run.

Two other phenomena are responsible for the occurrence of yield points, either in isolation or in association with

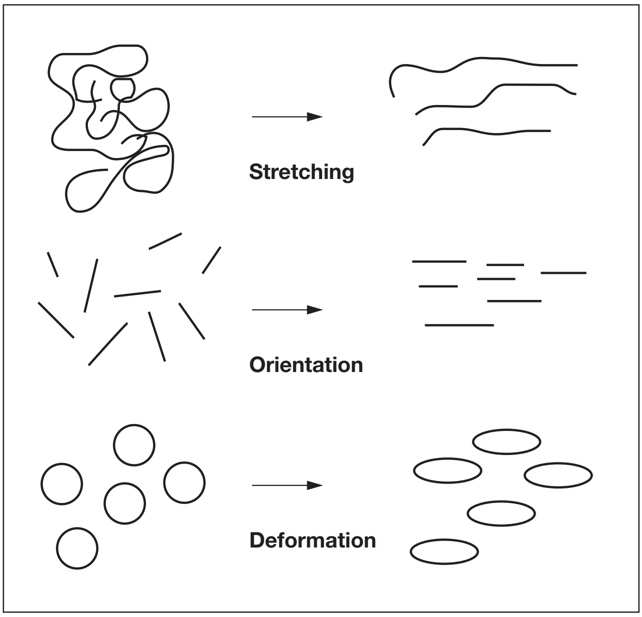


Fig. 2.3.15
Explanation for structural viscosity as stretching, orienting and deforming processes of the molecules

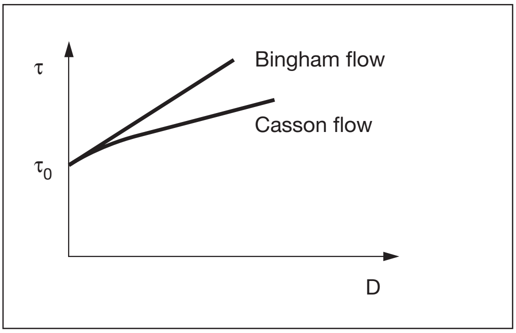


Fig. 2.3.16
Yield points of materials with Bingham flow and Casson flow behavior

pseudoplasticity: plasticity and thixotropy. Plasticity is a feature of all liquid substances which can only flow once a minimum shear stress τ_0 has been exceeded the yield point. Many pastes and fillers belong to this group of materials. After starting to flow they can exhibit Newtonian (*Bingham* flow) or pseudoplastic properties (*Casson*'s liquid).

In respect of their flow properties, therefore, paints and coating materials cannot generally be described using the linear function formulated by *Newton*. A mathematical relation which is more appropriate for practical application was developed by *Ostwald* [2.4.88].

$$(\tau - \tau_0)^n = \eta \cdot D$$

If n = 1 and $\tau_0 = 0$, these are *Newton*ian liquids. If n > 1 or n < 1 and τ_0 in turn is 0, the liquids are pseudoplastic or dilatant. In the case of substances with a yield point is $\tau_0 > 0$. All rheological phenomena described thus far are reversible processes without any time delays. By contrast, the changes in viscosity are also a function of time in the case of thixotropic liquids. The flow properties of coating materials therefore become a function of their history. Starting from the viscosity at rest, the viscosity decreases with increasing shear stress, but then initially reverts to a lower viscosity at rest when the shear rate decreases. Only after a time which is specific to each material is the substance regenerated and the original viscosity reestablished. In the τ/D graph there are, therefore, two different flow curves, for increasing shear stress from rest and falling stresses thereafter. The area enclosed by the curve traces in figure 2.3.18 is a measure of the degree of thixotropy.

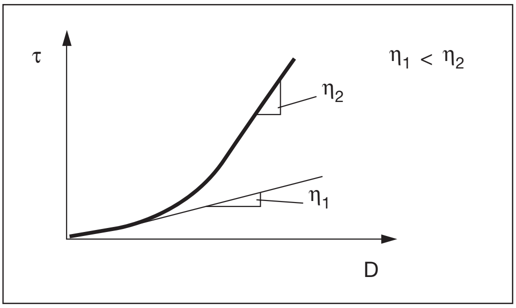


Fig. 2.3.17
Rheological profile of dilatant materials

The term thixotropy is derived from Greek and means change as a result of touch. In this phenomenon a gel liquefies in the event of mechanical action such as vibrating, agitating or stroking (sols) and gradually solidifies into a gel-like material again once the action finishes (gels). This reversible process is

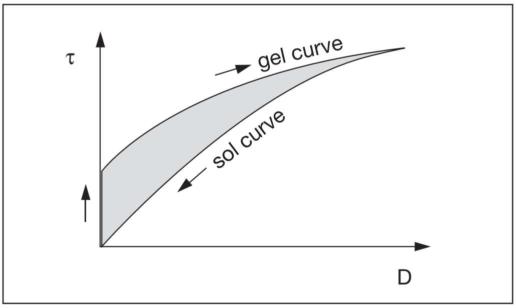


Fig. 2.3.18
Flow curve of a thixotropic liquid

therefore termed a sol-gel conversion. It is encountered in paints and numerous other materials. Some clay types, bentonites or hydrated metal oxides have a pronounced tendency when in static concentrated solutions with relatively large volumes of liquid to accumulate as honeycomb shaped, net- or matrix-like formations. Consequently, the viscosity of such a solution quickly rises. However, the intermolecular forces are not so large that the matrix remains intact during agitation or vibration. This process causes a rise in the yield point. On reverting to the material's rest state, the structures are reestablished within a certain time. It should be noted that thixotropy of a system decreases with increasing temperature and disappears entirely at temperatures around 100 °C.

Although thixotropy is problematic in the manufacture of paints and coating materials, it is a welcome property in processing [2.4.89, 2.4.90]. A feature of thixotropic paints, like paints with a set pseudoplasticity, is that they have less of a tendency to run on vertical surfaces.

In rare cases formulations exhibit the property of rheopexy, which is the opposite of thixotropy. In this the viscosity at rest is lower than the viscosity after the action of shear.

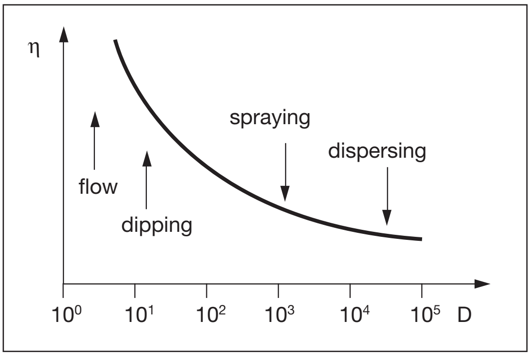


Fig. 2.3.19
Shear stress D and viscosity η of ideal pseudoplastic paints from manufacturing to application

Evaluating the complex flow properties of paints in practice requires accurate knowledge of the shear stress at every stage of manufacture and processing. A broad band of varying shear stress is covered, from the extremely high shear stresses when dispersing or spraying paints, via the lower shear gradient during processing by means of dip coating, to the extremely low shear during the flow of freshly applied films. The spectrum of the D-values ranges from 10^0 to > 10^5 s^{-1} when using paints. A for the application ideal pseudoplastic paint always exhibits the desired viscosity within the shear gradient spectrum. This is the only way of explaining how coating materials can meet the seemingly contradictory demands outlined above of easy brushability or sprayability without dripping while achieving good flow at the same time.

A liquid coating material can only meet the sometimes very heterogeneous requirements during the entire feed and processing stage by means of an adapted pseudoplasticity and plastic flow properties appropriate to the requirements if the temperature dependency of the viscosity is also addressed when characterising the rheological properties.

Of the numerous empirical and scientific attempts to quantify the impact of temperature on the viscosity of resin solutions and liquid coating materials, the Andrade equation has proved its value in practical operations.

The Andrade equation is based on work by *Arrhenius*, *Prandtl* and *Eyring*. This work explains the temperature dependence of liquids which is derived from the energy involved in the individual molecules changing position during the flow process.

$$\eta = A \cdot e^{\frac{B}{T}} \qquad A, B = \text{material specific constants}$$

The temperature dependency of the viscosity of solvent free polymer melts, as involved in the manufacture and processing of powder coatings, is better explained by the *Williams*, *Landel* and *Ferry* equation (WLF). However, this only describes viscosity properties with a good level of accuracy within a relatively narrow range above the melting point.

$$\lg \frac{\eta}{\eta_0} = \frac{-B \cdot (T - T_0)}{C + (T - T_0)}$$

B,C = material constants

η_0 = melt viscosity

T_0 = reference temperature, e.g. melting temperature

For resin solutions and melts the reduction in viscosity with increasing temperature can be considerable, particularly at higher viscosities. Depending on the chemical structure, viscosity reductions of 4 – 10% are measured per degree of temperature rise.
It is therefore important to ensure good temperature control in dispersers and agitators, and particularly sensitive measuring instruments for determining viscosity.

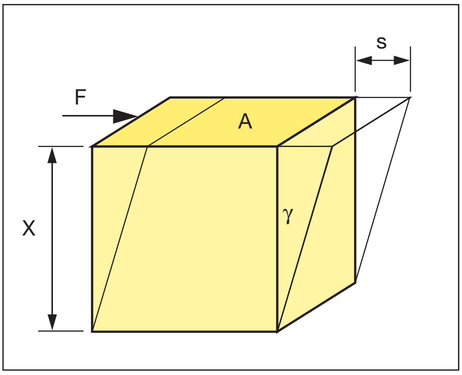


Fig. 2.3.20
Model to estimate the heat generation during flow of a liquid

Under the known condition that the deformation work during the flow of viscous liquids is converted quantitatively into heat, the following applies with regard to estimating the heat increase. An imaginary cube of side length x is sheared with a force F along a path s at a shear angle γ.
The quantity of heat $\dot{q}$ relative to the volume V arising in the time t is then

$$\dot{q} = \frac{F \cdot s}{V \cdot t} \quad \text{where} \quad F = \tau \cdot A \quad \text{and} \quad V = A \cdot x$$

$$\text{follows} \quad \dot{q} = \frac{\tau \cdot A \cdot s}{A \cdot x \cdot t} = \tau \cdot D = \eta \cdot D^2$$

Heat generation during flow is thus directly proportional to viscosity, but quadratically proportional to the shear gradient. This fact is important, among other things, for the design of the temperature control system of sensitive measuring instruments and for the development of manufacruring procedures for paint formulas (see below).

Measurement methods

A range of measuring instruments is available for measuring viscosity which locate the desired indicators by directly determining the shear stress at a specified shear rate (gap flow), by measuring the discharge rates when flowing through pipes (capillary flow) or by determining the sedimentation rate of a defined solid content in liquids (creeping movement).
In every case it is important to ensure that laminar flow conditions obtain during measurement. Only then can *Newton*'s fundamental law be used to calculate the

viscosity. If capillaries or pipes are used in the measurement process, the flow conditions in pipes can be characterized by calculating the *Reynolds*' number as a nondimensional link for all the flow influencing physical variables. These are viscosity, density, flow rate and diameter of the piping.

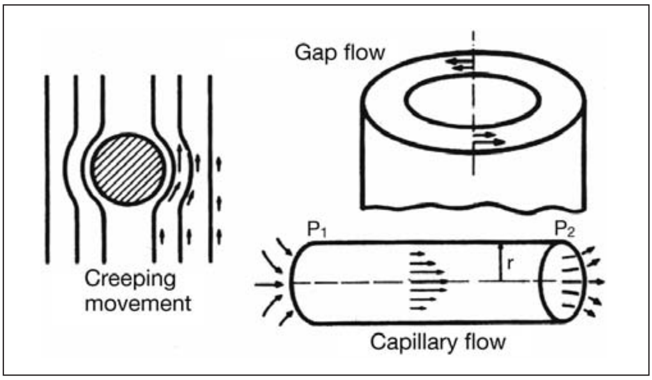


Fig. 2.3.21
Characteristic laminar flows for different measurement techniques of viscosity

If the *Reynolds*' numbers are below 2000, the flow is laminar and suitable for conducting measurements. Above 2000 the liquid threads start to develop mixed flows, while if the *Reynolds*' number continues to rise, turbulent flow sets in completely.

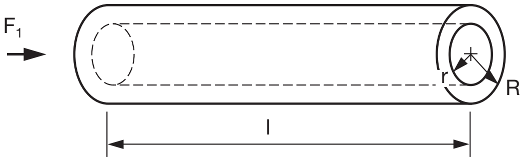
The measurement principle of **capillary viscosimeters**, which are widely used in coating technology in the form of flow cups, involves a defined volume of the liquid under analysis flowing through a nozzle of known diameter and length. The measured discharge time is converted to a viscosity reading with the aid of *Newton*'s fundamental law.

To this end the law has to be adapted to the flow conditions in pipes. If the force necessary for flow in pipes is F_2, the counterforce which occurs as a result of friction during flow is F_1 after *Newton*'s law.

$$F_1 = \eta \cdot A \cdot \frac{du}{dr} \qquad F_2 = \Delta p \cdot r^2 \cdot \pi$$

for stationary condition follows

$$F_1 + F_2 = 0 \quad \text{or} \quad \Delta p \cdot r^2 \cdot \pi = -\eta \cdot A \cdot \frac{du}{dr}$$



Preparing, inserting the boundary conditions and resolving the differential equation results in the following where r = 0 to R = radius of the capillaries of length l:

$$u = \frac{\Delta p}{4 \cdot \eta \cdot l} \cdot (R^2 - r^2)$$

The flow profile u(r) corresponds to a parabolic function. The liquid adheres to the side walls with $u_{min} = 0$, while attaining a maximum u_{max} in the centre.

The conveyed or discharged volume $dV = 2\pi r \, dr \, l$ is calculated by using the speed equation $u = l/t$.

The result yielded by resolving the new differential equation is

$$V = \frac{\Delta p \cdot \pi \cdot R^4}{8 \cdot \eta \cdot l} \cdot t$$

This equation, which is known as the *Hagen-Poiseuille* equation, enables the viscosity to be calculated for a specified flow volume by measuring the discharge time.
Since the effective pressure Δp is defined by gravity and is a function of time with $\rho \cdot g \cdot h(t)$ because of the reducing height of the liquid column, this dependence must also be determined. The mean $\bar{h}$ for h(t) is calculated from this.
None of our considerations to date has addressed the fact that the effective static pressure $\rho \cdot g \cdot \bar{h}$ is reduced during flow for reasons of energy conservation.
The consequence of this effect, first described by *Bernoulli*, is that the dynamic pressure $\rho \cdot u^2/2$ of the now flowing liquid has to be deducted from the total pressure $\rho \cdot g \cdot \bar{h}$ as a so called *Hagenbach* correction. The following is yielded once all the variables affecting the measurement process have been taken into account:

$$V = \frac{\left(\rho \cdot g \cdot \bar{h} - \frac{\rho}{2} \cdot u^2\right) \cdot \pi \cdot R^4}{8 \cdot \eta \cdot l} \cdot t$$

After mathematical processing it follows that:

$$\frac{\eta}{\rho} = \nu = \frac{g \cdot \bar{h} \cdot \pi \cdot R^4}{8 \cdot V \cdot l} \cdot t - \frac{V}{16 \cdot \pi \cdot l \cdot t}$$

or

$$\nu = A \cdot t - \frac{B}{t}$$

Fig. 2.3.22
Flow cup according to DIN EN ISO 2431

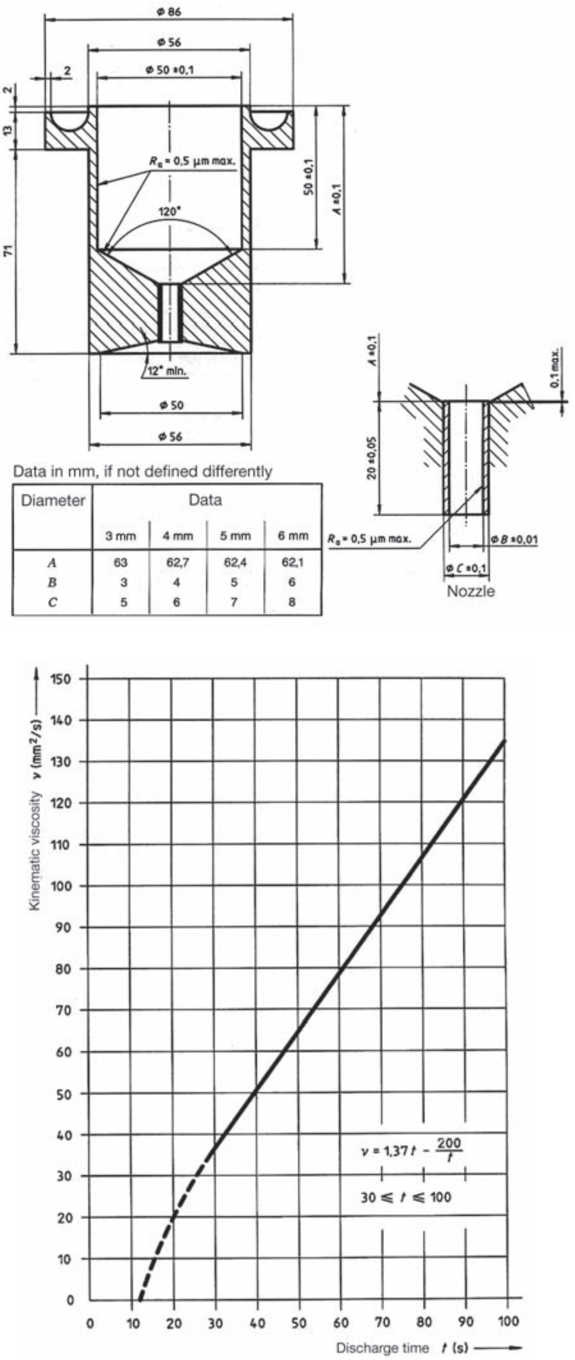
After calculating and aggregating the constant values into A and B the kinematic viscosity for *Newton*ian liquids can be calculated by converting the results of the discharge times.
In the case of pseudoplastic materials certain reservations apply to use of the flow cups. Because of the continually changing flow rate which is set by gravity, it is not possible to set a defined shear gradient, let alone maintain it at a constant level. τ/D graphs for characterising the flow properties as a function of defined shear cannot, therefore, be plotted with flow cups. In such cases flow cups merely serve ultimately to check the identity of coating materials, and even then only where there is the

same level of pseudoplasticity. Flow cups are not suitable at all for thixotropic coating materials.

The relevant standards specify geometries and calibration curves with the permissible viscosity ranges for the individual cups. The DIN cup, which was the standard in the past, has now been superseded by the ISO cup. The discharge nozzle has been lengthened five-fold compared with the DIN cup, which slows the flow rate down and increases the accuracy and reproducibility of the results.

Because of the known temperature dependency of viscosity it is important to ensure good temperature control for the samples under analysis.

International standard DIN EN ISO 2431 describes four flow cups with the same dimensions but different nozzle diameters (3, 4, 5 and 6 mm). By varying the nozzle width it is possible to cover a broad viscosity spectrum. The permissible working ranges for all cups use discharge times of between 30 s and 100 s.



Data in mm, if not defined differently

Diameter	Data			
	3 mm	4 mm	5 mm	6 mm
A	63	62,7	62,4	62,1
B	3	4	5	6
C	5	6	7	8

Fig. 2.3.23
Cross section of an ISO cup and a respective calibration curve

Rotary viscosimeter

Rotary viscosimeters are the appropriate measuring instruments for analyzing non-*Newtonian* liquids with a high pseudoplasticity, dilatancy or thixotropy which involves setting defined shear gradients. The flow states in the measuring part of the instrument are similar to the laminar flow between the two plates of the *Newtonian* model. Cylinder and cone-plate instruments have proved themselves

in practical operations. In the first case two concentrically configured cylinders with a narrow gap between them move relative to each other. Either the outer cylinder or the inner cylinder can be stationary. In the second case a flat cone rotates on a fixed plate. The liquid under analysis in the space between the cylinders or the cone and the plate can be sheared in a defined manner by varying the rotational speed. The torque which is generated for a given rotational speed can be measured by the power consumption of the driving motor. Both instrument types permit rheograms (flow curves) to be plotted in every stress range to which coating materials are subjected in practice.
If the outer cylinder of a **cylinder viscosimeter** is driven, this is termed a *Couette* viscosimeter, while the design featuring a driven inner cylinder is known as a *Searle* viscosimeter. In both instrument types the speed gradient is specified, and the resulting shear stress is then measured.

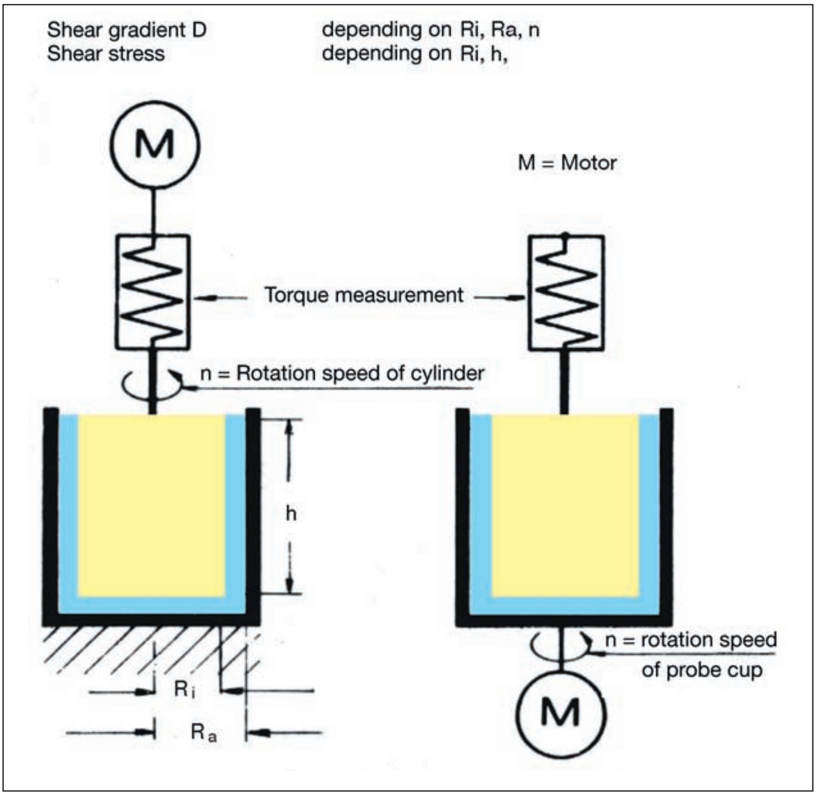


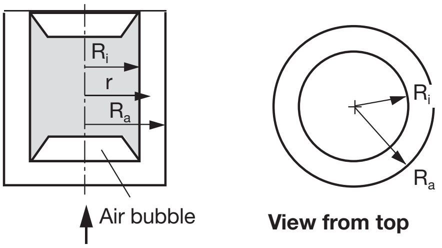
Fig. 2.3.24
Cross section of a cylinder viscosimeter

In the case of substances with time dependent flow properties care must be taken to ensure that an adequate rest time is allowed before the measurement process starts to enable the full development of the gel state. The sample must also be checked to ensure that it has reached the specified temperature before measurements begin. Once all the requirements for reproducible readings have been met, flow curves can be plotted, from which the viscosity corresponding to the particular D-value can be calculated. If the rheograms are identical at increasing and decreasing speeds, this is an indication of dilatancy or pseudoplasticity, depending on the increase or decrease in the viscosity. If the curves vary with increasing speed (gel curve) and a subsequent decrease (sol curve), this indicates thixotropy or rheopexy.

Newton's fundamental equation is again used to process the readings.

In this

$$\tau = \frac{F}{A} = \frac{F \cdot r}{A \cdot r} = \frac{M}{2 \cdot \pi \cdot r^2 \cdot h} \qquad M = \text{torque}$$



where the generated surface of the liquid $A = 2\,\pi\, r\, h$ and h is the height of the measuring cylinder. If the liquid cylinder is expanded to any radius r, a correlation is found between the shear stress τ and the torque M. The following applies to calculating D:

$$D = \frac{du}{dr} = \frac{d\omega \cdot r}{dr}$$

When incorporated in the Newtonian fundamental equation, this yields

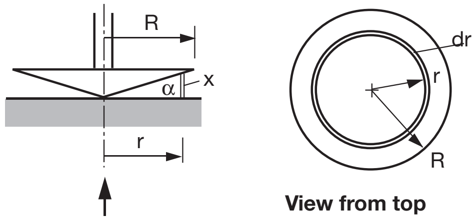
$$\frac{M}{2 \cdot \pi \cdot r^2 \cdot h} = \eta \cdot \frac{d\omega \cdot r}{dr}$$

Resolving the differential equation, taking account of the boundary conditions (external radius R_a/internal radius R_i or max. angular velocity $\omega = 2\pi n$), yields

$$M = \frac{8 \cdot \pi^2 \cdot R_a^2 \cdot R_i^2 \cdot h}{R_a^2 + R_i^2} \cdot \eta \cdot n$$

The formula ceases to be valid when the gap to be sheared exceeds a certain width. The ratio between the radius of the outer and inner cylinders should not exceed 1.1 in order to maintain a linear shear gradient and to create the necessary conditions for rapid heat dissipation.

Apart from cylinder type rotary viscosimeters **cone-plate rotary viscosimeters** are also in common use. The coating material to be measured is located in this case between the rotating cone and the stationary plate. The advantages these instruments have over cylinder viscosimeters are the very small sample quantity, the rapid attainment of the test temperature and the short measuring and cleaning time. Because of the very small angle of the cone envelope high shear gradients can be achieved even at low speeds. Calculation of the viscosity is similar to the method used with cylinder viscosimeters.



$$D = \frac{\omega \cdot r}{x} = \frac{\omega}{\tan \alpha} \approx \frac{\omega}{\alpha} = \frac{2 \cdot \pi \cdot n}{\alpha}$$

The D-value is a function of the rotational speed ωr and x, the gap between the cone and the plate at the location r. x/r can also be described by tan α which corresponds to α at very small angles. Since $\omega = 2\,\pi\,n$ this results in the calculation formula for the shear gradient as a function of the rotational speed.

Calculation of the torque is somewhat more complicated than with cylinder viscosimeters. A differential segment dM of the torque M must first be taken into account to obtain a usable relation by resolving the differential equation.

$$dM = \tau \cdot dA \cdot r$$

due to $dA = 2 \cdot \pi \cdot r \cdot dr$

follows after solution of differential equation → $\tau = \frac{3 \cdot M}{2 \cdot \pi \cdot R^3}$

When incorporated in the Newtonian fundamental equation $\tau = \eta \cdot D$, this yields

$$M = \frac{4 \cdot \pi^2 \cdot R^3}{3 \cdot \alpha} \cdot \eta \cdot n$$

Apart from the cone-plate instruments which permit a continuous change in the speed gradient, there are also simple viscosimeters which only operate with a fixed shear gradient. Because of their efficient operating method, these instruments have proved suitable for routine tests both in monitoring production and in R&D laboratories. They have thus become a serious competitor for flow cups which are frequently used where not permitted, i.e. with non-Newtonian liquids. Cone-plate instruments are therefore used not least because they also allow viscosity measurements at higher temperatures. Resin melts and powder coatings can be measured without difficulty at temperatures up to 200 °C.

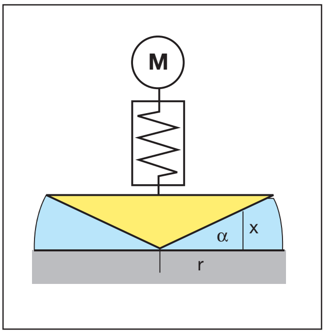


Fig. 2.3.25
Scheme of a cone-plate viscosimeter

A further principle relating to viscosity measurement is based on observing the motion of balls in a pipe filled with the test liquid. If the diameter of the ball is only slightly less than that of the pipe, and the ball moves downwards (Δρ positive) or upwards (Δρ negative) because of the difference in density between itself and the test liquid, the viscosity can be calculated from the time taken to cover a specified distance. These instruments include the **falling ball viscosimeter** after Höppler and the **bubble viscosimeter**. The viscosity is determined from the resulting rate of fall or rise of the test body in the form of a ball or air bubble. The following applies to the stationary state for the ball travel u:

$$m \cdot g = 6 \cdot \pi \cdot \eta \cdot r \cdot u$$

After resolving this and replacing u = s/t it follows that

$$s = \frac{k}{\eta} \cdot t \quad \text{where} \quad k = \frac{m \cdot g}{6 \cdot \pi \cdot r}$$

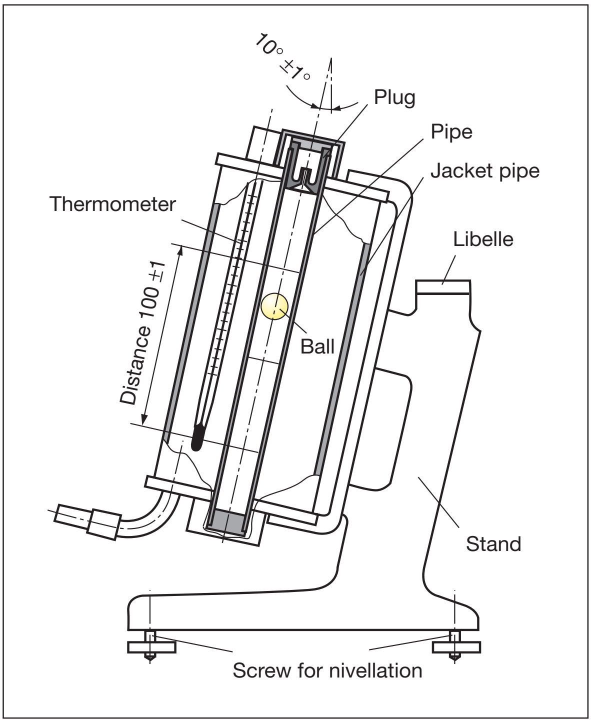


Fig. 2.3.26
Scheme of a Höppler viscosimeter

Different measurement ranges can be covered using balls of different density (glass, steel etc.). Viscosity measurements are also possible by means of a simple comparison of the travel speed of a bubble in liquids of known viscosity. In bubble viscosimeters to ASTM D 1545 test tubes are filled with liquids of rising viscosity (A–Z10). The liquid under test is then poured into a corresponding empty tube and compared with the rate of rise of the bubbles in the reference standards. The test substance is labelled with the letter corresponding to its viscosity.

All the instruments discussed so far are suitable to a greater or lesser extent for viscosity measurements to evaluate the molecular structure of resins and their interaction with solvents, but also to describe pigment dispersions and transport in pipelines and to evaluate atomization processes. They are not suitable, however, for evaluating the film forming process and

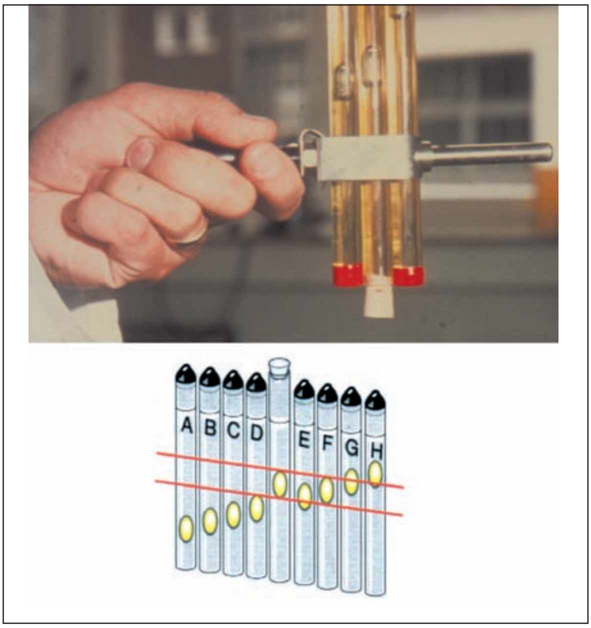


Fig. 2.3.27
Bubble viscosimeter according to ASTM D 1545

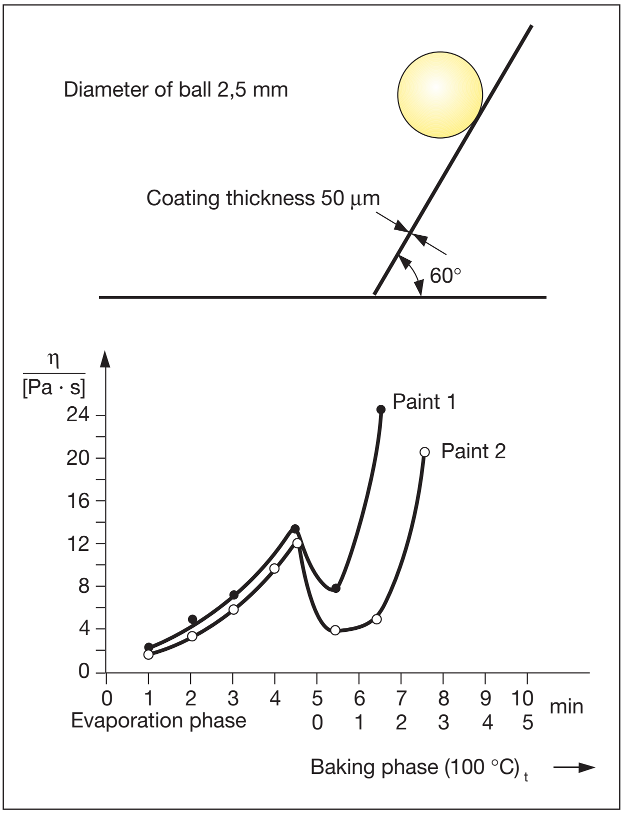


Fig. 2.3.28
Generalized curve of viscosity of coatings during film formation

the resulting high viscosities. The transition from the liquid to the solid phase with the discharge of solvents, overlapping with chemical reactions, cannot be simulated in the instruments described.

Since flow, the tendency to run and surface faults such as pinholes and craters are very greatly affected by the time profile of the flow properties right up to the set film, there is great interest in measurement methods which can record the rheological properties of paints throughout the entire film forming process.

A very old, yet at the same time also very simple method of determining changing viscosity semiquantitatively, is available in the ”**rolling ball method**” developed by *Wolff* and *Zeidler* in 1938 [2.4.91]. Immediately after application of the coating material to be tested steel balls with a diameter of 2.5 mm are placed on the test panel which is inclined at an angle of 60°. The speed at which the balls roll down is a measure of the viscosity at the time of the measurement. If balls are then dropped onto the curing coating at regular, short intervals and the travel of the last ball is subtracted from that of the preceding one, the distances s determined in this way provide the basis for calculating the particular viscosity η. If s is plotted against t, the viscosity is calculated from the proportionality factor. The proportionality factor is formed from the density and size of the ball, the density of the film, the acceleration due to gravity g and two empirical constants.

$$s = \frac{(\rho_b - k_1 \cdot \rho_p) \cdot g \cdot r^2}{k_2 \cdot \eta} \cdot t$$

ρ_b = density of rolling ball
ρ_p = density of paint
k_1, k_2 = empirical constants

Figure 2.3.28 shows the results for two different paints. Because of its lower reactivity in the baking phase paint 2, which has a tendency to run, falls to a lower viscosity level than the chemically more reactive and therefore faster curing paint 1. The poor flow of paint 1 and the tendency to run of paint 2 are clearly confirmed by the flow curves of the ”rolling ball method”.

Accurate viscosity measurements during the entire curing period of reactive paints are possible using rheometers whose shear travel is shorter than the maximum possible elastic deformation after curing of the film. This can be achieved by replacing the rotation of the rheometer by oscillation. Usually sine-shaped oscillations, whose amplitude must be below the film's yield point, are imposed on the film which is located between the oscillation plates.

$$\tau = \tau_0 \cdot \sin(\omega \cdot t)$$
$$\gamma = \gamma_0 \cdot \sin(\omega \cdot t - \delta)$$

Such measurement systems allow both the viscous and the elastic components to be measured as a result of the time shift in the deforming shear stress and the resulting deformation. It is therefore possible to record the complex viscosities of viscoelastic substances (see chapter 3.2.5).

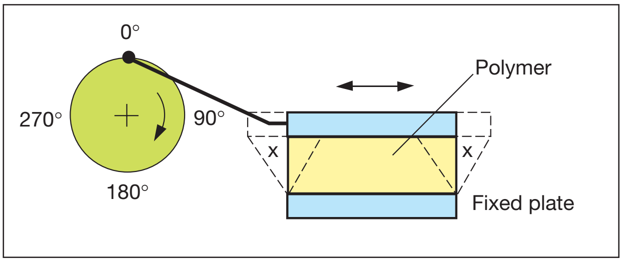


Fig. 2.3.29
Scheme of an oscillation rheometer

Surface tension

Many coating technology processes, e.g. the wetting of pigments, atomization of coating materials and flow of fresh films, the emulsification process, capillary action when penetrating pigment agglomerates, floating effects, running away from edges, crater formation and similar, are affected by the higher potential energy of molecules at interfaces and the resulting surface tension.

The surface tension, in its interaction with the rheological properties, is the most important physical variable in evaluating coating materials.

Materials with finite extension properties, such as liquids and solids, exhibit a higher energy level at their interfaces than in the rest of their volume. As a result liquids, if gravity effects are excluded, always take on the minimum surface area. Cohesive forces are generated by the *van-der-Waals*' forces as a consequence of dipolar and dispersion forces in conjunction with hydrogen bridges. These cohesive forces are equal in all spatial directions within the liquid. The force resultant assumes the value 0. The molecules at the interface with an imaginary vacuum or vapour space with comparatively few molecules, on the other hand, behave differently.

In this case the sum of all the forces acting is not equal to 0. All the molecules at the surface have an attraction to the inner component of the liquid and consequently a higher potential energy. This enables them to move into the inner part of the liquid if space is or becomes available to them. If, therefore, a

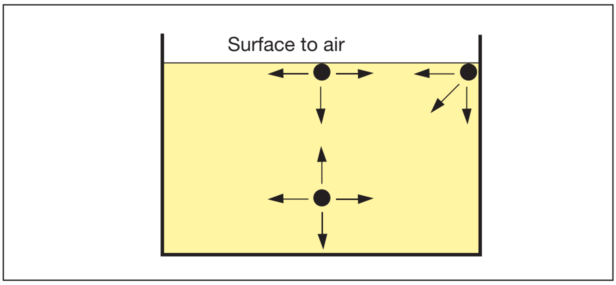


Fig. 2.3.30
Explanation of forces to create surface tension

form change is possible which involves reducing the surface area, this will occur because of the effective surface tension. Thus, excluding external influences such as gravity, liquids always have the minimum possible surface areas. They transform themselves into spheres because these occupy the least possible surface area for a given volume. Conversely energy has to be expended to increase surface areas. The definition of surface tension σ is consequently the work per unit area which has to be performed to increase the surface area.

$$\sigma = \frac{F \cdot s}{A}$$

The dimension of surface tension is N/m. It acts tangentially to the surface. The force counteracting expansion is directed towards the inner part of the liquid.
From a thermodynamic perspective the surface tension σ is equal to the change in the free enthalpy G of the system if surface areas A are changed without material change under isothermal and isobaric conditions.

$$dG = \left(\frac{dG}{dA}\right)_{p,T} dA \qquad \text{d.h.} \quad \sigma = \left(\frac{dG}{dA}\right)_{p,T}$$

Surface expansions area are thus also only possible from a thermodynamic perspective if the free enthalpy in the system increases. The system must therefore perform work to expand surface areas.
The work which has to be performed per unit area to expand the surface area varies very greatly for individual liquids. It is determined by the molecular interactions described above. These consist of the polar interactions σ^p as the sum of the effect of permanent dipoles (orientation forces), induced dipoles (induction forces), hydrogen bridge bond forces and the nonpolar dispersion forces σ^d.

$$\sigma = \sigma^d + \sigma^p$$

σ^d = disperse contribution
σ^p = polar contribution

Since the surface tensions of liquids of relevance to coating technology are relatively low, the surface tension is given in mN/m rather than N/m. Thus polar water has a surface tension of 73 mN/m. Other liquids, such as xylene or benzene, are substantially lower, at 30 and 24 mN/m, respectively. The illustration below gives an overview of the surface tensions of the most important resins and solvents.
Surface tension is a temperature dependent variable. *R. von Eötvös*, *W. Ramsay* and *I. Shields* formulated the following semiempirical relation which is valid for almost all liquids:

$$\sigma(T) = A - B \cdot T$$

Substances	σ^d	σ^p	σ_{total}
water	21,8	51,0	72,8
ethanol	17,5	4,6	22,1
ethylenglycol	29,1	20,3	49,4
n-hexane	18,4	0	18,4
n-decane	24,0	0	24,0
glycerine	37,2	27,3	64,5
toluene	26,1	2,3	28,4
alkyd resin	26,9	6,3	33,2
acrylic resin	25,8	7,2	33,0

Fig. 2.3.31
Surface tension of resins and liquids in mN/m

A and B are constants which have to be determined empirically.
By contrast with viscosity which reacts to temperature changes by 4 – 10%/°C, surface tension is less sensitive, with a figure of only 1%/°C.

Measurement methods
Since the surface tension of liquid materials is lowered by tensides, but these can only act if they are able to be deposited at the interface, i.e. take on a state of equilibrium, a distinction must be drawn in the measurement methods between measuring static and dynamic surface tension.
In the **static measurement methods** the surface area is expanded in various ways in a defined manner slowly such that an equilibrium can always be established for additives at the interface. The work to be performed to achieve this or the potential energy which is increased as a result is measured directly or indirectly. The force-pull methods after *du Nouy* and *Wilhelmy*, the capillary, drop and rotary methods, have proved particularly successful.
In the force-pull method a platinum ring to DIN 53914 (*du Nouy*) or ISO 304 or a platinum rod (*Wilhelmy*) is immersed in the liquid under analysis whose viscosity should be < 2 Pa s. The test bodies are slowly moved to the interface. As it is raised further, the surface area of the adhering liquid expands. The force expended to achieve this reaches a maximum before falling again as the lamella constricts and then breaks. The maximum force enables the surface tension to be calculated.
The work performed is F h. This corresponds to the surface tension, multiplied by the surface area generated. In the case of a ring, because of the doubled surface area internally and externally, this is $\sigma\ 4\ \pi\ r\ h$, while for the method after *Wilhelmy* it is $\sigma\ 2\ l\ h$ whereas l is the length of the platin stick.
The following applies with regard to the maximum:

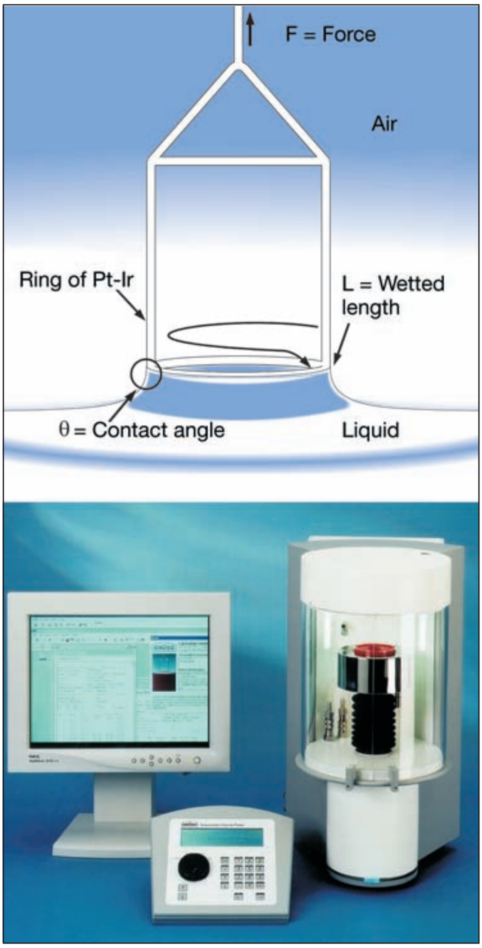


Fig. 2.3.32
Tensiometer according to DIN 53914 and ISO 304

$$\sigma = \frac{F}{4 \cdot \pi \cdot r} \quad \text{de Nouy} \qquad \sigma = \frac{F}{2 \cdot l} \quad \text{Wilhelmy}$$

The force-pull properties of the lamellae provide supplementary information about the foam persistence of the tested liquid. If the lamella breaks quickly once the maximum

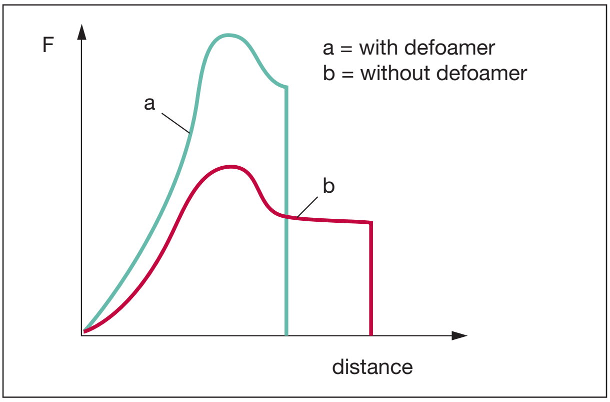


Fig. 2.3.33
Force-pull behavior of stable and unstable lamellas during measurement of static surface tensions according to Wilhelmy or deNoy

has been exceeded, there is no risk of foaming. Liquids with a tendency to foam, on the other hand, form stable lamellae which only break much later.

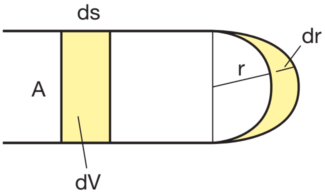
In the capillary or drop method a correlation is assumed between the cohesive pressure of the liquid and the surface tension. This can be established by means of a simple theoretical method.

At one end of a liquid filled pipe is a liquid hemisphere of surface area O = 2 π r^2. The influence of the pressure p results in an amount of work being performed which corresponds to the work required to create the new surface area.

$$\sigma \cdot dO = p \cdot dV$$

dO = change of surface area

dV = change of volume



or

$$\sigma \cdot 2 \cdot \pi \cdot \left[(r + dr)^2 - r^2\right] = p \cdot \frac{2}{3} \cdot \pi \cdot \left[(r + dr)^3 - r^3\right]$$

Ignoring dr^2 and dr^3, the resolution of the equation yields

$$p \approx \frac{2 \cdot \sigma}{r}$$

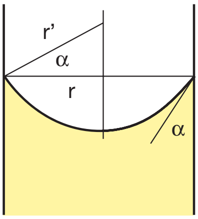
The cohesive pressure p is thus directly proportional to the surface tension and indirectly to σ the radius of the liquid hemisphere r. Decreasing diameters of liquid drops consequently result in an increased cohesive pressure.

The cohesive pressure p = 2σ/r acting in the capillary method draws a wetting liquid into the capillaries. With increasing lift height gravity also increases, resulting in the establishment of a stationary state. With a known capillary radius and wetting angle, the lift height is then a measure of the surface tension.

if $p = \frac{2 \cdot \sigma}{r'}$ follows $p = \frac{2 \cdot \sigma}{r} \cdot \cos\alpha$

because of $p = \rho \cdot g \cdot h$ follows $\frac{2 \cdot \sigma}{r} \cdot \cos\alpha = \rho \cdot g \cdot h$

$$\sigma = \frac{\rho \cdot g \cdot h \cdot r}{2 \cdot \cos\alpha}$$



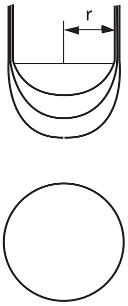
If the capillaries are wetted completely, the relation is simplified to

$$\sigma = \frac{1}{2} \cdot \rho \cdot g \cdot h \cdot r$$

In the drop method drops whose size or mass m is determined by the surface tension σ are formed by gravity m·g on a glass tube of radius r. In this process the cohesive pressure p_1 counteracts the gravity per unit area p_2. Measurements are made at $p_1 = p_2$.

$$p_1 = \frac{2 \cdot \sigma}{r} \qquad p_2 = \frac{m \cdot g}{A}$$

$$\sigma = \frac{m \cdot g}{2 \cdot \pi \cdot r}$$



To improve the accuracy of the measurement process several drops are generated and the total mass is then divided by the number of drops.
Another means of determining the surface tension of liquids, while taking account of gravity, involves analyzing the geometry of a drop hanging from a needle (pending drop method). The drop, which is spherical in a gravity free state, is transformed into an ellipsoid by gravity. Since the pressure difference between the exterior and interior of an interface is indirectly proportional to the radii of curvature, the surface tension of the liquid can be calculated from the changing geometry of the ellipsoid, where Δp = pressure difference between the interior and exterior of the interface.

$$\Delta p = \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

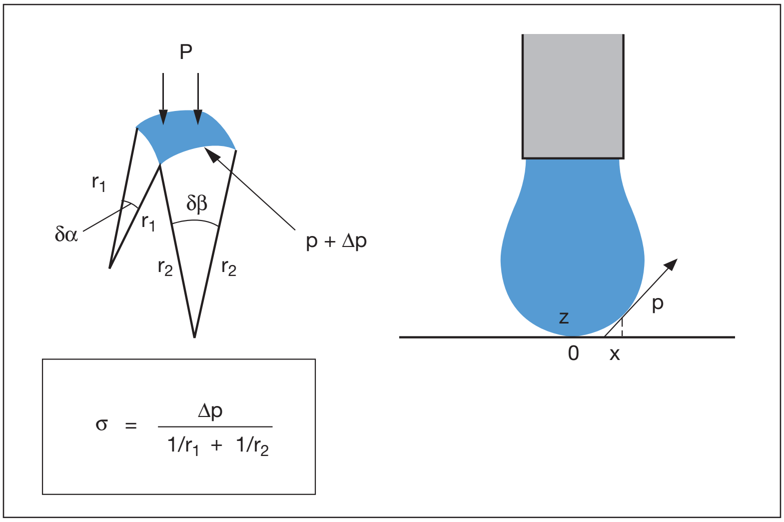


Fig. 2.3.34
Measurement of surface tensions with the pending drop method

r_1 and r_2 are the main radii of curvature of the ellipsoid. They can be calculated by image analysis of the drop. To do so, the pressure difference at the summit point Δp_s and at all the coordinates of the drop profile must be measured. The difference is

$$\Delta p_s - \Delta s = z \cdot \Delta\rho \cdot g$$

where z represents the vertical coordinate as per figure 2.3.34.

The methods presented here are not suitable for measuring extremely low surface tensions or interfacial tensions between two liquids. For such cases the spinning drop method is used. In this a drop of the sample under analysis of density ρ_{Pr} is injected into a heavier, continuous liquid of density ρ_s which is not miscible with the sample and which is located in a tube. This is then rotated at an angular velocity ω. The test drop, which is spherical at rest, is first transformed into an ellipsoid by the centrifugal forces. With increasing rotational frequency the ellipsoid is then converted to a cylinder with 2 hemispherical caps. If the length exceeds the radius r at least four-fold, the interfacial tension can be calculated [2.4.92].

$$\sigma = k \cdot r^3 \cdot \omega^2 \cdot (\rho_s - \rho_{Pr})$$

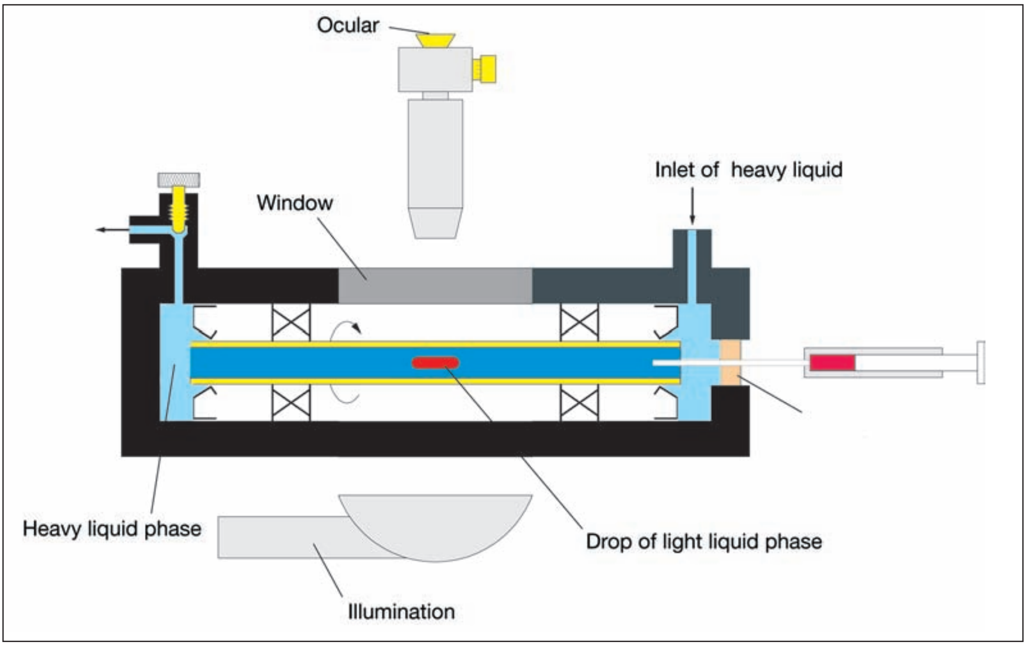


Fig. 2.3.35
Scheme of the spinning drop method for measuring interfacial tensions of liquids

Dynamic methods

Paints are always complex mixtures with ingredients which have an effect on surface tension. These have to be deposited at the interface to develop their full impact. However, many processes in paint manufacture and processing operate at such high speeds that it is impossible to achieve an equilibrium and thus the maximum possible effect of interfacially active additives. In order to achieve a quantitative analysis of

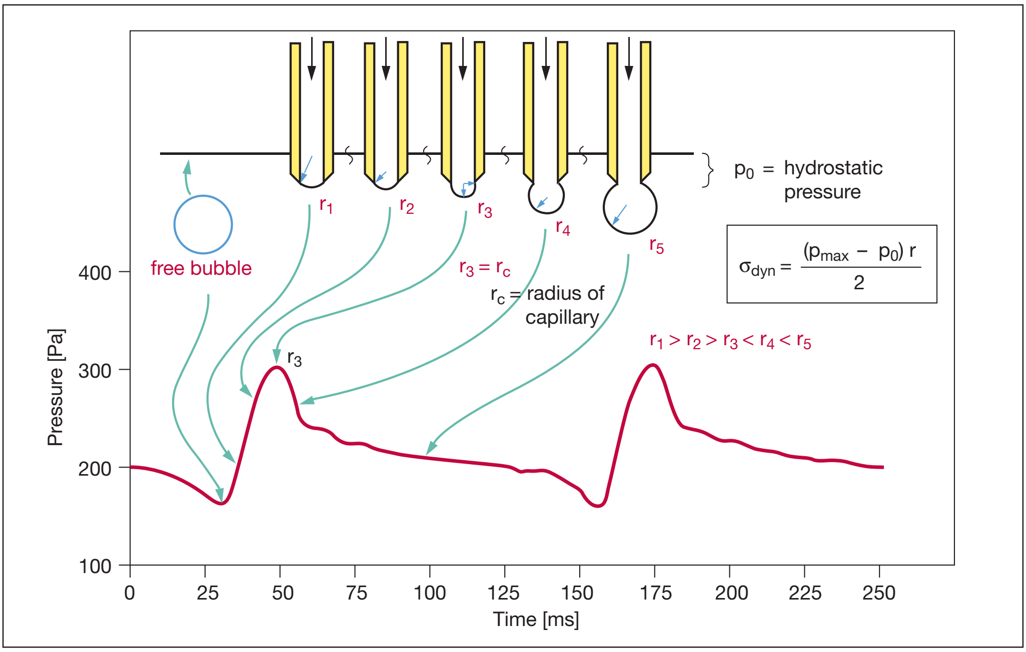


Fig. 2.3.36
Measuring the dynamic surface tension of tenside containing liquids

surface tensions, but also to measure the time required to establish equilibrium, readings have to be conducted on rapidly changing surface areas. The **bubble pressure method** is a measurement method which enables the surface tensions of newly generated surfaces to be measured. A capillary of radius r is immersed in the solution under analysis of density ρ. A specified number of bubbles per unit time is ejected from this capillary into the solution by means of a pressure p. The measured pressure required to release the bubble is p_{max}. At that moment the pressure is composed of $p_0 = \rho\, g\, h$, the hydrostatic pressure and the pressure required for bubble formation $2\, \rho / r_{min}$.

$$p_{max} = \frac{2 \cdot \sigma}{r_{min}} + \rho \cdot g \cdot h_l$$

The minimum radius r_{min} of the forming bubble is equal to the radius r of the capillaries.

$$\sigma_{dyn} = \frac{(p_{max} - \rho \cdot g \cdot h) \cdot r}{2}$$

If the bubble generation frequency is increased, p_{max} rises, and thus also the surface tension. Such a rise is an indicator of the kinetics underlying the setting of equilibrium in surface active substances.

Above a certain rate of volumetric flow, orientation of the tenside molecules at the interface cannot take place synchronously. If time dependent tenside effects are present, therefore, the surface tension is also a function of the number of bubbles formed per unit time.

The short time available to the molecules to reach the interface results in incomplete cover of the interface and thus to a higher surface tension. The time range of the surface age which can be set in this way ranges from 5 ms to 60 s.

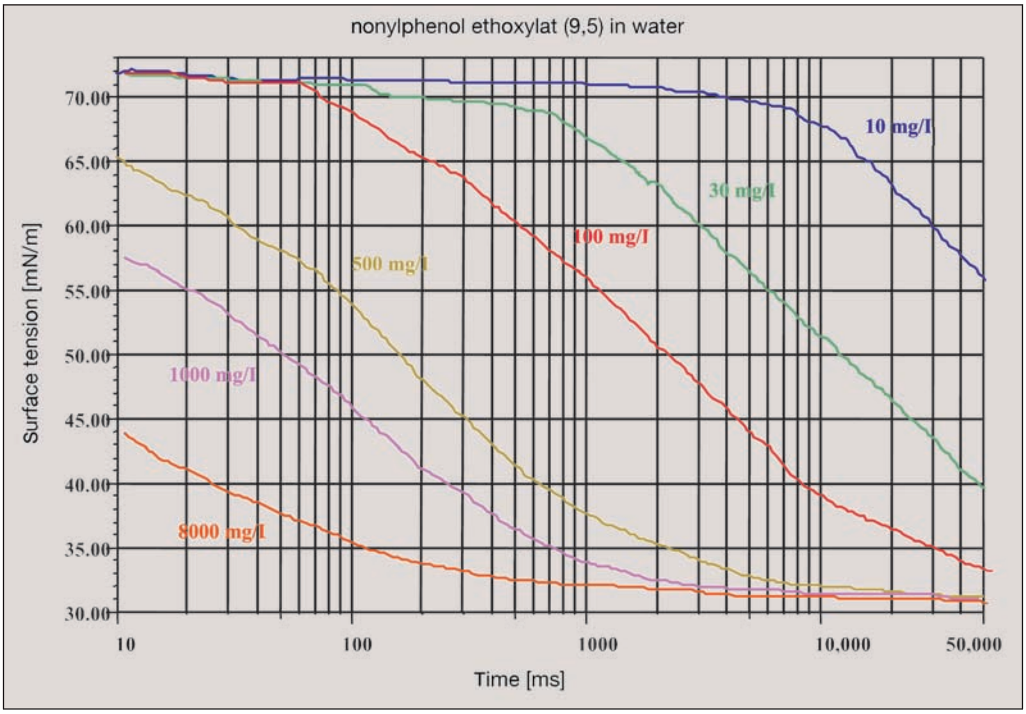


Fig. 2.3.37
Time dependency of surface tensions

The graph in figure 2.3.37 shows the time dependence of the surface tension generated with the addition of various quantities of tenside. The lower the rise in the curves, the faster the tenside reaches the interface. Assuming comparable molecular weights, equilibrium is established fastest with anionic tensides, followed by cationic ones. Nonionic tensides are generally the slowest products to be oriented.

Density

The density of coating materials and coatings is a significant variable with regard to the storage, processing and, in particular, yield of paints. Since the protective effect is mainly determined by the film thickness and thus, for a specified surface area, a certain volume ultimately has to be applied, a low density results in lower material consumption and thus to a better yield (see chapter 5.7).

The density ρ is defined in DIN EN ISO 2811-Parts 1-4 as the mass per unit volume in kg/m^3.

$$\rho = \frac{m}{V}$$

It is also a temperature dependent variable because volume is a function of temperature. The degree of temperature dependency is specified by the coefficient of expansion γ:

$$\rho(T) = \frac{m}{V_0 \cdot (1 + \gamma \cdot T)}$$

It is therefore essential when measuring density to ensure that the temperature is also measured or set to a specified value.

Measurement methods

Direct and indirect processes are used to determine the density of liquids. Pyknometers belong to the direct type of density measurement, while the indirect type includes immersed bodies, areometers and the oscillators.

Pyknometers as defined in DIN EN ISO 2811-1 are various shapes of vessel of known volume. Metal pyknometers are preferred in the paint and coatings industry because of their stability, ease of handling and good cleanability.

The uplift provided by air must be taken into account when weighing the mass where accurate readings are required. It is also usual to eliminate the pyknometer volume as a possible source of errors by means of comparative measurements with water, a medium of known density ρ_W. Because of the uplift of the ambient air, the density established by weighing is not the density of the paint, but the difference between the densities of paint ρ_{Pa} and air ρ_{Ai}.

Fig. 2.3.38
Pyknometers according to DIN EN ISO 2811-1

$$\rho_{Pa} - \rho_{Ai} = \frac{m_{Pa}}{V}$$

If this figure is divided by the result of the comparative reading with water, the outcome is

$$\frac{\rho_{Pa} - \rho_{Ai}}{\rho_W - \rho_{Ai}} = \frac{m_{Pa}}{m_W}$$

Solution to ρ_{Pa} results in a formula which permits readings with accuracy down to the per mill level.

$$\rho_{Pa} = \frac{m_{Pa}}{m_W} \cdot \rho_W + \rho_{Ai} \cdot \left(1 - \frac{m_{Pa}}{m_W}\right)$$

The measuring instruments which use the Archimedean principle of uplift include the **areometer**. The glass spindle of the areometer (see figure 2.3.39) is immersed in the liquid under analysis. Since the immersed body of volume V + h q of the part to be immersed loses the amount of weight equivalent to the weight of the displaced quantity of liquid m, the following applies to the equilibrium

$$m \cdot g = \rho_{Pa} \cdot g \cdot (V + h \cdot q)$$
$$\rho_{Pa} = \frac{m}{V + h \cdot q}$$

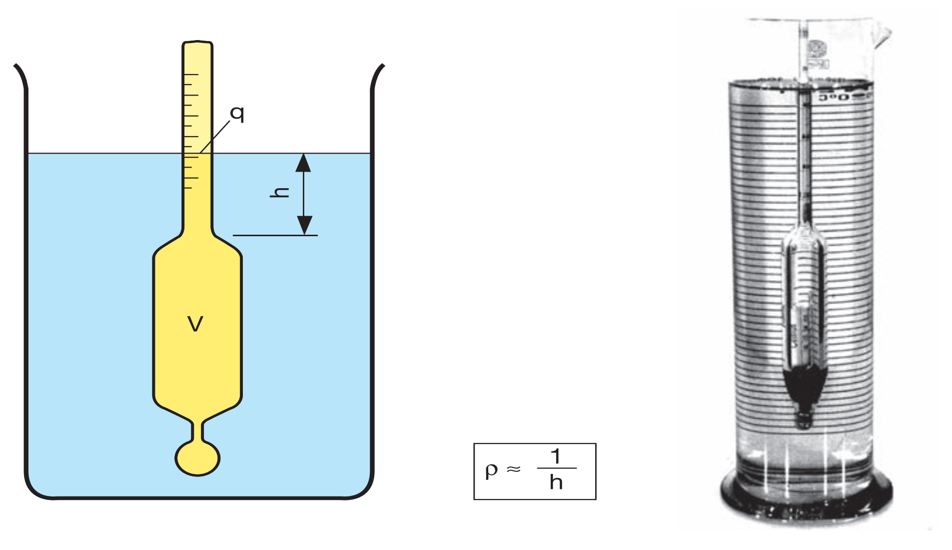


Fig. 2.3.39
Scheme and picture of an areometer

The distance h on the aerometer scale is a measure of the liquid's density.
The aerometer is, of course, unsuitable for use with highly viscous and especially with pigmented, thus opaque test liquids. In such cases the more precise method with the **immersed balls** to DIN EN ISO 2811-2 can be used. The material under analysis is

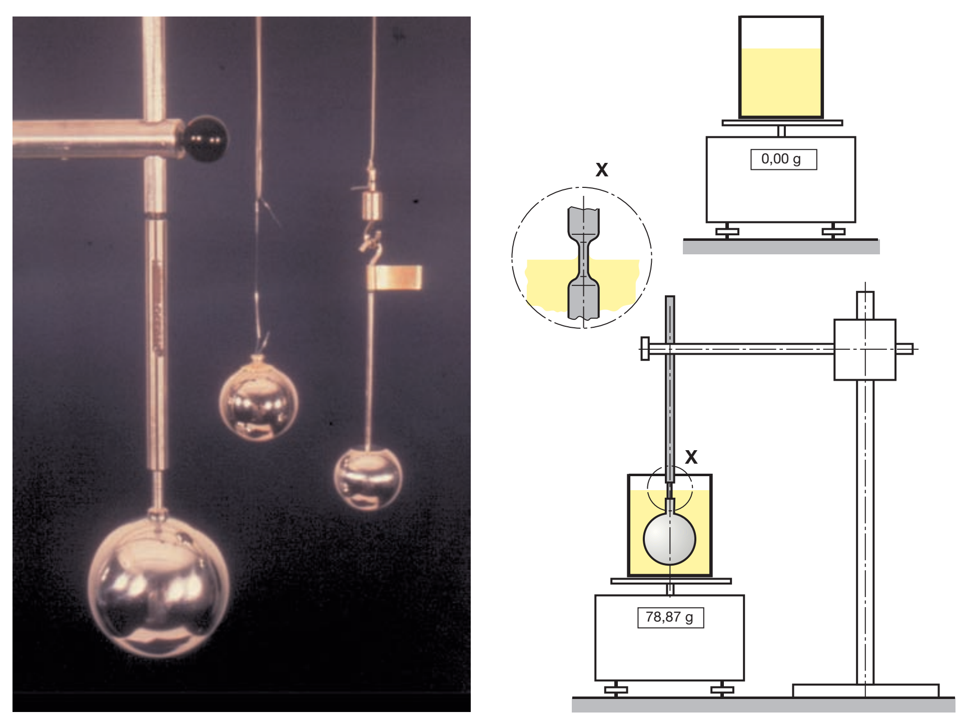


Fig. 2.3.40
Picture and scheme of measurements of densities with the immersed body method

located in a test vessel on a balance. After immersion and fastening of a metal ball with a volume of exactly 100 ml the increase in weight caused by the displacement of the paint is related to the volume and in this way the density is calculated. The measurement error is less than 0.1% and is especially low for an immersion process.

The immersed body method is universally applicable and easy to use. It is especially suitable for fast testing in the plant.

Another indirect method, though one which operates according to a completely different principle, is the **oscillator** method**.** The method according to DIN EN ISO 2811-3 uses the fact that the generated frequency of a tuning fork-like glass tube is a function of the densities of its contents.

If a ratio is formed of the period of vibration T_1 of the empty resonator tube to that of the resonator tube filled with test liquid T_2, the density ρ can be determined when the mass m_1 and the volume V of the measuring tube are known. The oscillator as a physical pendulum permits density measurements with accuracies to fractions of a per mill.

$$T_1 = 2 \cdot \pi \cdot \sqrt{\frac{m_1}{D}} \qquad T_2 = 2 \cdot \pi \cdot \sqrt{\frac{m_1 + \rho \cdot V}{D}}$$

$$\rho = \frac{m_1 \cdot \left(\frac{T_2^2}{T_1^2} - 1 \right)}{V}$$

The density of coatings (dry film density) and also that of the liquid coating materials are important technical and economic variables (see chapter 5.7). Means of determining the dry film density are described in chapter 3.2.2.

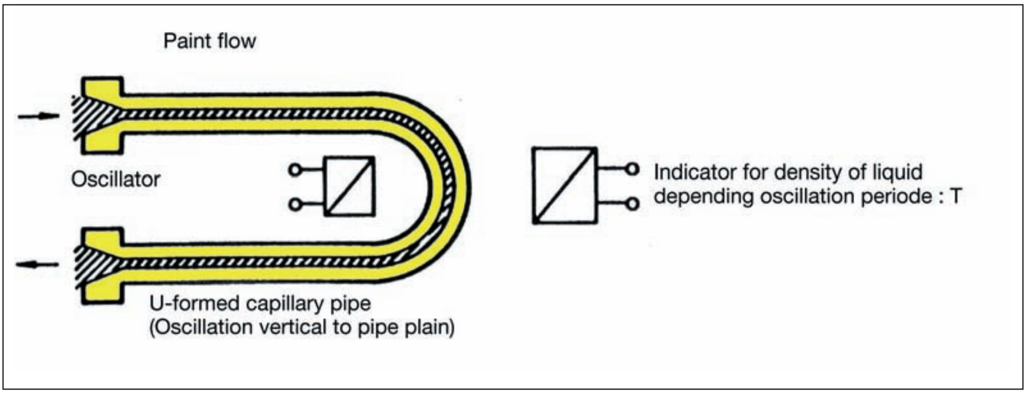


Fig. 2.3.41
Principle of measuring densities with the oscillator method

Other indicators

When solvents and resins are being delivered in tankers, the necessary identification checks are frequently carried out in the form of rapid tests to reduce waiting times. The **fractional analysis** of solvents, which used to be the standard method, has now been largely superseded by the recording of gas chromatograms. In a distillation system in conformity with relevant standards the distillate quantities are determined as a function of temperature and compared with those of a reference standard.

An even easier method involves determining the **evaporation number VDZ** to DIN 53170. A defined quantity of the solvent under analysis is dripped onto a filter paper at a test temperature of 23 °C. The evaporation time t_x is determined by comparison with the evaporation time for the same quantity of diethyl ether t_{Ether}.

$$VDZ = \frac{t_X}{t_{Ether}}$$

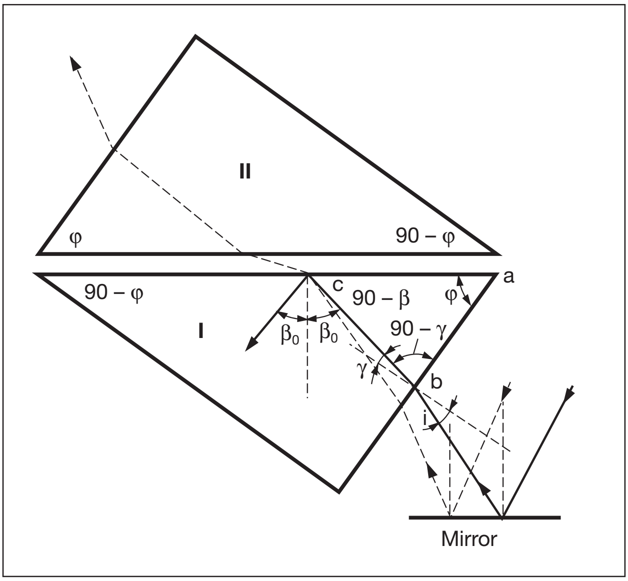


Fig. 2.3.42
Way of rays inside the prism of a Abbe refractometer

Determining the **refractive index,** (see DIN 51423-2) is the simplest and one of the most accurate methods of checking the identity of raw material mixtures. It is usually established using the *Abbé* refractometer and the total reflection principle. A beam of light passes through a glass prism after being deflected by a rotatable mirror and then, after exiting and being deflected by an angle corresponding to the refractive index of the liquid, it enters a second prism.
From here the light beam enters the observer's eye. By changing the incident angle the light beam can be totally reflected in the test liquid. Consequently the observer can no longer see any light. Since sine $\alpha = 1$ in accordance with figure 2.3.42, the refractive index of the sample can be calculated after Snell's law.

2.3.3 Pigment Specific Tests

The most important requirements for pigments can be classified in two categories; firstly, the ageing resistance under the influence of light, outdoor exposure and chemicals as discussed in chapter 3.3 and, secondly, the processing properties in coating materials. They are characterized by pigment indicators such as the average particle size, their size distribution, specific surface area, weight per unit volume (bulk density) or volume per unit weight, but also the moisture content, watersoluble components, specific resistance, pH value, acid or alkali number and abrasiveness (hardness).
In order to achieve a complete description the interactions of the pigments with the film forming agent must also be included in the characterization. The flow, softening and wetting points, in the form of the oil absorption value or water equivalent, fineness, tinting strength, tinting strength development and dispersion hardness of the formulations are useful variables in this regard.

2.3.3.1 *Indicators of the Pigment as a Raw Material*

Particle size/particle size distribution

Pigment particles are adjusted to their optimum particle size by crystallization or grinding processes. The random processes of growth and crushing almost always result in size distributions. If ideal growth is achieved, the particle distributions almost obey a Gaussian curve, but for decomposition, on the other hand, they obey a logarithmic distribution. Of the various measurement methods for describing pigment sizes in practice the distribution curve established empirically by *Rosin*, *Remmler*, *Sperling* and *Bennet* (RRSB distribution) has proved the most successful. This permits the distributions to be characterized with two indicators to DIN 66145. The variables d’ and n can be calculated by plotting the cumulative frequency as a residual sum R as a function of particle size d and subsequent mathematical processing involving double logarithms.

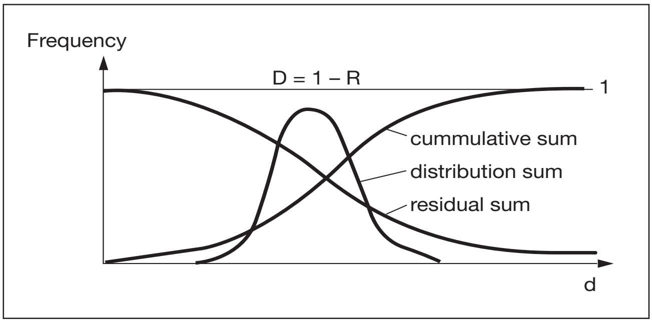


Fig. 2.3.43
Definition of average parzicle sizes d’ and the partzicle size distribution n of pigments according to Rosin,Remmler,Sperling and Bennet

$$R = e^{-\left(\frac{d}{d'}\right)^{n}}$$

Because of the e-function 36.8% of all particles are > d’. The distribution curve is clearly defined in association with the particle parameter n which characterizes the distribution range. In a double logarithmic graph the RRSB curve is a straight line where the distribution is ideal. Irregularities in the

$$\underbrace{\lg\lg\left(\frac{1}{R}\right)}_{y} = \underbrace{n}_{a}\cdot\underbrace{\lg d}_{x} + \underbrace{(\lg\lg e - n\lg d')}_{b}$$

distribution can be seen as jumps (cluster of equal particle sizes) or plateaus (paucity of particles).

In addition to the calculation of d’ as the mean particle distribution described above, there are other mathematical methods of determining the mean particle diameters. *Megele* and *Evans* have proposed a calculation [2.4.93] for these with the general formula:

$$d_{ab} = \left(\frac{\sum_{i=1}^{n} n_i \cdot d_i^{a}}{\sum_{i=1}^{n} n_i \cdot d_i^{b}}\right)^{\frac{1}{a-b}}$$

in which n_i is the number of particles in the categories of diameter d_i, and a and b are positive integers which characterize the type of distribution by volume (3), surface area (2), diameter (1) and number (0). The means d_{10}, d_{30} and the *Sauter* diameter d_{32} from the table in figure 2.3.44 have proved successful in practical operations.

Averaged diameter	**a**	**b**	**characterized by**	**Equation**
d_{10}	1	0	Particle diameter related to particle number	$d_{10} = \frac{\sum_{i=1}^{n} n_i\, d_i}{\sum_{i=1}^{n} n_i}$
d_{20}	2	0	Particle surface related to particle number	$d_{20} = \sqrt[2]{\frac{\sum_{i=1}^{n} n_i\, d_i^2}{\sum_{i=1}^{n} n_i}}$
d_{21}	2	1	Particle surface related to sum of diameters	$d_{21} = \frac{\sum_{i=1}^{n} n_i\, d_i^2}{\sum_{i=1}^{n} n_i\, d_i}$
d_{30}	3	0	Particle volume related to particle number	$d_{30} = \sqrt[3]{\frac{\sum_{i=1}^{n} n_i\, d_i^3}{\sum_{i=1}^{n} n_i}}$
d_{31}	3	1	Particle volume related to sum of diameters	$d_{31} = \sqrt[2]{\frac{\sum_{i=1}^{n} n_i\, d_i^3}{\sum_{i=1}^{n} n_i\, d_i}}$
d_{32} (Sauter diameter)	3	2	Particle volume related to particle surface	$d_{32} = \frac{\sum_{i=1}^{n} n_i\, d_i^3}{\sum_{i=1}^{n} n_i\, d_i^2}$

Fig. 2.3.44
List of common average particle sizes according to Megele and Evans

Various processes for measuring particle sizes can underpin these mathematical characterization methods. Since the pigment particle sizes or size distributions exert a special influence on the color and rheological properties, particle measurement methods are extremely important. The same applies to powder coatings. The selection of the methods described is also important in determining the drop size and distribution when processing liquid coating materials using spray application methods.
Mechanical, laser diffraction, electrical and optical methods are used in practice, depending on particle size. The following merit particular mention:

- Dry sieveing
- Wet sieveing
- Sedimentation (including sedimentation balance)
- Accelerated sedimentation (disc centrifuge)
- Coulter counter
- Electron microscope and image analysis
- Laser scatter (if < 1 µm)
- Laser diffraction (if > 1 µm)

Sieveing processes are only successful if relatively coarse pigment or extender particles are to be analysed. Standardized dry sieve sets are used for coarse extender particles. The substance under analysis is placed in the uppermost one of 16 sieveing drums configured one above the other. As a result of intensive oscillation (vibrating sieve) the particles are offered up to the openings in the top sieve and, if they are smaller than the openings, drop into the next sieve chamber. Here the particles are again offered up to the finer sieve tray, and the process is repeated a further 14 times. The mesh sizes start at 1500 µm and end at 50 µm. Weighing the individual sieve fractions gives an overview of the particle size distribution. The residual sum function obtained in this way can be converted after RRSB into a distribution function to determine d' and n.

The sieve separation process becomes more sensitive and thus feasible for analyzing finer particles if the sieveing is carried out in suspension. Particles with sizes of up to one micrometre can be analyzed in this way.

Another measurement process is **sedimentation**. In the gravity sedimentation process a particle suspension layer is added to a less dense liquid. The particles which are deposited because of gravity migrate to the bottom at a sedimentation rate u which is a function of the density difference Δρ between the particle and liquid, the square of the particle diameter d^2 and the viscosity η. In addition, a specific form factor f and a concentration dependent interaction factor b must be included for the particles in order to achieve accurate calculations.

$$u = \frac{\Delta\rho \cdot g \cdot d^2}{18 \cdot \eta} \cdot f \cdot b$$

By measuring the particle speeds during their downward travel or by weighing the particle quantities being deposited on a sedimentation balance as a function of time, the particle sizes or particle size distributions can be calculated. The particle travel can be followed directly after sampling or at a certain time at different levels. The simplest way is to measure the intensity of scattered light in the test configuration itself.

For particles with a diameter of less than 1 µm and at the same time a small density difference between the fluid and the migrating particles the sedimentation rates with

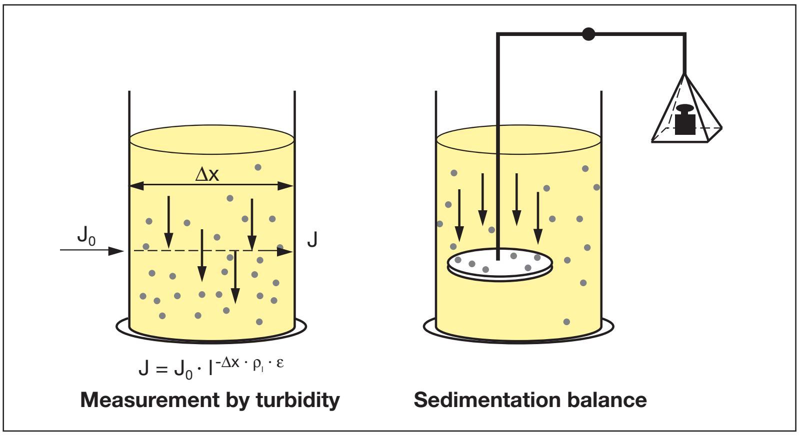


Fig. 2.3.45
Measuremenet of particle sizes by sedimentation and different indication methods

the earth's gravity are so low that excessive test times and results distorted by Brownian movement are inevitable. For such particles accelerated sedimentation processes in ultracentrifuges have proved successful. A variant of interest to the pigment industry is the disc centrifuge. Practically all pigment particles in the range 0.01 – 1 µm can be analyzed accurately by setting appropriately high speeds.

The measurement principle corresponds to that used in gravity sedimentation. It differs only in that it has a centrifuge to increase acceleration. In the sedimentation formula the acceleration due to gravity must be replaced by the centrifugal acceleration ω^2 r or 4 π n^2 r. The migration rate u is then

$$u = \frac{\Delta\rho \cdot 4\,\pi^2 \cdot n^2 \cdot R}{18 \cdot \eta} \cdot d^2$$

R is the radius of the centrifuge.

The suspension under analysis is injected into the centre of the rotating disc. The migration rate can be determined in this test configuration by measuring the scattered light of laser beams.

When evaluating the results it should be borne in mind that the calculations are valid initially only for spherical particles. Where form factors are known, however, the average diameters of irregularly shaped particles can also be calculated.

A **particle counter** developed by *Coulter* uses a completely different process for analysing particle distributions. The *Coulter* counter makes use of the low electrical conductivity of the particles relative to the liquid. If a highly diluted suspension passes through a capillary containing a metering pipe for determining the electrical conductivity, the electrical conductivity falls if a pigment particle passes through. The change in the conductivity is proportional to the particle size.

Assuming a sufficiently high dilution, the *Coulter* counter is capable of registering each individual particle and converting the results into a particle size distribution curve using appropriate software.

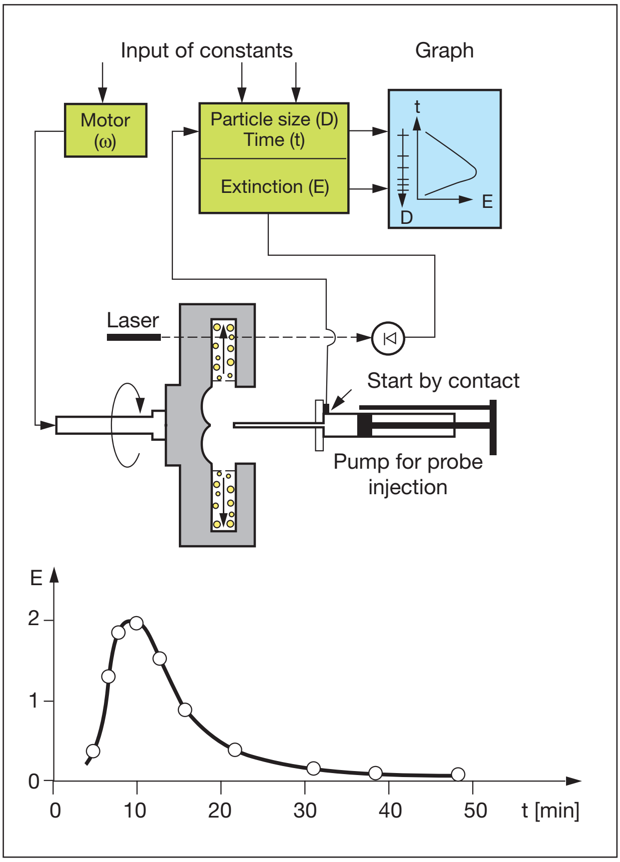


Fig. 2.3.46
Process and graph of a measurement by disc centrifuge

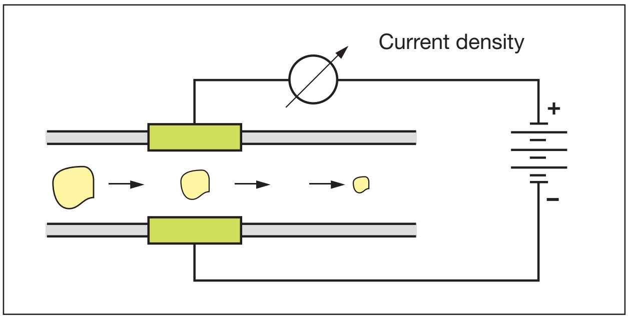


Fig. 2.3.47
Scheme of a Coulter Counter

Optical methods to ISO 13320-1 are suitable for the direct characterization of extremely fine particles, such as are present in dispersions of resins and organic pigments. They can detect particle sizes down to the molecular range. Two phenomena are used as the basis of analysis: either light scattering or light diffraction, depending on particle size. In light scattering the interaction of a particle with the light beams reacts differently depending on the size of the particle. The deciding factor is $\alpha = D\pi/\lambda$ which can be calculated from the particle size D and the wavelength λ of the incident light. I is the intensity of the diffusion effect, φ the diffusion angle and n the refractive index.

If particles which are smaller than $\lambda/20$ (α much smaller than 1) are analyzed, either the light scattering of a laser beam vertically to the beam direction is determined or the attenuation of the primary beam itself. In the former case the scattering density I is converted into the particle size D in accordance with

$$I = I_0 \cdot k \cdot \frac{D^6}{\lambda^4}$$

In the latter case *Lambert*'s law permits the attenuation of the primary beam intensity to be converted into a turbidity factor which is correlated with the particle size [2.4.94].

At the magnitude of the particles described to date other measurement methods record Brownian movement. The *Doppler* effect generated by the self-motion of the particles results in an expansion of the diffusion frequency, as a result of which the incident light is overlapped by higher and lower frequencies. It is then not the intensity of the diffused light but its frequency expansion which is the relevant measurement variable. This method is termed quasielastic light scattering (QELS) or dynamic light scattering (DLS) in the literature [2.4.95].

Type	α	**Functionality**	**proportional to diameter**
Rayleigh scatter	<<1	$I = f(\alpha, n, \varphi)$	$I \sim \frac{D^6}{\lambda^4}$
Mie scatter	≈ 1	$I = f(\alpha, n, \varphi)$	$I \sim D^2$
Fraunhofer diffraction	>> 1	$I = f(\alpha, \varphi)$	$I \sim D^4$ (wenn $\varphi = 0$)

there is $\alpha = \frac{\pi \cdot D}{\lambda}$

I = intensity of diffraction
φ = angle of diffraction

Fig. 2.3.48
Valid areas and the respective calculation formula of particle sizes

If the particles under analysis are larger than figure 2.3.48 Valid areas and the respective calculation formula of particle sizes $\lambda/20$ and α approx. 1, interference (*Mie*'s scatter) occurs in the range of the scattered light.

If two different scattering centres of one and the same particle are observed and there is a sufficiently large distance between points A and B with discrete angles of diffusion,

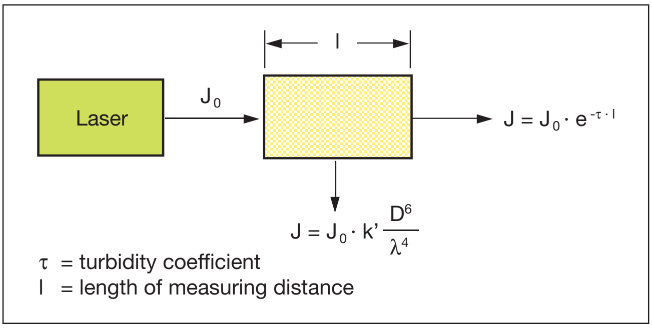


Fig. 2.3.49
Methods of particle measurements by light scattering

shifts in the wavelengths occur which result in interference, and this in turn permits calculation of the particles after *Rayleigh*'s formula [2.4.96].

If α significantly exceeds a value of 1, the evaluation of diffraction spectra is the most suitable way of determining particle sizes. By diffraction of the light we mean the deviation of the light propagation from the laws of geometric optics. It occurs if the free propagation of the wave is changed by objects such as openings or particles [2.4.97]. If a light beam passes a solid surface tangentially, it departs from its original direction all the more, the closer it passes to the particle. The effect is a function of particle size. To meet the conditions for the *Fraunhofer* theory and enable relevant readings, the light source is beamed through the focal point of a convex lens, as a result of which the light source is focused at infinity, and parallel beams of light are formed. By observing the diffraction phenomenon again in the focal plane of a second lens, the diffraction image is also focused at infinity.

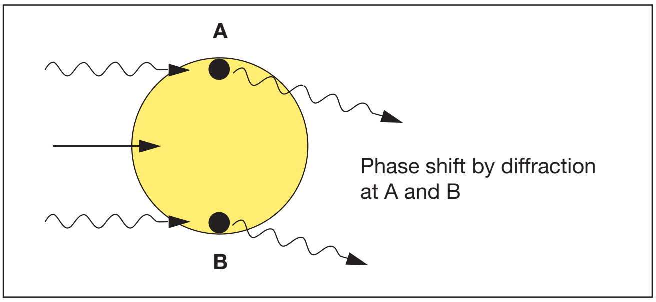


Fig. 2.3.50
Shift of wave length and interference of scattered light on particles

Under these conditions the simplified *Fraunhofer* integral can be used for quantitative discussion of the diffraction phenomena [2.4.98, 2.4.99].

The diffraction spectra of particles can be calculated with the aid of this equation or the particle size of spherical particles can be determined from diffraction images on the basis of this theory.

$$I = I_0 \cdot \left[\frac{2 \cdot J_1(x)}{x} \right]^2$$

$$x = \frac{2 \cdot \pi \cdot r \cdot s}{\lambda \cdot f}$$

I_0 = intensity of incoming light
J_1 = Bessel equation
r = radius of particle
s = radiant distance to the optical axes
λ = wavelength of laser
f = focal distance of lens

Particle sizes can also be determined using **electron microscopy**. If the concentration is sufficiently low, the size, size distribution and shape of pigments or ”frozen” dispersion particles can be established by means of digital image analysis (see chapter 6.2). At the same time it is possible to derive information about the distribution state such as primary particles, agglomerates and aggregates. This requires specific sample preparation which changes the original state of the sample as little as possible [2.4.100].

As outlined in the descriptions of the individual methods for measuring particle sizes, the methods each have specific ranges in which they deliver the best results.

It is essential to take this into account when selecting the

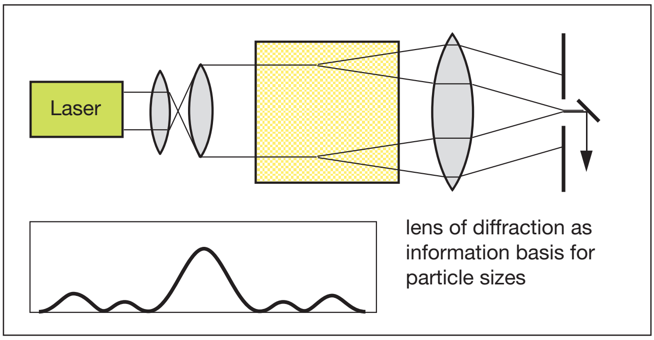


Fig. 2.3.51
Deviation of light used for information about particle sizes

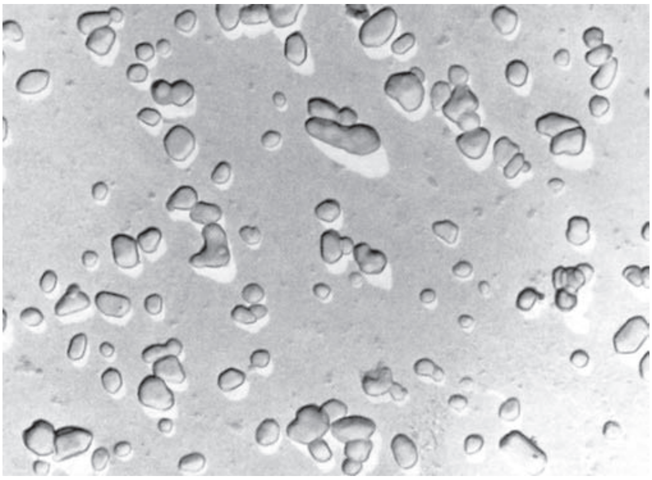


Fig. 2.3.52
Photograph of titaniumdioxide powder in a resin matrix by electron microscopy

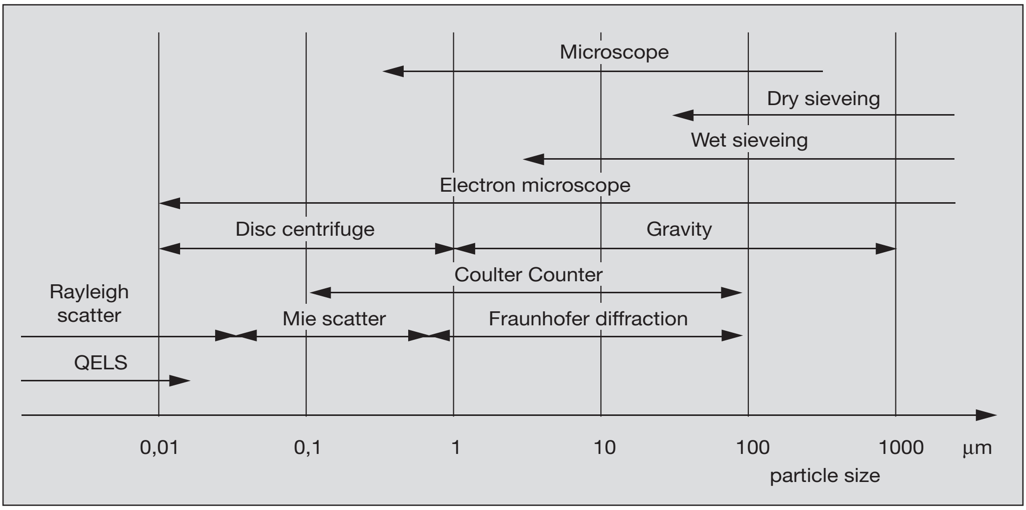


Fig. 2.3.53
Optimum particle sizes for the different measurements techniques

methods for the particular measurement problem. Please refer to figure 2.3.53 for the measurement ranges.

Specific pigment surface area

An indicator which is functionally linked to the particle size and is important for pigment dispersion is the specific surface area. This is defined as the pigment surface area either per unit mass or per unit volume. Direct determination is not possible because of the small size of the particles. For this reason the surface area is determined indirectly by means of interaction with gases or liquids.

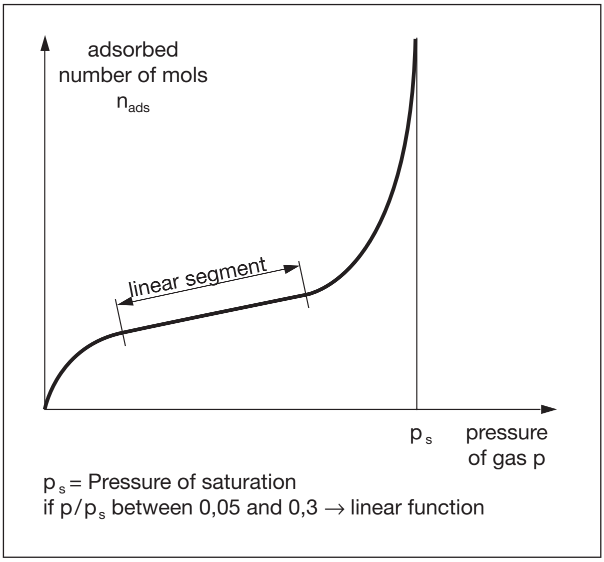


Fig. 2.3.54
Isothermal gas adsorption n_{ads} depending on gas pressure p

A measurement method which is also known from other spheres uses the quantity of gaseous nitrogen adsorbed by the pigment at the temperature of liquid nitrogen. Comparative pressure measurements with helium enable conclusions to be drawn about the number of nitrogen moles adsorbed n_{ads} from the reduced quantity of gaseous nitrogen calculated in accordance with the gas law. The adsorbed number of moles at different pressures and constant temperature yields a typical curve as shown in figure 2.3.54. Mathematical processing after *Brunauer*, *Emmet* and *Teller* (BET method) enables the specific surface area of the pigment to be calculated.

The BET function, which represents the basis for conversion from the adsorbed number of nitrogen models n_{ads} to a monomolecular cover n_0, applies to the linear section in the p/p_s range of ~ 0.05 – 0.3. Knowledge of the space requirement of a nitrogen molecule enables the surface area per unit mass to be calculated, taking account of the weighed-in amount.

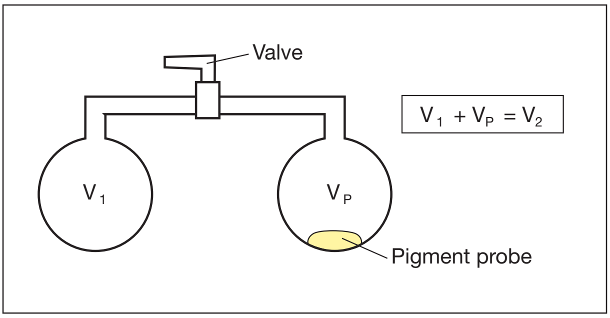


Fig. 2.3.55
Scheme of a measurement device for the gas adsorption on pigments

To measure n_{ads} as a function of gas pressure in accordance with DIN 66131 a closed apparatus of known volume V_1 is used which is correlated with a volume V_p. This contains the sample. If the gas pressure in V_1 is determined with a closed valve after complete evacuation of V_p, then $p_1V_1 = n_1RT$.

On opening the valve the volume increases from V_1 to V_2.

However, the pressure p_2 measured then does not correspond to the value calculated according to the gas law. Instead, it is lower than expected because of the surface area specific gas adsorption and associated reduction in the number of moles from n_1 to n_2. Consequently

$$\frac{p_1 \cdot V_1 - p_2 \cdot V_2}{RT} = (n_1 - n_2) = n_{ads}$$

The number of moles n_0 necessary for a monomolecular cover can be calculated using the BET formula for a known saturation vapour pressure p_s by measuring p and the corresponding number of moles adsorbed n_{ads}.

$$\frac{p}{n_{ads} \cdot (p_s - p)} = \frac{c - 1}{n_0 \cdot c} \cdot \frac{p}{p_s} + \frac{1}{n_0 \cdot c}$$

$$y \quad = \quad a \quad \cdot x + \quad b$$

If $p/[n_{ads}\,(p_s–p)]$ is plotted against p/p_s, n_0 is determined from the gradient and the section on the ordinate. If n_0 is multiplied by the space requirement ϑ for one millimol nitrogen (= 97.5 m^2) and this figure is related to the weighed-in quantity of pigment in g, the result is the mass specific surface area O_m in m^2/g.

$$O_m = \frac{n_0 \cdot \vartheta}{E}$$

An alternative for determining n_{ads} consists of single point measurements of the changing thermal conductivity of a helium/nitrogen mixture as a result of nitrogen adsorption.

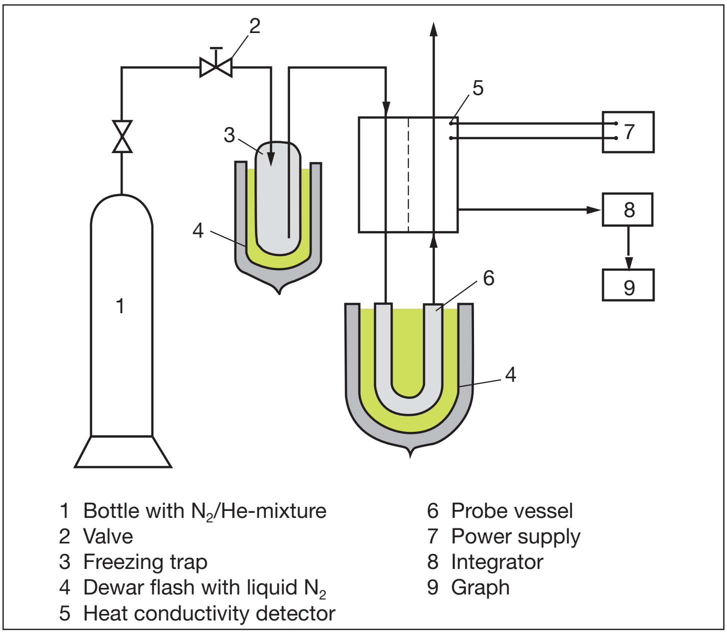


Fig. 2.3.56
Determing the specific surface by measuring thermal conductivity

In the flow apparatus shown in figure 2.3.56 the difference in the thermal conductivity of a defined gas mixture of helium and nitrogen before and after nitrogen adsorption at the pigment surface is measured in the test vessel and converted into n_{ads}. Mathematical processing is carried out again as for the gas pressure method [2.4.101].

The determination of the specific surface area can be used to calculate the particle size if the pigment shape is known. To put it another way: the joint determination of particle size and specific surface area also enables form factors to be calculated.

Particle sizes, shapes and distributions also determine the space requirement of pigments in bulk. The **tamped volume** or **tamped density** to DIN EN ISO 787-11 is used to describe this. Both variables depend on the orientation of the particles in the bed. Thus they are not material specific properties. The type of transport and storage influence the result. The pigment powder must be precompressed before the test so that comparable and thus reliable data can nonetheless be obtained. The mass per unit volume is termed the tamped density, while the tamped volume is the reciprocal of this.

Because of their large and frequently polar surface area pigments contain a certain quantity of adsorptively bound **moisture**. Depending on the pigment and the storage conditions (temperature, relative humidity) up to 1% water can be retained. Since water can have a significant adverse effect on pigment dispersion in solventbased paints, and CO_2 gas is generated from the interaction with isocyanates, the moisture contents must be determined before processing the pigments. To do so, the powder is dried in a dessicator until a constant weight is achieved, and the percentage mass loss is recorded. In order to ensure that only the adsorptively bound water is recorded, if water of crystallization is also present, the drying temperature must be exactly 105 °C.

The goal underlying the determination of the **weight loss at heat** to DIN EN ISO 3262 is different. In this test, which is primarily important for analytical purposes, the pigment under analysis is heated to 1000 °C in a porcelain crucible and the residue in percentage by weight is termed the weight loss at heat.

Since electrolytes in coatings contribute to bubble formation under the action of water, the content of osmotically active salts in pigments must be analysed as they are potential sources of damage. To do so, the **electrical conductivity** of an aqueous extract of the pigment powder is generally measured in accordance with DIN EN ISO 787-14.

If pigments contain soluble acid or alkali components, these can easily be registered in the form of an **acid or alkali value** by mixing them with alkalis or acids. In accordance with DIN ISO 784-4 100 g pigment must be titrated after extraction in the suspension with 0.1 n NaOH or 0.1 n HCl.

Determining the **pH value** of pigment suspensions to DIN EN ISO 787-9 can provide similar information. The pigment powder is first boiled in water and then analysed with a pH meter after removing any still dissolved carbon dioxide.

Coating materials are sometimes exposed to high shear forces during their manufacture and processing. Hard pigments can cause a high level of material wear in system pumps and valves because of the high flow rates induced by constrictions. Data on **abrasiveness** is also required to provide a complete description of pigments and extenders. To test this property a defined pigment quantity is incorporated in a standard paint and agitated with steel balls of a defined type and quantity in a planetary ball mill. The loss in weight of the steel balls measurable after an agreed test period is given as a percentage by weight.

2.3.3.2 *Tests with the Pigmented Coating Material*

The incorporation of pigments in the liquid resin matrix results in new test demands on the pigments because of the interaction with the binder matrix. Compliance with the entire specification profile to which the coating material is subjected, such as the binder requirement when dispersing, the necessary pigment distribution fineness, the desired tinting strength or the required hiding power, yield, and storage without flocculation or sedimentation can only be obtained by pigment specific tests in the overall system.

Pigments have a different requirement for the resin solution depending on their form, size and size distribution if the intention is to convert them into a flowable, homogeneous mixture. To describe this property in a way which is as pigment specific as possible, the various influences of the film forming agents and solvents must be eliminated. DIN EN ISO 787-5, therefore, specifies linseed oil with standardized properties to determine the **oil absorption value**. A precisely weighed quantity of pigment is therefore mixed drop-by-drop from a burette with standardized linseed oil and homogenized with a spatula until a coatable, paste-like mass has been produced. The quantity of oil used is related to 100 g pigment and then used as an oil absorption value to evaluate the dispersion properties. To characterize pigments for processing in waterbased paints the hydrophobic linseed oil is replaced by water as specified in DIN 55608.

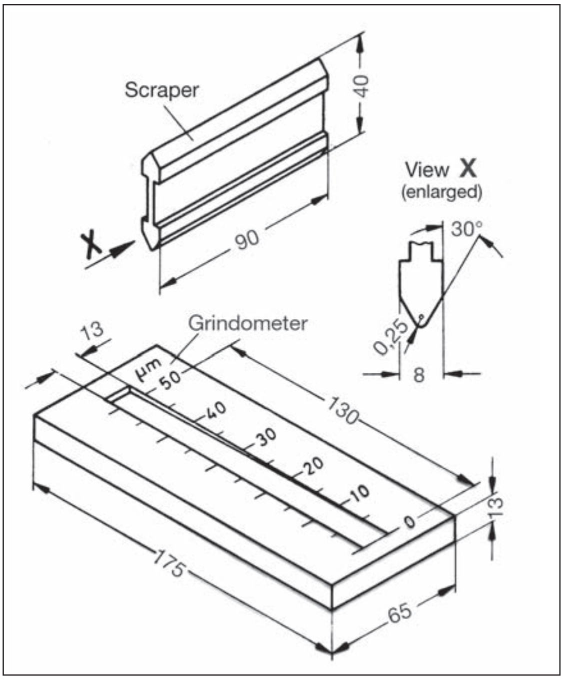


Fig. 2.3.57
Device to determine the fineness of grind according to DIN EN ISO 1524 (Hegman method)

The oil absorption value is a pigment specific indicator which should only be used with certain reservations for determining the optimum mill base formulation. In many cases the standardized linseed oil should be replaced by the film forming agent solution specified in the formulation (see chapter 2.2.3).

Important indicators for pigment properties during the dispersion process relate to the degree of decomposition of the agglomerate. This can be carried out directly or indirectly.

The standard test in everyday use involves determining the **fineness of grind.** In this process the material to be dispersed which is under analysis is tested at regular intervals using the grindometer to DIN EN ISO 1524. In the test a small quantity is taken from the batch for grinding and spread with an applicator over the wedge shaped indentation of a grindometer from the deepest to the shallowest part. In areas in which the particle size exceeds the wedge depth, stripes and grooves are created. The wedge depth, which can be read off on a scale for this range, is a measure of the largest agglomerates still present.

Because of the subjective assessment, the evaluation of grindometer measurements results in a great divergence of results. To objectify and thus to reduce the error range, instruments have been developed which fix the grindometer profile using a high resolution camera and objectively process it after digitisation [2.4.102]. The very simple and therefore commonly applied measurement method is particularly used to determine progress in the dispersion process. It only permits an approximate estimate of the maximum possible tinting strength of the individual pigments, especially if fine grain organic pigments have to be dispersed.

In such cases and when testing primary batches the more complex but therefore more precise measurement method of determining the tinting strength which involves test panels manufactured using the material to be dispersed is chosen. The tinting strength, which increases with increasing dispersion level, cannot, however, be measured directly because of the scattering power S which changes at the same time. According to *Kubelka* and *Munk* the quotient from the absorption coefficient K and the scattering coefficient S can be calculated from the reflections R as a function of the wavelength λ of the test samples.

$$\frac{K}{S} = \frac{(1 - R(\lambda))^2}{2 \cdot R(\lambda)}$$

K = absorption coefficient
S = scattering coefficient
R = share of reflection

In order, when testing the progress of the dispersion process, to keep the test equipment needed to determine increases in tinting strength within reasonable bounds despite the varying scattering coefficients, testing is limited to measuring the relative tinting strength. To this end the batches for grinding under analysis are mixed with a sufficient quantity of white paste, which results in the scattering coefficient remaining constant, irrespective of the progress of the dispersion process. If the K/S values determined after *Kubelka* and *Munk* are then related to standard values K(St) and S(St) determined by means of complete dispersion, it is possible to plot curves of changes in tinting strength F as a function of time.

$$F_{rel} = \frac{K(t)}{S(t)} \cdot \frac{S(St)}{K(St)} \cdot 100$$

if $S(t) = S(St)$ follows

$$F_{rel} = \frac{K(t)}{K(St)} \cdot 100$$

It is possible to derive theoretically from this that curves of changes in tinting strength obey a hyperbolic or e-function, depending on the pigment concentration [2.4.103]. The constants of such functions such as the half value period provide information on the speed and degree of dispersion quality already achieved. The half value period is defined as the passed time until the color strength of the starting point has been increased to 50% of the difference F_E - F_{A1} (see figure 2.3.58).

DIN EN ISO 8781-1 describes dispersion properties using a simple indicator. The **dispersion hardness** DH in % is calculated according to

$$DH = \frac{F_{60} - F_6}{F_6} \cdot 100$$

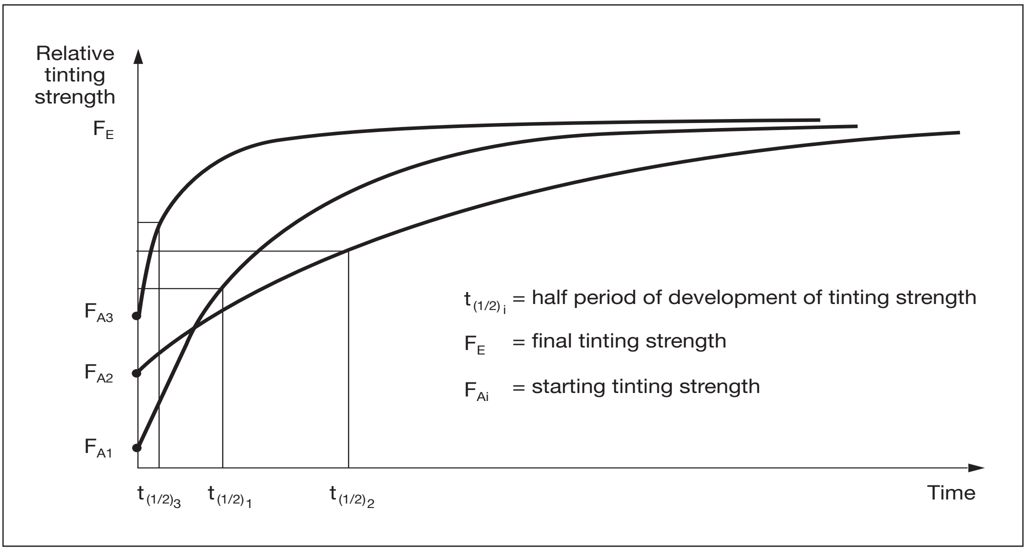


Fig. 2.3.58
Development of the relative tinting strength of different pigment dispersions during grinding

from the tinting strengths F_6 and F_{60} for dispersion times of 6 and 60 minutes. A comparison of the maximum tinting strength of several pigments which are identical in color terms can be made using relative measurements by defining the final tinting strength of one of them as 100% and relating the readings of the others to this. Figure 2.3.59 shows the curves of changes in tinting strength of two blue pigments. They differ from each other only in their pigment shape and size. The needle shaped, coarser pigment has a higher initial tinting strength and low dispersion hardness (DH = 12). The isometric, finer alternative product has a lower tinting strength initially because of the high degree of agglomeration, but with a significantly higher dispersion hardness (DH = 67) develops a higher final tinting strength.

When evaluating the value of a coating, the quantity of paint used in its production is also a deciding criterion, in addition to the quality achieved. Since the protective effect is already achieved in many cases before the substrate is optically covered, the **hiding power** becomes a variable which determines the paint consumption of coatings that provide color. The hiding power is the reciprocal of the

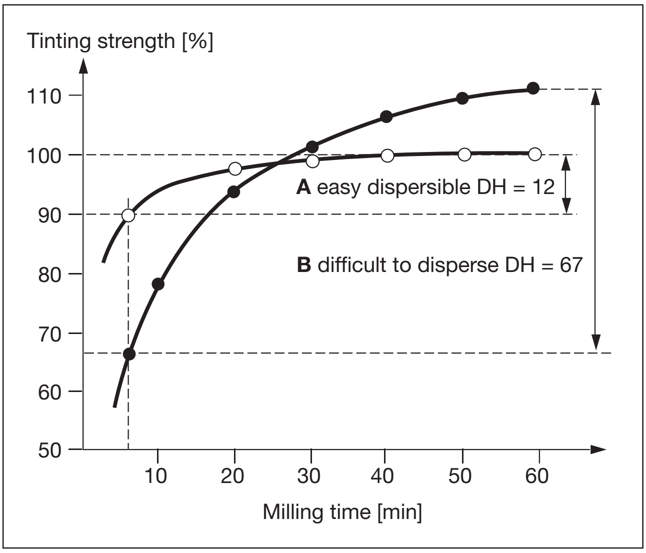


Fig. 2.3.59
Development of tinting strength and dispersion hardness of two types of Cu-phtalocyanine pigments

film thickness of a pigmented coating, in which the ratio of the intensity of the reflected light on a white R_W and black substrate R_B has taken on a value > 0.98.

In many cases testing involves the visual evaluation of a wedge shaped paint film in the wet or film formed state on a chequered black and white substrate. The two values are not identical because of the changing relative refractive index during the film forming process.

Other processes for determining the hiding power use the possibilities of colorimetry (see chapter 3.2.4), by plotting reflection curves (R_∞ and R_b) of a covering and a noncovering coat, respectively, of thickness h and calculating the scattering coefficient according to

$$S_V \cdot h = \frac{1}{b} \cdot \operatorname{arc\,coth} \frac{1 - a \cdot R_B}{b \cdot R_B} \qquad \text{where} \quad a = \frac{1}{2} \cdot \left(\frac{1}{R_\infty} + R_\infty \right) \quad \text{and} \quad b = a - R_\infty$$

The volume related scattering coefficient S_v can be converted to the hiding power D_v in m^{-1} as specified in DIN 55987 by means of a correction factor which is a function of the reflection from the covering coat.

$$D_V = \alpha \cdot S_V$$

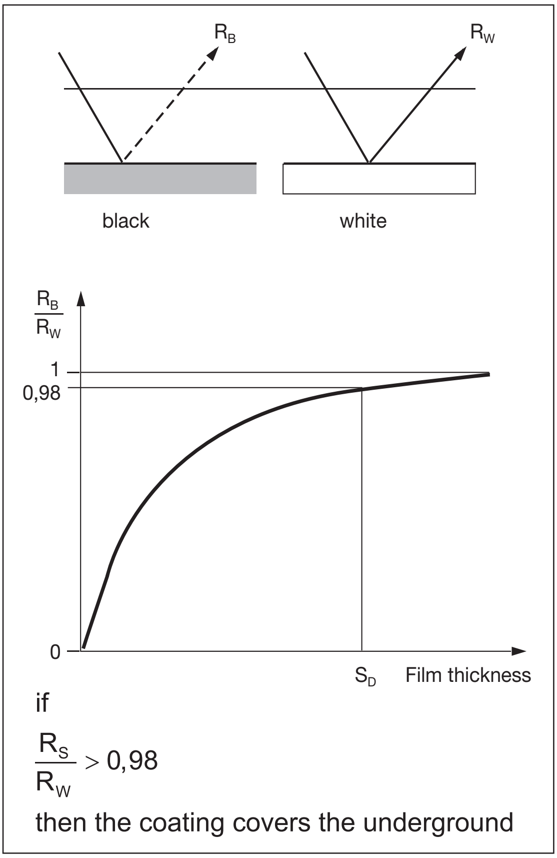


Fig. 2.3.60
Definition of hiding power according to DIN 55987

The hiding power specifies the minimum film thickness and, in conjunction with the solid content and the dry film density (see chapter 3.2.1), largely determines the material consumption and thus the yield per quantity of paint (see chapter 5.7).

Despite carefully developed formulations and precise knowledge of the important physical processes in the dispersion of pigments it is not always possible to prevent reagglomeration of the pigments occurring during the storage and processing of coating materials. These conglomerations, which are known as flocculation, result in increased **sedimentation**. Sediment in stored paint tins can be qualitatively detected by simple stirring manually. Better, but also more complex measurement processes have proved successful in providing more accurate information on the sedimentation properties of pigmented coating materials.

The most important method of determining the tendency towards sedimentation consists of immersing a test body into the liquid coating material at a defined speed. The resistance to the penetration of the test body is measured and related to the depth of penetration. Whereas only a slight rise in the counterforce is recorded in the upper part of the test vessel, it increases dramatically on penetrating the sedimentation area. This measurement method permits sedimentation profiles to be recorded with a high degree of accuracy [2.4.104].

Another measuring principle involves the attenuation of X-rays passing through the paint sample. The presence of a nonhomogeneous pigment distribution is detected by means of differing levels of absorption of the X-rays or light [2.4.105].

The degree of flocculation can also be determined indirectly by mechanically rubbing the paint film of a freshly applied paint. This test, known as the **rub out test**, visually evaluates the change in tinting strength caused by rubbing or measures it colorimetrically. If flocculates are present, these are converted to primary particles again. If the rub out process is carried out under defined conditions and if changes in tinting strength are determined colorimetrically by measuring the rubbed out F_r and the nonrubbed out surface areas F_{nr}, it is possible to obtain very accurate information on flocculation during storage or film formation. Quantitative values relating to the degree of flocculation can be derived by determining the rub out number RBN in %.

$$\mathrm{RBN} = \frac{(F_r - F_{nr})}{F_{nr}} \cdot 100$$

2.3.4 Processibility of Coating Materials

Coating materials are processed by different methods depending on the field of application. Even if brush application plays only a subordinate role in industrial scale paint processing, this application method is still extremely important in the housepaint and craft fields. Brushes and rollers are important tools when painting doors, windows, façades and similar surfaces.

For the housepainter, therefore, an analysis of the criteria for good brushability is just as important as the analysis of the variables for sprayability and ability for dipping in the industrial sector. The different methods of spraying and dipping must be viewed separately. For example, coating materials for conventional spraying must be set and evaluated differently from materials which are to be processed hydraulically, pneumatically or electrostatically. Electro-

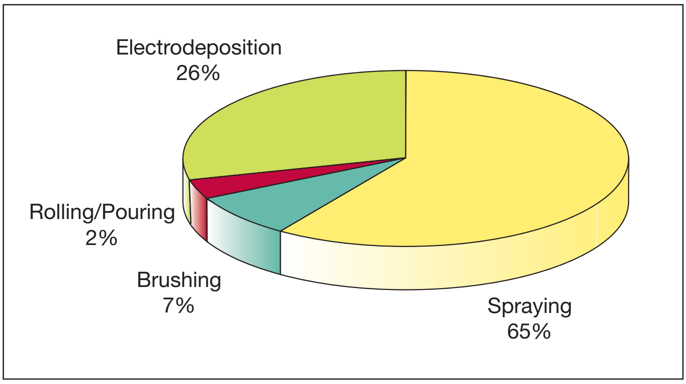


Fig. 2.3.61
Share of appication methods of coatings in North America 1999

coating requires different paints from conventional dip coating with solventbased or waterbased coating materials.

En route from the paint to the finished coating different material settings have to be drawn up for the coating materials, despite the same quality demands on the coating. Only in this way is it possible to meet the set target in view of the variety of objects to be painted and the resulting different application methods.

The processibility test (see chapter 6.3) is intended to ensure that the coating material can be processed without problems. In addition to the surface finish of the material under analysis, a range of external conditions exerts a great influence on processibility. Particular mention may be made of the substrate, the adjustment of the coating material to the processing form, the process sequence, with manual processing the individual working method, with automatic processing the setting and condition of the application equipment, and the environmental conditions (temperature, air pressure, relative humidity).

For all paints and all application methods the relevant variables are the viscosity profile as a function of temperature and shear stress, surface tension, density, evaporation properties of the solvents and from case to case other specific properties.

Brushability

Brushability is the term used to designate a material profile which enables optimum processing by brushing. Thixotropy in conjunction with an appropriately ”long” solvent design is a key property. Only in this way is it possible to equalize the applied coating still further by applying another coat. The solvent composition of a brush applied paint therefore differs substantially from that of a spray paint. The question of the substrate also has to be addressed to achieve good brushability. When painting absorbent timber it is possible to reduce absorption by the substrate by choosing a high processing viscosity and a correspondingly high degree of thixotropy. Other features used in evaluating brushability include flow, tendency to run, drying properties, and the hiding power. These properties are most usefully tested by means of special wedge shaped applicators. The evaluation of brushability depends very much on subjective variables and in practical terms is thus only a relative variable with reference to a standard which also has to be tested.

Brush applied paints are subject to a high shear stress. The resulting viscosity at any given time determines the application work involved. If, for example, shear gradients of 10^4 s^{-1} are specified, reliable forecasts of brushability can be obtained. An additional brush applied coat is then superfluous. Simple, inexpensive cone-plate viscosimeters have proved suitable for such forecasts.

Ability for dipping

The requirements of coating materials are completely different if a dip application process is to be used. Rigorous demands are made of material stability depending on bath turnover, quantity of components to be coated per unit time and bath size.

Good ability for dipping also means achieving optimum wetting of all areas of the object to be painted in the shortest possible time. A low viscosity is desirable to ensure that the cavities of complex objects are also reached by paint. At the same time it is also a precondition for rapid drying of the excess material after removal from the bath. In addition, fast drying prevents the paint from running away from the edges. In order to achieve a good compromise between flow and the avoidance of running away from edges, a balance between viscosity, evaporation properties and surface tension has to be aimed for.

Quite different criteria have to be applied in turn when evaluating the ability for dipping of paints for the ecoating process. The electrical precipitation equivalent, pH value, degree of neutralization, electrical conductivity and throwing power, to mention only some of the numerous indicators, are data which have to be precisely determined. They permit more binding forecasts of the anticipated coating result than can be achieved, for example, for manual processing by brush or roller. When processing pigmented dip-coating paints, pigments with a high specific mass should not be used, regardless of whether a conventional or electrochemical method is being used. Lasting homogeneity of the bath material can only be guaranteed, while also keep costs to a reasonable level, by using light to medium-weight pigments. A low tendency towards sedimentation is thus also an important criterion for dip-coating paints. Regular testing of the pigment/binder ratio and monitoring of the solvent components and their composition are further important criteria for constant processing properties.

Sprayability

Account must be taken of the atomization methods when evaluating sprayability. Spraying with compressed air with and without supplementary heating of the material, airless atomization at extreme pressure, electrostatic assistance or the high speed rotary method are based on very different physical principles. One feature they all have in common is that the liquid paint is broken down into more or less small droplets by generating free surface energy and that these droplets are then given kinetic energy to transport them to the object to be painted where they form a closed film in contact with the object. The fundamental difference from the dip and brush processes lies in the interim atomization of the paint. The brief but significant enlargement of the total surface area of the material to be processed and the associated faster solvent release must be taken into account when drawing up the formulation and testing it for this application method.

As far as hot application is concerned, generally carried out at 60 – 80 °C, the material must be adapted to the changed conditions by appropriate selection of the solvents. Checking that the formulation is right to ensure applicability is then carried out at these temperatures.

Because of the very small nozzle diameter used for airless atomization (0.1 – 0.8 mm) special demands are also made of the fineness of grind. At the same time hard and thus abrasive extenders should not be used because of the extremely high tangential speed of the paint at 150 – 200 m/s. Only in this way is it possible to limit nozzle wear.

Very different factors come to the fore when formulating paints for electrostatic processing. The electrical conductivity determines the degree of charge to a very large degree and therefore determines the atomization. Physical indicators which influence the spray angle and the droplet size and therefore also the yield and quality of the coating, are the surface tension and the dielectric constant.

At this stage it becomes apparent that in all the important processing stages for liquid paints, whether for spray, brush or dip application, material related properties such as flow properties, wettability, surface tension, evaporation properties and chemical reactivity are interlinked in such a complex fashion that it is impossible to make forecasts about the processibility of paints based purely on theoretical considerations. Predictions relating to the properties of paints with a specified processing system are therefore only ventured after extensive simulations and experiments. The more accurately the practical conditions can be simulated, the more authoritative the comment.

2.3.5 Summary

Coating materials and their raw materials are subjected to various basic mechanical and thermal process engineering operations during their manufacture and processing. This places certain demands on the individual components and on the coating material. The physical properties of viscosity and surface tension are without doubt the most important fundamental variables with regard to conveying in pipes, pigment dispersion and application with subsequent film formation. The solid content, density and hiding power then complete the material characterization.

A complete evaluation of the property profile of coating materials also includes occupational health and safety indicators and systems for measuring them. The flash point, solvent content in the emissions from spray booths and driers, ignition temperatures of explosive gas/air mixtures, but also the concentration of hazardous work materials must be known if coating plant is to be operated safely.

If pigmented coating materials are to be evaluated, attention must be paid to specific pigment properties of the raw material in isolation and in its interaction with the film forming agent. Particle size, particle size distribution, oil absorption value, bulk density, moisture content, watersoluble components and agglomerate strength on the one hand, and the reduction in fineness of grind, development of tinting strength, but also stability of the dispersion achieved, on the other hand, are just some of the noteworthy properties of coating materials.

In order to provide a comprehensive quality guarantee, in depth application tests also have to be carried out, including processibility, sprayability and the specific properties when pouring or rolling.

If, in addition to identifying the properties, there is a need to comment on the chemical composition, recourse must also be made to the varied analytical methods using appropriate instrumentation.

2.4 Literature

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3 Coatings

3.1 From Coating Material to Coating : The Film Formation

Coating material i.e. paint is a semi-finished product. Only by coordinating the application process, the subsequent curing, the design requirements and various materials used in the item being coated can the surface properties expected of the coating be achieved. However, there is no doubt that, regardless of how different the demands may be, coating materials will always have to be transformed into a continuous, smooth film with good adhesion in order to be able to meet the requirements made of them in the long term after the drying and curing processes.

The rough texture of droplets in a fresh coating which has been created by spray application, for example, must be sufficiently flowable to seal any voids remaining and level out the application-related peaks and valleys. In addition to viscosity, the degree of levelling and the rate of levelling are essentially dependent on surface tension and wet film thickness. The temperature characteristic and rheological behaviour affected by it as well as evaporation of the solvents overlie the physical and chemical processes in the transition from paint to a coating. Evaporation of the solvents and the formation of cleavage products which starts in the case of systems curing by polycondensation involve additional film shrinkage. Reproductions of the substrate are therefore not only a function of the solids content but in the same way they are also dependent on the quantity of cleavage products and the reactivity of the system. If local changes in density and surface tension also occur during solvent flash-off, flows can also be expected within the film as it forms.

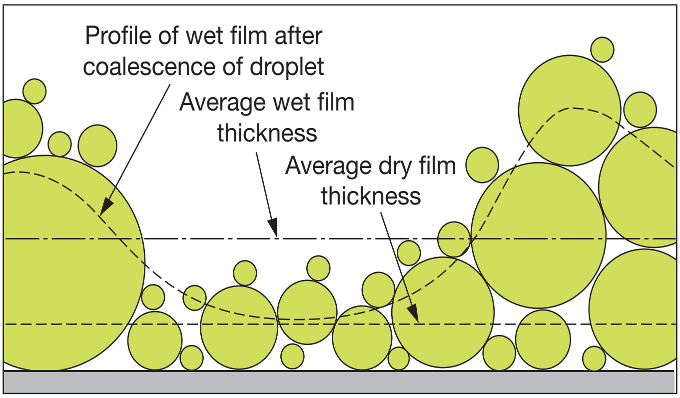


Fig. 3.1.1
Schematic texture of a film freshly applied by spray coating as starting point for film formation

Owing to the importance of the film forming process for the desired properties of the coating we ought to provide a detailed description of the metamorphosis from coating material to coating.

3.1.1 Wetting and Flow

Wetting the substrate is subject to the laws described in chapter 2.1.4. The liquid coating material or the melting powder paint wets the substrate if the surface tension of the coating material is less than that of the substrate. The individual droplets created during spray application unite after wetting and, after release of enclosed bubbles of gas, form a continuous film, provided viscosity is sufficiently low.

Owing to brush processing or various sizes of droplet created by atomization with the spray gun the primary stage of the wet film provides more or less pronounced unevenness. After wetting, an integral part of film formation is the flowing, smoothing and solidification of surface textures. Eliminating the wet film contour and also preventing flow down vertical surfaces thus constitutes the major task in the second stage of the film forming process.

Although flow is facilitated by low viscosity, the actual driving force required to create a smooth surface is to be found in the surface tension and gravity. Whilst surface tension in vertical and horizontal surfaces endeavours in the same way to reduce the size of the surfaces, gravity only enhances flow on horizontal surfaces. On vertical surfaces, on the other hand, it can cause runs. Although as high a surface tension as possible is desirable for flow, it does cause increased drag of the still liquid paint away from the edges of the item on account of cohesive pressure p.

$$p = \frac{2 \cdot \sigma}{r}$$

σ = surface tension
r = radius of edge

To facilitate flow and at the same time prevent sagging and running away from edges, another parameter, viscosity, has to be included in considerations. Flow without sagging can only be achieved by balanced compensation of viscosity taking into account viscous or thixotropic behaviour with the surface tension at all stages of film formation.

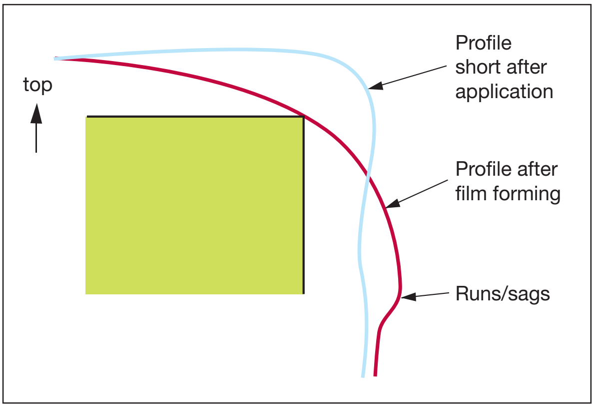


Fig. 3.1.2
Conditions of coatings running away from edges

Detailed investigations into fresh films with defined primary textures were conducted by *Orchard* [3.4.1]. Surface textures made under defined conditions with an initial height of h_0 lose height in relation to time t, whilst the minimums increase in the same manner. Levelling down to height h in relation to time takes place according to an e-function.

$$h = h_0 \cdot e^{-\frac{t}{\tau}} \quad \text{thereof} \quad \tau = k \cdot \frac{\eta}{\sigma} \cdot \frac{\lambda^4}{s^3}$$

The initially fast levelling of the peaks and valleys to form a smooth film is increasingly decelerated as time progresses. Information about the absolute rate is provided by parameter τ in the exponent of the function. By experiment one has to prove that in addition to the material properties mentioned the flowing process is also influenced by application-related variables. The flow determing value τ is composed of the material variables of viscosity η, surface tension σ and process-related variables: the distance between the excess heights of primary roughness λ and wet film thickness s. What is worth noting is that this influence is much greater than that of material parameters. If one considers that parameter λ in the case of spray application is determined by droplet size or droplet size distribution, the substantial dependence of flow on droplet size and film thickness, which will be familiar to paint formulators from experience, is substantiated by theory.

3.1.2 Solidification of the Film

The essential stages in the transition from a liquid paint to a physically firm coating occur in the fundamental changes to which rheological properties are subjected. The originally thin paint solidifies more and more and passes through various intermediate stages before it ultimately turns into an elastic or durومeric body.
The transformation from paint to a coating can be described by examining the change in viscosity with the following mathematical relationship for resin solutions [3.4.2].

$$\lg \eta = k \cdot \sqrt{M_n} \cdot NV$$

The equation can be applied to high-viscosity solutions and melts in order to describe film forming processes with sufficient accuracy. Accordingly viscosity η depends on molecular weight M_n and solid content NV. The viscosity rise necessary for film formation after the application of coating materials, into the range of physical resistance, can be achieved in two ways. First of all, evaporation of the solvents brings about an increase in the concentration of film forming agent i.e. NV. The molecular chains approach each other and increase the mutual interaction and physical entanglement, and hence viscosity. If reactive resins are present, chemical curing reactions overlie physical drying. This involves an increase in the average molecular weight by crosslinking of the molecular chains. Solidification is therefore the result of combined influences exerted by physical and chemical processes.
Since crosslinking of the resin molecules beyond a rise in viscosity ultimately has to produce a resistance of the film to solvents and weathering, in the graphic shown in figure 3.1.3 the range of physical hardness is supplemented by that of chemical resistance.
If one follows the transition from the low molecular monomers via the paint resin through to the finished coating with all the intermediate stations, applying the

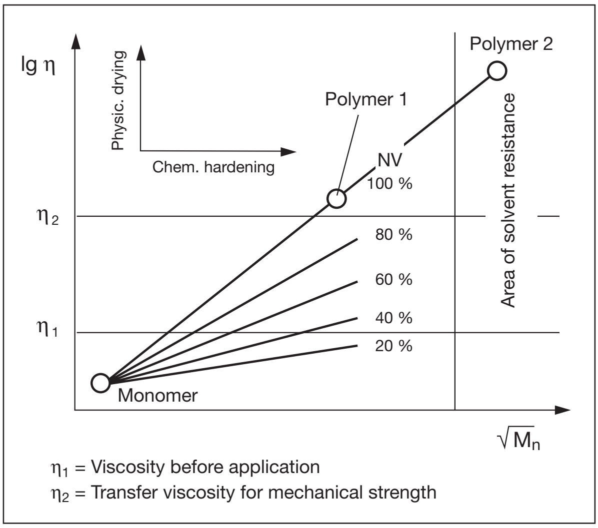


Fig. 3.1.3
Correlation of viscosity and molecular weight M_n as well as the solid content NV of paints for the film formation process

formula presented, the two fundamentally different formulation principles become easier to understand. Based on the monomeric basic building blocks of resin manufacture chemical reactions bring about such a molecular enlargement that the substance solidifies. For application this raw material has to be liquefied again by adding solvents and thus transformed into a state where it can be applied to a surface. After application and during film formation these solvents are released. Physical drying therefore means a vertical displacement of the coordinates into the range of physical hardness. There is no change in molecular weight.

The situation is different with film forming agents for chemical curing. In this case one assumes smaller resin molecules which are not yet physically stable. Molecular enlargement, which only starts to takes place after application and an associated increase in molecular weight with simultaneous crosslinking, causes a horizontal displacement as shown in figure 3.1.4. If the coating has to be resistant to solvents and aggressive chemicals, the crosslinking of growing film forming molecules in particular has to create a dense network.

With the aid of figure 3.1.4 it is possible to characterize all the paint systems schematically in terms of their film forming behaviour. Physically drying paints (A), that is, ones which cannot suffer any more chemical changes during film formation, contain film forming agents with relatively high molecular weights. Owing to the absent crosslinking these type of paints are only of limited quality in terms of their resistance to solvents. Another disadvantage of physically drying paint systems, also due to the high molecular weight of the film forming agents, consists in a relatively high proportion of solvents in the application state. Physically drying paints therefore always have a low solid content. Due to the associated high emission during their application, physically drying paints containing dissolved film forming agents have no great future for ecological reasons. The only advantage which can be attributed to them is their drying at room temperature. Examples of physically drying paints are thermoplastic acrylates, cellulose derivatives such as cellulose nitrate, cellulose acetobutyrate, chlorinated rubber and cyclized rubber.

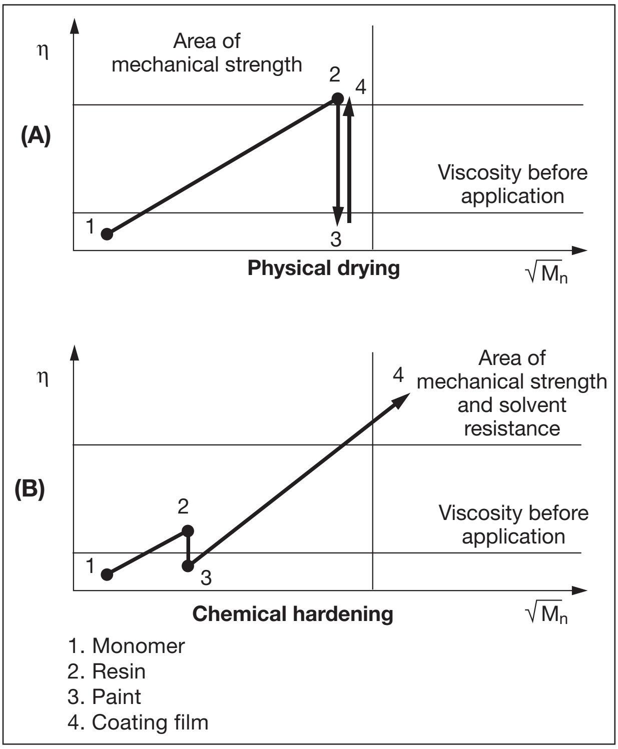


Fig. 3.1.4
Principles of film formation : physical drying (A) and chemical hardening (B)

The situation is different when applying chemically hardening paints (B). Their film forming agents have lower molecular weights and so they have a much higher solid content in the application state owing to better solubility. However, the lower solidification due to physical drying is more than compensated for by chemical processes during the film forming phase. Molecular weight, and hence the viscosity, can be raised by any amount and the resulting film can be transformed by chemical crosslinking into an insoluble duromeric high molecular network which can be no longer melted. In this way it becomes understandable that coatings with maximum physical and chemical stability take priority, without exception, over chemically curing reaction paints. For such advantages extra investments into the curing process has to be accepted. The achievable quality of coating justifies this approach in many cases.

3.1.2.1 Physical Drying

In the case of physical film forming processes one must differentiate between solidification of the polymer due to solvent emission from polymeric solutions and solvent emission from dispersions. The latter can take the form of organosols or hydrosols, but also plasticizer-containing plastisols. Whilst in the case of plastisols the plasticizer penetrates the polymer being plasticized during film formation, with organosols and hydrosols the liquid constituents, i.e. solvent or water, leave the resulting film in the same way as with solventborne paints.

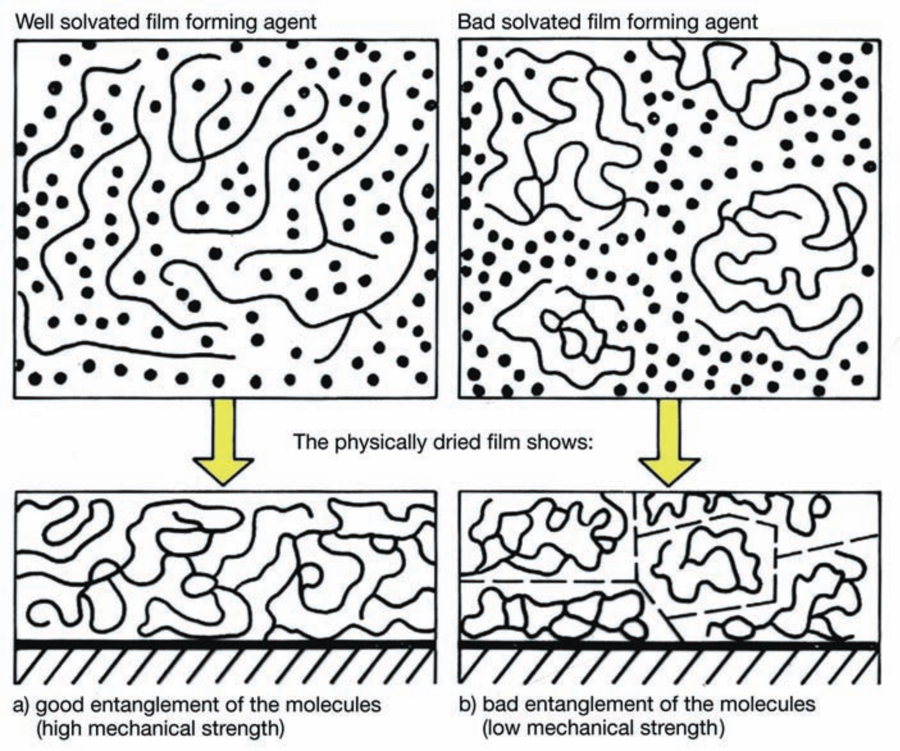


Fig. 3.1.5
Orientation of molecules of good and bad solubilized paints before and after film formation

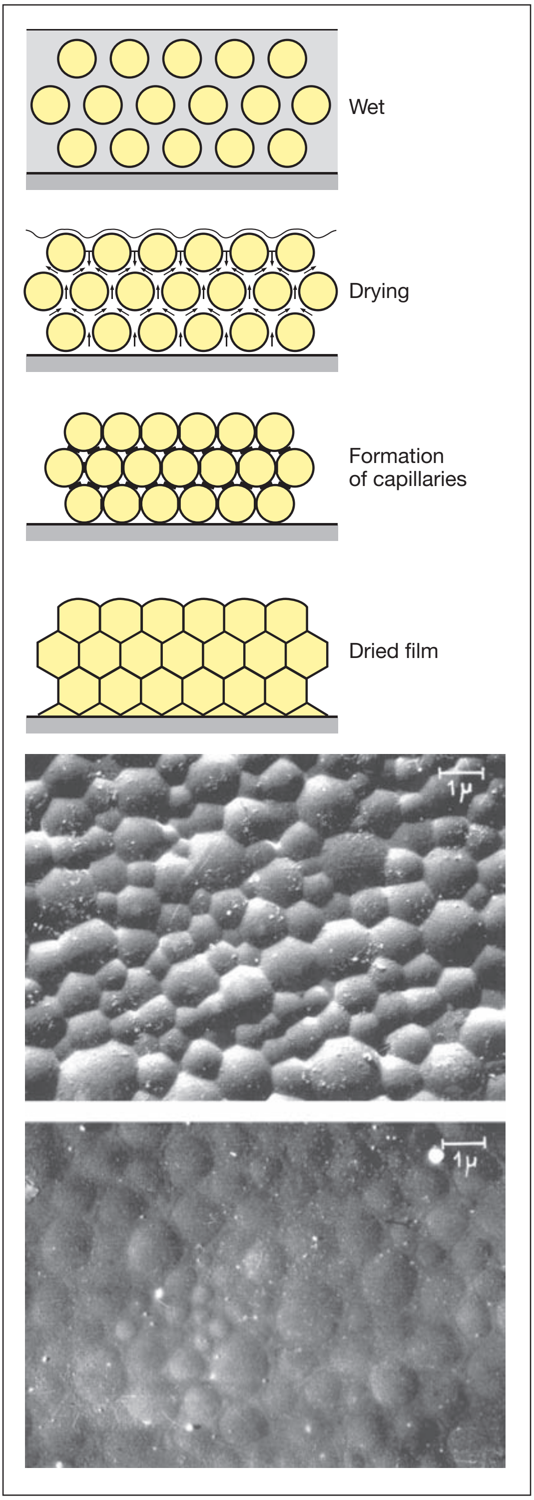


Fig. 3.1.6
Schemes and pictures by scanning electron microscope (SEM) of film formation of dispersions

Compared to dispersions, the film forming process of resin solutions as a homogeneous mixture of film forming agents and solvents with freely mobile resin molecules in their liquid environment seems to be the simpler case, but only superficially. With a molecularly dissolved liquid paint solvents flow round virtually all the resin molecules. As a result, the polar groups of the film forming agent are saturated via bridging bonds with the also polar groups of the solvent molecules. The macromolecules highly coiled in the solventfree resin are more or less stretched (solvated), depending on interaction with the solvent molecules. Interaction of the resin molecules among each other is consequently reduced. As solvent evaporation increases this state is changed continuously. Mutual influence of the resin molecules increases, the macromolecules become more and more entangled and solidify, forming spatial structures. The degree of uncoiling caused by solvation thus has an influence on subsequent entwinement and therefore on the physical resistance of the coating. Although solvents are used for applying coating materials and they leave the film almost entirely, they can exert various influences on the physical/technological properties owing to the resulting tertiary structures, despite the same composition of coating. This fact applies particularly if the systems only dry physically without chemical crosslinking.

Film formation in the case of dispersions takes place according to completely different physicochemical principles. With the polymer particles dispersed in the water and stabilized, film formation commences during evaporation and the associated shrinkage of volume when the discrete dispersion particles are touched. Owing to forced convergence the repulsion barrier is overcome so that the forces of attraction prevail. At the moment of contact the surface forces are so strong that there is a complete unification of the various particles. In the capillaries of the film, which still exist at the beginning, convergence is even supported by capillary forces. For complete fusion of dispersions the originally spherical particles are deformed by the forces of attraction to such an extent that the intervening spaces disappear completely. The thermodynamic driving force behind film formation in dispersions is therefore due to the gain in free energy on account of a reduction in the total surface area of the particles originally dispersed as individuals. The gain in area-related free energy corresponds to cohesive pressure 2 σ/r and is therefore inversely proportional to particle diameter. Consequently, film forming forces are high whenever the dispersed particles are particularly small. At a particle size of 0.05 – 0.1 µm cohesive pressures are calculated to be more than 100 bar. Owing to such high pressures the solid polymer particles are deformed by hexagonal stacking to create rhombic dodecahedrons. This theory is confirmed by electron microscope images (see figure 3.1.6).

Formation of the textures described is only possible if the viscosity of the polymers in the particles permits the necessary flowing processes. On account of the dependence of viscosity on temperature there is therefore a characteristic minimum film forming temperature (MFT) for the various dispersions. If necessary it can be lowered by adding organic solvents. For this purpose only water-miscible solvents are suitable, the relative evaporation rate of which exceeds that of water. When all the water has evaporated, they act as genuine solvents and soften the mini-spheres of the dispersion, which were previously too hard for deformation. They create conditions that will allow complete fusion to create a homogeneous film. Another method of achieving lower minimum film forming temperatures is to reduce the molecular weight of the film forming agent. The dispersion becomes softer and thus becomes film forming without solvent, albeit compromising some properties such as abrasion resistance.

Film formation with plasticizer-containing plastisols (see chapter 2.1.4) is completely different. By briefly warming the plasticizer penetrates the hard dispersion particles, thereby separating intermolecular forces in the polymers, and thus causes elastification and simultaneous solidification of the liquid, which was previously viscous.

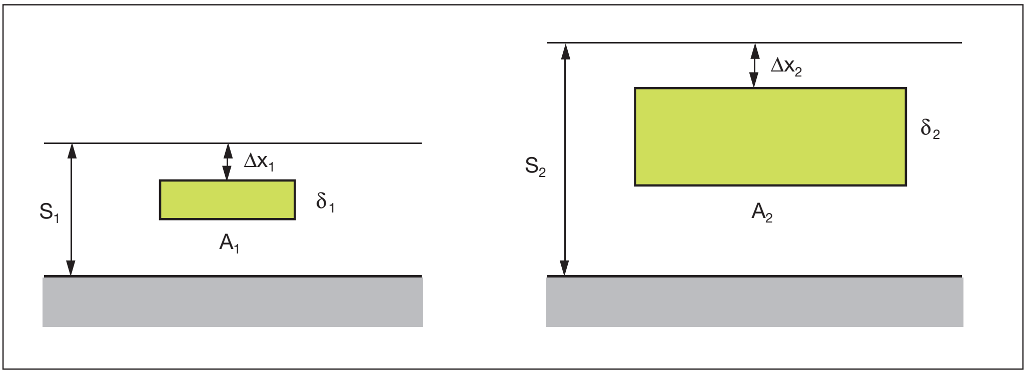


Fig. 3.1.7
Model for estimation of the material transport during film formation

If one endeavours to quantify film forming processes in terms of their exchange of materials with the gaseous phase, one encounters a highly complex situation. Known physical laws of kinetics offer no satisfactory basis for calculating the evaporation behaviour of the coating materials. Two of the reasons for this are the constantly changing composition of the complex solvent mixtures in the transition from the paint film to the headspace and the dependence of evaporation rate on film thickness. If one assumes that the solvent mixture has a consistent composition over the entire period of the evaporation process, semi-quantitative statements can be made about the dependence of the exchange of materials on film thickness if the calculations are isothermally related to such short intervals that *Fick*'s first diffusion law remains valid. A simple intellectual experiment then leads to the result.

In two, still solvent-containing films of different thickness S_1 and S_2, two geometrically similar, cuboid volume elements V_1 and V_2, calculated from the base area A and height δ, are analyzed by comparison. In view of the geometric similarity of the two volume elements with diffusion distances Δx_1 and Δx_2 as well as heights δ_1 and δ_2 it follows that:

$$\frac{\delta_1}{\delta_2} = \frac{\Delta x_1}{\Delta x_2} = \frac{S_1}{S_2}$$

Next step is looking for the times that elapse in order to cause the same reduction in concentration Δc, in both layers. Δc is the ratio of the mass of the evaporating solvents, Δm, and its volume V.

The requirement is therefore $\Delta c_1 = \Delta c_2$.

Since $\Delta c_1 = \frac{\Delta m_1}{V_1}$ and $\Delta c_2 = \frac{\Delta m_2}{V_2}$ and $V_i = A_i \cdot \delta_i$ follows that

$$\Delta m_1 \cdot A_2 \cdot \delta_2 = \Delta m_2 \cdot A_1 \cdot \delta_1$$

The area-related flow of material is subject to

$$\dot{m} = \frac{\Delta m}{\Delta t} \cdot \frac{1}{A}$$

Related to the present case it follows that:

$$\dot{m}_1 \cdot A_1 \cdot A_2 \cdot \Delta t_1 \cdot \delta_2 = \dot{m}_2 \cdot A_2 \cdot A_1 \cdot \Delta t_2 \cdot \delta_1$$

In addition, according to *Fick*'s first law it applies:

$$\dot{m} = -D \cdot \frac{\Delta c}{\Delta x}$$

$$D_1 \cdot \frac{\Delta c_1}{\Delta x_1} \cdot \Delta t_1 \cdot \delta_2 = D_2 \cdot \frac{\Delta c_2}{\Delta x_2} \cdot \Delta t_2 \cdot \delta_1$$

Since $D_1 = D_2$ (same paint, same solvent composition), it follows that:

$$\frac{\Delta t_1 \cdot \delta_2}{\Delta x_1} = \frac{\Delta t_2 \cdot \delta_1}{\Delta x_2} \quad \text{or} \quad \frac{\Delta t_1}{\Delta t_2} = \frac{\Delta x_1 \cdot \delta_1}{\Delta x_2 \cdot \delta_2}$$

On account of the geometric similarity required

$$\frac{\delta_1}{\delta_2} = \frac{\Delta x_1}{\Delta x_2} = \frac{S_1}{S_2} \quad \text{it follows that} \quad \frac{\Delta t_1}{\Delta t_2} = \left(\frac{S_1}{S_2}\right)^2$$

The ratio between the evaporation times of two paint layers of different thickness thus equals the square of the ratio between the film thicknesses. The old painter's experience that "two thin coats are better than one thick one" is thus underpinned by theory [3.4.3]. For a comprehensive analysis of the exchange of materials during the film forming process the temperature dependence of the diffusion coefficient and the vapour pressure of the solvents, the viscosity of the coating material and the crosslinking reactions must also be included in calculations. Since the material transfer processes are complex and cannot be calculated accurately, practical experience on the part of paint formulators will be crucial in avoiding incorrect coatings, pinholing, runs, craters, lack of gloss and inferior flow as a result of inadequate coordination of paint components.

3.1.2.2 Chemical Curing

Whilst physical drying covers the change in film state due to solvent evaporation, chemical curing relates to changes in the molecular structure of the resins or resin combinations by creating new chemical bonds. This involves an enlargement and crosslinking of the film forming agent constituents, which were previously single individuals. In the case of chemically curing paints the application of energy serves to speed up the emission of solvent, overcoming activation energies and accelerating the ensuing crosslinking reactions. Depending on the number of reactive groups per molecule they bring about more or less close-knit chemical molecular bonding with a substantial increase in molecular weight.

The bonding of the individual molecules via functional groups can take place by polyaddition, polycondensation and polymerization (see chapter 2.1.1). In the case of polycondensation high levels of activation energy have to be overcome. Above a minimum temperature, which is therefore defined, the crosslinking reaction occurs automatically with the formation of low molecular cleavage products. This has consequences for the adjustment of air flows in the baking ovens (see chapter 4.3.1). Examples of coating materials curing by polycondensation are baking paints based on alkyd resins or acrylic resins in conjunction with phenolic resins, urea resins or melamine resins.

Crosslinking baking paints require a larger supply of reaction-capable groups than is consumed during crosslinking because the rise in viscosity impairs the activity of crosslinking. To perform the polycondensation reaction as completely as possible within the set curing time of 30 minutes normally, the curing times and curing temperatures

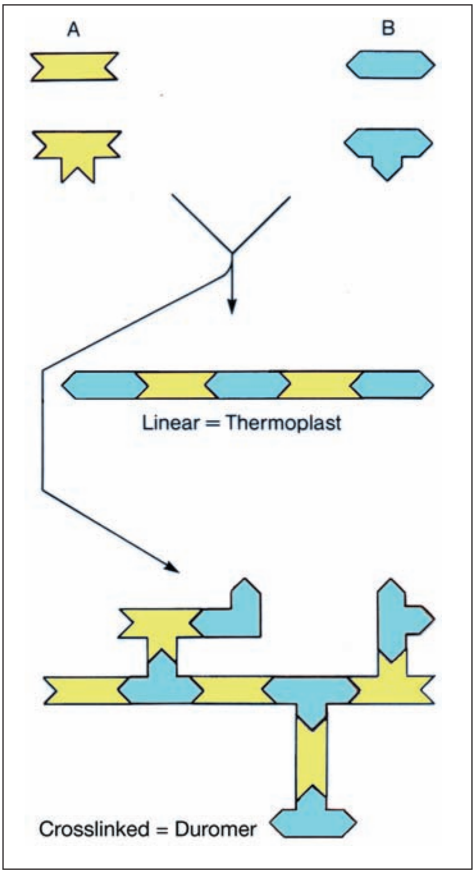


Fig. 3.1.8
Schemes of bonding and crosslinking of film forming agents during chemical curing

exert a special influence on film properties owing to the higher activation energy compared with the other crosslinking reactions. Excessively high temperatures and excessively long curing times cause the coating to become brittle owing to exaggerated crosslinking, whilst excessively low temperatures and excessively low curing times fail to achieve the hardness necessary for coating performance [3.4.4] (see chapter 4.3).

Curing reactions based on polyaddition or polymerization have this drawback to a much lesser extent. The two mechanisms permit chemical curing even without additional heating. Polyaddition systems already react after mixing the reactive components without cleaving off low molecular reaction products. The normal practice of heating during film formation merely serves to speed up a crosslinking reaction already occurring. Owing to the higher reactivity than in the case of the polycondensation reaction, less reactive residual groups remain in the cured film. 2-component paints such as polyurethanes or epoxy resin paints are consequently much more resistant to overbaking. In the case of polyurethane coatings this property is even reinforced owing to fast hydrolysis and the associated inactivation of the remaining isocyanate groups. By comparison with polyaddition, polymerization-curing coating materials require extra initiation. This can be achieved by adding suitable catalysts or by means of high-energy radiation. The crosslinking reaction is then exceptionally fast and therefore leads to very hard, chemically resistant films. Important examples of polymerization-curing film forming agents are unsaturated polyesters and acrylic acid derivatives specially developed for radiation curing.

3.1.2.3 Flows in the Solidifying Film

On account of the low-density of the volatile solvents in relation to the dried film an increase in density occurs at the surface losing solvent during the film forming process. The heavier but still mobile paint components sink in the substrate, which has a lower specific density. To the same extent ligh-weight components containing more solvent are moved upwards. Surface tension, which therefore rises in the areas close to the boundary surface, reinforces flows in the resulting film. Local vertical and horizontal flows take material from the top downwards and transport it upwards again at a different point. This process creates cavities and rises in the coating as it solidifies.

These surface textures known as *Bénard* cells run counter to the conventional flow of application-related local rises. If a paint contains several pigments with varying mobility, cell formation is accompanied by floating effects, pigment separation and flocculation. The decrease in color intensity and therefore changes in color are the result. As a measure of the mobility of pigments one normally uses the reciprocal product of density and the square of particle size. The effect is particularly pronounced if the resulting films have a low viscosity, film thicknesses are large and there are considerable differences in the surface tension and density between upper areas of the film losing solvents and the lower areas of the film containing more solvent. If the solvents are ones which are particularly "short", a temperature gradient occurs in addition owing to their rapid evaporation. This even reinforces the effect (see chapter 2.1.4).

3.1.3 Film Shrinkage

Solidification of the film, be it physically due to the emission of solvents or chemically due to the formation of low molecular cleavage products from the crosslinking reaction, brings about a reduction in film volume. That causes irregularities in the paint substrate to be reproduced, depending on the degree of shrinkage. Such substrate unevenness creates rises of several micrometres in automotive steel panels for reasons of deep-drawing capability and formability in the press shops. Even sanding processes cause unevenness in the form of sanding grooves.

Figure 3.1.9 shows two wet films with a different solid content. At the beginning of film formation the two paints fill both grooves in the substrate completely and create a smooth surface. The film shrinks owing to the emission of solvent and cleavage products by chemical crosslinking. As solid content increases, shrinkage declines and thus causes the substrate to be reproduced less. Some of these irregularities in the film, which is still not crosslinked, tend to flow again, depending on the viscosity of the wet film.

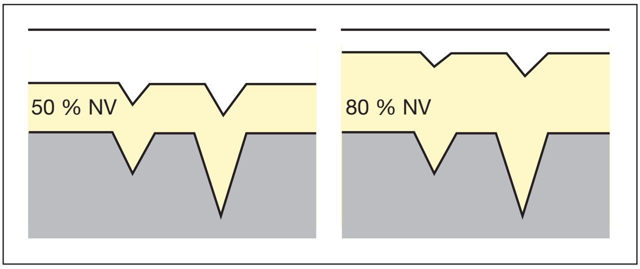


Fig. 3.1.9
Textures of substrate and their reflected images in the surface of coatings

The approximately 10% share accounted for by cleavage products in polycondensation-curing paints, in relation to the quantity of solvent, seems to be a negligibly small contribution to shrinkage. However, cleavage products only occur on account of chemical curing, that is, at temperatures where solvents have largely evaporated. On account of the high film viscosity at that point in time it becomes more difficult to level out the hollows caused by cleavage products. From this it becomes evident that the only relatively small quantities of cleavage products can cause a more substantial effect in reproducing substrate irregularities than the quantity of solvent evaporating, which is approximately 10 times the amount.

A deterioration in visual attractiveness associated with the reproduction of microstructures must therefore be regarded as an interaction between the formation and levelling of textured surfaces. A high solid content, in conjunction with small quantities of cleavage products, is therefore a good basic requirement for a smooth and hence high-gloss coating with good build. This is particularly pronounced in the case of radiation-curing paints.

3.1.4 Special Features of High Solid Paints and Waterborne Paints

Owing to the differences between ecological material options, special features also have to be taken into account during film formation (see chapter 5.6).
High solid paints, that is, coating materials rich in solids, suffer less film shrinkage than solventborne paints, and hence less pronounced reproduction of surface irregularities, on account of the lower proportions accounted for by solvents. If one adds that high solid paints drop to a much lower level of viscosity during film formation on account of the lower molecular weight of their resins, it is easy to understand that the less pronoun-

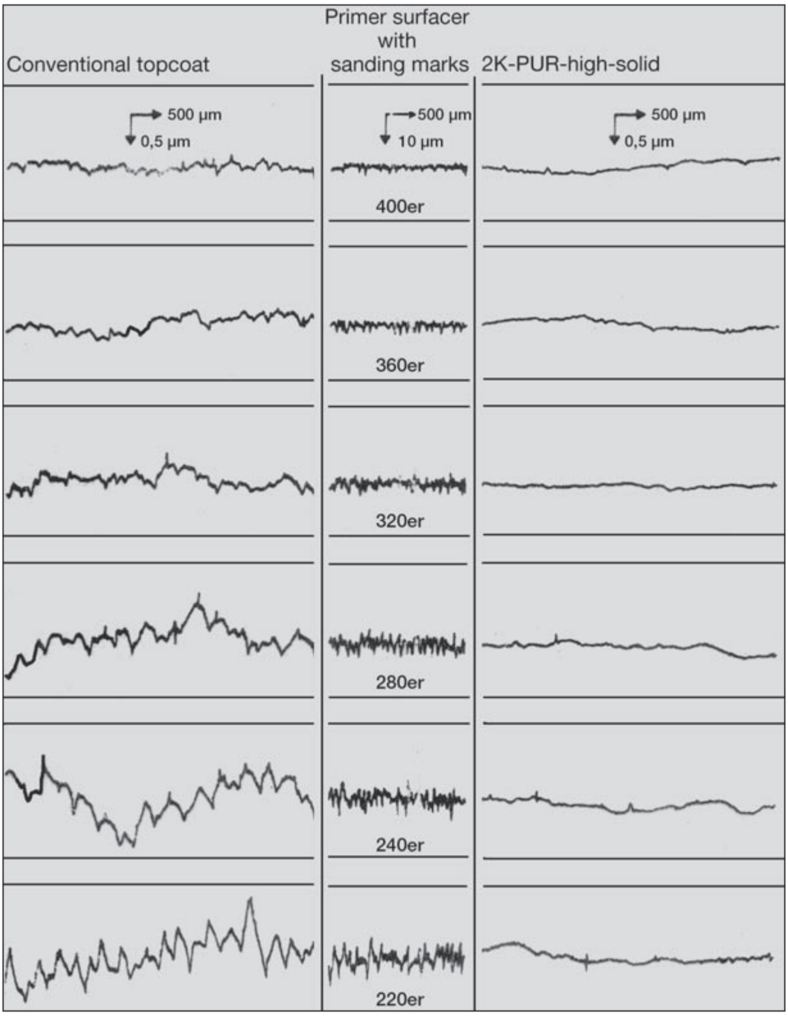


Fig. 3.1.10
Surface profiles of a conventional 1-component paint and a 2-component high solid paint in correlation to substrate textures by means of defined sanding marks (= 20 x less magnification)

ced microstructures are compensated by the excellent flow of high solid paints, although this is an effect which goes hand in hand with an increase in the tendency to run. One must not overlook the fact that with polycondensation-curing high solid paints the cleaved condensation products tend to increase on account of the larger number of crosslinking points than with solventborne paints. The resulting larger degree of volume shrinkage can offset the advantages achieved by raising solid content.

With 2-component high solid paints the situation is better. Here there are absolutely no cleavage products owing to the polyaddition crosslinking. Moreover, by comparison with 1-component paints a higher solid content can be achieved so the formation of macrostructures and microstructures is largely prevented. Also, by optimizing the coordination of solvent release, reactivity and thixotropy it is easier to control the tendency to sag and run away from edges, which is characteristic of 1-component high solid paints.

The excellent build of 2-component high solid coatings compared to solventborne ones is illustrated in figure 3.1.10. The surface textures scanned physically with a profilometer (see chapter 3.2.4) vary enormously. Whilst the solventborne baking enamel show textures which have a direct functional relationship with the depth of sanding grooves in the primer, there are virtually no gloss-reducing microstructures or long-wave irregularities in the solid rich coating.

Even waterborne paints manifest specific features during film formation. On the one hand, there is a dependence of evaporation behaviour on the level of moisture in the ambient air, which thus makes air-conditioning systems a necessarily integral part of coating lines if waterborne paints are to be applied without any problems (see chapter 4.2.4 and chapter 5.6). With physical drying there is an additional variable owing to the degree of neutralization and the resulting pH. The amines necessary for the solubility of anionic film forming agents exert an influence on viscosity, depending on the type and quantity of the neutralizing agent.

Figure 3.1.11 provides information on the viscosity of a dissolved waterborne paint depending on the degree of neutralization, adjusted with various amine additives. Since during film formation it is not only water and organic cosolvents that evaporate but also the neutralizing agent amine, the rheological behaviour and hence the flow properties of waterborne paints compared with solventborne coating materials cannot be controlled solely by altering the composition of the solvents.

The situation is completely different with the film formation of

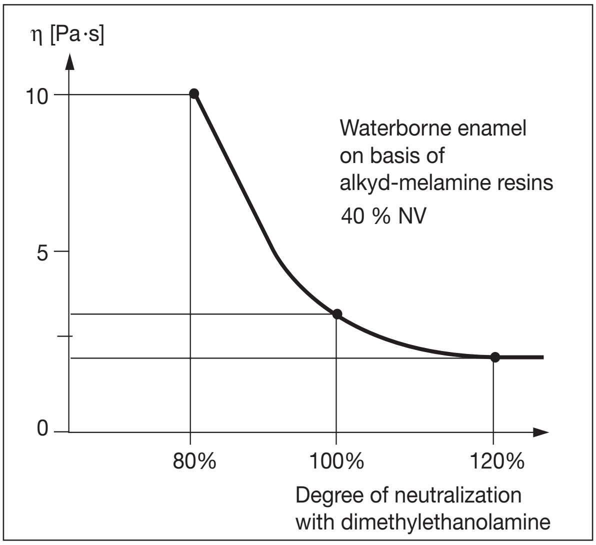


Fig. 3.1.11
Correlation of viscosity of waterborne paints and the degree of neutralization

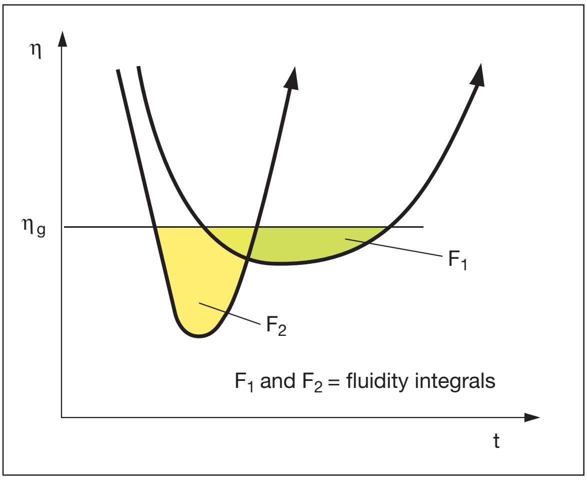


Fig. 3.1.12
Fluidity integrals during baking of powder coatings with good (F_1) and bad (F_2) flow properties

powder coatings. After melting on the sprayed object, solid particles made by grinding have to be transformed into a smooth, continuous film. Owing to the absence of solvents and the molecular weight being higher than that of solvent-borne paints the bake-on viscosities are relatively high. Consequently, there are less problems with running, but particularly flow and ventilation, that have to be overcome. Good-flow coatings with film thicknesses equalling those of liquid paints are still subject to development. Research work is aimed not only at adjusting the flow properties but also at optimizing particle size and particle shape. Spherical and also finer particles with a close size distribution might improve flow even when applying thin layers [3.4.5].

Viscosity-time curves can assist in characterizing the flow properties of powder coatings if they can be used to calculate dimensions in the form of so-called fluidity integrals. Time intervals within which an agreed viscosity η_g limit is fallen short of play a vital role. With the aid of computer programs the fluidity integrals, and hence the flow properties, can, after determining material-specific constants by experiment, be calculated for any heating gradients with considerable accuracy [3.4.6].

3.1.5 Monitoring the Film Forming Process with Measuring Instruments

For the purpose of describing film forming processes quantitatively methods are used which can detect with measuring instruments the physical drying, chemical curing and, as is usual in most cases, both phenomena, one overlying the other. The transition of the liquid film to a viscoelastic protective layer has to be monitored by simulating practical conditions accurately. That can either be performed by lengthy exposure to room temperature or by brief thermal stress. If the second method has to be adopted, defined conditions of film formation have to be set so that the entire range of

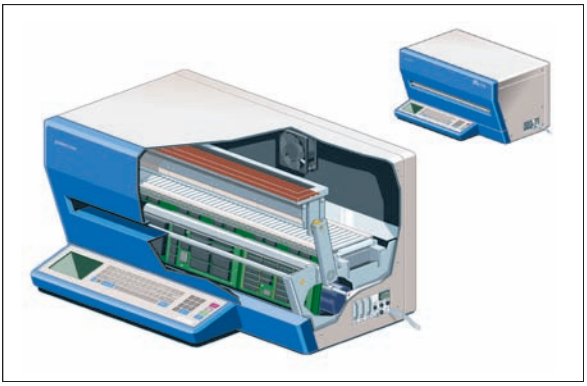


Fig. 3.1.13
Gradient bar oven according to Byk-Gardner

baking conditions occurring in practice is covered with as few individual tests as possible. Devices have proved successful which bring about different temperature conditions on one and the same test panel by setting temperature gradients. The gradient bar oven used most frequently (Byk-Gardner) consists of a long narrow hot-plate, on which an appropriate metal panel is placed. The temperature gradient selected can then be adjusted from one end of the panel to the other. That way it becomes possible to implement the film states relevant to quality assurance on just a single test panel. The measurements of visual and physical/technological properties then have to be performed at various points on the test piece.

3.1.5.1 Flow and Sag

If one wishes to make reliable forecasts about the flow properties of coating materials, one must first of all ensure that the state of the film at the time of measurement is equivalent to the practical conditions of manual application and of industrial paint shops. Flow applicators and run applicators specially developed for manual application are consequently only suitable for dip and brush coating methods of application by contractors. The devices for measuring flow each have five dual apertures with heights from 250 µm to 4 mm.
The test panels placed horizontally (A) are assessed by giving grades from 1 to 10, whereby grade 1 means that no pair of double strips has flowed together and grade 10 means that all the pairs of double strips have flowed together. The run applicator is of similar design. Ten apertures with heights from 75 µm to 300 µm, rising continuously, make it possible to apply film thicknesses with defined varying heights. If the test panel is then placed upright, the sagging limit is determined by measuring the film thickness at which the runs in the wet film extend to the next strip (B).

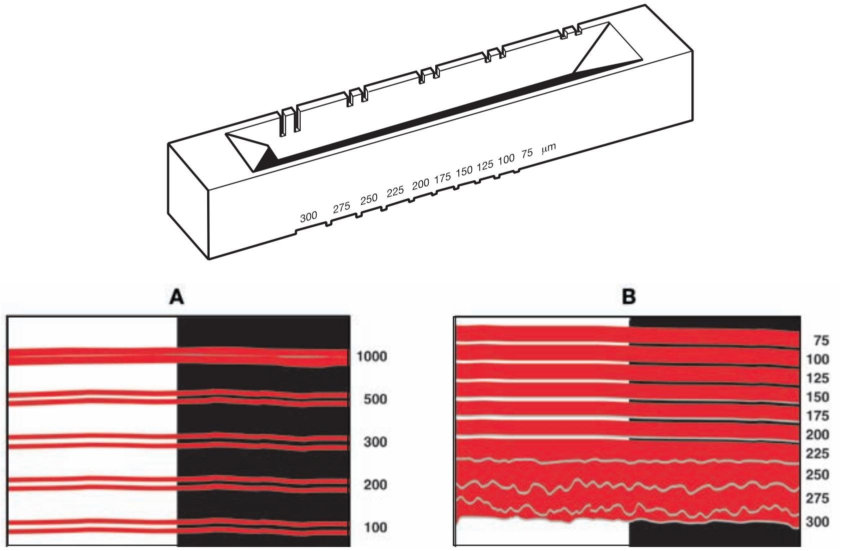


Fig. 3.1.14
Flow and sag doctor blade according to Stieg

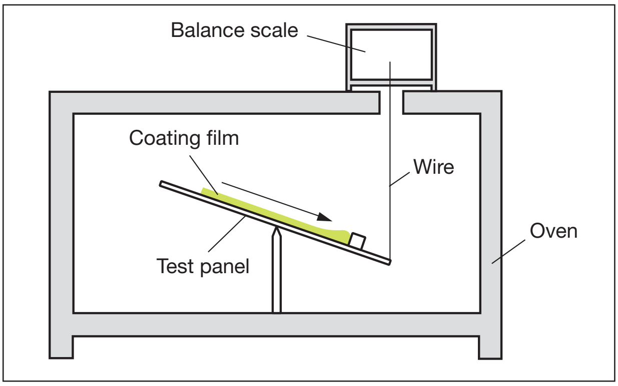


Fig. 3.1.15
Scheme of the sag balance according to TNO

A different technique with a similar effect on measurement is to use wedge applicators. The wet film to be tested should exceed the sagging limit at its thickest point. After introduction of defines cavities in the fresh paint the test plate is placed vertically to the cavity lines in order to determine the tendency to sagging.

The film thickness as of which a run into or out of the cavity can be observed serve as a parameter for the tendency to sag. Such a measuring technique can be used for flow measurements on films made by spray application if the test panels are made according to application methods in practice.

A different test method for quantifying the tendency to sag is the TNO sag balance [3.4.7]. On a test plate placed at an angle the change in weight associated with sags can be seen on a weigher connected to the test panel. Such a technique also permits measurements in a dryer and is therefore also suitable for characterizing baking enamels.

3.1.5.2 Film Formation of Air Drying Paints

Irrespective of whether the paint is physically drying, chemically curing or a combination of the two types of film formation, woollen threads or sand are placed on or pressed into solidifying films by machine with defined thrust. While the film is still liquid the threads and the sand sink at the beginning of the test and afterwards they remain at the surface, still sticking at first, but later on only lying detached after sufficient solidification [3.4.8].

A different testing tool for making detailed statements about the entire process from the paint to the cured coating is a steel hoop which is drawn through the solidifying layer at a defined velocity and with an adjustable weight applied. Whilst the traces of the hoop refill in the still liquid paint, traces will remain in the second stage of drying in order to break up the surface of the film again after further solidification. In the next stage of solidification the hoop will not leave any traces at all (see figures 3.1.16 and 3.1.17).

3.1.5.3 Indirect Methods

Numerous indirect methods have proved successful for describing film formation in the case of baking enamels to be applied in industry. Apart from the “rolling ball” technique presented in section 2.3.2 all methods which detect the chemical changes in the film forming agent during film formation quantitatively are to be recommended. Methods worth mentioning are instrumental analysis such as nuclear magnetic resonance, infrared or Raman spectroscopy, measurement of the dielectric constant or dielectric loss, or the caloric effects of Differential Thermoanalysis (DTA) and Differential Scanning Calorimetry (DSC). For detecting the degree of crosslinking the determination of glass temperature is just as important as that of the still reactive residual groups (see chapter 2.3.2).

Monitoring the reduction of dielectric constant must be emphasized because it provides reliable measurements with simple measuring probes quickly and without any damage. What is measured is the crosslinking related reduction in the capacitance of a capacitor made up of the coated metal item, the film of paint and the measuring probe applied. If film thickness and the area of the probe are known it is possible to calculate the dielectric constant [3.4.9].

Furthermore, it is also possible to make statements about the degree of crosslinking by performing dissolving tests with aggressive solvents. Different degrees of softening provide qualitative information about the degree of crosslinking. If one dilutes the solvent being used with a soluble dye, the latter will penetrate the coating if there is insufficient crosslinking and changes color depending on the degree of crosslinking. To make the test result more objective effects can be measured by colorimetry and stated in absolute color differences.

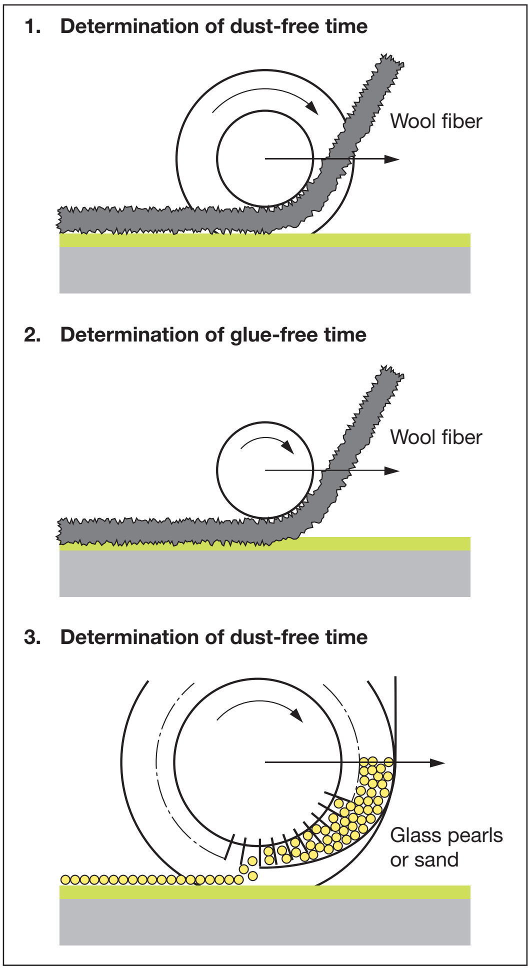


Fig. 3.1.16
Methods to measure the film formation of air drying paints and oxidatively hardening paints

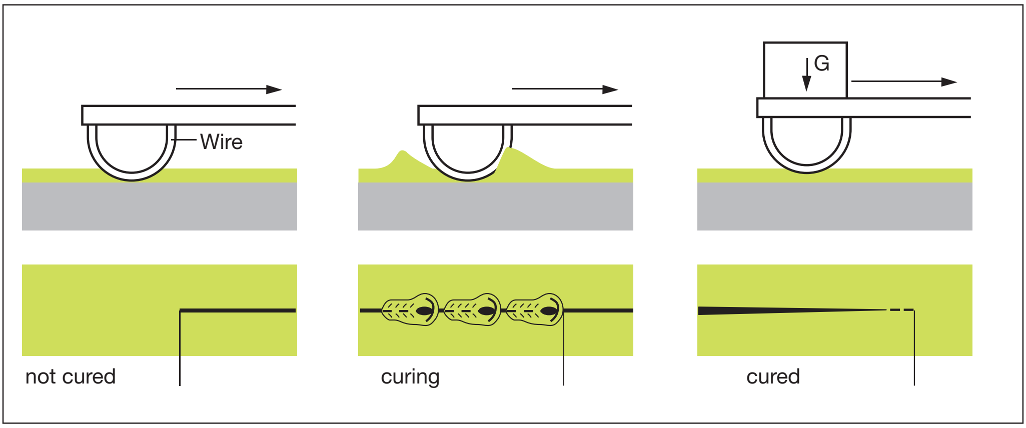


Fig. 3.1.17
Method to examine the solidification process of coatings

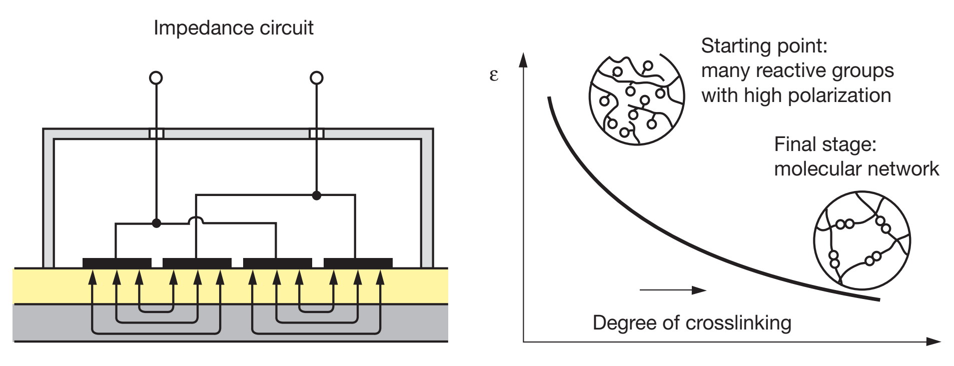


Fig. 3.1.18
Correlation of the dielectric constant and the crosslink density

Special reference has to be made for powder coatings. Due to their solid state during application the flow and curing mechanism is of great importance. Melting, flowing, the gel point and final crosslinked state of the film are distinct situations which have to be monitored for successful powder coating formulation [3.4.10].

3.1.6 Summary

The transition from paint to a coating is determined by numerous physical and chemical changes. The wetting, flow, solidification due to solvent emission and chemical crosslinking reactions are the most important individual steps in the process between the coating material and a coating suitable for use. Coating materials themselves can be used in various forms: molecularly dissolved, dispersed or solid powder. The desired quality of coating in the form of good visual properties, good adhesion and excellent physical/technological properties is defined by the interaction of solvent emission, changes in rheological properties and the reactivity of the film forming agents. The latter leads to chemical crosslinking reactions by polycondensation, polyaddition and polymerization. The process of solidification is superimposed by other physical phenomena such as currents in the solidifying film and volume shrinkage.
Numerous test methods have been developed for making films easily and reproducibly, constantly monitoring the course of solidification and smoothing. In this way it is possible to use a description of the film forming process to conduct targeted interventions and thus improve quality.

3.2 Properties and Testing the Coatings

When the film forming process has been completed, the requirements made of the coating with regard to performance properties should have been fulfilled. Apart from film thicknesses and the physical/technological properties such as adhesion, hardness and elasticity the visual properties and resistance when exposed to practical conditions play an important role when assessing performance of coatings.

3.2.1 Film Thicknesses

In addition to visual attractiveness, the selection of coating materials and application technique are vital to long-lasting protection of commodities. For all requirements made of the coating there is an optimum thickness for the layer applied. High film thicknesses are desirable to ensure good flow, visual covering of the substrate and good protective action against gases and water vapour. However, they can be offset by a deterioration in physical/technological properties with increasing film thickness and not least by the profitability of the coating process. Definition of optimum film thickness and film thickness distribution and the monitoring of it are therefore important preliminary reviews for the quality assurance of coatings.

Owing to the more or less rough paint substrates to be coated an exact statement of film thicknesses is frequently a difficult task. The term film thickness can therefore only be defined as a mean value in relation to the method of measurement and roughness. For this reason industrial standards assume that film thickness is to be regarded as a result of measurement which has been obtained by an agreed, exactly defined method. Figure 3.2.1 demonstrates that the common integral measurement of film thicknesses does not detect its local deviations.

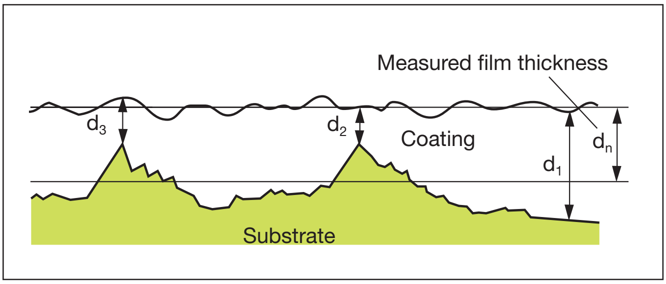


Fig. 3.2.1
Determination of film thicknesses d_n as an average value of coatings on rough substrates

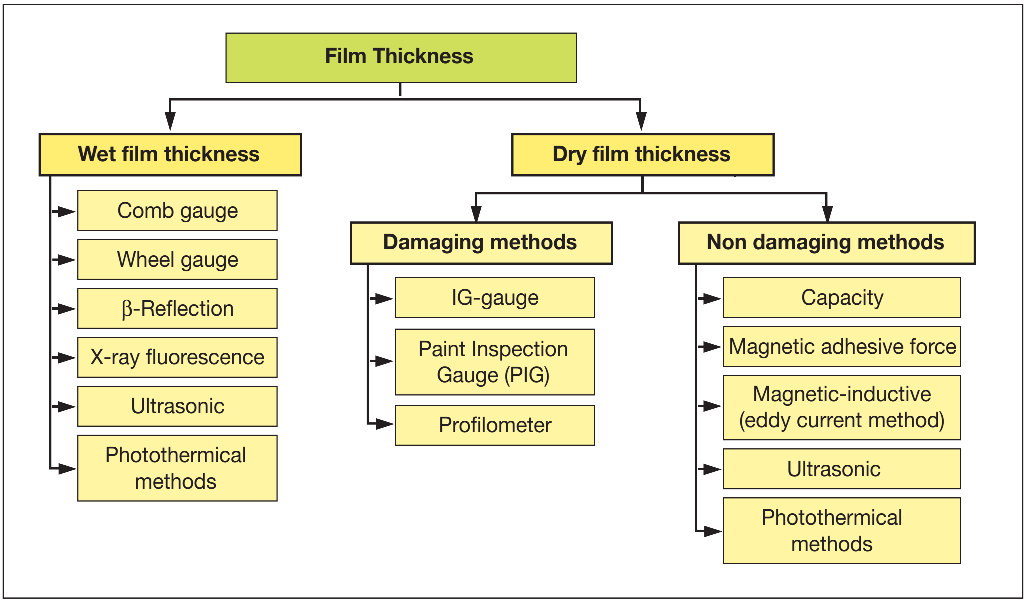


Fig. 3.2.2
List of relevant methods for determination of film thickness

To assess the protective action of a coating it is therefore necessary to add other criteria. Essentially these are definition of the roughness of the substrate and the voids and irregularities in the organic protective layer due to the application process.
Most methods of determining film thicknesses relate to measurement of the applied and cured coating. In many cases it is necessary to determine the thickness of the film as it develops in order to be able to correct it if necessary during application. This also applies to brush or roller application by contractors and to high-speed industrial application of paints by coil coating.
Measurement of film thickness is defined in industrial standards such as DIN EN ISO 2808 and many ASTM-standards. The methods of measuring film thicknesses can be divided into ones for dry films and ones for wet films, of which some can be used for both cases. The methods for dry film thicknesses can be split up into damaging and nondamaging methods.

3.2.1.1 Wet Films

To measure the wet film thickness there are simple and inaccurate devices available as well as more elaborate and more accurate ones. One of the simple devices is the measuring comb.

Fig. 3.2.3
Measuring comb for determination of wet film thickness

The measuring comb, which has prongs of different length, is pressed into the fresh coating at right angles. The longest pin not yet covered by the paint indicates the wet film thickness. The rolling rim is based on the same principle. The centre wheel of three parallel wheels is smaller than the others and is positioned off-centre. As a result, when pressed into the paint there are various distances from the substrate depending on the position of the wheel. By rotation the place is determined at which the off-centre wheel is just being wetted by the paint.
The beta backscatter method as per DIN EN ISO 3543 and X-ray fluorescence as per DIN EN ISO 3497 are more convenient, with measuring errors of ± 1% to 4% they are much more accurate and what is more, there is no contact. Both methods can be used for fresh films and cured films in the same way. Owing to their accuracy and particular suitability for online measurement of film thicknesses these methods will be explained later (see below).

3.2.1.2 Dry Films

Film-damaging methods

Film-damaging methods assume a defined clearing off the coating down to the substrate. With the so-called wedge cut method, e.g. with the paint inspection gauge (PIG) as per DIN 50986 a wedge-shaped cut is made in the coating down to the substrate.

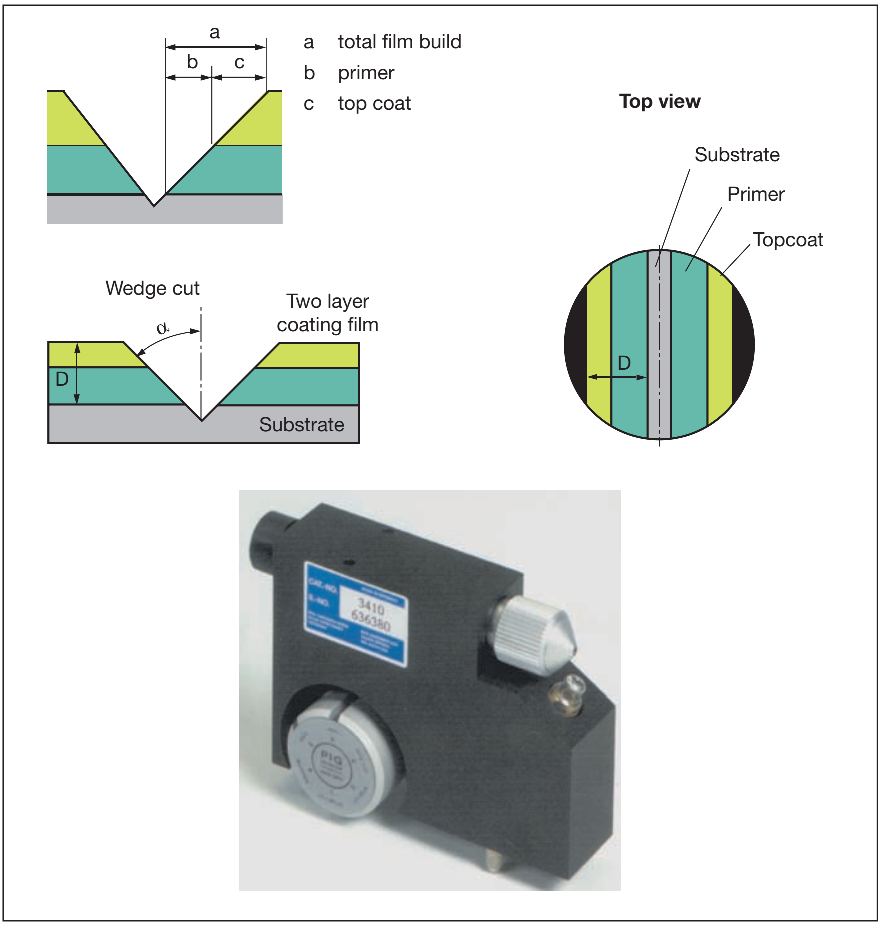


Fig. 3.2.4
Principle of measurement and respective instrument of the Paint Inspection Gauge (PIG) according to DIN 50986

By measuring distance a for the total layer as well as distances b and c for the individual layers with a measuring microscope the figures are converted to corresponding film thicknesses assuming the angle of inclination, α, of the resulting edge is known. The wedge cut method is suitable for simultaneously determining individual layers of multilayer systems. It has also proved reliable for measuring the film thicknesses of coatings on various nonmetallic substrates such as wood or plastics.

Another device, albeit only suitable for measuring total film thickness, is the IG gauge as per DIN 50933 or ASTM D 1005. It has three feet, two fixed ones and another which is connected to a gearwheel via a rack. This probe is placed on the coating with its point at a distance from the substrate so that the fixed feet are on the coating and the sensing foot is in the cavity on the substrate. The probe now transmits the height difference to the rotating gearwheel in proportion to the film thickness.

Profilometers (see chapter 3.2.4) are modern, more accurate devices. They are used for measuring surface structures but if the samples are prepared accordingly they can also be used for measuring film thicknesses. A diamond or laser beam scans the surface and transforms the detected height differences into electronic information about the surface

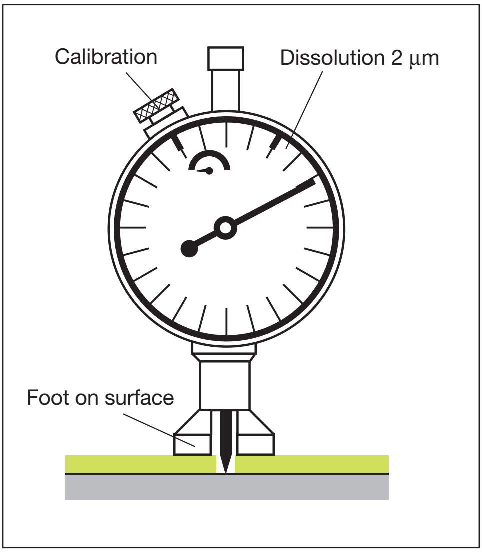


Fig. 3.2.5
Scheme of an IG gauge

texture. If the coating is damaged before measurement and part of the coating is pulled off down to the substrate, the profilometer is able to detect this difference in height and thus supply information about film thicknesses.

The measurement of individual layers in multilayer systems is extremely accurate using microscopic examination of cross sections. Modern image analysis techniques permit precise digital processing of the microscopic images made with a video camera.

Nondamaging methods

If the coatings to be measured are on metal substrates, there are several methods of measurement available which allow nondestructive determination of film thicknesses. The devices are based on measuring principles which exploit the material properties of the films and their dependence on film thickness. Three physically different methods have proved reliable in practice.

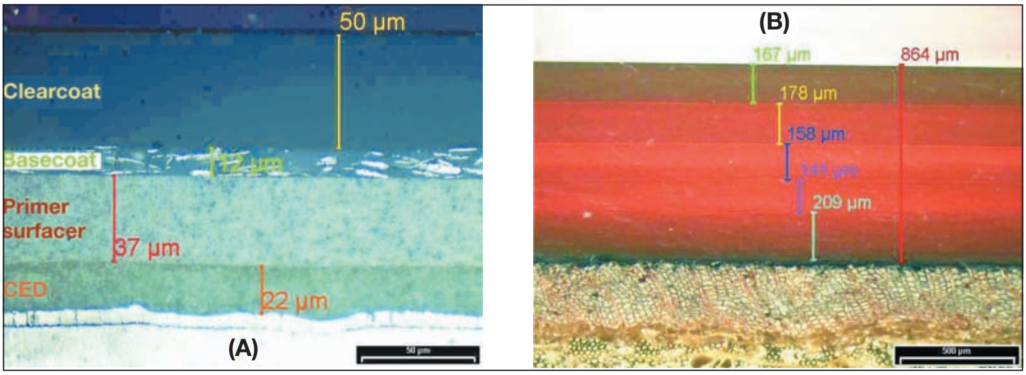


Fig. 3.2.6
Results of cross section measurement of an automotive OEM coating (A) and a wood coating (B) by microscope

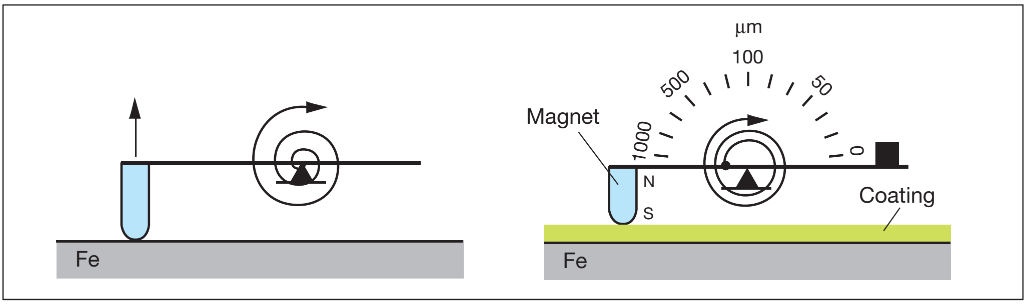


Fig. 3.2.7
Principle of film thickness measurements by a permanent magnet for ferromagnetic substrates

In the application on ferromagnetic substrates, i.e. iron or steel, there are two measuring principles which can be used. DIN EN ISO 2178 is based on the methods of **measurement involving magnetic adhesive force** of a permanent magnet and the influence of magnetic flux exerted by inductance on an electromagnetic alternating field as parameters. The former exploits the layer-thickness-dependent force of attraction of a permanent magnet. Its measurement is performed by continuously increasing counter-acting force. The force applied at the moment of tear-off is a measure of the film thickness of the coating. A diagram of how the principle works is shown in figure 3.2.7.

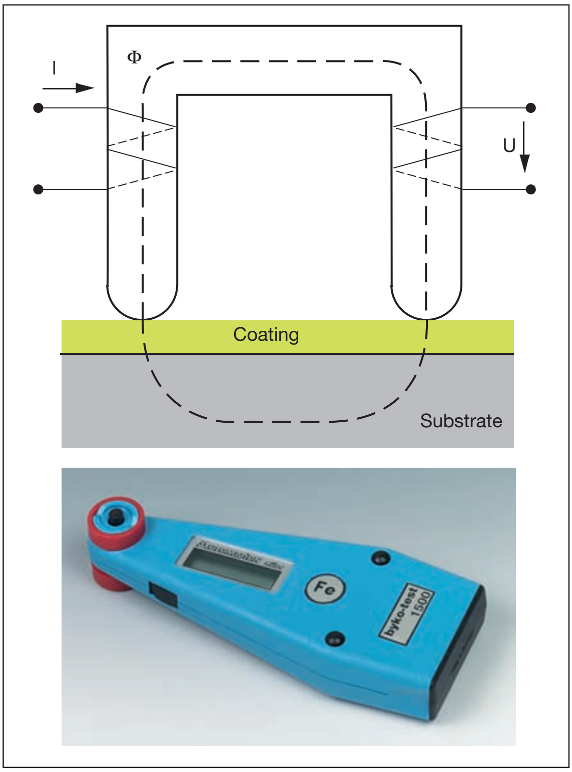


Fig. 3.2.8
Film thickness measurements using the magnetic-inductive effect

Film thickness measuring instruments which exploit the inductive influence of the magnetic substrate on an electromagnetic alternating field for measuring film thicknesses are of more elaborate design and are more sensitive in use but they produce more accurate results.

Current I (see figure 3.2.8) generates magnetic flux Φ in the primary coil of an electromagnet, which in turn generates induced voltage U dependent on it. In the measuring set-up the film thickness of the coating influences magnetic flux Φ and hence the measured induced voltage U.

Measurement of the change in inductive resistance, i.e. impedance, of a measuring coil conducting current by the retroactive influence of inductive eddy currents in an electrically conductive substrate is not restricted to use on magnetic substrates but can be employed for all metal materials, that is, not only

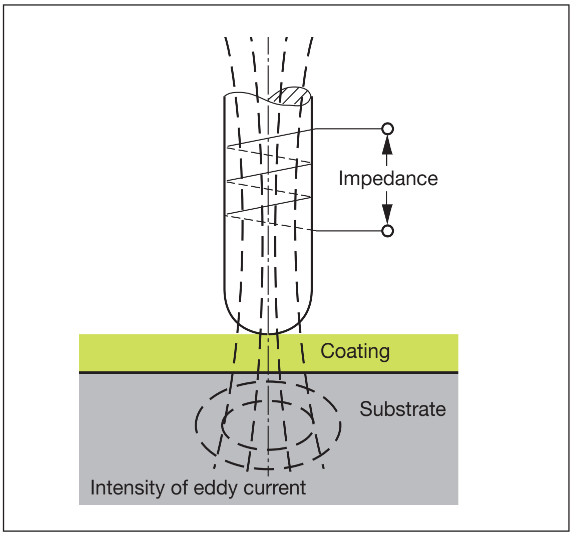


Fig. 3.2.9
Determination of film thickness according to the eddy current method on metallic conductive substrates

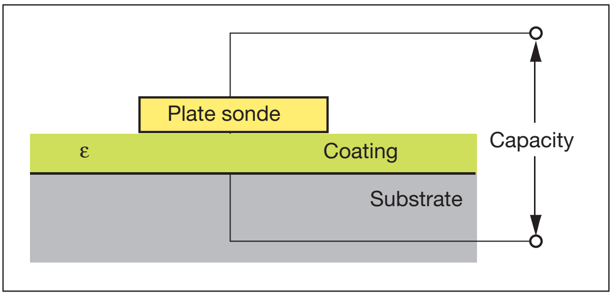


Fig. 3.2.10
Principle of the capacity method of measurement for the determination of film thickness

for iron but also for aluminium, zinc, copper and magnesium. In the case of the **eddy current method** it is the change in inductive resistance of the measuring coil which constitutes the layer-thickness-dependent variable. Details are described in DIN EN ISO 2360.

Capacitive methods of measurement are not quite so common but in principle they can also be used for all electrically conductive substrates. A plate-shaped measuring probe is placed on a flat, painted metal substrate and is used as an electrode of a plate capacitor, the dielectric of which is the coating.

By measuring capacitance C of the capacitor, film thickness d can be calculated provided the dielectric constant ε and the measured area A are known.

$$C = \frac{\varepsilon \cdot A}{d} \quad \rightarrow \quad d = \frac{\varepsilon \cdot A}{C}$$

Since the dielectric constant is substantially influenced by the film forming agents, the pigments and the moisture content of the coat, this method cannot be used universally. Moreover, measuring errors can be expected if there are irregularities in the coated surface. If, however, identical conditions can be created and measurement proper can be preceded by calibration measurements, film thickness measurements by the capacitive method are by no means inferior to the methods described above.

The approach to achieve automated paint application involves the development of new, nondestructive, contactless measuring techniques.

Contactless methods

Film thickness measurements by means of ultrasound, X-ray fluorescence, beta backscatter or photothermal methods have reached maturity so they are ready for use.

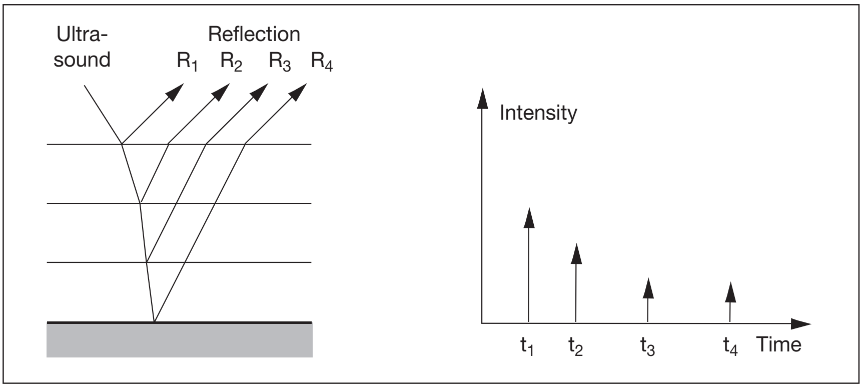


Fig. 3.2.11
Principle of measuring film thicknesses by ultrasonic reflection of a multi layer coating according to ISO 2808

Although they are all elaborate and expensive, some of them permit measurement of noncured films a very high degree of accuracy.

If an ultrasonic source with a sufficiently high frequency is used, it becomes possible to determine film thicknesses by means of interference effects as per ISO 2808. The **ultrasound** hitting the coating system is partially reflected at the surface. The remainder penetrates the coating and is split up again at all other boundary surfaces into a reflected component and a component that continues to penetrate. The waves now emerging from the coating with a phase shift, R_2 to R_4 (see figure 3.2.11), superimpose themselves on the previously reflected ones and also produce layer-thickness-specific interference manifestations owing to the dependence of phase shift on film thickness. One major advantage of this technique is that as opposed to the nondamaging methods described above it also becomes possible to measure the individual layers of multilayer systems on nonmetallic substrates. Devices with contact probes are suitable for the measurement on plastic substrates [3.4.11]

The characteristic secondary radiation occurring in the substrate or in the film of paint when exposing to **β- or X-rays** is also used to determine film thicknesses accurately. Here two layer-thickness-dependent principles of measurement are exploited.

Either β-rays or X-rays penetrate the coating film and are scattered back by the substrate. If suitable pigments are used the backscatter already occurs in the film of paint. The scattered radiation and secondary radiation are measured in a detector. If the atomic numbers of the elements in the paint and in the substrate are sufficiently different, scattered radiation of the β-rays and fluorescence radiation in the case of X-ray have to be applied to two types of film thickness measurement. If one uses the scattered radiation and fluorescence radiation from the coating as a basis, intensity is directly proportional to film thickness. If one uses the secondary radiation from the substrate, the dependence is indirectly

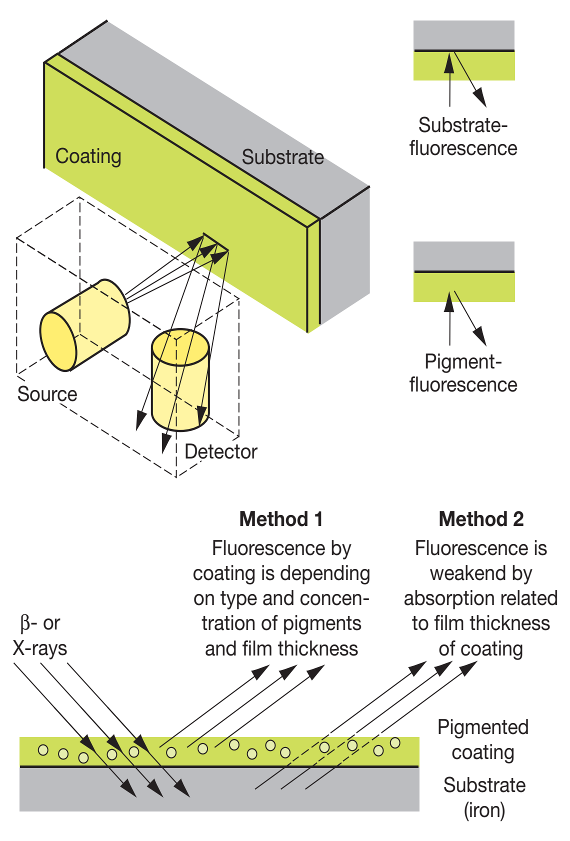


Fig. 3.2.12
Reflection of β- or X-rays and fluorescence radiation by organic materials

proportional to film thickness. Especially on high-speed continuous coating lines the less distance-dependent principle of measurement, beta backscatter as per DIN EN ISO 3443, has become most widespread but on the other hand it is less sensitive. The radiation sources normally used are radioisotopes. In practice one must bear in mind the hazards due to exposed sources of radiation.

Owing to their fast feedback to the coating process both measuring principles have managed to acquire importance in continuous measurement for the coil coating process, which is extremely fast at a rate of up to 200 m/min (see chapter 7.4).

One method which is suitable both for powder coatings and for liquid paints that have not yet dried is photo-thermometry [3.4.12]. The intermittent radiation pulses of frequencies in the IR range being emitted by a radiation source, e.g. a laser, warm the near-surface zones briefly by a few degrees. The rise in temperature, transport of thermal waves to the substrate and the ensuing reflection at the surface of the substrate lead to a film-thickness-dependent temperature-time profile in the coating.

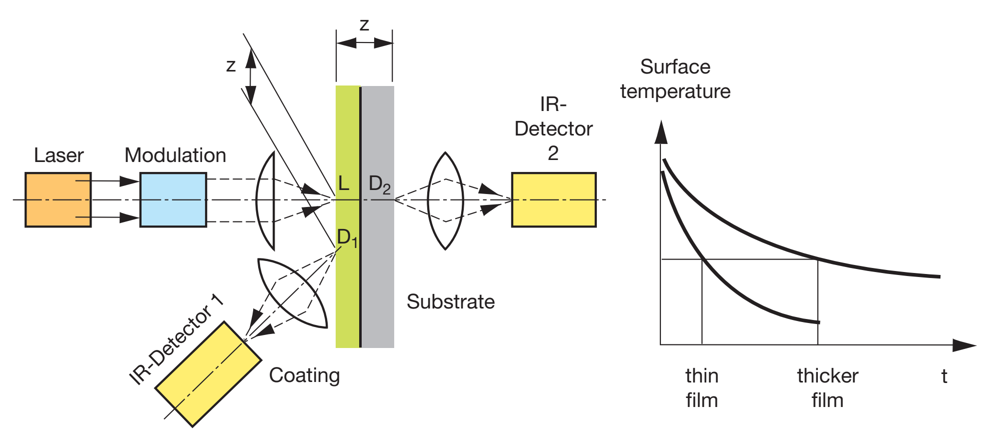


Fig. 3.2.13
Film thickness measurement by photo-thermometry

The measuring probes used are fast-response thermometers, so-called photothermal detectors. On account of the sensitive response of the IR beam to the molecules of water in the film, detailed statements can be made about the drying process with the aid of the thermal wave technique, in addition to rapid film thickness measurement. Special infrared spectrometers are also used, particularly for film thickness measurement and monitoring film formation in waterborne paints. The residual water content is indicated by the intensity of the absorption bands characteristic of water and is proportional to film thickness [3.4.13].

A comparison of the film thickness measuring instruments normally used in practice with regard to their accuracy, expediency in use and prices/cost of operation always lead to the same result. The reliability of the test result and the speed with which the test results are obtained are always directly proportional to the cost of the method.

The established, no doubt expedient but also low-cost devices, no matter whether they are ones which operate on the principle of adhesive power or magnetic induction, capacitance or the eddy current method, are all relatively inaccurate at ± >5%, as are the damaging techniques of the IG gauge or of the Paint Inspection Gauge. It is therefore necessary to minimize the errors by conducting multiple measurements and mathematical processing. Elaborate methods of X-ray fluorescence, beta backscatter and laser thermometry, on the other hand, must be given a different classification. Installation of the measuring apparatuses is correspondingly elaborate and additional sources of error are taken into account and eliminated so levels of reproducibility amounting less than ± 1% can be achieved.

Different methods of microscopic examination of cross sections, which are also accurate, have the drawback, however, of damaging the film by sample preparation so they are restricted to analyzing and determining the causes of coating defects.

3.2.2 Dry Film Density

Whilst determination of the density of liquids in a pycnometer poses no problems, density measurements in solids has to be performed indirectly, and hence in a more complicated manner, because the volume is seldom known.

One way of measuring dry film density is to determine the solids volume as per DIN 53219. For this purpose a coating is applied to a plate of known mass and calculated volume V_1. Calculation of the volume V_1 is conducted by determining the weight in air m_1 and water m_2 in accordance with

$$V_1 = \frac{(m_1 - m_2)}{\rho_1}$$

m_1 = weight of the test panel in air
m_2 = weight of the test panel in water
ρ_1 = density of water

Then the panel is coated and weighed again to determine m_3 and, after immersion in water, to determine m_4. The volume of the coated plate, V_2, is then:

$$V_2 = \frac{(m_3 - m_4)}{\rho_1}$$

m_3 = weight of coated test panel in air
m_4 = weight of coated test panel in water

The volume of the dried film, V_3, is then $V_3 = V_2 - V_1$, and $m_3 - m_1$ equals the initial weight of the film. Consequently, dry film density ρ_T is

$$\rho_T = \frac{m_3 - m_1}{V_2 - V_1}$$

Furthermore it is possible to calculate dry film density from the material data of the liquid paint if the density of the wet coat, the density of the solvents and the percentage quantity of the solids (% NV) are known.

Since the volume of the liquid paint, V_{Pa}, is the sum of the volume of the dried film V_T and volatile fraction V_{fl}, it follows that:

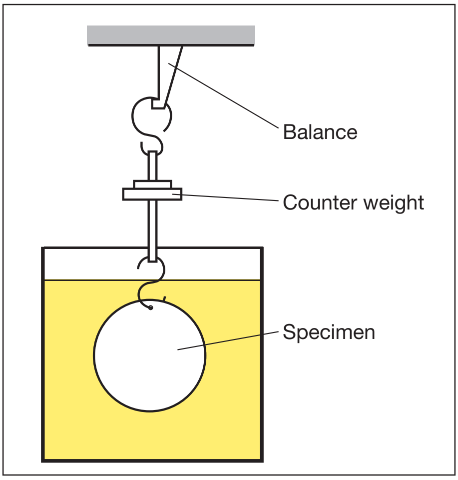


Fig. 3.2.14
Measurement of dry film density according to DIN 53219

$$V_{Pa} = V_T + V_{fl} \quad \text{or} \quad \frac{m_{Pa}}{\rho_{Pa}} = \frac{m_T}{\rho_T} + \frac{m_{fl}}{\rho_{fl}}$$

Since the mass of the paint constituents m_T and m_{fl} is also equal to the mass of the liquid paint m_{Pa}, it follows that:

$$m_{Pa} = m_T + m_{fl}$$

After resolving the equation to find ρ_T and substituting m_T/m_{Pa} x 100 by the solids (% NV) it follows that:

$$\rho_T = \frac{NV \cdot \rho_{Pa} \cdot \rho_{fl}}{100 \cdot \rho_{fl} - (100 - NV) \cdot \rho_{Pa}}$$

On closer analysis this simple relationship proves to be highly sensitive to small errors when determining the nonvolatile fraction. This becomes important particularly because baking temperatures which occur in the oven when determining in the laboratory are often different from those in industrial application. In an initial approximation the density of the volatile fraction ρ_{fl} can be equated with the density of the solvents in the paint.

On coating lines it often also happens that one has to determine densities of solids for which there is no relevant data concerning the liquid paint. Pigment powders and powder paints are examples where density calculation fails. In such cases one resorts to a modified pycnometer method. As described in DIN EN ISO 787-10 the density of solid powders is calculated from the weighings by the pycnometer with the pigment powder being examined, the pycnometer is then topped up with petroleum ether and it is finally weighted with pure petroleum ether. The density is determined from

$$\rho_T = \frac{m_{Pi} \cdot \rho_{Pe}}{m_{Pe} - m_{PiPe} + m_{Pi}}$$

ρ_{Pe} = density of petroleum ether
m_{Pi} = weight of pigment
m_{Pe} = weight of petroleum ether
m_{PiPe} = weight of pigment and petroleum ether

To achieve accurate test results it is essential that the powder be completely wetted with the petroleum ether.

3.2.3 Measurement of Voids in Coating Films

For the protection of substrates susceptible to corrosion film thickness is an important criterion but it is not the only one. Adhesion to the substrate and the continuity of the closed protective layer are additional factors determining quality. Depending on the rheological properties of the paint, extremely fine air inclusions or wetting flaws introduced by the application process can leave voids in the coating. These may stay only in one part of the coating or may extend in the form of continuous capillaries from the substrate into the surface of the coating, depending on the number of individual layers applied. Such voids tend to weaken the protection. They allow water and electrolytes to advance down to the substrate without any hindrance. Quantitative determination of voids is an absolutely indispensable task for assessing the protective action of anticorrosive coatings.

It is relatively easy to visualize channels in the coating extending down to the steel substrate by immersing the item in a copper sulphate solution containing surfactant. In the area of the voids the nonnoble iron in the substrate is dissolved and elementary, clearly visible copper is separated.

$$\mathrm{Fe} + \mathrm{Cu}^{2+} \longrightarrow \mathrm{Fe}^{2+} + \mathrm{Cu}\downarrow$$

The number of voids in relation to dm^2 is converted to a void ratio. P1 means no continuous voids, P2 less than 20, P3 20–100, P4 101–400 and P5 more than 400 voids.

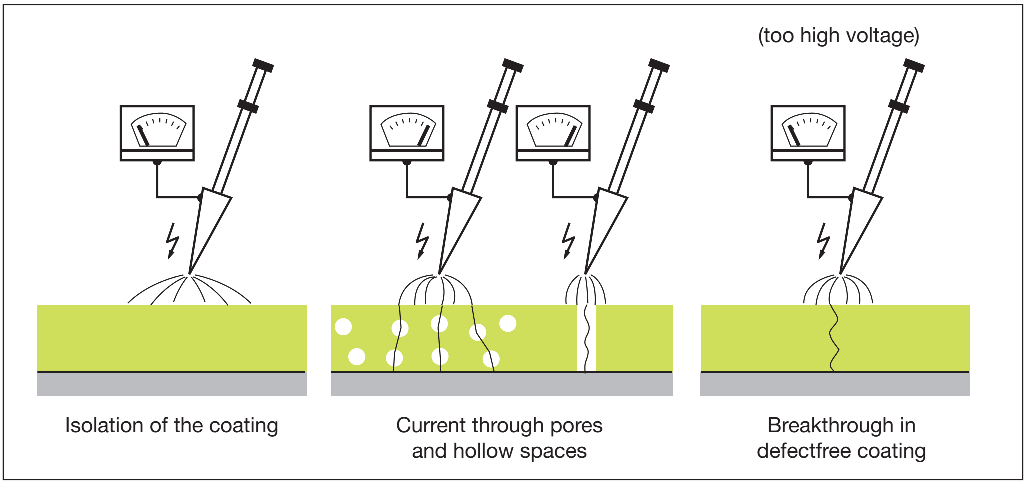


Fig. 3.2.15
Principle of determing voids in films with the help of high voltage

If the voids are not continuous, they cannot be identified by simply marking with copper. Weak points in the coating then have to be detected by other methods. In the search for continuous voids but also latent voids electrical spark discharges generated by high voltage have proved reliable. As described in DIN 55670, wire brushes or electrically conductive rubber wipers connected to high voltage are passed over the item being examined. Depending on the depth and the voltage applied, voids are indicated by disruptive discharges audibly or electrically.

This method is also used to determine edge coverage and the protective action on highly textured substrates.

3.2.4 Visual Properties

The color, color effects and gloss of surfaces are sensory impressions and hence subjective perceptions of the light changed by the interaction with coatings.

Color stylists examine the subjective perception of color, gloss and effect in conjunction with the shape of the coated item and thus help combine aesthetic and functional properties with one another. New visual effects are often transformed into beauty and elegance in order to provide incentives and arouse desires, but not only in the automobile sector.

The overall visual impression a person acquires is essentially created by two different physical phenomena. Part of the light hitting the coating is reflected at the surface and passes without further interaction with the constituents of the coating – irrespective of their color – into the observer's eye. If it is a directed reflection on a smooth surface, it is perceived to be glossy. By far the largest part of the light penetrates the coating where, after interacting with the pigments and effect substances, it creates color, hiding power and additional effects.

3.2.4.1 Gloss

Traditional definition of gloss

The traditional definition of gloss considers the light reflected at the surface of coatings. The reflection of light varies depending on the smoothness of the surface so the illuminated environment is reproduced more or less efficiently. The sensory impression perceived by the eye is recognized as gloss.

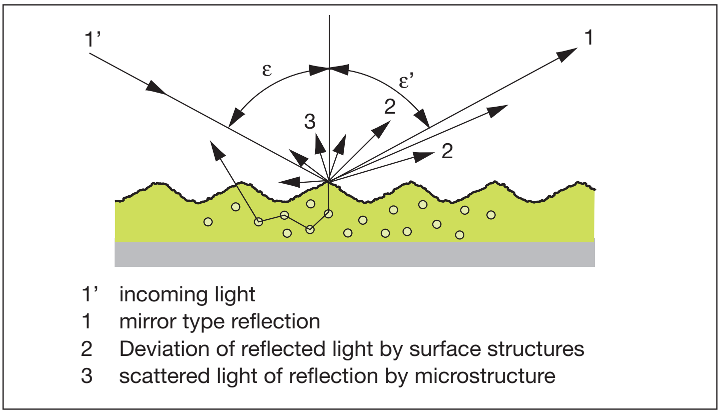


Fig. 3.2.16
Reflection pattern of light on coated surfaces

The proportion of the light reflected at the surface R is to calculate for coatings without effect pigments, depending on the angle of incoming light, with the aid of *Fresnel*'s formula by analogy with DIN EN ISO 2813.

$$R(n,\varepsilon) = \left[\frac{n^2 \cdot \cos\varepsilon - (n^2 - \sin^2\varepsilon)^{\frac{1}{2}}}{n^2 \cdot \cos\varepsilon + (n^2 - \sin^2\varepsilon)^{\frac{1}{2}}}\right]^2 + \left[\frac{(n^2 - \sin^2\varepsilon)^{\frac{1}{2}} - \cos\varepsilon}{(n^2 - \sin^2\varepsilon)^{\frac{1}{2}} + \cos\varepsilon}\right]^2$$

The graph of the intensity of reflected light is shown in figure 3.2.17, a plot in correlation to the relative refractive index from the ratio of the refractive indices n of the coating and air and the angle of incoming light ε : Over a large range of the angle of incoming light surface reflection is calculated to be 4% to 8%, which are relatively low proportions. Nevertheless, it is perceived by the eye as being intense. As opposed to penetrating light at smooth surfaces it is either not distributed at all, or only diffusely. If the surface texture is less pronounced, the light is chiefly reflected in a directed manner, thus leading to a sharp reflection of the light source.

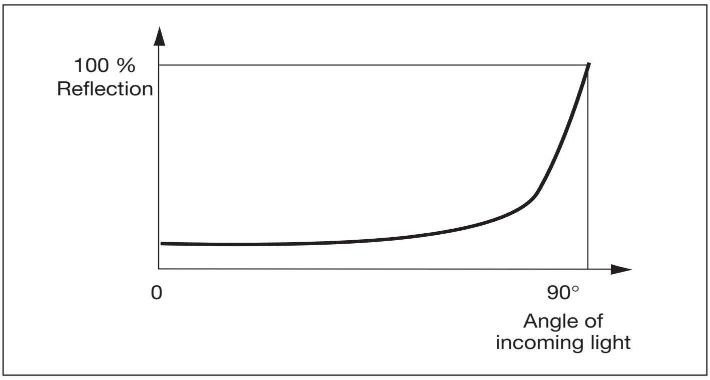


Fig. 3.2.17
Reflection depending on the angle of incoming light

Since gloss is evidently perceived as being intense if an illuminated object on a coating of paint is reflected brightly with little distortion and high contrast, it seemed advisable when defining the term 'gloss' to use the proportions of directed reflected light as a measure of gloss. This is the method specified by DIN 67 530.

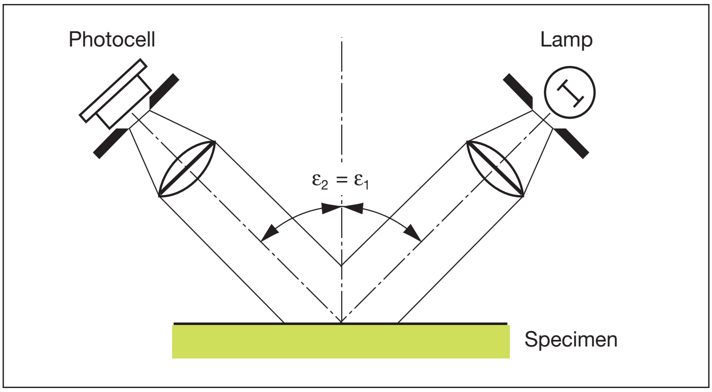


Fig. 3.2.18
Scheme of a reflectometer according to DIN EN ISO 2813 resp. DIN 67530

For gloss measurement reflectometers are used. These are devices which send from a defined light source light with an area of several square centimetres at an angle ε_1 onto the coated item. The intensity of the reflected light ($\varepsilon_1 = \varepsilon_2$) is measured at the appropriate angle of reflection, ε_2. Compared to a rough or wavy surface a smooth one will create higher reflection values. High reflectometer values are therefore indicative of high gloss. In practice simple devices have become established which make it possible to measure directed reflection on a reproducible basis and convert it to reflectometer values. The measurements are always relative and they relate to the reflected flux of light from a black, polished glass plate with a refractive index of 1.567.
To increase the measuring accuracy and improve the reproducibility of the measurements it has become reliable procedure with samples manifesting different gloss to also set various angles of incidence and reflection for the measuring beam. Owing to the higher proportion of reflected light with larger angles of incidence matt surfaces are

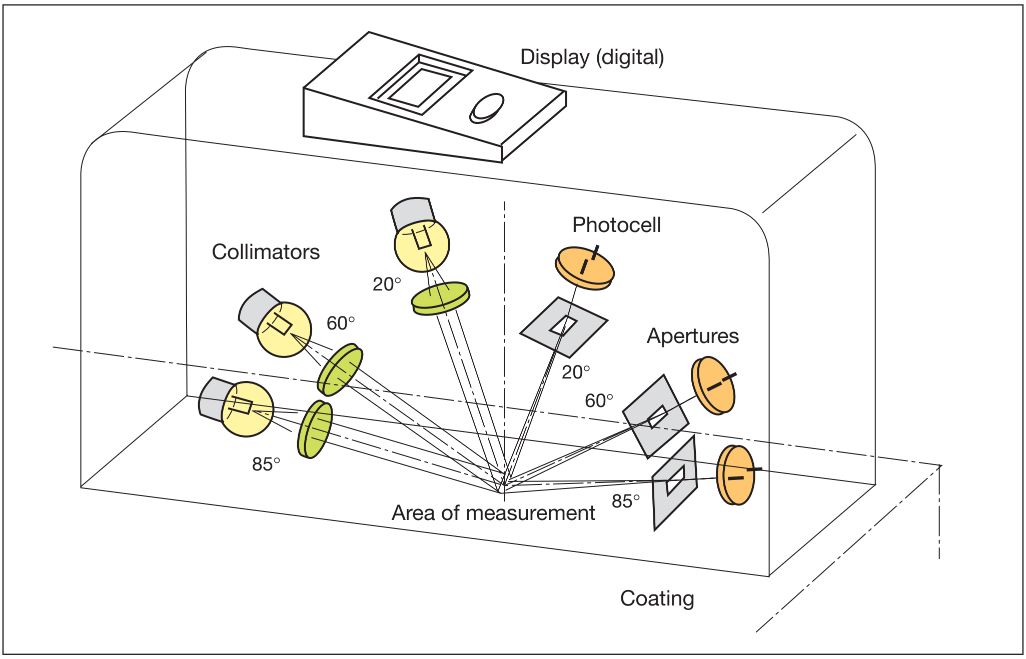


Fig. 3.2.19
Scheme of a measurement device for gloss at different angles

measured with a large angle of incoming light (85°), semi-gloss ones are measured with a medium angle (60°) and high-gloss ones with only a very small angle (20°) [3.4.14]. Modern devices contain all 3 measuring geometries and can be used universally by switching to the various ranges.

It is certain that if the directed reflection is of relatively low intensity the sharpness of reproduction will be impaired in different ways owing to the increasing nondirected and diffused components. The nondirected and diffused components are not detected by the reflectometer. However, they exert an influence on the observer's visual perception of surfaces.

To detect the light/dark effects of metallic coatings the reflectometer measurement is performed at various angles. One parameter of this effect is calculation of the relative reflection of the angle of 0° in relation to 45°, which is also the angle of incoming light.

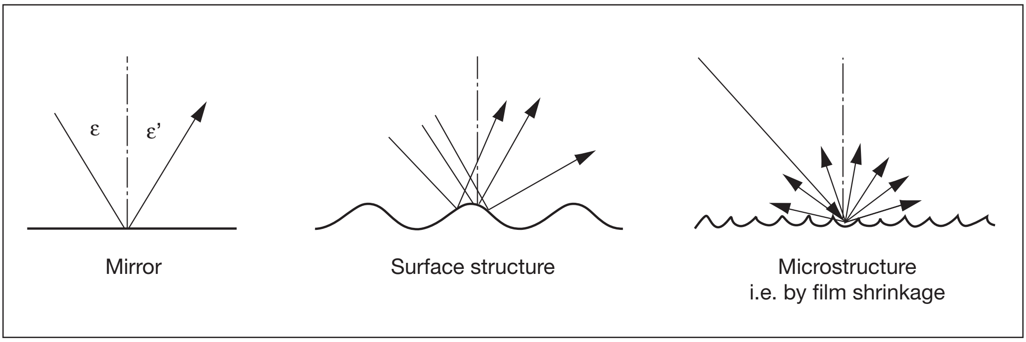


Fig. 3.2.20
Reflection of light on differently structured surfaces

Extended consideration of the term gloss

Long-wave structural deviations from the absolutely continuous flat surface mean slight local changes in the angle of incoming light and therefore in the angle of reflection as well. Short-wave surface disturbances in addition to those create larger local changes in the angle of incoming light. Fine and ultra-fine textures, on the other hand, scatter the light in all directions. Correlations between a sensory impression and physical effects can therefore only be found if the nondirected reflected light is also detected accurately and quantified with figures.

If one extends the measuring options of the reflectometer so that other angles of reflection are also detected beyond the setting $\varepsilon_1 = \varepsilon_2$, statements can be made about the whereabouts of the light flux for nondirected reflection as well.

Such devices, known as goniophotometers, have a mobile measuring probe and can thus cover all angles of reflection from 0° to 90°. Consequently, one no longer measures the gloss peak as the only reflectometer value but an entire reflection curve, the gloss indicatrix.

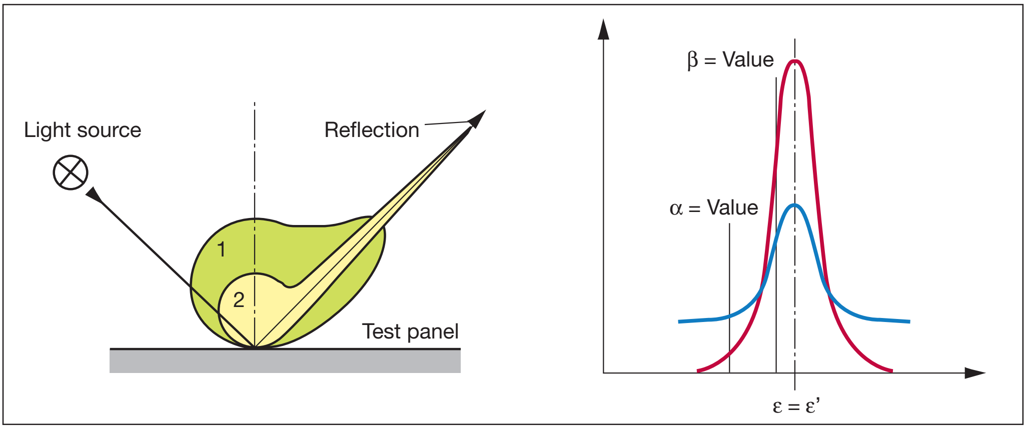


Fig. 3.2.21
Distribution curves of light from different coating films (gloss indicatrix)

The gloss indicatrix, with its information about the angle-dependent distribution of all the reflected light, makes it possible to gain a much more detailed analysis of the integral sensory impression of gloss using numerical values concerning light flux components. As with simple reflectometer measurement, the curve maximum at the angle of reflection $\varepsilon_1 = \varepsilon_2$ provides information about so-called specular gloss. In addition, owing to the different course of gloss indicatrix statements can be made about the reflected components near the angle of reflection (small angle scatter), also at a larger distance (wide angle scatter). The former indicates the coarse-wave textures with only a slight deviation from the horizontal whilst the latter indicates the fine textures which largely create nondirected scattering effects. In this way it becomes possible to differentiate between long-wave disturbances and microstructures in the coating.

For fast comparative measurements devices have been developed in which the mobile measuring sensor has been replaced by four firmly installed photosensors. The first is positioned at an angle of reflection $\varepsilon_2 = \varepsilon_1$, the second one at $\varepsilon_2 = \varepsilon_1 + 0{,}3°$, the third at $\varepsilon_2 = \varepsilon_1 + 2°$ and the fourth at $\varepsilon_2 = \varepsilon_1 + 5°$ (R_β). By subjecting the individual reflection values to mathematical processing it becomes possible to make quantitative statements

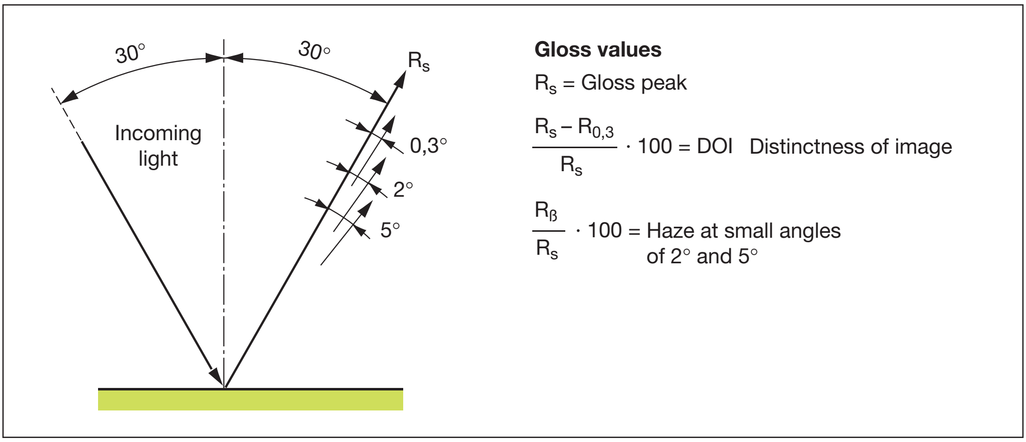


Fig. 3.2.22
Principle of a reflectometer for gloss measurements at different and fixed reflection angles

about specular gloss R_s, disturbances in the form of Distinctness of Image (DOI) and the fine textures that can be perceived as haze H_β or a gloss fog. Haze is a special feature of specular gloss. It is created by near-surface disturbances (e.g. pigment agglomerates) in dimensions of the wavelength of the light.

There is no doubt that owing to the extension of the reflectometer in the form of the goniophotometer it was possible to arrive at a much better explanation of the discrepancies between sensory impression and the test result. A reliable forecast of the subjective perception of complex textured coatings can still not be achieved with it. The physiological impression is more complex because as opposed to the measuring instrument the observer does not process the sensually perceived images with a sensor but with two eyes. Another reason is that on account of the constant movement of the eyes an integrated overall impression ultimately results from a large number of individual items of information. Moreover, by contrast with the measuring instrument, the eyes adapt unconsciously either to the surface or to the environment reproduced in a glossy surface depending on gloss level and the distance from the object [3.4.15].

Indirect methods

To explain the causes of gloss even better and possibly also obtain better forecasts of the observer's impression, efforts have been undertaken which completely dispense with examinations of light reflections and devote themselves to the direct measurement of surface textures. Based on different methods of measurement the aim is to use a geometric description of the surface structures to find out ways of detecting causes of the formation of textures beyond the relationships involved in subjective perception. If one knows the influences exerted by the formula, dispersion, application or the substrate, it becomes possible to not only describe phenomena but also take useful measures to optimize product quality.

The textures of the surfaces of coated objects are the result of the addition of complex reproductions of substrate irregularities as well as application-related and material-related textures. The application-related, usually coarse-waved structures overlie the reproductions of textured substrates. They are caused by the interaction between the levelling of primary structures and the formation of rises due to flows in the resulting

film (see chapter 3.1.1). In all cases the flow and film forming disturbances covered with substrate structures are accompanied by an additional ultra-fine texture due to film shrinkage. Its wavelength and amplitude depend just as much on the solid content and the quantity of the cleavage products escaping while curing as on the fineness of the pigments and extenders (see chapter 2.2.3).
Measuring such complex textures and giving them indicators which then allow correlation with the sensory impression of gloss is the task of these measuring techniques. A proven method for measuring surface textures consists in scanning the surfaces mechanically with a diamond tip which can be moved vertically (profilometer). With amplitudes of up to 50 µm a diamond tip with a curvature of approx. 5 µm scans the surface mechanically in order to transform the data electronically into a height profile afterwards. Surface structures are divided up into a long-wave component under the term 'waviness' and a medium-wave and short-wave component under the term 'roughness'.

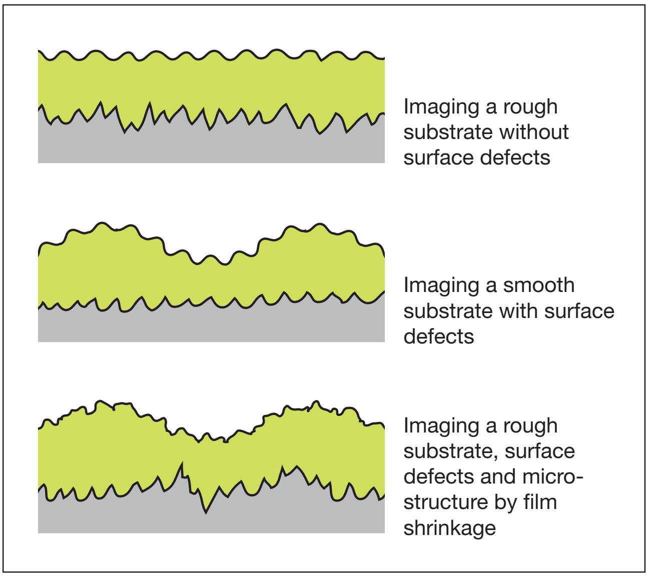


Fig. 3.2.23
Superimposed surface structures of films and substrates

The long-wave component above 0.24 mm is caused by flow defects and can be assessed by conducting DOI measurements (see above). The short-wave component stated between 0.02 mm and 0.06 mm reflects the microstructures by shrinkage-related reproduction of the substrate and pigments and can be detected integrally by haze measurement [3.4.16].

Better fine resolution is provided by measurement with a laser beam, which is focused on the relevant height of the microscopic roughness being measured. Such a method can be used successfully with pigmented systems but it fails in the case of metallic coatings because reflection at the surface is only partial. Penetration of the basecoat and additional reflection at the effect substances allows objective quantitative analysis of the metallic effect (flip-flop) if an appropriate measuring technique is used.

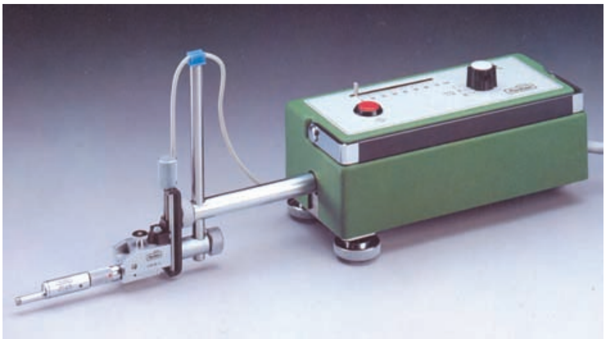


Fig. 3.2.24
Profilometer

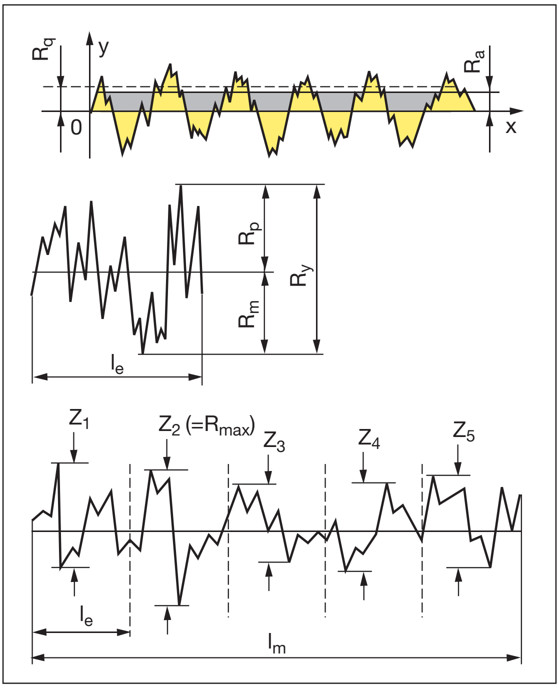


Fig. 3.2.25
Definition of measurable data of surface structures

Diagrams obtained by scanning to analyze the morphological features of surfaces have to be given various parameters on account of the cataloguing of roughness profile proposed according to DIN EN ISO 4287. They include the mean roughness value R_a as the arithmetic mean of all the profile values in the roughness profile and R_q as the geometric mean.

Supplementary information is supplied by the profile depths R_p and R_m. These are the distances of the highest and lowest profile points from the reference line. The sum of the two variables is R_y, the vertical distance between the highest profile value and the lowest one within test section l. For an even better description of surface profiles the test section l may be divided up into a larger number of individual sections. In the individual subsections the individual peak-to-valley height Z_i corresponding to the R_y value and the peak-to-valley height R_z averaged from the individual peak-to-valley heights of consecutive individual test sections can be stated and calculated.

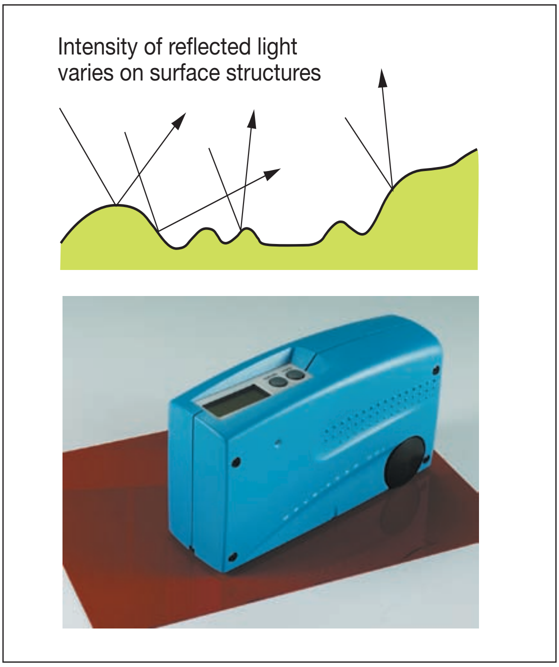


Fig. 3.2.26
Principle and device of the wavescan method

A different principle for measuring surface textures with laser beams is to determine the angle of reflection as it changes when the textured surface is being scanned. The device, which is referred to as a Wavescan, initially resembles a reflectometer. The fundamental difference is the area measured. Whilst the light source of the reflectometer scans the surface integrally with a measured area of several square centimetres producing an average, the Wavescan uses an ultra-fine laser beam (D < 1 µm) to scan a section of several centimetres and thus detects the intensity of the beam reflected depending on the distance covered.

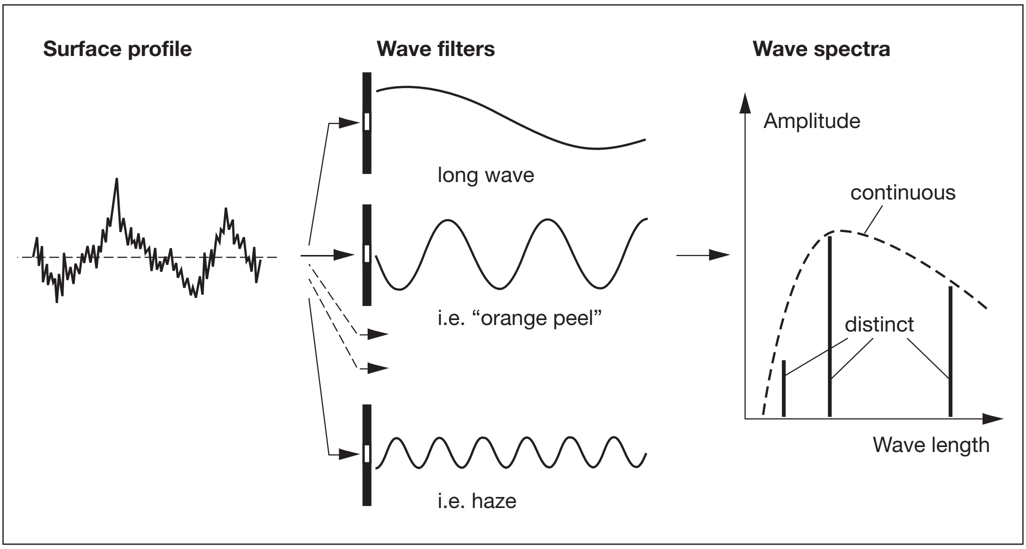


Fig. 3.2.27
Calculation of wave profiles according to the Fourier analysis

Peaks and valleys appear light-colored whilst slopes are shown correspondingly darker depending on their inclination or rise [3.4.17].

Mathematical processing makes it possible to classify the components of the individual structures according to wavelength ranges and amplitudes and state them separately. All curves can be converted to a multitude of sine and cosine curves with different wavelengths and amplitudes, no matter how complex they may be, whilst adding them together restores the original curve. This operation, which is known by the name of Fast Fourier transformation, produces discrete indicators for the short-wave, medium-wave and long-wave fractions of textured surfaces, depending on the desired resolution. The surface profiles obtained primarily by mechanical and optical profilographs or by the Wavescan are transferred by means of these conversions to waviness spectra, through waviness filters [3.4.18].

The Wavescan is restricted to two wavelength ranges relevant to the assessment of surfaces. These variables, which are known as short-wave and long-wave, provide information about fine and coarse textures measuring 0.3 – 1.2 mm and 1.2 – 12 mm.

In the meantime an additional measuring system has been developed for the Wavescan which also records matt surfaces, i.e. ones

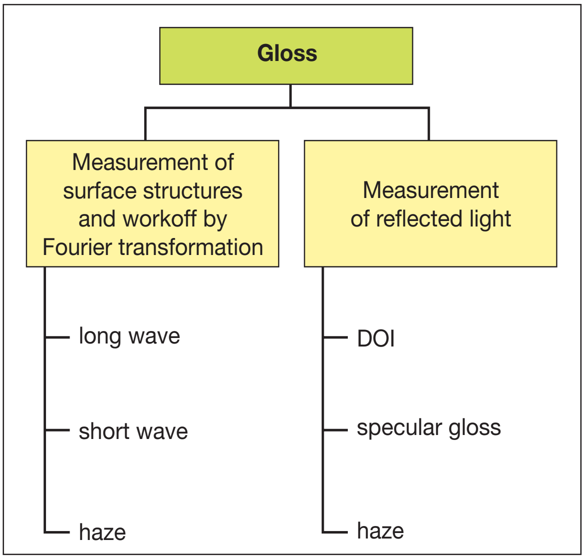


Fig. 3.2.28
Variables for describing surfaces

which are highly textured, with satisfactory accuracy. This makes it possible to objectively assess the surface texture of less glossy fillers and primers as well.

In the search for other simple instruments for measuring surface textures another device has become established which is referred to as the Autospect Quality Measurement System (AQMS). With a digital camera it creates a test image of the coating and evaluates distortions as well as attenuations of light/dark transitions mathematically. In this way it becomes possible, as with a goniophotometer, to obtain analogue values for the gloss peak, Distinctness of Image (DOI), appearance and haze [3.4.19].

The technical and physical variables for measuring gloss are not always adequate for covering the subjective sensation of gloss. Another approximation of subjective overall impression can be achieved by combining several methods, whereby each one describes partial aspects which can be applied to specific comparisons.

Unambiguous classification of the measurements as the observer's subjective perception continues to remain the subject of current research activities [3.4.20].

3.2.4.2 Color and Coloristic

As opposed to gloss, which is a sensory impression created by the reflection of light at the surface, color impression is the result of a physiological effect due to the interaction of light within the coating with its constituents. Chroma occurs whenever wavelength components are removed from the visible spectrum of available light from 380 – 760 nm. Within the spectrum of sunlight that section represents its maximum radiation intensity (see figure 3.2.30).

Depending on the ability of the color pigments to remove individual wavelength components from the white light by means of selective absorption or interference, reflection spectra occur which cause the observer to perceive different color impressions with regard to color, chroma and luminosity. The human eye is so sensitive that can differentiate several million individual colors. Unfortunately, despite the extremely high sensitivity to color perception, color impression is subjective, not only among different observers but also in one and the same person at different times or in a different environment.

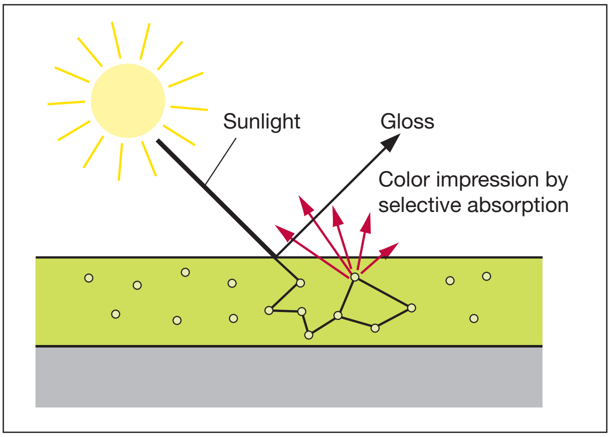


Fig. 3.2.29
Description of the basic difference between gloss and color

In order to assess colors objectively it is therefore necessary to search for numerical values and measuring methods for the description of colors.

Causes of chroma

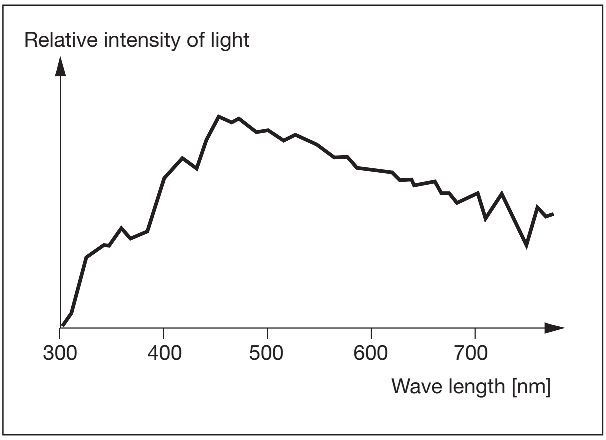


Fig. 3.2.30
Spectral distribution of sun light

The requirement for perception of colors is a light source with wavelength components in the range from 380 nm to 720 nm, an object with which the light can interact, a coating containing color pigments in this case, and an observer who perceives with his eyes the light changed and reflected by the coating [3.4.21]. As with a camera, the human eye reproduces the environment on the retina and, on account of sensors positioned there in the form of rods and cones, it is in a position to sense different levels of luminosity and color impressions. The rods are responsible for seeing light and dark and the cones are responsible for detecting color. There are three variants with different degrees of sensitivity to the individual wavelength components and they create the conditions required for sensing color. The levels of sensitivity of the three sensor groups are in the long-wave, medium-wave and short-wave ranges of the visible spectrum. If a coating is in a position to completely absorb white light over the entire visible wavelength range, the coating is seen as being black. Vice versa, the observer sees a coating to be white if there is no selective absorption.

If, however, individual ranges are absorbed from the spectrum of incident white light more than other ones, the body appears to be colored. If the body is perceived to be blue, the long-wave yellow and red radiation is absorbed more than the short-wave blue radiation. A green body reflects green, absorbing blue, yellow, orange and red entirely. A yellow body reflects yellow and red whilst it only absorbs green and blue to varying degrees. A red body reflects red, whereby blue, green and yellow are absorbed to varying degrees.

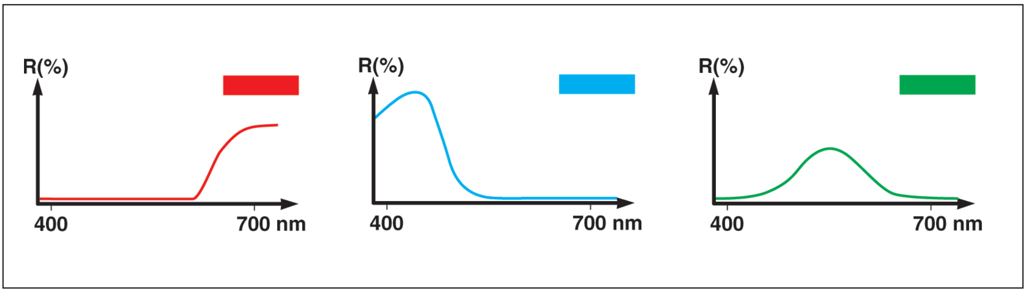


Fig. 3.2.31
Examples of reflection curves of red, blue and green coatings

If one assembles the various degrees of reflection R depending on the wavelength λ in order to create a curve, one obtains the reflection curve characteristic of a certain body color. Figure 3.2.31 shows the reflection curves for some colors.

When illuminated with identical light sources, two bodies with identical reflection curves have the same color physically speaking. The reflection curve of a coating thus permits an objectively accurate description of the physical property of color without any subjective influences, as are bound to occur if the human eye perceives a color impression.

The number of colors can be increased as required by mixing color pigments. The individual components extract from the light their specific components and combine from incident light the individual absorptions to create a new color impression, which can be seen on a new reflection curve. On account of the principle of such subtractive color mixing it becomes possible to adjust reflection curves, and hence colors, systematically by mixing pigments.

By contrast with subtractive color mixing, one refers to the superimposition of colored light sources as additive color mixing, a phenomenon which, for example, is used to create television pictures. Here addition of several light sources leads to addition of the individual light components, ultimately through to white light.

For the color design of coating materials pigments, which act by absorption and thus use the principle of color subtraction, consequently play a key role.

Colorimetry

The new spectral distribution which remains after interaction of incident light with the coating and ultimately creates the color impression is naturally dependent on the light source. Different light sources and different coatings lead to different color impressions.

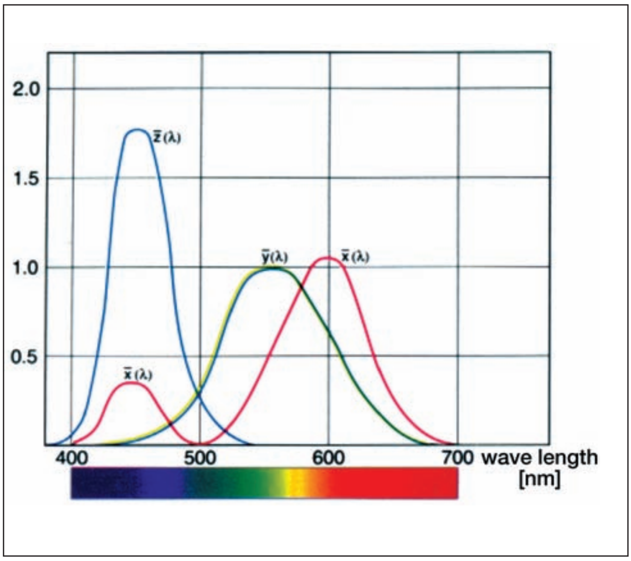


Fig. 3.2.32
Sensitivity diagram for eyes of a 2°-observer

As a result, when exposed to light from an incandescent bulb with a high proportion of radiation in the long-wave red range a coating with reflection in the red range appears to be redder than when exposed to the white light of the sun.

Consequently, if one wishes to make general statements about chroma, the “subjective” cones of the human eye and transmission of impulses to the brain as well as the processing to create a color impression have to be substituted by the photosensors with appropriate mathematical transformation of the signals. The requirement for this is that the sensitivity of the cones of the human eye is known in full detail. Since human beings perceive color subjectively, it was necessary to define the color sensation capacity of a fictional standard observer. For this purpose, the International Commission of Illumination (CIE) defined the spectral sensitivity functions of the human being with standard color eyesight back in 1931. The standard color matching functions shown in figure 3.2.32 reflect the averages of the so-called standard eyesight observer. They represent the viewing ability of over 90% of all human beings.

An objective and hence general statement about chroma can only be made if standardized light sources provide a constant supply of light. In order to meet the various conditions encountered in practice the CIE (see chapter 8) has, among other things, standardized the following types of light:

- Standard light A for viewing in incandescent bulb light with high components in the long-wave range
- Standard light D 65 for daylight under an overcast northern sky
- Standard light B for sunlight
- Standard light TL 84 for department stores

Bearing in mind the standardized light source, the reflective and absorptive behaviour of the coating and the defined sensitivities of the standard observer it is then possible to describe color impressions unambiguously. The most common types of light for coatings are standard lights A and D 65.

If standardized light of intensity S(λ) hits the coating, it is changed by absorption and scatter depending on the wavelength. The reflected light R(λ) arrives at a measuring probe where it is detected by sensors and converted to the standard trichromatic values X, Y and Z according to human eye sensitivities $\overline{x}(\lambda)$, $\overline{y}(\lambda)$ and $\overline{z}(\lambda)$.

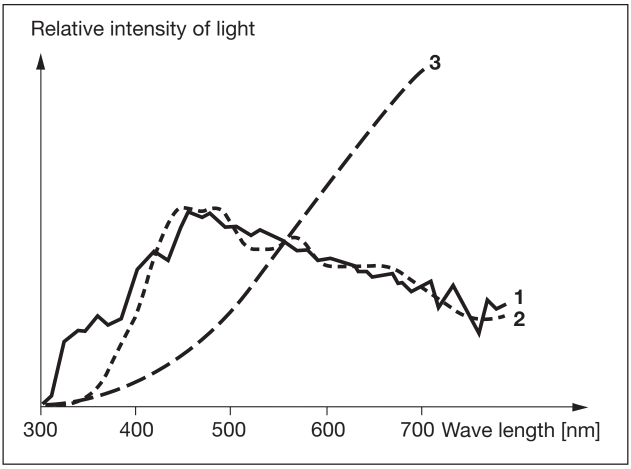


Fig. 3.2.33
Distribution of spectral density of standard light A (3) and D65 (2) in comparison to the sun light (1) according to CIE

$$X = \sum_{380}^{720} S(\lambda) \cdot R(\lambda) \cdot \overline{x}(\lambda)$$

$$Y = \sum_{380}^{720} S(\lambda) \cdot R(\lambda) \cdot \overline{y}(\lambda)$$

$$Z = \sum_{380}^{720} S(\lambda) \cdot R(\lambda) \cdot \overline{z}(\lambda)$$

The standard trichromatic values of body colors are therefore the product of spectral radiation distribution depending on the type of light S(λ), reflectance R(λ) and the standard spectral values of the observer $\overline{x}(\lambda)$, $\overline{y}(\lambda)$ and $\overline{z}(\lambda)$.

Since the spectral sensitivity of the eye depends on the angle of view and therefore on the size of the object, the CIE originally defined a field of measurement and field of view of 2°. The sensitivity curves of the so-called 2° standard observer were supplemented in 1964 by those of the 10° (wide-field) observer.

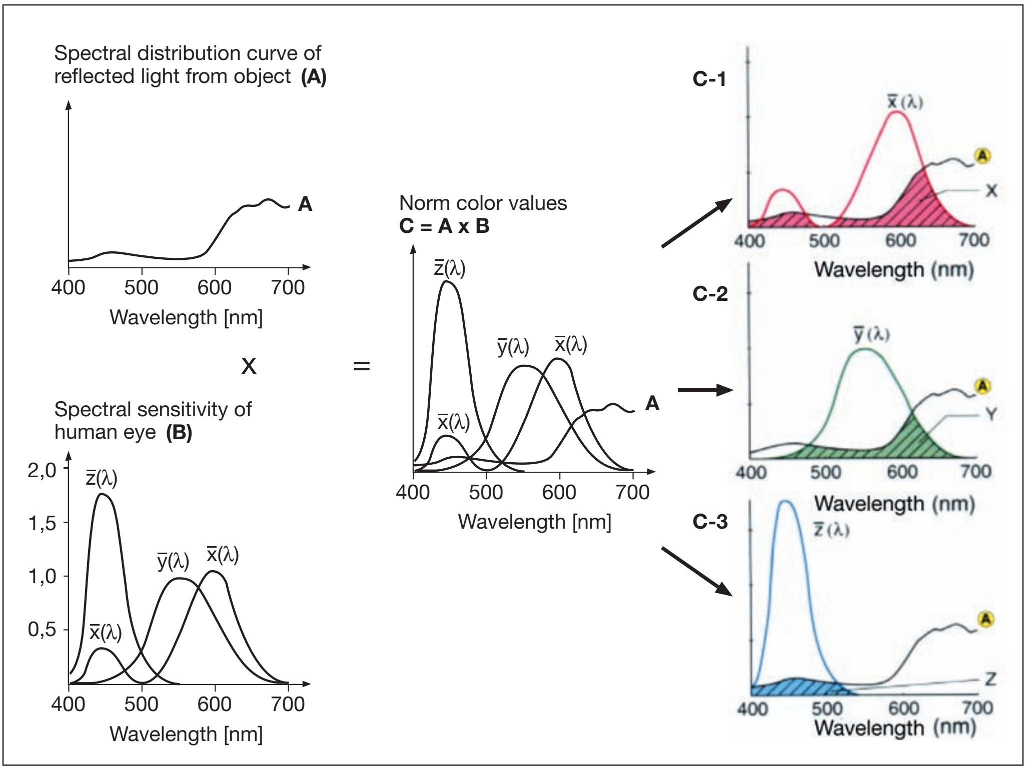


Fig. 3.2.34
Determination and calculation of X, Y and Z

The measured standard trichromatic values X, Y and Z are converted to the standard trichromatic value components x, y and z in order to determine further useful indicators and achieve further representations:

$$x = \frac{X}{X+Y+Z}$$

$$y = \frac{Y}{X+Y+Z}$$

$$z = \frac{Z}{X+Y+Z} = 1 - (x+y)$$

The value for z can be obtained from z = 1 – (x + y). The standard trichromatic value component x represents the relative red component, y the relative green component. The standard trichromatic value Y is stated as the third numerical value of color for characterising luminosity. All colors with the same standard value components x and y have the same type of color. The only difference is the luminosity Y.

This method permits calculation of a standard chromaticity diagram derived from determined X and Y values. Achromatic colors such as white, grey and black have a so-called equal energy spectrum with standard trichromatic value components x = y = 0.333.

All naturally occurring colors are within the spectral locus presented (see figure 3.2.35). The pure spectral colors from 380 nm to 720 nm correspond to the points on the spectral

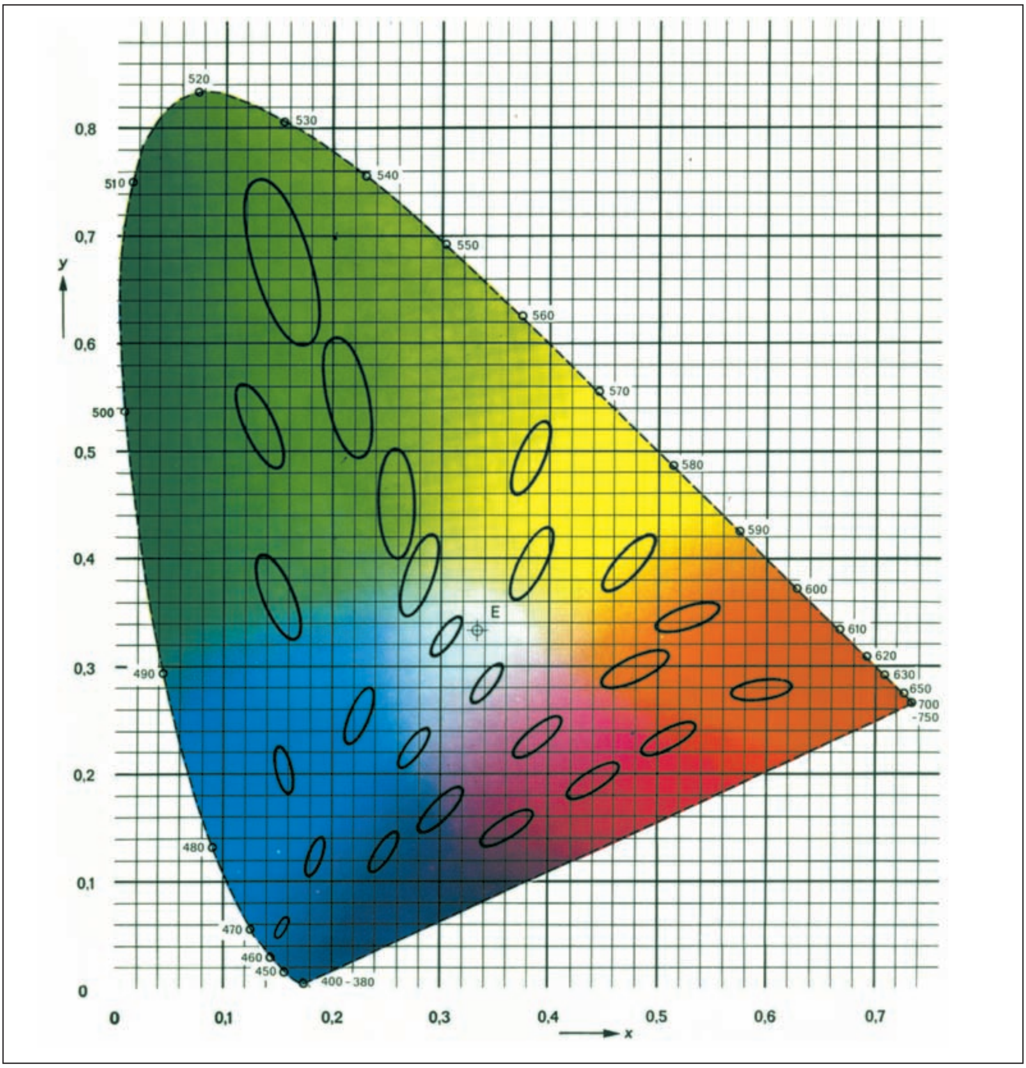


Fig. 3.2.35
Standard chomaticity diagram according to CIE of 1931

locus. The straight connecting line between points 380 nm and 720 nm are referred to as the purple straight. It cannot be represented by spectral colors. At the centre of the standard chromaticity diagram is the achromatic point. The more colorful color is, i.e. the more saturated it is, the further away it will be from the achromatic point and the closer it will be to the spectral locus. If the numerical color values x, y and Y have each been defined for two colors, it is possible to describe the difference in color quantitatively.

One drawback with the system is that the calculated color differences do not always coincide with the subjective sensation of color difference. Many experiments have therefore been performed in order to eliminate this drawback of the CIE system and develop a system with equal differences in accordance with perception. To strike a compromise, in 1976 the CIE recommended a transformation formula based on the standard trichromatic values X, Y and Z, which is nowadays commonly used and recognized internationally. In practice a reliable procedure has been to apply the transformed numerical color values L*, a* and b* as coordinates of a color space (CIELAB system).

$$L^* = 116 \cdot \left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - 16$$

$$a^* = 500 \cdot \left[\left(\frac{X}{X_n}\right)^{\frac{1}{3}} - \left(\frac{Y}{Y_n}\right)^{\frac{1}{3}}\right]$$

$$b^* = 200 \cdot \left[\left(\frac{Y}{Y_n}\right)^{\frac{1}{3}} - \left(\frac{Z}{Z_n}\right)^{\frac{1}{3}}\right]$$

In these transformation equations X_n, Y_n and Z_n are, specific to each type of light and each standard observer, the standard trichromatic values of the completely matt white standard of barium sulphate. Transformation of the standard trichromatic values X, Y and Z to the CIELAB numerical values L*a*b* is quite a substantial benefit in practice

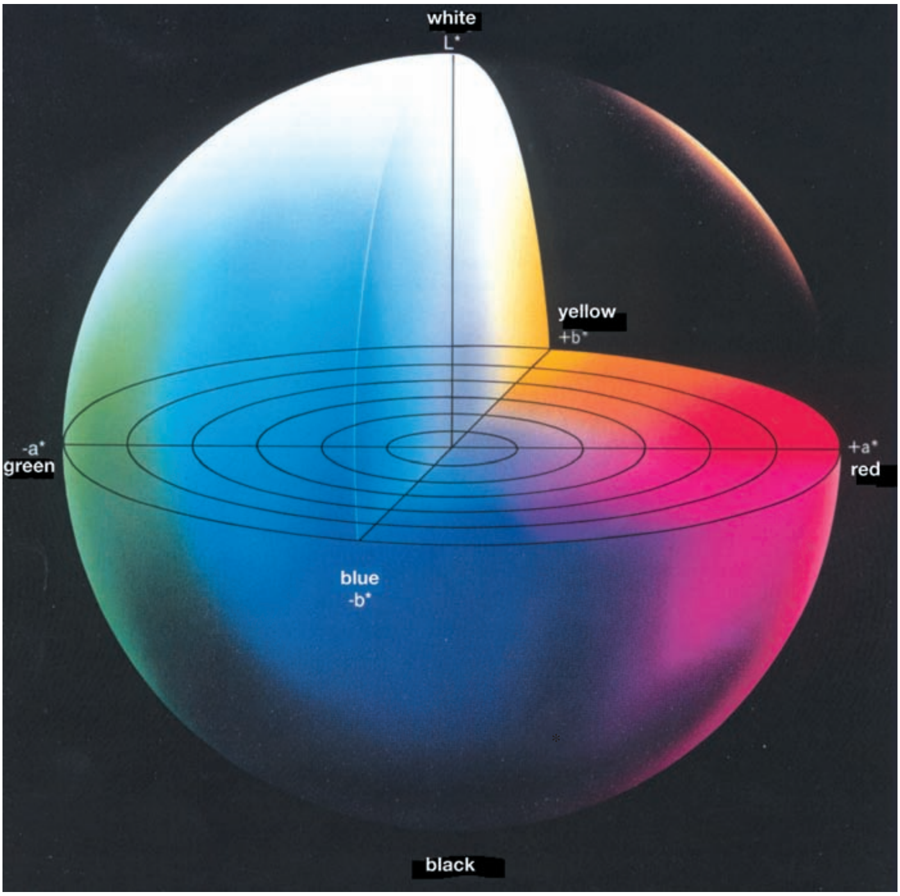


Fig. 3.2.36
Threedimensional graph of the L,a*,b*-color space*

because on the a*b* plane differences in hue and chroma can be represented more clearly.

The graphic representation of the color loci of measured colors L*, a* and b* is three-dimensional. As shown in Fig. 3.2.36 the positive and negative directions of the perpendicular a* and b* axes describe the red-green and yellow-blue color range. The individual quadrants contain orange and brown colors, yellow-green, blue-green and violet ones, whilst the L* axis is perpendicular to axes a* and b*. The latter is calculated from Y and is the measure of luminosity.

The achromatic colors of white, grey and black are on the L* axis. With regard to these, a* and b* = 0, which corresponds to the achromatic axis. The farther a color is from the achromatic axis, the more chromatic (saturated) it will be.

A different representation of colors in the color space described is made possible by the L* C* h* chromatic system.

By contrast with the L*a*b* system, definition of colors is conducted not with right-angled coordinates but with polar coordinates, stating an angle for the hue h and a radius vector from the centre point for chroma C*.

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad \text{and} \quad \tan h = \frac{b^*}{a^*}$$

C stands for chroma and h for hue. The luminosity L* is identical in both systems. Colors which are on a radius ray have, by definition, the same hue h. Colors with the same L* all have the same luminosity; they are in the same plane parallel to the a*b* plane.

Calculation of color difference

Although it is useful to be able to classify a number of colors in a color space systematically, when defining color specifications it is much more expedient to be able to calculate color differences, as can occur between a standard (original color) and a delivery (sample).

In practice nowadays the L*a*b* numerical color values for a standard type of light and a standard observer, e.g. D 65 and 10° standard observer, are determined and assessed in order to verify the color consistency between the original color and deliveries.

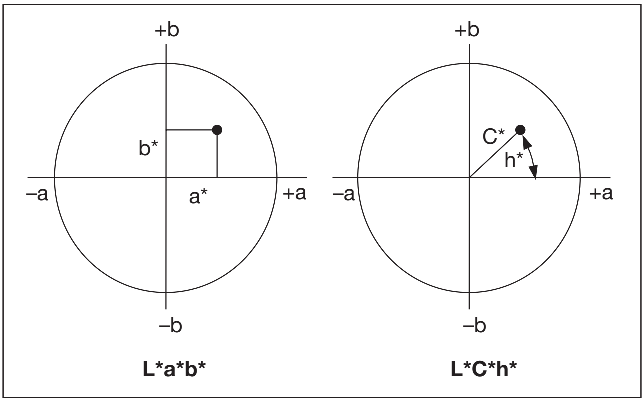


Fig. 3.2.37
*Comparison of L*a*b* and L*C*h* coordinates*

DIN 6174 quotes two different distance formulas for the L*a*b* system and the L*C*h* system and both lead to the same result.

$$\Delta E^*_{ab} = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{1/2} \quad \text{for} \quad L^*a^*b^*$$

$$\Delta E^*_{ab} = \left[(\Delta L^*)^2 + (\Delta C^*_{ab})^2 + (\Delta h^*_{ab})^2\right]^{1/2} \quad \text{for} \quad L^*C^*h^*$$

ΔL^* means the difference in luminosity, ΔC^* the difference in chroma and Δh^* the difference in hue, whilst Δa^* refers to the difference towards the red-green axis and Δb^* indicates the difference towards the yellow-blue axis.

One aim of describing color differences is to analyze by measuring instruments the product batches released by a colorist and define specifications with numerical values. Achromatic colors with a chroma C < 10 are better represented by the L*a*b* system whilst more chromatic colors are better represented by the L*C*h* system [3.4.22].

Metamerism

The special feature of human color perception leads to the fact that despite different reflection curves coatings exposed to certain illuminations can create the same color

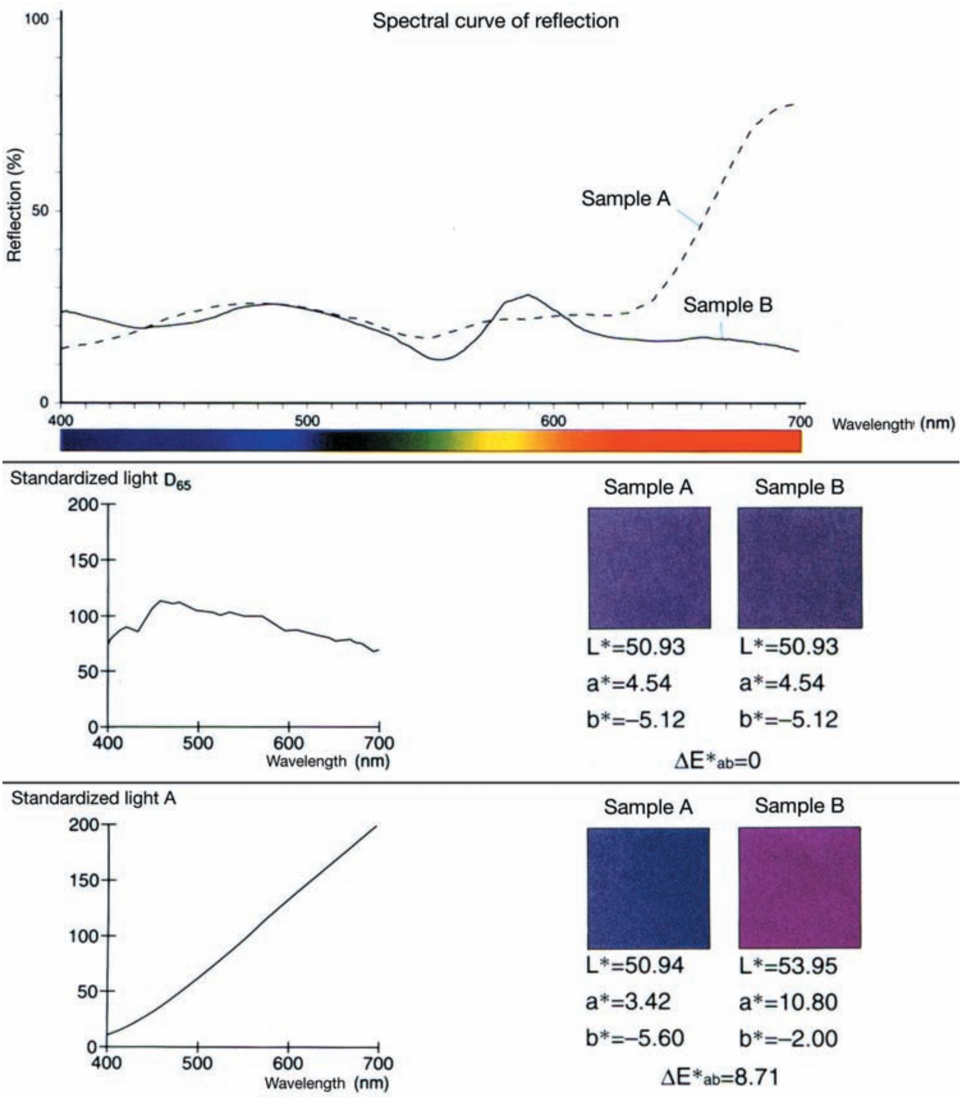


Fig. 3.2.38
Example of measurements for metameric coating films

impression. This phenomenon is termed metamerism. Two coats are metamers whenever they look the same in one type of illumination but look different in at least one other type of illumination. This phenomenon assumes that two samples have different reflection curves, integrals of which with one type of light add up to the same color values but not in the case of another type of light. The result is identical colors with the first type of light and different colors in the other case (see figure 3.2.38).

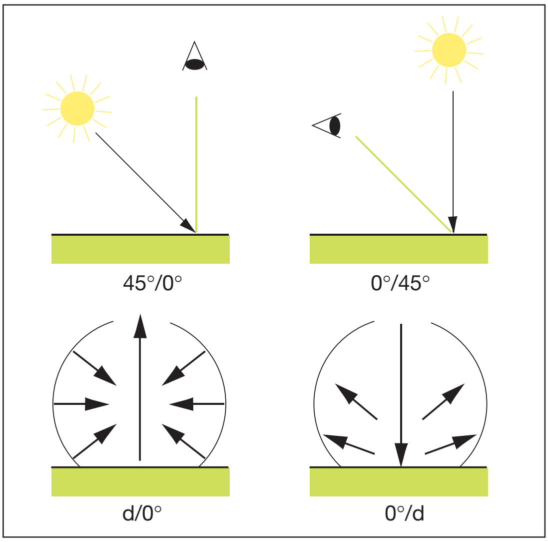


Fig. 3.2.39
By CIE recomended geometrical data for color measuring devices

Measuring instruments

As already indicated, the sensory impression complex resulting from light consists of the interactions of the light reflected in the surface (gloss) and of the component penetrating and then scattered back diffusely (color). This reflectance R(λ) is measured with the aid of a spectrophotometer. To monitor the gloss factor, the CIE recommends four different geometries of measuring probe for the various coatings:

1. Illumination at 45°/measurement at 0° (45/0)
2. Illumination at 0°/measurement at 45° (0/45)
3. Diffused illumination/measurement at 0° (d/0)
4. Illumination at 0°/measurement diffused (0/d)

An additional d/8° arrangement permits simultaneous measurement of gloss and color in a single measuring instrument close to sensory impression.

In order to determine the standard trichromatic values the spectrophotometers mentioned have proved reliable.

A spectrophotometer measures the entire spectrum of reflectance R(λ) and uses the individual measurements to calculate the standard color values X, Y and Z. By means of continuous calibration the reflectance R(λ) has to be

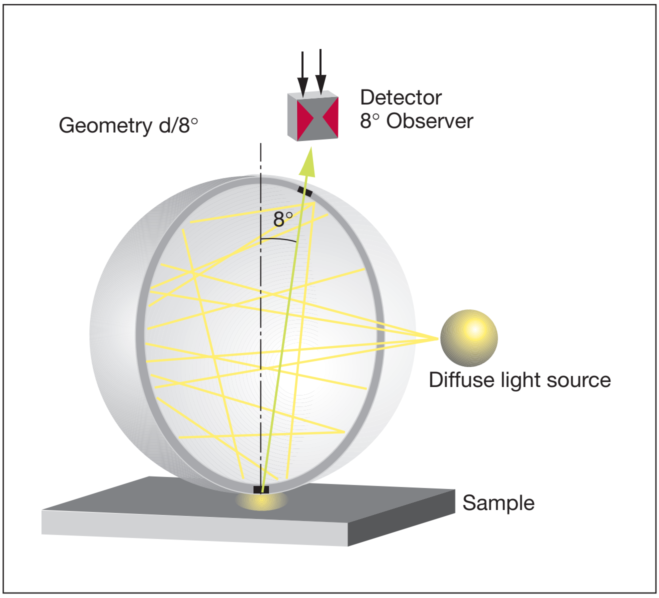


Fig. 3.2.40
Principle of a d/8°- measuring head

related to white and black standards irrespective of the source of illumination used in the spectrophotometer. For measuring purposes polychromatic light is split up into monochromatic light by a prismatic or grid monochromator or by narrow-band filters. A photoelectric cell determines the quantities of light reflected by the standard and the sample and evaluates their ratio. Since two beams, i.e. the sample beam and the reference beam, are measured, instruments are referred to as two-beam spectrophotometers. Understandably they have the advantage of compensating for device and power fluctuations and thus eliminating errors. The most accurate measuring instruments known nowadays are therefore based on the two-beam method.

Although spectrophotometers only have one type of light, they can perform conversions into various types of light because they register the entire spectrum so they cover metamerism.

Measuring the color of effect pigments

The color effects of traditional pigments described so far are largely independent of the angle of observation on account of diffused backscatter and can be measured by using color measuring instruments described above.

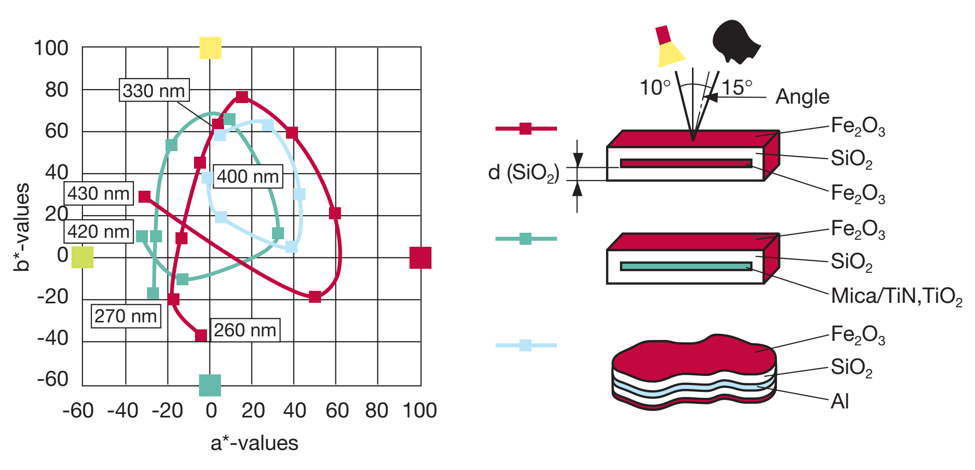


Fig. 3.2.41
Color shift by interference pigments depending on the view angle

The situation is different, however, in the case of metallic paints and paints with interference pigments (see chapter 2.1.3). The former show angle-dependent luminosity differences whilst the latter manifest angle-dependent chroma owing to beam differences between the rays of light reflected at the surfaces and on the undersides of the pigment particles. Both call for new methods of characterizing color coatings with test equipment. The crucial element here is multiangle measurement. The market offers devices with varying measurement geometry. Normally the angle of incoming light is constant at 45° with five deviations from 15° to 110° from the angle of reflection (effect angle). Other devices permit variable adjustment of the angle of illumination in order to then measure at fixed effect angles. Even a continuous increase in steps of 1° on the side of the illumination and effect angle is possible nowadays.

Figure 3.2.41 shows an example of the color shift depending on the angle of observation and illumination.

The curves show the color loci of interference pigments with a face view in relation to SiO_2 film thickness. The measurement was conducted with a Zeiss spectrometer, whereby both the angle of illumination and the angle of measurement were altered irrespectively of one another. The angle of illumination set was 10° and the angle of measurement set was 15° so measurement took place 5° outside the gloss angle. This 10°/15° setting is roughly equivalent to the color impression in face view.

The diagram shows three curves. They can be attributed to three chemical systems: the red curve reproduces the $Fe_2O_3/SiO_2/Fe_2O_3$ system, the silver one the $Al/SiO_2/Fe_2O_3$ system and finally the blue one the structure of $mica/TiO_2/SiO_2/Fe_2O_3$. The color loci on a curve result solely by varying the SiO_2 film thickness of a given layer system. As the SiO_2 film thickness increases the colors blue, green, gold and red of the first interference order and finally of the second and higher interference orders are passed through.

Fig. 3.2.42
X-Rite-multiangle spectrophotometer

Investigations into effect coatings comprising the latest generation of interference pigments using a wide variety of measuring instruments indicates that color measuring instruments available at the moment do not entirely reproduce visual impression yet. Although reasonable goniospectrometers, i.e. ones where the angles of measurement and observation can be varied continuously, do exist, they involved elaborate handling and are still much too large to be able to be used as portable devices for online quality assurance [3.4.23].

Color classification systems

The principle of color classification arose from the need for designers and other people interested in color to be able to select colors usefully. It consists of compiling color sample catalogues with as close an arrangement of the individual colors as possible which are perceived physiologically to have the same color differences in relation to one another. For the classification of pigments and dyes as well, color classification systems have a certain amount of importance despite the existence of sophisticated colorimetry (see chapter 2.1.3). With all the principles of color classification distinctions are made between the empirical, unsystematic color collections and the color classification systems based on colorimetric facts [3.4.24].

One of the most important empirical scales is the American *Munsell* catalogue. This largely fulfils the requirements for approximately equidistant individual samples. *Munsell* color collections are current and are available in the trade. In addition, mention should be made of a large number of proprietary color files indexes. The colors represented are selected according to subjective, arbitrary aspects taking marketing policy into account, with numbers and, to a certain extent, with color names. In Germany and neighbouring countries the nonproprietary color charts include the RAL register 8040 HR which is widespread. Among the matt RAL samples there is a selection of high-gloss RAL charts (RAL 841 GL), the pigmentation of which is state-of-the-art. The government institutions such as authorities, the police and the armed forces have defined some of these colors as being binding for themselves.

The German DIN system is regarded as the most important of the systematic scales. The DIN color charts are based on the criteria of color saturation and darkness step as a parameter in contrast with luminosity. The colors represented were selected so that the resulting color saturation and darkness step series are all divided up with same differences according to sensation. The system also published as of 1960 showing matt samples relates to the standard type of light C customary at that time and to the 2° standard observer. Conversion to the 10° observer with type of light D 65 and high-gloss samples with modern pigments is now also available.

The Uniform Color Scale System issue by the Optical Society of America (OSA-UCSS) must be mentioned as a systematic color collection. Based on the CIE it provides a collection of formulas and samples but its use is restricted to the USA.

3.2.5 Mechanical Properties

If a coating is to fulfil its requirements from the outset over a lengthy period, various properties have to be observed. For each requirement good bonding of the organic layer with the substrate is essential. That is the only way in which the destructive influence of water, atmospheric oxygen or chemicals on the substrate to be protected can be prevented. Furthermore, physical stresses in the form of expansion, compression or torsion must not reduce the bond with the substrate or affect the cohesive strength of the coating. The coating must also durably withstand stresses due to abrasion and impact.

The appropriate parameters for adhesion, elasticity during slow or rapid exposure to stress, and for physical hardness, which are summarized in the term of physical/ technological properties, have to reach a certain minimum level over such an extreme temperature range as occurs in the various climatic zones of the world.

Specification and testing of the quality level can be conducted in two different ways: on the one hand, coatings are exposed to the usual stresses encountered in practice with varying intensity. Physical elongation by bending coated metal sheets, firing metal balls or road chippings, artificially damaging or peeling off with defined tools are examples of methods of testing which have been used for decades. Their aim is to characterize the performance of coatings. Indicators determined in this way often involve complex links between various physical properties, the assessment of which can often only be performed by giving grades.

On the other hand, modern paint research is endeavouring to describe performance properties of coatings by physical parameters such as modulus of elasticity, adhesive force, relaxation times or retardation times. Such indicators that have to be measured accurately are beneficial when it comes to making test results objective and for online tests on production to be controlled. They help effectively whenever there is a distinct relationship between the indicators and the performance of the coating. The aim of completely objective analysis, however, has not been achieved yet. Test methods such as the *Erichsen* cupping test, *Buchholz* and pendulum hardness tests, the cross hatch test or the mandrel bending test, are all still standard tests nowadays which are used for quality assurance purposes.

3.2.5.1 Adhesion

Theory of adhesion

If a coating even only partially becomes delaminated from its substrate, it no longer fulfils its purpose. Firm attachment of the coating to the substrate which also remains intact under the effect of moisture, light, salts and gases, i.e. under the influences encountered in practice, is a necessary requirement for long-lasting protection. On metal substrates good attachment suppresses the formation of corrosive products even if the coating is physically damaged.

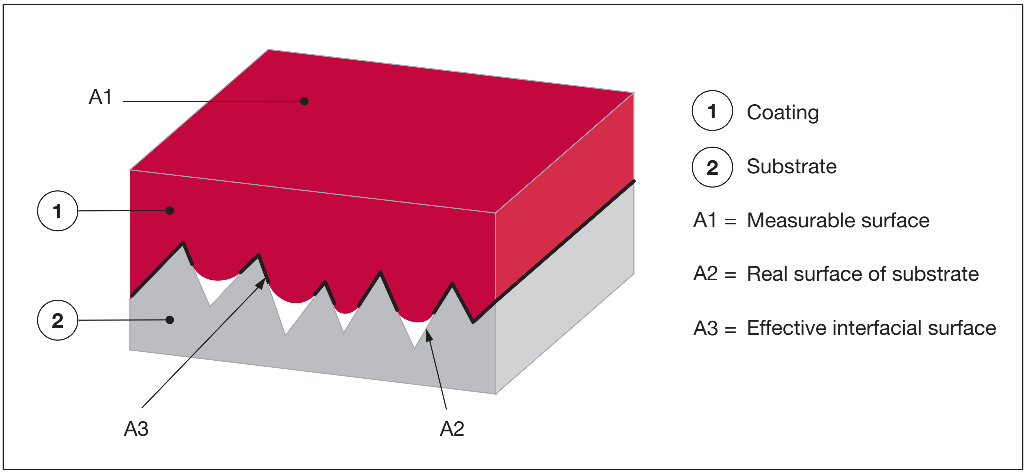


Fig. 3.2.43
Scheme of surface effects determing the measurement of adhesion

The adhesion of a coating is not solely determined by the paint. Similarly, the special characteristics of the coated object also have to be taken into account. To create optimum adhesion, the coating process has to be preceded by cleaning processes or layer-forming pretreatments. Good levels of adhesion are therefore not solely due to the paint but result from appropriate selection and adaptation of paint materials and the substrate (see chapter 4.1).

For the adhesion of coatings, in addition to the term adhesion, terms such as adhesive strength, adhesive ability and bond strength are also used. If one defines all the terms as synonyms for the area-related force which has to be applied to delaminate the coating, one encounters problems because the reference parameter, area, has to be defined more precisely. The measurable surface area of coating A1, the surface area of the partially highly textured substrate with all its A2 irregularities or only the effective common boundary surface area A3 are the reference parameters that can be considered. The two latter parameters may be identical if the wetting of the substrate is good, but they are always very different from the macroscopically measurable area A1.

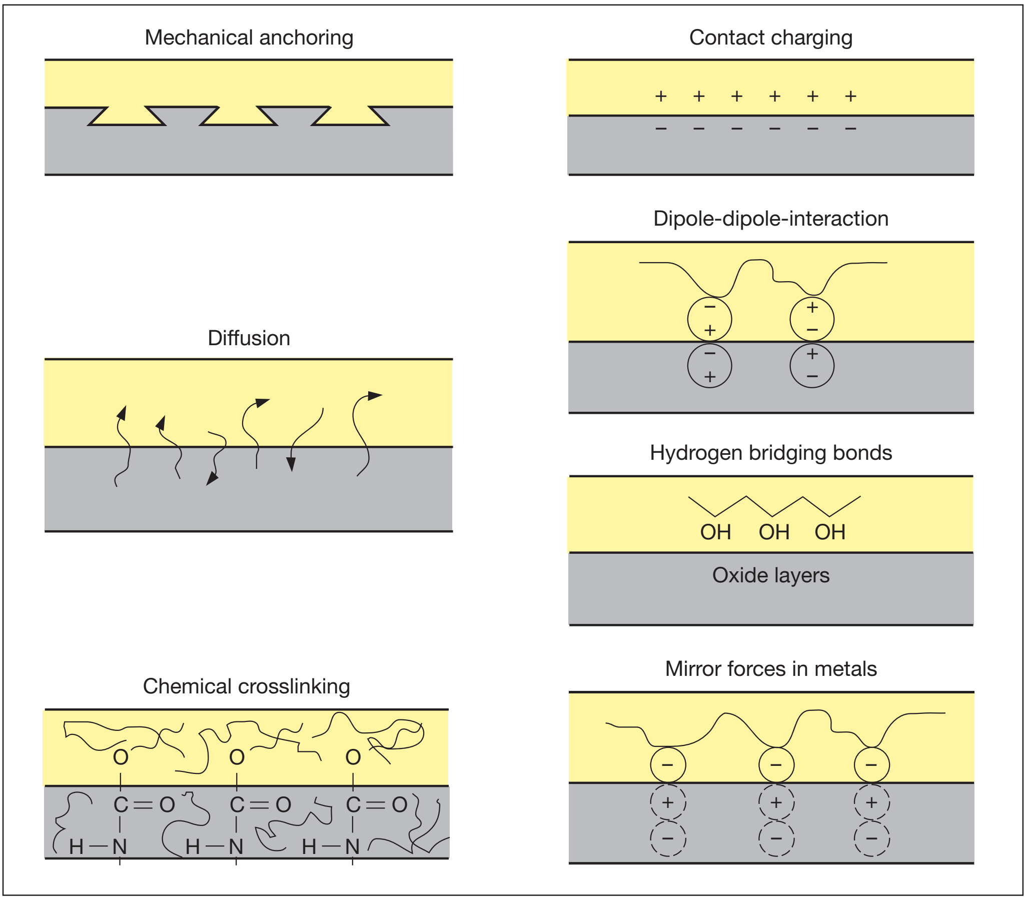


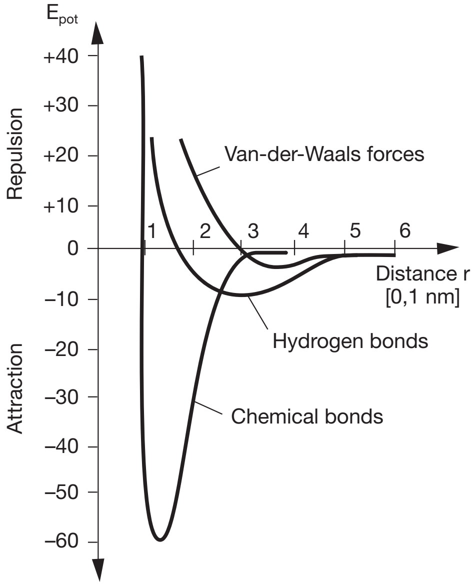
Fig. 3.2.44
Physical and chemical causes for the adhesion of coatings to the substrate

For scientific examination of adhesion mechanisms it is useful to consider only the real common area, taking surface texture into account. To characterize the performance properties, however, an indicator calculated in this way is of little interest. Here the macroscopically measurable substrate surface or coated surface represents the more pragmatic reference parameter.
If one endeavours to establish the causes of interactions, one encounters numerous theories in the literature, some of which are very different [3.4.25, 3.4.26]. The explanations range from mechanical attachment of the coating in the cavities and fissures in the substrate (press-stud theory or mechanical anchoring) and attachments of film forming agent molecules by diffusion or contact charges and the creation of mirror forces through to interactions of polar functional groups, hydrogen bridging bonds or chemical links between the coating and the substrate.
It is definite that all the mechanisms mentioned can affect bond strength and adhesion. It is also undisputed that the individual mechanisms of adhesion only make significant contributions if the prerequisites have been met. Mechanical attachment to rough metals and wood are without doubt beneficial for bond strength. Links by means of penetration when coating plastics, primers and fillers are as well. When coating glass and polished

metals it would be wrong to chiefly hold the press stud and diffusion theories responsible for the bond. The interactions summarized by the term *van-der-Waals* forces have to be classified differently. Regardless of the type and morphological features of the substrate these are generally the main causes of adhesion.

Van-der-Waals forces are orientation forces (dipole-dipole), induction forces (dipole/induced dipole) and dispersion forces. Assuming a suitable chemical structure and an appropriate substrate there are also effective hydrogen bridging bonds [3.4.27].

With fractions of nanometres the ranges of *van-der-Waals* forces and the hydrogen bridging bonds are extremely short. For optimum adhesion it is therefore absolutely essential to ensure good wetting by the coating material applied, thus creating ideal conditions for causing the film forming agent molecules to approach the substrate. The conditions for good wetting are always fulfilled whenever the surface tension of the substrate is higher than that of the still liquid coating material (see chapter 2.3.2 and 3.1.1). Such a requirement can easily be fulfilled when coating metals on account of the high surface tension. With various unpolar plastics such as polyethylene or polypropylene with values less than 30 mN/m it is not possible to achieve good adhesive coatings on account of the inferior wettability without polarizing surface treatments.



Type of van-der-Waals forces	Average energy	Range
Orientation forces Dipole-dipole (Keesom forces)	25 kJ / mol	$E = \frac{2\,\mu^4}{3kTr^6}$
Induction forces Dipole-induced dipole (Debye forces)	15 – 20 kJ / mol	$E = \frac{2\alpha \cdot \mu^2}{r^6}$
Dispersion forces (London forces)	5 – 10 kJ / mol	$E = \frac{3h\nu_0 \cdot \alpha}{4r^6}$
Hydrogen bridging bonds	40 – 50 kJ / mol	$E = e^{-kr}$

Fig. 3.2.45
Curves and numbers of the potential energies of van-der-Waals forces as well as hydrogen bonds as causes for adhesion

Fulfilment of all the physical boundary surface requirements is not sufficient to achieve the best possible bond. In addition, viscosity has to be sufficiently low in order to give the functional groups capable of bonding an opportunity for orientation towards the substrate. Furthermore, the rise in surface tension due to evaporation of the solvents,

Substrate	σ [mN/m]
Stainless steel	1000
Phosphated steel	34
Mercury	480
Glass	74
Polypropylene	30–35
Polyamide	40–43
PVC	36
Polystyrene	32
Polycarbonate	37
Polyester	40–45

Fig. 3.2.46
Surface tensions of selected subtrates

which normally have lower surface tensions, has to be set so that the wetting behaviour is not negatively influenced by film formation. If it should happen that at still relatively low viscosity the surface tension of the paint exceeds that of the substrate, coating defects in the form of wetting disturbances can be expected because of the dewetting. It is therefore useful to adjust the values of surface tension in paint in such a way that in the cured film there are similar, or rather the same, surface tensions in relation to the substrate. Material adjustments which meet these requirements can only be formulated if surface tensions of solids are known and can be measured.

Whilst for determining the surface tension of liquids there are numerous methods available (see chapter 2.3.2), direct measurement of the surface tension of solids is not possible. It can only be performed indirectly by measuring the contact angle of droplets of liquid which have been applied to the solid surface being examined. If the surface tension of the liquid σ_L is higher than that of the substrate σ_S, a different contact angle α is created in relation to it.

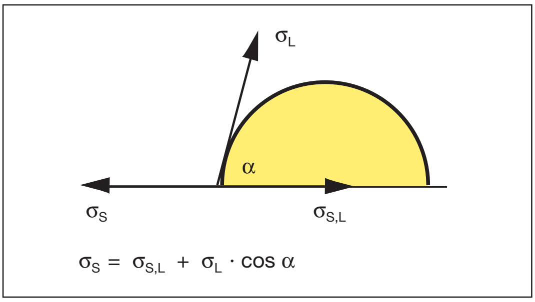


Fig. 3.2.47
Definition of the contact angle according to DIN EN 828

If the contact angle α approaches 0, the boundary surface tension $\sigma_{S,L} = 0$ and hence $\sigma_L = \sigma_S$.

Since small contact angles α cannot be determined with sufficient accuracy, one uses the *Zisman* method whereby several liquids a, b and c with different but also higher surface tensions than the substrate are measured with regard to the resultant contact angle and each calculated cosine is plotted in relation to the surface tension of the liquids. Then the curve has to be extrapolated to the value $\cos\alpha = 1$ [3.4.28]. To perform the measurement optical benches are available which allow precise recording of the wetting angles.

From experience in dealing with the determined critical surface tensions σ_c it is known that in many cases deviations from the surface tension of the substrate can occur. However, conversion of the critical surface tension σ_c to the surface tension of the substrate σ_s becomes possible by means of adjustment using *Good*'s interaction parameter Φ.

$$\sigma_c = \Phi^2 \sigma_s$$

The interaction parameter says something about the spatial fulfilment of the interacting groups and hence about the quantity of the maximum number of bonding sites. Its

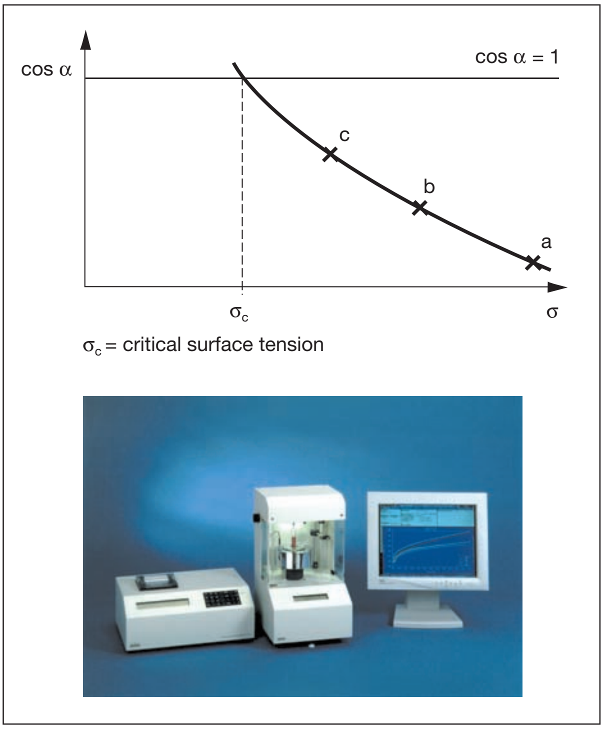


Fig. 3.2.48
Zisman diagram to determine the critical surface tension and picture of an instrument for measuring contact angles

calculation is difficult for interactions of polymers. It is therefore usually determined by experiment. The *Good* factor assumes the value 1 if all the polar groups of coating material and substrate can interact. However, it can also drop to values of around 0.3 [3.4.29].

With regard to adhesion, experience teaches that even if the surface tensions of coating and substrate are optimally adapted the expected optimal values are not always found. Better conformities between experiment and theory are obtained if the surface tension does not enter the calculation as a total value of all the *Van-der-Waals* forces and hydrogen bridging bond forces. After splitting the surface tension into polar and dispersed components σ^d and σ^p

$$\sigma = \sigma^d + \sigma^p$$

better forecasts can be made regarding the maximum adhesion possible if the polar components of substrate and coating assume the same value. The best adhesion possible is therefore achieved if

$$\frac{\sigma_L^p}{\sigma_S^p} \rightarrow 1$$

One must bear in mind that best possible adhesion of the system says nothing about the absolute level of the adhesive forces. These are performed owing to the polarity of the interacting surfaces and are merely optimized by adaptation of the surface tensions.

The importance of the ratio between polar components of surface tensions in the substrate and the coating for adhesion has been verified using various plastics [3.4.30]. Taking acrylic resins and alkyd resins as examples there are systematic interrelationships as shown in figure 3.2.49.

To determine the polar and dispersed components several teams have produced practicable approaches. According to *Owens* the boundary surface tension is represented as the geometric mean of the individual constituents [3.4.31]. If $\Phi = 1$, it follows that:

$$\sigma_{S,L} = \sigma_S + \sigma_L - 2 \cdot \sqrt{\sigma_S^d \cdot \sigma_L^d} - 2 \cdot \sqrt{\sigma_S^p \cdot \sigma_L^p}$$

After taking *Young*'s equation into consideration (see chapter 2.3.3) and conducting wetting tests with liquids of known dispersed components σ^d_L for measuring contact

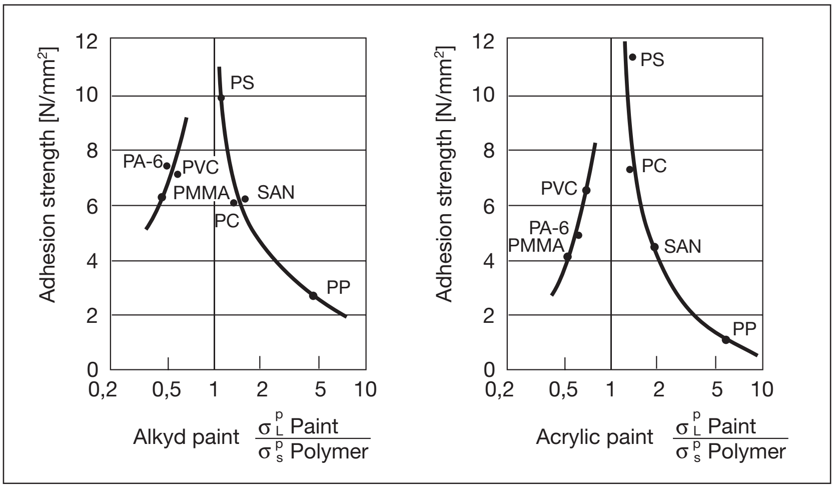


Fig. 3.2.49
Adhesion in N/mm² as a function of the share of polar adhesion forces of alkyd and acrylic resins on different substrates

angles, after further mathematical processing it becomes possible to calculate dispersed and polar components of the surface tension of the substrate $\sigma^d{}_S$ and $\sigma^p{}_S$.

$$\frac{\sigma_L \cdot (1+\cos\alpha)}{2 \cdot \sqrt{\sigma_L^d}} = \sqrt{\sigma_S^p} \cdot \sqrt{\frac{(\sigma_L - \sigma_L^d)}{\sigma_L^d}} + \sqrt{\sigma_S^d}$$

$$(\quad y \quad = a \cdot \quad x \quad + b)$$

Despite all optimizations, it is frequently only possible to obtain satisfactory conformities between theory and practice using model substances. The reasons for this includes undefined changes in the boundary surfaces due to water vapour adsorption and cross contractions during the curing of coating materials on textured surfaces.

Since the range of bonding forces is extremely small, the substrate has to be freed, with the utmost care, of all impurities that could impair wetting. Pretreatments which serve to remove dirt, dust and residues of oil are therefore standard procedures which have to precede the coating process. Layer-forming surface pretreatments such as phosphating and chromating have proved reliable especially for the coating of metals (see chapter 4.1.2). The systematic formation of insoluble, crystalline, tenacious salts or oxides supports the bond strength by additional attachment, one of the reasons being the significant enlargement of the surface area.

The influence of solvents on swellable substrates, as in the case of plastics and multilayer coatings, can have positive or negative effects on adhesion depending on the degree of crosslinking (see chapter 4.1.3). For instance, the bond strength of overbaked coatings is impaired owing to the reduced ability to start swelling.

Investigations into the dependence of adhesion on temperature if the real common boundary surface is known and if interfering factors at the surface are eliminated permit calculation of the activation energies required for adhesion. In this way it is then possible to find details of the nature of the bonding forces. Nevertheless, the theories on the adhesive strength of polymer coatings has still not been sufficiently completed to allow reliable forecasts of bond strength or adhesion in all cases [3.4.32].

Methods of measuring the adhesion of coatings

For practical assessment of bond strength and adhesion empirical methods have long since been customary (performance tests). Although they are not based on any physically unambiguous principles, they are relatively easy to perform and provide largely reproducible test results.

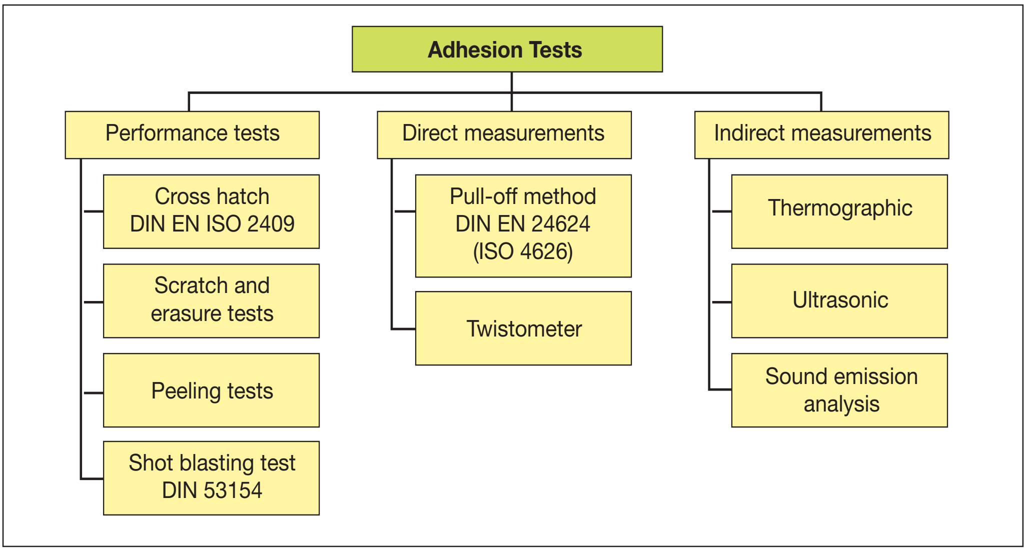


Fig. 3.2.50
List of measurement methods for adhesion of coatings

Since they are easy to apply the cross hatch test as per DIN EN ISO 2409 as well as scratch and erasure tests are used for quick results. Although the test result does not provide direct measurements, it can be assessed with a graded degree of damage in relation to reference images.

To obtain numerical values for the bond strength of coating systems one can determine the minimum tensile stress or torsional stress that has to be applied in order to separate the coating from the substrate. Ultrasonic and thermal flux measurements are further indirect methods of characterizing the adhesion of coating systems.

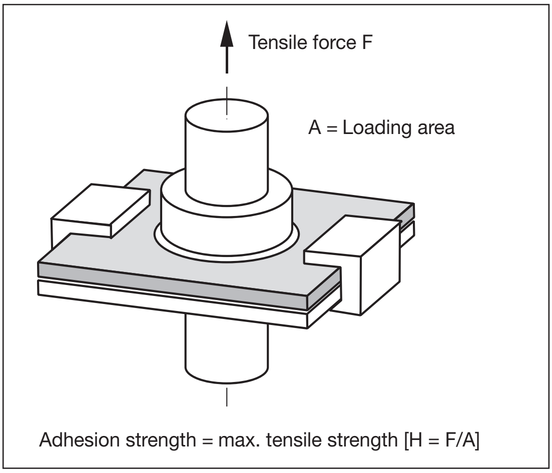


Fig. 3.2.51
Adhesion measurement by the pull-off method according to DIN EN 24624

Pull-off method as per DIN EN 24624 (= ISO 4624)

For testing purposes the coating material is applied to a flat test panel of the substrate being examined. When film formation has been completed a test punch is stuck on the sample coating and pulled off vertically after curing. The tensile force must be distributed perpendicularly, increasing to such an extent over the entire test area that the break occurs within 90 s after beginning the absorption of stress. If in cases where substrates are thin there is a risk of deformation which could falsify the result. The specimen is fixed between two test punches using a centring device. Care must be taken to ensure that the two test punches are positioned coaxially above one another.

Special attention must also be paid to the selection of adhesives. It is important that the bond of the adhesives is better than that of the coating being tested. Moreover, adhesives must not cause any swelling in the coating being tested.

The measurement is then conducted with the aid of a tensile testing machine.

The parameter determined is the adhesion value H resulting from the force F which has to be applied until separation, in relation to the measured area A. Depending on the paint system at least three measurements are performed. Analysis of the fracture pattern, i.e. position and size of the delaminated surface, leads to further information about the adhesion of the coating, especially multilayer coatings.

Torsion method with the Epprecht twistometer

The *Epprecht* twistometer is used to determine the bond strength of coatings by torsion. For this purpose the punch bonded to the panel as in the previous test set-up is subjected to a torsional load. In this set-up the bonded area is a ring with an outside diameter D and inside diameter d. The torque M which is effective at the moment of fracture is converted to the area-related separating force H. By analyzing the fracture patterns it is relatively easy to locate the point of lowest cohesion within the coating system.

If the coating becomes entirely delaminated from the substrate in the form of an adhesion fracture, the measurements obtained are representative of the bond.

$$H = M \cdot \frac{16}{\pi} \cdot \frac{D}{D^4 - d^4}$$

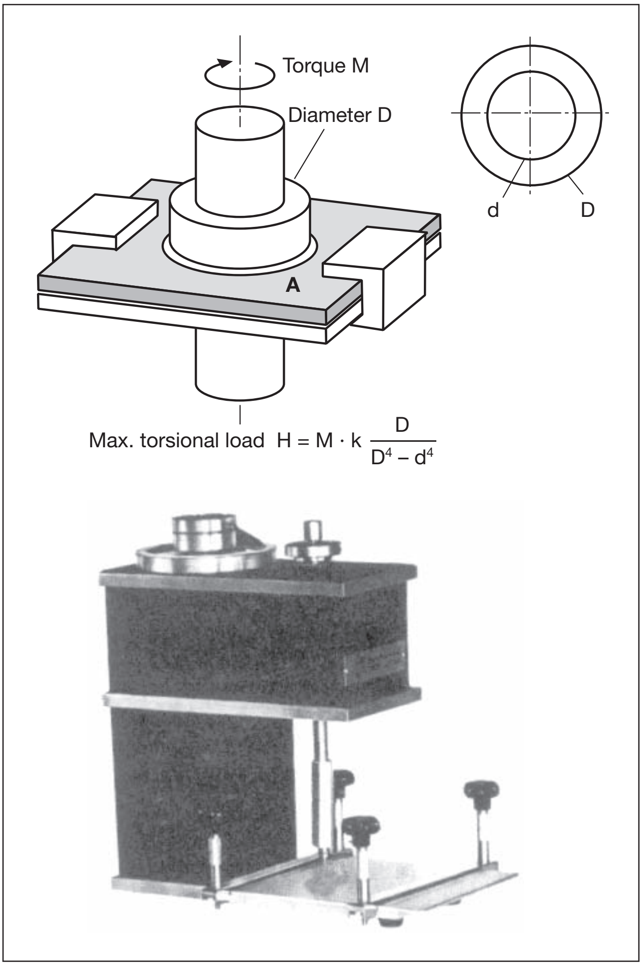


Fig. 3.2.52
Measuring device and picture of an Epprecht twistometer

In the case of a cohesion fracture within the coating it is not possible to make any direct statement about adhesion. The measured value merely indicates that the actual adhesion to the substrate or between two layers of paint is higher than that measured.

Cross hatch method as per DIN EN ISO 2409

The cross hatch test is a simple empirical test for assessing the bond between single-layer and multilayer coatings and the substrate and between the individual layers [3.4.33]. Comparative interpretations of the test results are only possible if the viscoelastic properties of the coatings are the same. Films with higher elasticity are easier to deform, as a result of which the delaminating forces are reduced during mechanical loading.

On anisotropic substrates such as wood the test results measured at various points may be scattered to such an extent that no absolutely reliable statements can be made about adhesion. For such substrates the cross hatch test is unsuitable.

The test instrument specified by the standard is the cutting knife with a certain shape and certain dimensions. The selection of cutting device depends on film thickness and the type of coating. Consequently, instruments with more than one cutting edge require considerable force on very hard films so it is often not possible to make all the cuts down to the substrate. In such cases an instrument with a single cutting edge is to be recommended.

For measurement with the multicutter instrument a continuous longitudinal band of cuts comprising six parallel notches is made in the sample coating down to the substrate. Then another band of cuts is made at right angles to them. This results in a grid of 25 squares, the so-called cross-cuts.

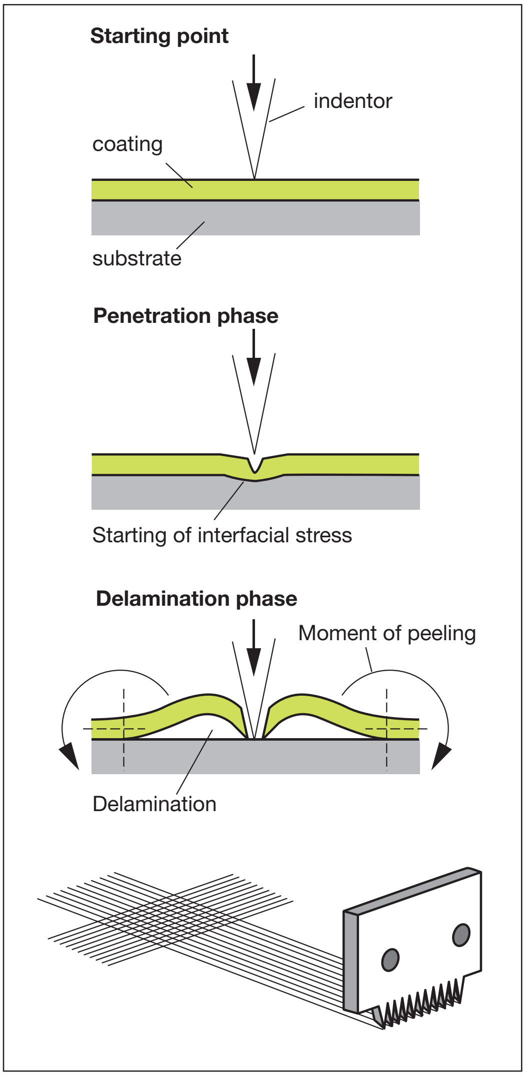


Fig. 3.2.53
Scheme of delamination by cross hatch testing according to DIN EN ISO 2409 and multicutter device

With the single-cutter instrument a folding ruler is preferably used which guarantees the required cut spacing and parallel cutting.

For evaluation purposes an adhesive tape with a defined adhesive force is pressed on to the loaded point and then pulled off the surface keeping pull-off velocity as consistent

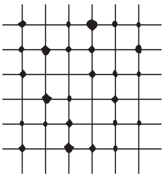
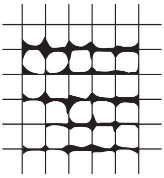
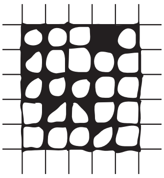
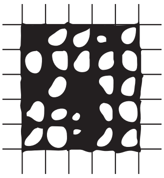
Cross Hatch Index	Description	Reference Picture
Gt. 0	The cutted edges are completely smooth, no partly delamination	—
Gt. 1	At the point of cross cuttings no fragments are seen; delaminated area ca. 5%	
Gt. 2	The coating is delaminated along the cutting lines or/and the cross sections; delaminated area at about 15% of the cuttings	
Gt. 3	The coating is delaminated partially or all along the cutting lines partially in full stripes; delaminated area is about 35%	
Gt. 4	The coating is delaminated along the lines in full stripes and/or totally in segments; delaminated area is about 65%	

Fig. 3.2.54
Cross hatch numbers according to DIN EN ISO 2409 for evaluations

as possible. By comparison with the standard patterns indicators Gt0 to Gt5 are assigned. To increase reproducibility of measurements and make the results more objective the cuts are made in the coating by automatic devices. These are able to adapt cutting depth to film thickness. Evaluation of the test result can be performed by pattern analysis [3.4.34].

A practical variant of the cross hatch test is the jet stream test dominantly used for adhesion tests on plastic substrates. In this test a cross hatch is applied followed by a defined jet stream treatment.

Peel-off method

Apart from the pull-off and torsional methods devices are sporadically used which make it possible to measure the work required to peel off the coating and then convert it into adhesion values.

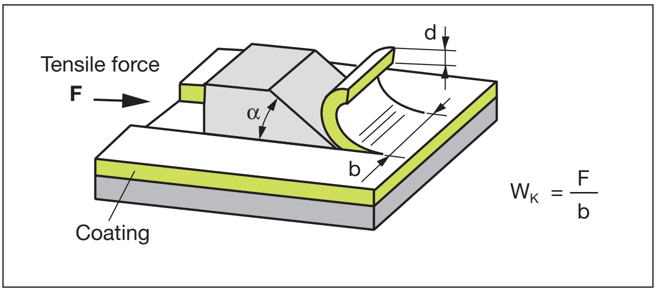


Fig. 3.2.55
Measuring principle of the wedge feed method

With the **wedge feed method (hesiometer)** a wedge is positioned in the boundary surface between the coating and the substrate and moved parallel to the substrate so that the coating becomes delaminated. The work is the product of pulling power F and distance covered s and in relation to the peeled area A it is then a direct measure of the bond strength of the two layers. From A = b s one obtains the area-related peeling work W_K as a measure of adhesion:

$$W_K = \frac{F \cdot s}{A} = \frac{F}{b}$$

With the wedge feed method it is not only possible to make statements about adhesion by assessment of the fracture pattern but also provide information about the hardness and elasticity of the coating.

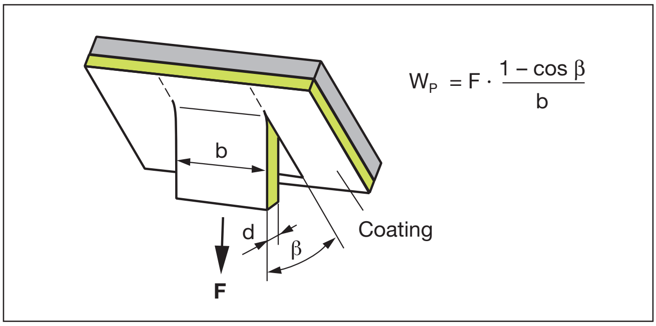


Fig. 3.2.56
Measuring principle of the peeling test and calculation of adhesion strength

The **peeling test** has a similar measuring effect but uses a different measuring technique. In this case a strip of coating to be tested with a specified width b is peeled off the substrate at an angle β. To ensure that the film does not tear in the event of insufficient cohesive strength, a reinforcing wire is placed in the centre of the coating of paint when making the test pieces. A tensile force F normally acts as weight at the end of the wire. The weight is determined at which delamination commences.
In the final calculation of adhesion the measuring angle β at which the delaminating force acts has to be taken into account.
Adhesion strength tests with the **scratch and erasure methods**, where the coating is stressed by rubbing or scratching with a knife, are of little interest although they are still used by experienced experts. Even though it is difficult to give absolutely reliable grades, the fracture at break provides experts with information about the adhesion, elasticity and hardness of the coating.
Another variant is *Peters* shaving test. Here a razor blade is guided at an angle to cut shavings of the coat. Depending on the length of the shaving removed the coating is assigned indicators which allow a statement about adhesion.
Another less used method of determining adhesion consists in exerting defined impact stress by means of the **shot peeling test** as per DIN 53154. Since delamination due to

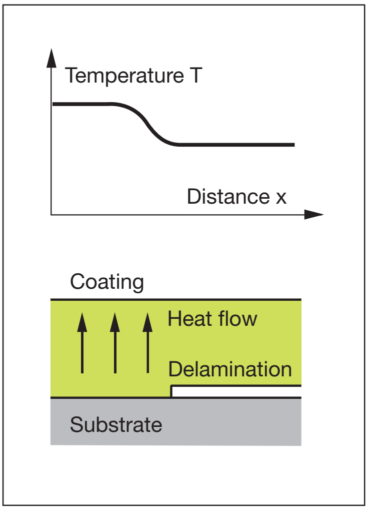


Fig. 3.2.57
Heat flow as a basis for adhesion strength

steel shot hitting the surface is influenced by elasticity beyond bond strength, this is rather a combined test of performance.

Nondestructive measurement methods are of great importance i.e. for online quality control and improved laboratory efficiency [3.4.35] So-called **thermographic methods** for determining adhesion forces belong to this class of tests. Heat applied to the substrate by convection or IR rays passes through the boundary surface with the coating depending on the bond and is recorded by an infrared camera in the form of a temperature profile T(x) on the surface of the coating. The thermal flux is detrimentally affected at a point where there is insufficient adhesion so that areas with inferior bond strength are indicated by a low temperature in the surface.

The drawback with this test method is the lack of differentiation. However, thermal flux measurements are excellent if one is conducting a search for weak points in the bond of layers without causing damage [3.4.36].

Bond weaknesses in multilayer systems can also be found with acoustic methods. The **ultrasonic pulse echo method** with frequencies above 1 MHz records the sound, Z and R, reflected at the individual layers and at the surface.

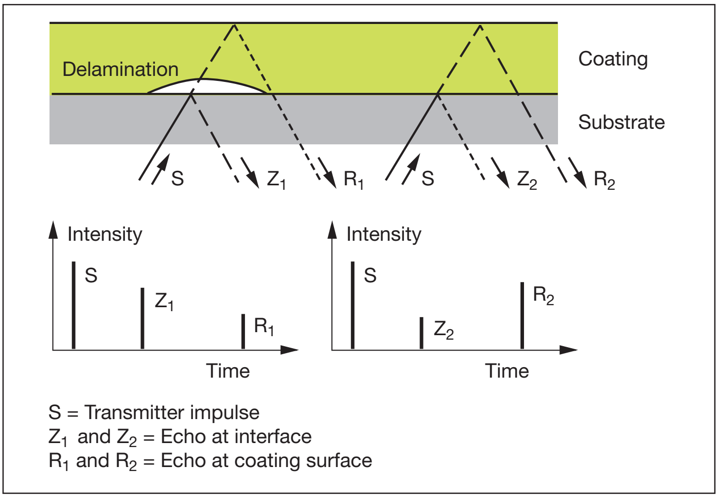


Fig. 3.2.58
Scheme of adhesion measurements by ultrasonic reflection measurements

Depending on the individual film thicknesses they reach the measuring instrument at different times and depending on defects in the bond they arrive with varying intensity. The method of **sound emission analysis** is based on the fact that a coating subjected to mechanical stress can emit sound signals. The energy stored by elastic deformation can spontaneously pass to new energy states if stress limits are exceeded. The energy

liberated in this way is manifested as a sound pulse [3.4.37]. To perform the measurement the coated steel panel is elongated at a defined velocity. The start of damage to the bond is indicated acoustically before it becomes visible macroscopically. Solvent emission is measured, amplified and analyzed.
This measuring method does not permit any fine differentiation of bond strength so only rough estimates can be made between good and less good adhesion.

3.2.5.2 Elasticity

Theory
Coatings are subjected to many different deformations throughout their service life, which have to be withstood without performance impairment, physical damage or loss of adhesion. The usual physical types of deformation are elongation, compression, shear, bending and torsion. In practice loads are caused by brief deformation stresses due to gravel impact or engine vibrations, e.g. automotive coatings. Permanent deformations, whether they are unintentional by denting a wing or intentional owing to drawing processes on coated panels when manufacturing precoated beverage cans, refrigerators or other bulding materials [3.4.38], must not affect the coat. On account of heat-related different volume changes in the coating and substrate internal stresses and strains can occur which must not lead to irreversible damage.
In the broadest sense, materials with pronounced elastic properties can satisfy most of these requirements. Ideal elasticity is obtained on account of the ability of reversible reorientation of molecules and molecular chains of the organic film forming agents and complete storage of the deformation energy being applied. In this way the prerequisites for quantitative restoration are met when the deforming force no longer acts.

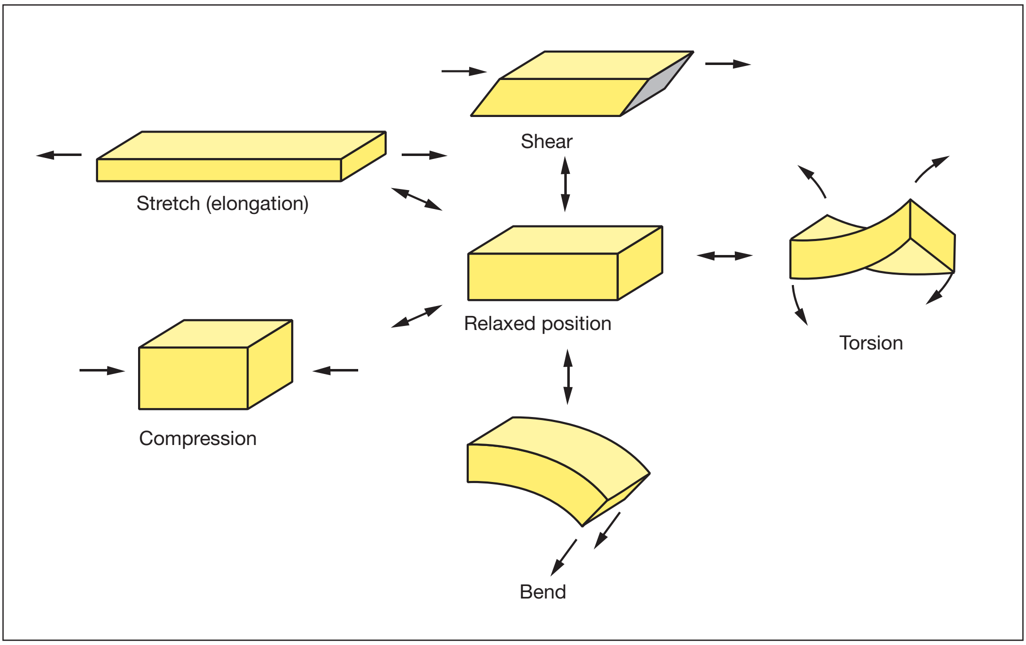


Fig. 3.2.59
Types of mechanical deformation

The interrelationships of ideal elasticity can be described by *Hooke*'s law between the tensile force F acting on a body in the case of elongation and the resultant deformation. Tensile stress σ as an area-related force is directly proportional to elongation Δl in relation to initial length l, the ε-value. The proportionality factor E in the appropriate stress-strain diagram is the modulus of elasticity by definition.

$$\sigma = E \cdot \varepsilon \qquad \text{where} \quad \sigma = \frac{F}{A} \quad \text{and} \quad \varepsilon = \frac{\Delta l}{l}$$

The other types of deformation such as shear and torsion can be simply described for ideal-elastic bodies, whereby the individual moduli for describing the elastic properties are functionally related to one another and can be converted to one another.

Taking shear as an example, if shear stress τ is acting tangentially on a test body there will be a shear angle γ. The quotient is the shear modulus G.

$$\tau = G \cdot \gamma$$

τ = shear stress
G = shear modul
γ = shear angle

The moduli E from the elongation test and G from the shear test can be converted to one another as follows:

$$G = \frac{E}{2 \cdot (1 + \mu)}$$

Since in practice *Poisson's* ratio μ, the quotient of relative transverse and longitudinal contraction, assumes values within the region of 0.5, the modulus of elasticity E is approximately three times the value of shear modulus G.

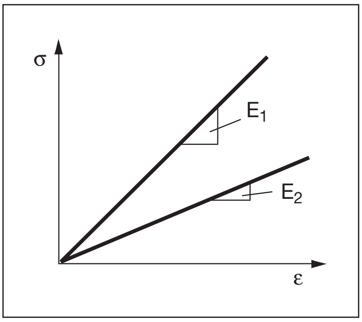


Fig. 3.2.60
Stress-strain diagram of energy-elastic material (Hooke's law)

The type of elasticity described so far, as applies to metals for example, is independent of deformation time and, within certain temperature intervals, also independent of temperature. We do not find such simple manifestations of elasticity in polymers and therefore coatings. Bending tests show linear dependencies only if deformations are small or if force applied is low. High shear and tensile stresses lead to considerable deviations in linearity. Dependencies on time and temperature are also observed. Slow deformations due to bending and fast deformation due to knocks or impact can lead to different results for one and the same coating. When determining the elastic properties of coatings one must therefore differentiate between bending elasticity as a slow deformation and impact elasticity as fast deformation.

In the range of small elongation the stress-strain diagram plotted during slow deformation (see figure 3.2.62) only complies with *Hooke*'s law up to point A. This short linear section is then directly followed by a range of disproportionate elongations A to C. The modulus of elasticity, the gradient of the locus, falls. The product consequently becomes more elastic. The causes are to be found in the separation of texture-

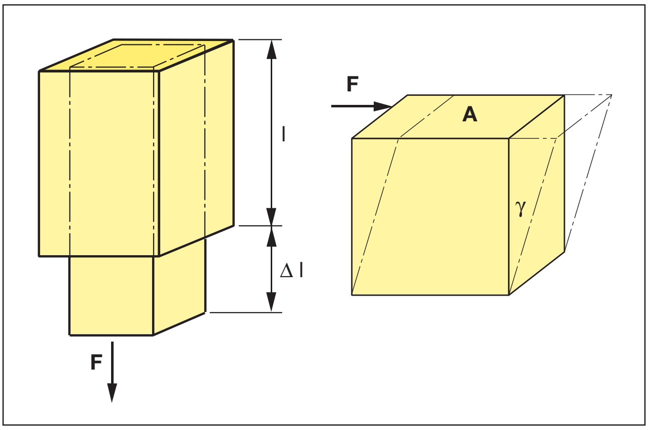


Fig. 3.2.61
Elongation and shear

stabilizing intermolecular interactions. The chains become more mobile and find it easier to glide past one another. In the case of fixed loops in thermoplastics or chemical linkage of the individual molecule segments in duromers the orientation of the previously statistically coiled macromolecules involves storage of free energy. The order increases so the entropy of the system declines. The restoring forces of deformed bodies are, in addition to exploitation of stored energy (see above), caused by the fact that polymeric material strives to take on the previous statistical arrangement of the molecular chains because entropy has increased.

Elastic deformation of coatings, also by analogy with the *Gibbs-Helmholtz* equation (see chapter 2.2.3), is entropy-related storage of free energy by "reversible" flow. Such properties are therefore fittingly described by the term viscoelasticity.

After complete orientation of the molecular chains due to commencing deformation of bond angles the stress-strain diagram resumes a steeper rise as of point C. The curve ends at point D because the tensile forces exceed the cohesion of the polymers. Cracking or complete fracture are the result.

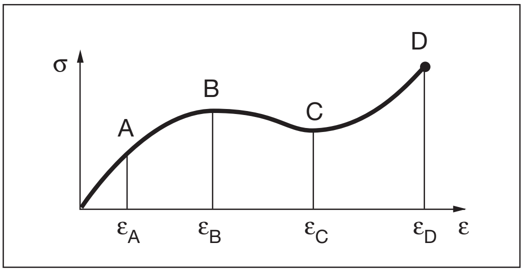


Fig. 3.2.62
Stress-strain diagram of viscoelastic films

The deformation of polymers is thus a superposition of energy and entropic state changes dependent on the mobility of the molecular chains. One therefore talks about the energy and entropy-elastic components of viscoelasticity. The substantial dependence of the elastic properties of coatings on temperature is thus provided with a molecular explanation.

For the practical behaviour of coatings it is important to know how dependent the modulus of elasticity is on temperature. In the low temperature range the segment mobility of duromers and thermoplastic materials is considerably

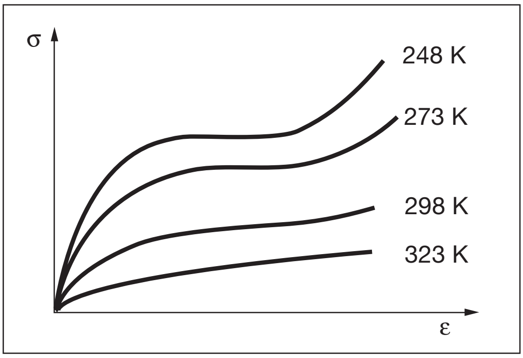


Fig. 3.2.63
Schematic dependance of stress-strain behavior of coatings from the temperature

restricted by fixation of the molecular structure. Deformations are only possible in the close range on account of the change in bond angles. The macroscopic changes in shape observed are minimal. Consequently, the moduli are high. The polymer is within the range of energy elasticity. As temperature increases the modulus of elasticity only shows a slight drop at first but after that it declines steeply to a much lower plateau at a temperature which is characteristic of each polymer. First of all the increase in temperature is not yet able to overcome the stabilizing intermolecular bridging bonds as fixed points. Only after a further rise in temperature are the stabilizations cancelled out so that entropy-elastic deformations with major effects become possible on account of the free mobility of the now evidently longer molecule segments. The turning point in this segment of the curve is referred to as the glass transition temperature Tg and it has become established as a characteristic material parameter in coating technology [3.4.39]. Glass transition temperature can fluctuate between –100 °C and +100 °C depending on the structure and molecular weight of the film forming agents. In the case of baking enamels it is normally between 20 °C and 40 °C. Owing to the enormous differences in viscoelastic behaviour testing and stressing temperature of coatings should always be on the same side of glass temperature. A correct forecast of behaviour in practice is then only a matter of chance.

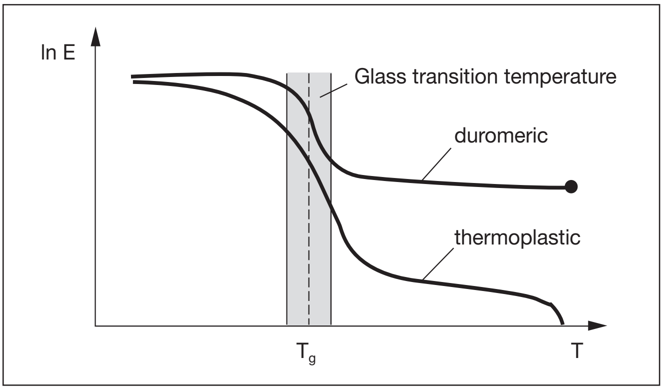


Fig. 3.2.64
Temperature dependance of the logarithmic E-modulus of polymeric films at constant stress

With thermoplastics, if there is a further rise in temperature, mobility increases, as of a certain temperature, to such an extent, depending on the molecular weight and the polar components, that long chain segments can glide past one another irreversibly. The material then acquires the properties of a liquid. In the case of duromers there is no such drop. They decompose at an appropriately high temperature (ceiling temperature), without previously having become flowable.

It becomes apparent that with duromeric coatings the difference in modulus of elasticity declines in the entropy-elastic range. Dependence of the modulus of elasticity on temperature can therefore also serve as a guide for the degree of crosslinking of reaction paints.

The difference between the slow bending elasticity and fast impact elasticity of identical coatings can be explained by the time-dependence of the molecular shifts over long distances which is responsible for viscoelastic behaviour.

The figure 3.2.65 shows the time-dependence of deformation of an energy-elastic steel spring and of a viscoelastic polymer film at constant tensile stress σ_0. Whilst the steel spring spontaneously assumes constant elongation, the stressed polymer film only becomes longer in the first phase of loading on account of the energy-elastic deformation

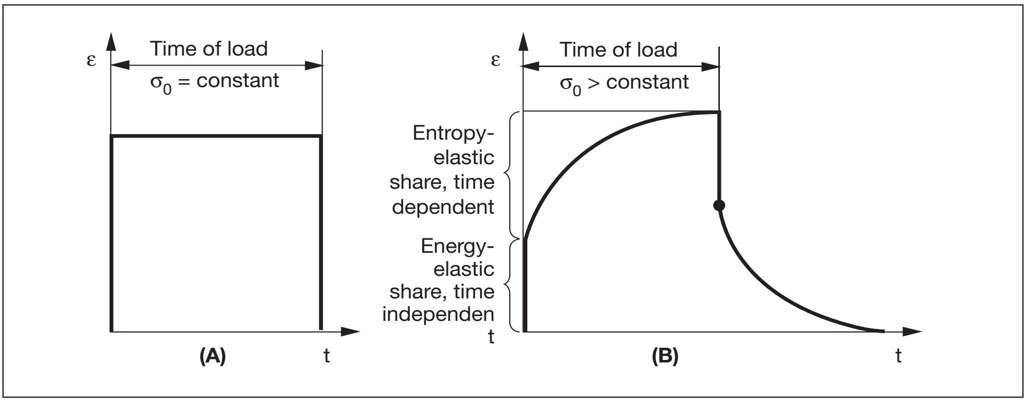


Fig. 3.2.65
Strain of energy-elastic (A) and viscoeleastic (B) materials depending of time

irrespective of time. The larger component of elongation caused by molecular segment shifts is only complete after a finite time. This behaviour, which is known as retardation, can be described quantitatively by the retardation time. It can be determined from elongation-time dependence and is defined as the time which elapses before $t = t_{ret}$. At this time the elongation ε(t) following an e-function has reached 63.2% of its maximum value.

$$\varepsilon(t) = \frac{\sigma_0}{E} \cdot (1 - e^{-\frac{t}{t_{ret}}})$$

Another viscoelastic parameter becomes accessible by experiment if at constant set elongation the dependence of the resulting stress on time is determined as a measure of internal stress.

The course of the curves of thermoplastics and duromers corresponds to an e-function as with retardation.

$$\sigma = \sigma_0 \cdot e^{-\frac{t}{t_{rel}}}$$

t_{rel} is the required time defined as relaxation time for re-orientation of the molecular chains until σ has dropped to 36.8% of σ_0. Ideal thermoplastics can drop to 0 if time is sufficient. Duromers always retain a crosslinking-related residual stress.

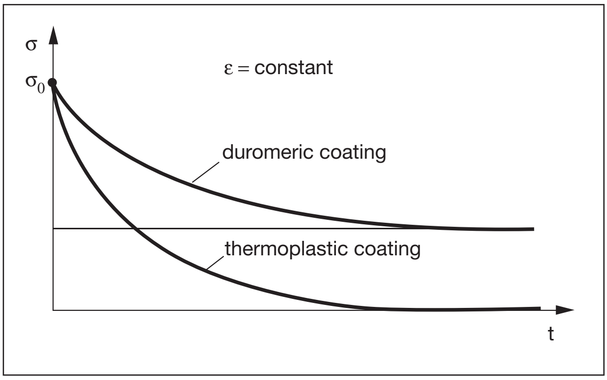


Fig. 3.2.66
Relaxation of inner stress at thermoplastic and duromeric coating films

Viscoelastic behaviour can be described with a graphic model. Application of a force and its effect on change of shape can be represented imaginarily by connecting steel springs and dampers in parallel and in series. The latter are cylinders filled with a viscous liquid and a fitting plunger inside [3.4.40]. The three rheologically relevant components of the model are represented by the steel

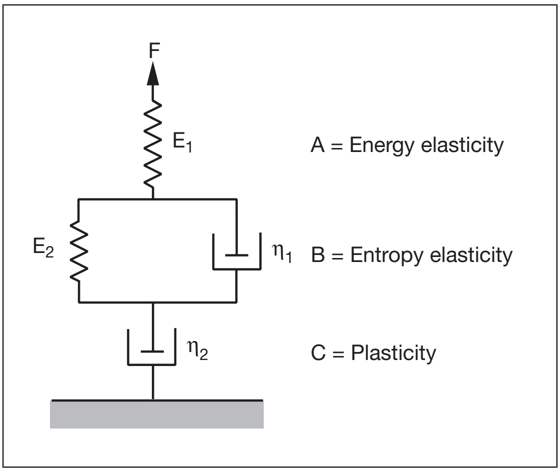


Fig. 3.2.67
Circuit to describe viscoelastic properties of materials according to Burger

spring with modulus E_1 for energy elasticity A, by combining the steel spring with modulus E_2 and the damper with η_1 for entropy elasticity B and by the damper with η_2 for plasticity C. Whilst energy-elastic component A is independent of time and temperature, the entropy-elastic and plastic components are parameters which depend on temperature and time. Deformations in accordance with A and B are reversible, those in accordance with C irreversible. On account of the model the dependence on temperature of visco-elasticity (see figure 3.2.63) known from experience acquires a plausible explanation because of the lower viscosity of the liquid in the dampers at higher temperatures. Entropy-elastic and plastic components are then manifested to a greater extent. A considerable drop in the modulus of elasticity is the result.

A complete description of the viscoelasticity of polymers is not possible with the so far described definition of the modulus of elasticity. For a more precise description of viscoelastic behaviour it is necessary to split it into a viscous component and an elastic component in accordance with the *Burger* model and describe it with appropriate individual moduli. On the complex numerical level the viscous components are identified by loss modulus E'' as an imaginary part whilst the elastic components are identified by storage modulus E' as the real part [3.4.41]. Addition then leads to the complex modulus of elasticity E*.

$$E^* = E' + i \cdot E''$$

The scalar value of the complex modulus can be calculated by obtaining the root of the sum of the squares of the individual modulus components. For assessment of the mechanical behaviour of coatings the quotient of the two moduli E''/E' as tan δ value is applied as the mechanical loss angle. Owing to the dependence of E'' on temperature the value of tan δ is also a function of temperature.

$$\tan\delta = \frac{E''}{E'}$$

For the engineer it is important to know that tan δ reaches a maximum in the region of glass temperature. In this temperature range the coating thus arrives at the best compromise between the dissipation of energy and mechanical resistance – a fact which should be taken into account when developing impact-proof elastic coatings.

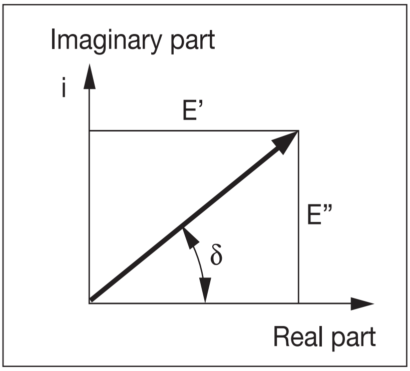


Fig. 3.2.68
Complex modulus

Viscoelasticity is therefore always a complex combination of viscous and elastic behaviour and provides an intermediate stage to be quantified individually between two extreme states of ideal elastic behaviour and ideal viscous behaviour.

Methods of measurement

The methods of measuring viscoelasticity can be divided into two different categories. On the one hand, performance indicators are obtained by simulating the practical stresses of coatings, on the other the temporal phase shifts are observed between a cyclic deformation force and deformation of the material. Owing to the time dependence of viscoelastic deformations it has proved reliable to split the individual test methods into procedures for determining bending elasticity and impact elasticity.

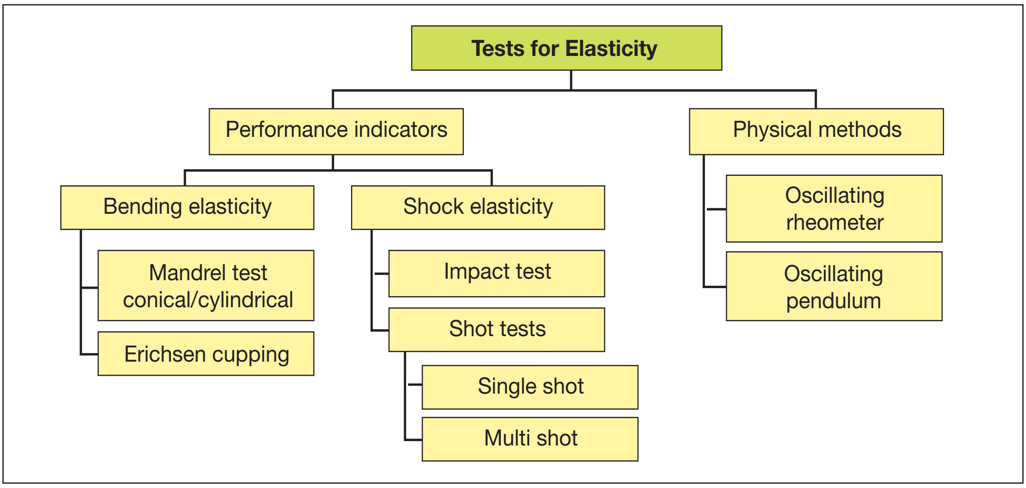


Fig. 3.2.69
Structure of testmethods for elasticity

Testing of bending elasticity

All tests for characterising the bending behaviour of coatings are basically practical stresses reproduced under defined conditions. In the case of the mandrel bending test in

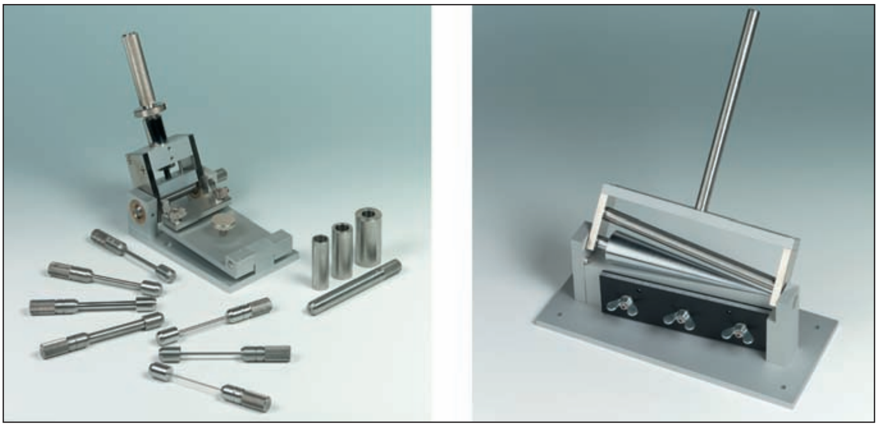


Fig. 3.2.70
Cylindrical mandrel test according to DIN EN ISO 1519 and conical mandrel test according to DIN EN ISO 6860

accordance with DIN EN ISO 1519 (cylindrical mandrel) sample strips coated at a defined velocity are bent round cylinders of different diameters. The diameter at which the coating cracks or flakes off after stress is used as an indicator of the elasticity of the coating.

Apart from the mandrel bending test with a cylindrical mandrel, for many applications the mandrel test is conducted with a tapered (conical) mandrel as per DIN EN ISO 6860. This has the advantage that with one test a whole range of varying bending radii can be covered. With the conical mandrel bending tester the bending mandrel consists of a truncated cone approximately 20 cm in length with a diameter decreasing from 38 mm to 3.2 mm. The test panel is covered with a sheet of paper, clamped firmly and bent through 180° at constant velocity in approximately 10 s. After the bending process the paper is removed and the point is marked where the cracking stops. The diameter of the bending mandrel at which the coating cracks or flakes off is stated. A different method of evaluation is to state the percentage elongation caused by the bending.

Fig. 3.2.71
Erichsen cupping test device according to DIN EN ISO 1250

The Erichsen cupping test

Apart from one-dimensional elongation until cracking, two-dimensional elongations are also used to describe the elasticity of coatings. In the *Erichsen* cupping test a plunger is used to punch a hardened, polished steel ball with a diameter of 20 mm into the back of the sample plate at a consistent feed velocity of about 0.2 mm/s until the first crack appears in the surface of the coating. The distance covered by the plunger is read off the measuring device as the cupping value. With cupping it is not only the film of paint is stressed with regard to deformability but the entire test panel. For this reason the substrate for the sample coating should only involve materials and pretreatment methods which conform to the practical application or have been standardized for development purposes.

All the tests presented so far merely provide information about the maximum elongation ability of the polymeric film. Reproducible results can only be obtained if, in particular, the film thicknesses of the substrate, but also the film thicknesses of the coating as well as test temperature, conform precisely to the values agreed in the specifications.

Shock and impact elasticity

In order to test dynamic deformation in the case of impact stressing the ball impact tester as per ASTM is used. The tester consists of a base plate with a die and a solid stand with a holding arm for a drop pipe. On the drop pipe there is a height scale and a device for setting the drop weight. The falling body itself must be defined with regard to geometric design and mass.

With the impact tester the aim is to test the resistance of a film of paint to cracking or flaking from a metal substrate when a falling body hits the coating. Depending on the question being asked, it can hit the coating directly or from the rear. The film of paint is compressed or elongated (impact or reverse impact). The test has to be repeated with increasing or decreasing drop height until the first signs of cracking or flaking appear.

The special devices for testing the resistance of coatings to stone impact can be divided into single-impact devices and multi-impact devices. When testing with single-impact devices a defined shock load is applied to the coated area. The test itself can be performed by two methods. The first one uses a hemispherical impact body with a diameter of 2 mm. To generate impact energy a fast-starting electric motor is used which propels the impact body and hurls it at the object. The impact energy is determined by the nominal rotational speed, the power and the mechanical time constant of the motor.

Especially in the automotive industry single-impact tests as per DIN 55996-3 have proved reliable as so-called mono-impact methods. A defined projectile is fired at the test coating with a pneumatic firing device at defined velocity and at a defined angle of impact. To assess the stone chip resistance, with both methods the damaged area in square millimetres is determined and the damage pattern is interpreted.

Fig. 3.2.72
Single impact test device according to ASTM B 279

When testing the stone chip resistance with multi-firing devices as per DIN 55996-1 the damage to the outer skin of vehicle bodies has to be simulated by a large number of small, often sharp-edged impact bodies which hit the surface simultaneously and in rapid sequence. The standardized device consists of a steel channel of standardized size, at one end of which there is a clamping device for holding the test panel at a defined firing angle. The feeding station for the impact bodies is located at the other end. The

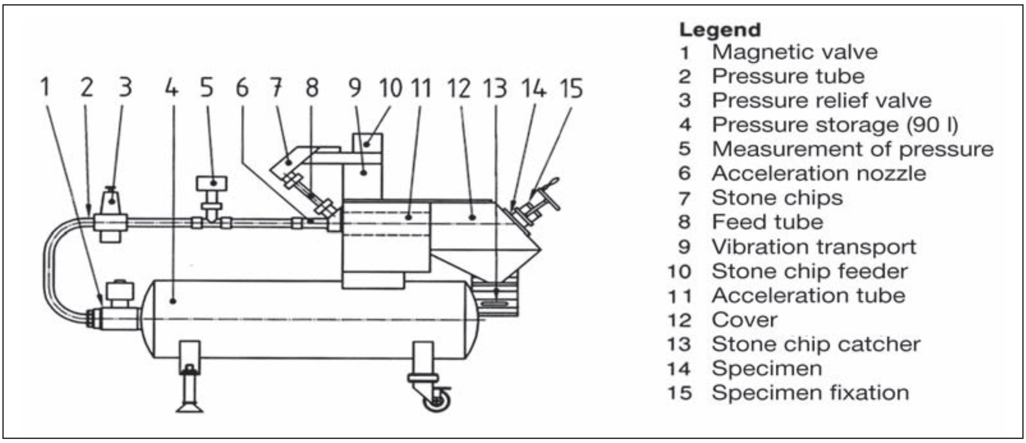


Fig. 3.2.73
Scheme of a multi stone chip testing equipment according to DIN 55996-1

firing material, consisting of steel shot, steel balls or road chippings of various grain sizes, is propelled by compressed air and fires it at the test panel.

If the effect of impact stress on the corrosion resistance of a coating is to be assessed, the test plate can be subjected to corrosion stress before and after firing. The test conditions and total duration of corrosion stress vary depending on the test method.

Physical methods of measurement

The methods of measurement for describing the viscoelastic behaviour of coatings are essentially aimed at recording the loss and storage moduli (see above) as an individual parameter of the viscoelastic material property directly or indirectly. Dynamic mechanical measurements with an oscillation rheometer or a torsion pendulum make it possible to determine viscoelasticity from the behaviour of films of paint stressed in cycles. The temporal phase shifts between deformation force and deformation on the one hand or the damping of pendulum oscillations on the other are the measurable effects from which individual moduli as well as the relaxation or retardation times can be calculated.

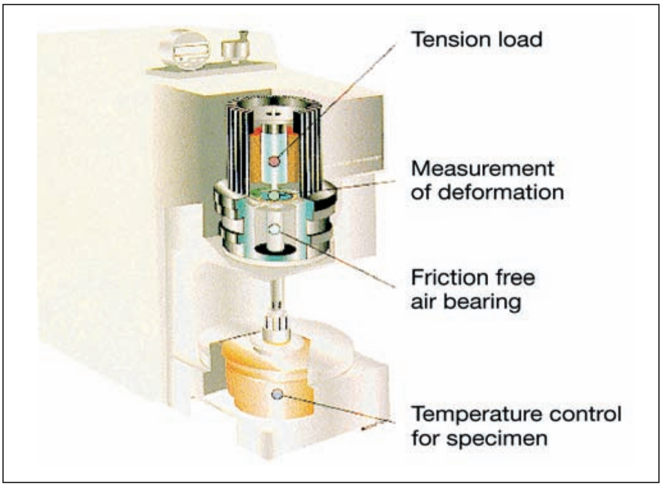


Fig. 3.2.74
Principle of an oscillating rheometer

Scientific physical methods are becoming more and more popular for characterizing physical/technological properties although a correlation between the data found and performance is not always in evidence. The principle of dynamic stressing with the oscillating rheometer is shown in figure 3.2.74.

By means of an oscillating drive a coating is subjected to cycling shearing. Owing

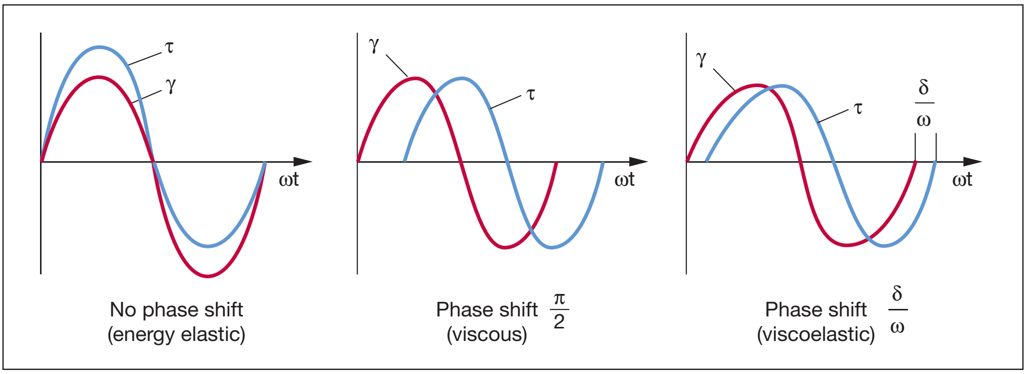


Fig. 3.2.75
Stress-strain curves of energy-elastic, viscous and viscoelastic materials

to the design of the devices the shear angle γ corresponds to a sine-wave function depending on time. According to the elastic properties of the coating the oscillation applied to the bottom plate is delayed by a more or less large phase shift angle. If the shift angle $\delta = 0$, the body is an ideal-elasticity body, and if it is shifted 90°, it is an ideal-viscosity body. For viscoelastic substances, assuming specified deformation γ, the phase shift of the transferred shearing stress τ is between $\delta = 0$ and $\delta = \pi/2$ depending on the components of the two properties, i.e. the purely elastic and purely viscous properties are shifted by 90° in relation to one another.

$$\gamma(t) = \gamma_0 \cdot \sin(\omega \cdot t)$$
$$\tau(t) = \tau_0 \cdot \sin(\omega \cdot t - \delta)$$

The smaller the phase shift δ, the more pronounced the energy-elastic properties. The shift angle δ can be split up by mathematical processing into a component in phase ($\delta = 0°$) and a component shifted by $\pi/2$ ($\delta = 90°$). Both parameters have to be converted to loss and storage moduli. The resulting quotient is then the mechanical loss angle tan δ (see chapter 2.3.3). Another way of obtaining information about the elastic properties of coatings is to measure the damping of artificially created oscillations without any further supply of energy.

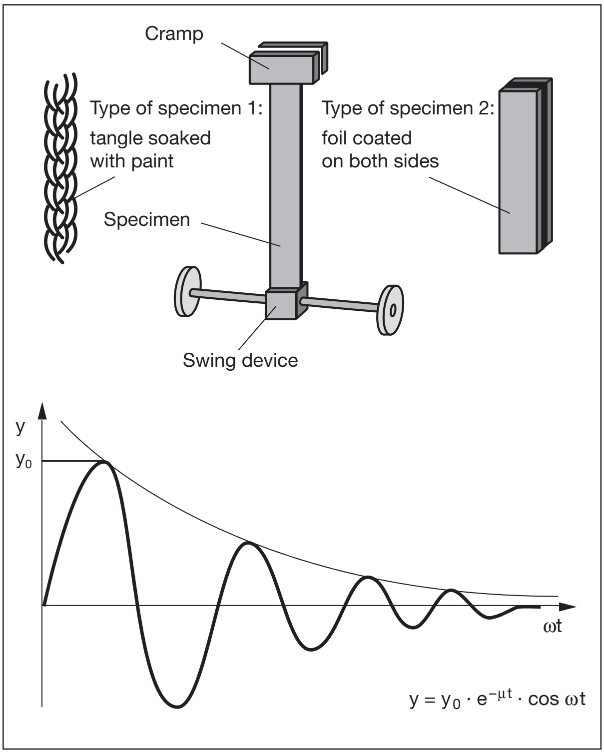


Fig. 3.2.76
Specimen and damping curves of oscillations by a pendulum

Free films, frequently reinforced by backing films, are fixed to one side and, after attachment of a flywheel, caused to oscillate by torsion. The oscillation time and damping can then be used to calculate the viscoelastic parameters. The pendulum oscillation y can be described at maximum deflection y_0 by

$$y = y_0 \cdot e^{-\mu \cdot t} \cdot \cos(\omega \cdot t)$$

The lower the damping factor μ, the lower the damping and the higher the energy-elastic component of the test piece. Conversion to mechanical loss modulus tan δ is possible.

3.2.5.3 Hardness

Coatings with good performance must not only have high adhesion and elasticity but also a level of hardness appropriate to requirements. In an attempt to define this property physically with precision, one encounters difficulties. One finds definitions of hardness as the material property of low elongation ability, i.e. a high modulus of elasticity, high resistance and cohesion or resistance to abrasive effects. If one follows a definition originating from Swiss experts, it is a quasi-static resistance of a body to strictly local, inhomogeneous deformations subjected to the action of point-shaped or linear force centres [3.4.42]. This definition indicates a relationship with elasticity and reciprocally combines it with the physical parameter of hardness. However, equating a high modulus of elasticity with high hardness only partially coincides with the general concept of the term hardness.

Hardness Scale	**Reference Material**
1	Talc
2	Gypsum
3	Calcite
4	Fluorite
5	Apatite
6	Feldspar
7	Quartz
8	Topaz
9	Corundium
10	Diamond

Fig. 3.2.77
Moh's scale of hardness from 1822

The hardness definition is extended by taking into account the hardness scale published by *Mohs* back in 1822, in which a total of 10 degrees of hardness are defined by appropriately hard minerals. According to that a material is harder than a different one if it withstands collision without damage when subjected to mechanical stress from both sides. Such a definition of hardness relates less to deformability and resistance to the action of force than to the internal resistance and hence to the cohesive forces of the material being assessed. Unfortunately the *Mohs* hardness scale [3.4.43] does not contain any polymers as reference substances. It is therefore not very suitable for assessing coatings. The definition in DIN EN ISO 4617, in which hardness is described as the mechanical property of a coating which is manifested in the resistance that the coating applies to a mechanical action, is a broader one and more suitable for polymers, but it also takes into account behaviour towards the influence of pressure, friction or scratching. If one adds that the result of stressing is assessed not only with regard to deformation but also with regard to possible damage in the form of fracture or other irreversible changes, one comes much closer to what is normally understood by hardness.

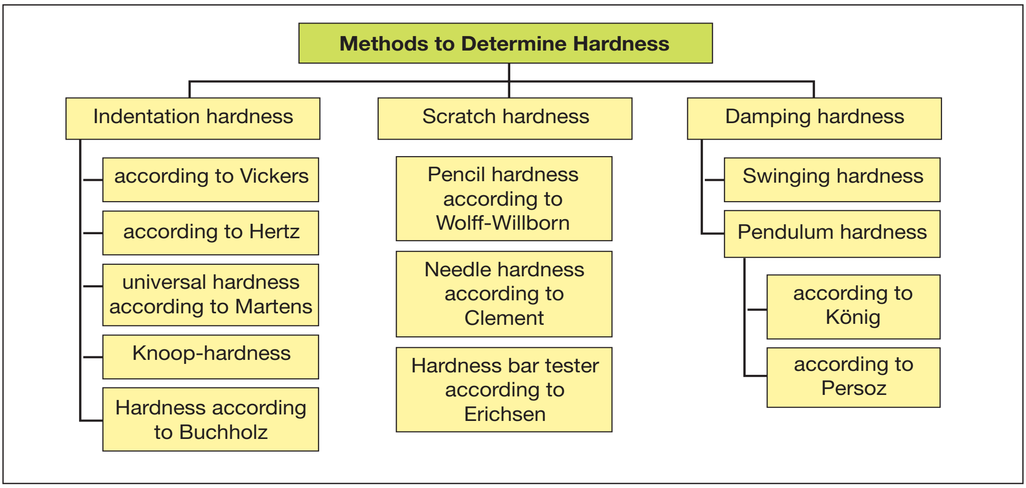


Fig. 3.2.78
Methods to determine the hardness of coatings

To avoid misunderstandings it has proved reliable to not only talk of absolute hardness but also to integrate the principal individual characteristics in the definition of hardness. This makes it clear that the term hardness involves various material properties which are covered by various test methods and seldom fully correlate with each other.

Test methods

For determining the hardness of coatings there are test instruments with which indentation resistance, the damping of oscillating free films or the resistance to the damaging effect of scratching tools can be measured.

The most common method of determining **indentation hardness** is the *Buchholz* test as per DIN EN ISO 2815. The tester used is a double truncated cone made of steel, which, after placing on the test coating, acts on it at right angles with a force of 5 N.

After a stressing time of 30 seconds the penetration body is removed in order to measure the remaining damage to the coating after a regeneration time of 35 seconds.

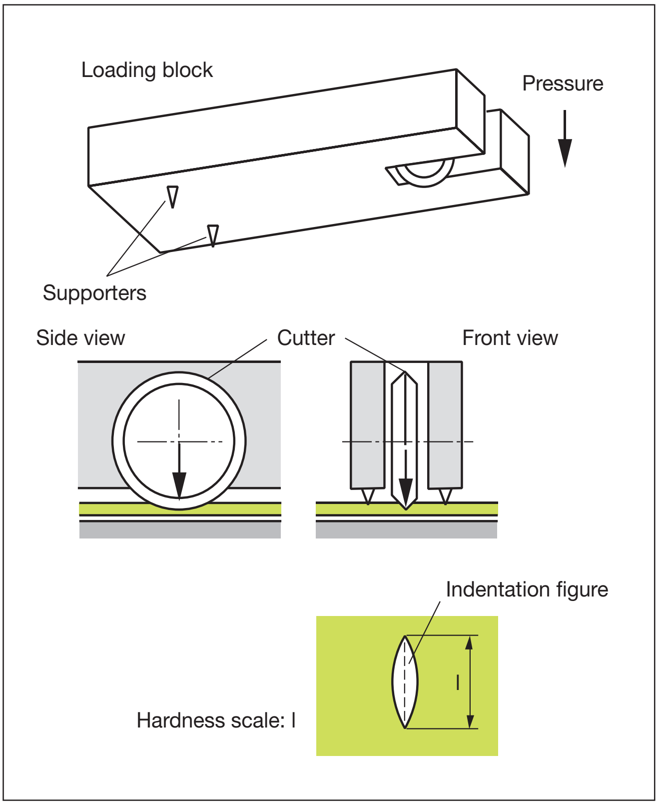


Fig. 3.2.79
Indentation hardness according to Buchholz and DIN EN ISO 2815

According to DIN EN ISO 2815 the indentation length is stated as a parameter for hardness in millimetres. The reciprocal value of indentation length multiplied by 100, known as *Buchholz* hardness, will thus be replaced in future. One of the most important prerequisites for the practicability of the test method is sufficient film thickness (see below).

Experience has shown that a short indentation length is associated with high mechanical strengths and hence good performance properties. The question as to what physical variables are measured in what bonding is difficult to describe and in terms of a correlation with performance properties it is ultimately of little consequence.

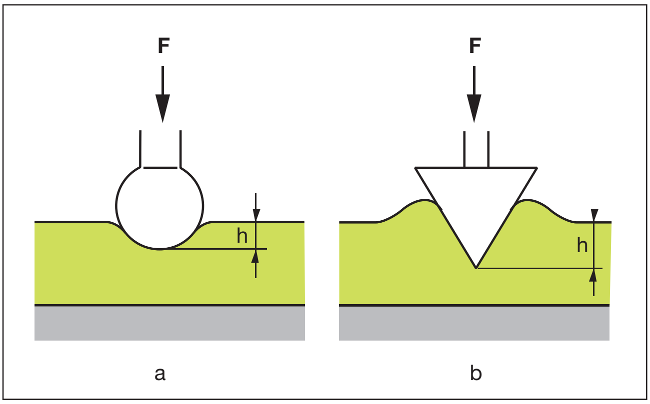


Fig. 3.2.80
Test specimen for indentation tests according to Hertz (a) and Vickers (b)

A rarely practised method of hardness testing is to determine *Knoop* hardness. The apparatus consists of a device with which a load of 250 mN is applied to the coating by the tip of a conical diamond. Measurement of the resulting deformation from indentation depth/length serves as a measure of hardness.

Also rare in the paint and coatings industry are the penetration hardnesses measured under load with reference to defined physical parameters. The most frequent test bodies are the *Hertz* ball and the four-sided *Vickers* pyramid.

From the ratio between force F acting on the test body and the resulting penetration depth h it is possible to calculate *Hertz* hardness H_K and *Vickers* hardness H_V. When calculating *Hertz* hardness the radius R of the penetration ball is used in the calculation whilst when calculating *Vickers* hardness it is the angle of inclination of the pyramid.

$$H_K = \frac{3 \cdot F}{4 \cdot \sqrt{R} \cdot h^{\frac{3}{2}}} \qquad H_V = 3{,}8 \cdot 10^{-2} \cdot \frac{F}{h^2}$$

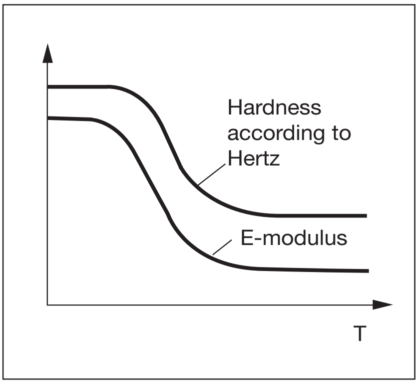


Fig. 3.2.81
Correlation of indentation hardness according to Hertz to the temperature and relation to the E-modulus

Both methods provide information about the hardness of coatings. However, the numerical values cannot be converted to each other. If there is no plasticity, deformation of the film is completely reversible according to the *Hertz* method. The hardness values largely correlate with the modulus of elasticity E. Figure 3.2.81 shows the temperature dependencies of the modulus of elasticity and the hardness values determined according to *Hertz* with a good degree of conformity.

The interaction of the *Vickers* pyramid with the polymeric film is different. The initially only very small load area leads to permanent damage owing to the sharp edges of the test body. Consequently there is no direct relationship between *Vickers* hardness and the modulus of elasticity.

Comprehensive studies incorporating all the important penetration hardness tests have repeatedly demonstrated that reproducible measurements are only possible if deformation of the film only accounts for a fraction of film thickness. For reproducible test results *Van Laar* specifies that the penetration depth should not exceed 1/12th of film thickness. At a film thicknesses of 60 µm deformations of > 5 µm are thus no longer admissible [3.4.44].

To satisfy these requirements two other test techniques have been developed. Either one uses very light weights for the penetration body or one determines the deformations with declining load and extrapolates the thus determined hardness curve by regression to the load 0. The latter method determines the gradient at the origin of the force-compression diagram.

The former method of measurement determines *Martens* universal hardness. The principle of operation of the device for determining it in accordance with DIN EN ISO 14577-1 to 3 is based on measurement of the penetration depth of a pyramid-shaped diamond with a square base and a 136° angle of inclination. The test load is divided up into ranges from 0.4 to 25.6 mN, from 4 to 256 mN and from 16 to 1024 mN or according to additional agreement. The measurements are obtained by test force F being increased quadratically at defined intervals in order to record the resulting penetration depth h immediately. The so-called universal hardness H_n is then calculated from

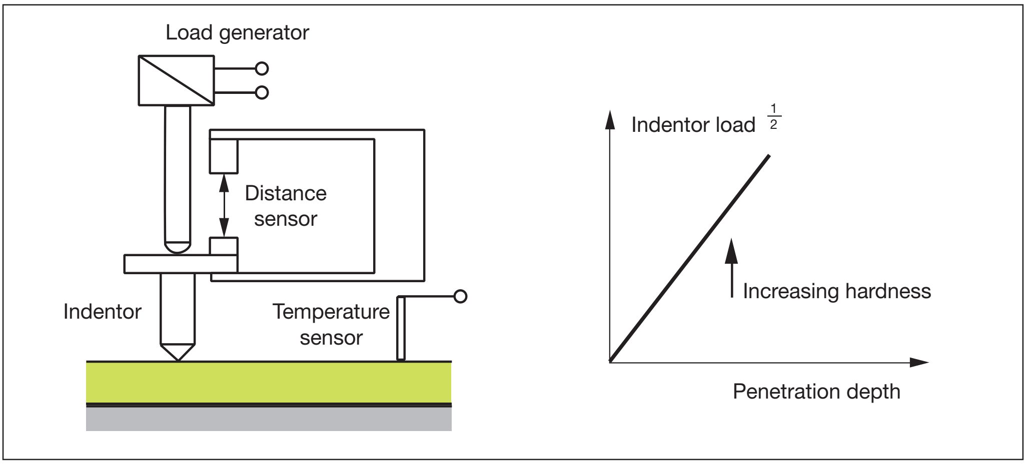


Fig. 3.2.82
Principle of measurement and scheme to determine the universal hardness according to Martens and ISO 6461-3

$$H_n = \frac{F}{26,43 \cdot h^2}$$

Apart from the successive increase in force, other loading processes also have to be set [3.4.45]. In this way test series with a declining load can supply additional information about the time dependence of restoration. The relative depth resilience can be calculated from the penetration depth h_2 measured under the test load after a specified time and the penetration depth h_3 remaining immediately after relief. Relative depth resilience t_r is then:

$$t_r = \frac{h_2 - h_3}{h_2} \cdot 100$$

The time dependence of penetration depth at constant test load produces supplementary data about creep characteristics, i.e. the irreversible deformation of coatings.

A device suitable for determining *Martens* hardness is the Fischerscope. With this device it is possible to not only record traditional penetration hardness but also viscoelasticity and plasticity.

Another method of eliminating errors due to substrate influences was developed by *Oesterle* [3.4.46]. The measuring principle of infinitesimal modulus determination (IMD) is similar to that of the *Hertz* and *Fischer* methods. Penetration depths h are measured in relation to the increasing test force F. The increasing compression alters the elasticity of the thin test body more and more. To eliminate the resulting errors, the gradient in the force-compression diagram is determined in relation to the test force and extrapolated to the gradient at the origin.

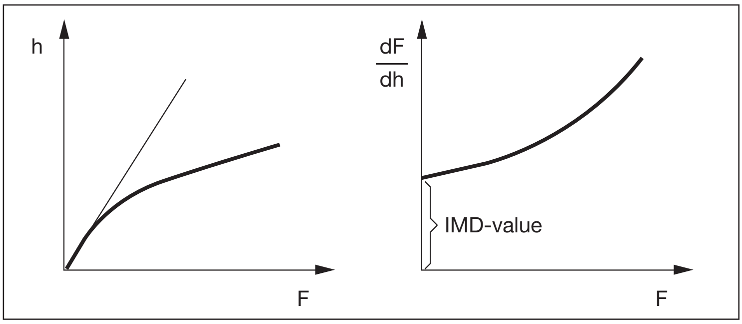


Fig. 3.2.83
Diagrams for determination of infinitesimal modulus determination (IMD) according to Oesterle

The results of the IMD method are irrespective of the shape of the test body. Owing to the extrapolation procedure and sensitivity obtained by it very small differences in pigment distribution can be seen, as can fluctuations in the physical/technological properties according to the varying relative humidity in the environment.

The critical discussion of penetration hardnesses makes it clear that the *Buchholz*, *Vickers*, *Hertz*, *Oesterle* and *Martens* methods ultimately tend to be used for measuring viscoelasticity and plasticity, whereby distinct attribution to the basic physical variables is just as impossible as attribution to performance properties.

In terms of test procedure the measuring techniques which take into account the influence of coatings on the damping of vibrations can scarcely be compared with that of penetration hardness tests. *König* **pendulum hardness** in accordance with DIN EN ISO 1522 is a method frequently encountered in practice. The device itself consists of a pendulum, to the support of which two agate balls are attached.

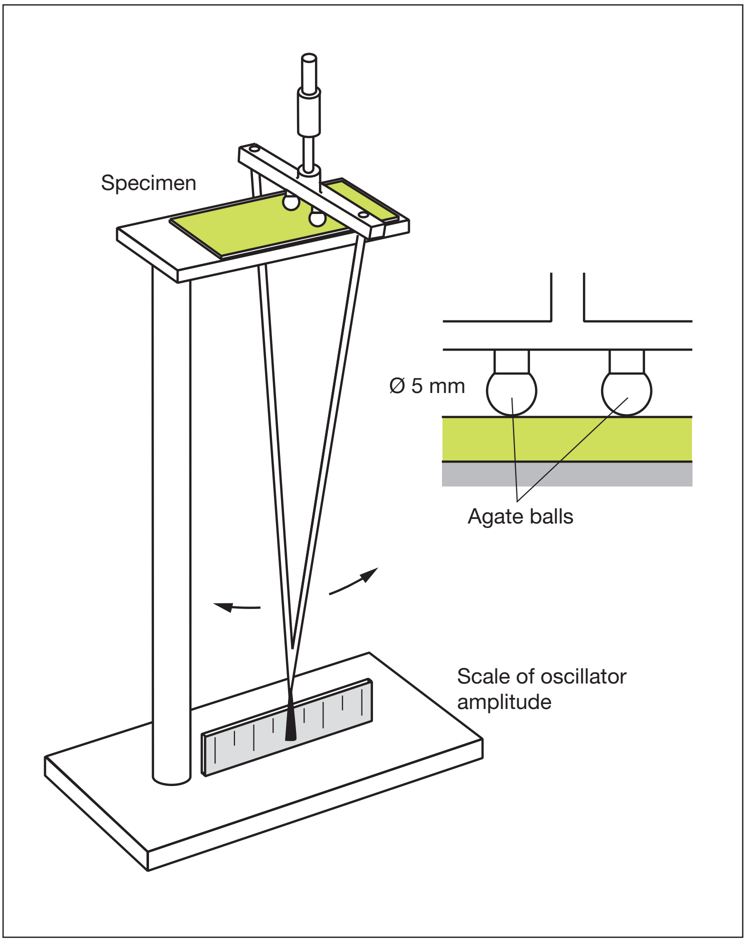


Fig. 3.2.84
Principle and scheme of a device for measuring pendulum hardness according to DIN EN ISO 1522 (König)

The pendulum is placed on the coating with the two balls 5 mm in diameter and moved 6° away from the position of rest. After releasing the 200 g pendulum the oscillations are recorded by a counter. The measure of damping is the number of oscillations or the time in seconds which elapses until the amplitude of the pendulum has dropped from 6° to 3°. For use in accordance with the standard the device with a standard plate has to be set with an adjusting screw in such a way that for an oscillation time of 1.4 s a total of 179 oscillations have taken place by the time half the amplitude has been reached.
A slightly different damping hardness measuring technique is that proposed by *Persoz*. The design and weight of the *Persoz* pendulum differ from the *König* pendulum so it produces different measurements. For example, the 8 mm balls have a much larger diameter than the *König* pendulum balls. The weight of the *Persoz* pendulum, 500 g, is also heavier. The measure of *Persoz* damping is the number of oscillations which are recorded with a pendulum deflection of 12° until a drop to 4°.
The cause of the oscillation damping is the cyclic change in deformation caused by the balls. In relation to the viscoelastic properties and especially retardation behaviour the

coating does not quantitatively recover the restored deformation energy on account of the delayed restoration.

The measured half-life $t_{1/2}$, oscillation time T_p, the length of the pendulum l and the radius of the balls r make it possible to calculate t_{ret}. To enable comparative measurements for coating materials it is half $t_{1/2}$ which is used for simplicity.

$$t_{\frac{1}{2}} = \frac{T_P^2 \cdot l \cdot \ln 2}{\pi^2 \cdot r \cdot t_{ret}}$$

Damping hardnesses record the viscoelastic properties in a similar way to penetration hardnesses.

Measuring techniques where damage is done to the coating with a scorer or suitably shaped test body come much closer to the definitions of hardness in accordance with DIN EN ISO 4617 and *Mohs*. These methods of determining **scratch hardness** use two principles:

Either several test bodies of varying hardness with the same weight or a single test body with various weights are moved horizontally over the coating. The former method is the *Wolff* and *Willborn* hardness test method. To determine this so-called pencil hardness there are17 different pencils with hardnesses from 6B to 9H. For hardness testing the pencils, starting with 6B, are moved over the coating with an appropriate device at a constant weight of 300 g and at an angle of 30 – 40°. The pencil with which the coating suffers permanent damage is regarded as the measure of hardness.

To eliminate sources of error special attention has to be paid to preparation of the pencils and a dust free test coating.

The other way of obtaining data on the hardness of coatings is to determine the resistance of a scorer pulled over the coating with different weights. The force applied as of which the scorer cuts into the coating is stated as being representative of the hardness. In physical terms fracture mechanics processes also play a role in addition to the peeling delamination of the coating. The proportion accounted for by the various influences is also affected by the rate at which the damage is done to the coating.

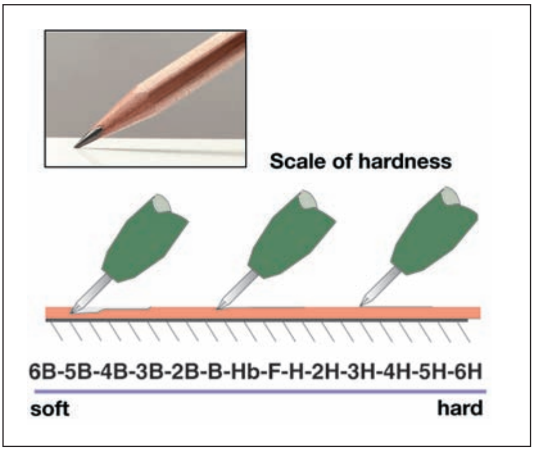


Fig. 3.2.85
Method to determine pencil hardness according to Wolff-Willborn

The scoring tools used are chisel-shaped tungsten-carbide cutters (*Clement* method) or needles with spherical steel heads.

The measuring procedure has to be repeated with systematic increases in load until traces of scratching become visible in the coating. The test result is recorded numerically in relation to weight by giving grades from 1 to 10. Starting with 50 g the weights are increased to a maximum of 500 g.

Measurements with a spherical engraving tip are performed with the *Erichsen* test bar. The tester consists of a cylindrical tube into which an adjusted coil spring has been inserted. The adjustable spring tension acts on an engraving pin, the tip of which projects from the bottom of the tube. To perform the test the hardness bar is placed on the coatings with the tip at right angles applying sufficient force to ensure that the engraving tip is pressed into the tube and guided over the coating at a constant velocity of approx. 10 mm/s over a length of 5 to 10 mm. The numerical value stated for bar hardness determined in this way is the spring tension at which the engraving tip just leaves a trace visible with the eye.

3.2.5.4 *Abrasive Resistance and Mar Resistance*

The abrasive resistance of coatings provides information about the ability to withstand without damage the influence of abrasive materials such as sand, dirt, chippings or corundum, but also scouring brushes. As with all physical/technological properties described so far, the background is extremely complex. Without a doubt the abrasive resistance is functionally linked both to the elastic properties and to the cohesive forces characterized by molecular looping and polar interaction. Owing to the complexity of this property pattern test methods for quantifying abrasive resistances do not aim to determine defined physical indicators. Basically they are nothing more than a simulation of practical stresses [3.4.47].

A method which has proved reliable for many years is the Taber abraser as per DIN 53754. A test panel is stressed “as if with emery paper” by rotating friction rollers exerting a defined force. Depending on the hardness or abrasive resistance the coating is stressed with friction rollers which have various degrees of roughness and hardness. The reduction in the weight of the test panel due to abrasion, measured after a specified test time, is regarded as a measure of abrasive resistance.

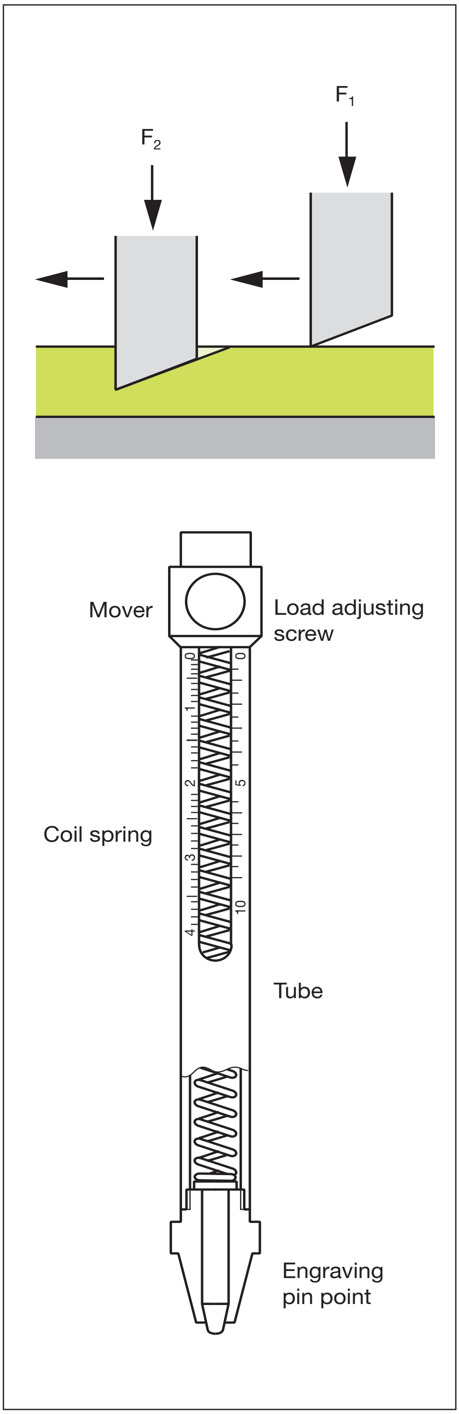


Fig. 3.2.86
Principle of measuring the scratch hardness

Fig. 3.2.87
Equipment for determination of abrasive resistance according to DIN EN ISO 11998

Quite different but no doubt no less aggressive stresses are provided by washing brushes in car washers or scouring brushes for cleaning coated façades. To determine the wear resistance or wash resistance of emulsion paints it is normally the DIN EN ISO 11998 test which is used. The *Gardner* device suitable for this stresses the sample moistened with water and wetting agents by moving a scouring brush horizontally at a defined force. Wash-resisting emulsions have to withstand 1,000 cycles with virtually no damage and wear-resistant ones more than 5,000 cycles.

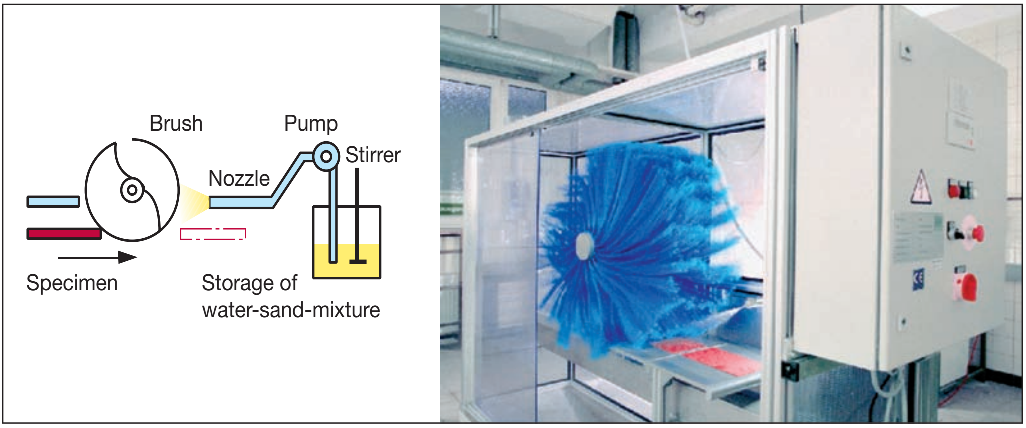


Fig. 3.2.88
Scheme and picture of an equipment to determine scratch resistance for the automotive industry

A particularly interesting type of abrasive resistance is the washing brush resistance of automotive coatings. Reliable tests have been sought for years. However, it has so far not been possible to find the ideal test showing absolute correlation with behaviour in practice.

One test method is based on the conditions in car washers. Test plates are stressed with rotating polyether or polypropylene brushes in opposite directions to the movement of the test bench and simultaneously sprayed with aqueous silica sand slurries (1.5 g/l). The evaluation of tests is performed by conducting gloss measurements on the unstressed and stressed samples at right angles to the direction of abrasion. Reproducibility of test conditions and that of the test device itself is still problematical.

Other test methods cause different materials to be drawn cyclically across test panels in simple apparatuses under defined weights. The scratches achieved thereby are usually measured as haze or gloss. The type of scratches is largely dependent on the materials used [3.4.48]. Further methods of increasing acceptance in the coatings industry are the nano-scratcher (nano-indentation), Taber abraser and Crockmeter [3.4.49]. To increase the hardness of coatings so-called organic-inorganic hybrid paints using the sol-gel-process have been developed to a commercial state [3.4.50]. Recently nano-particles are proposed to have an impact on surface hardness and scratch resistance especially in clear coats for automotive coatings [3.4.51].

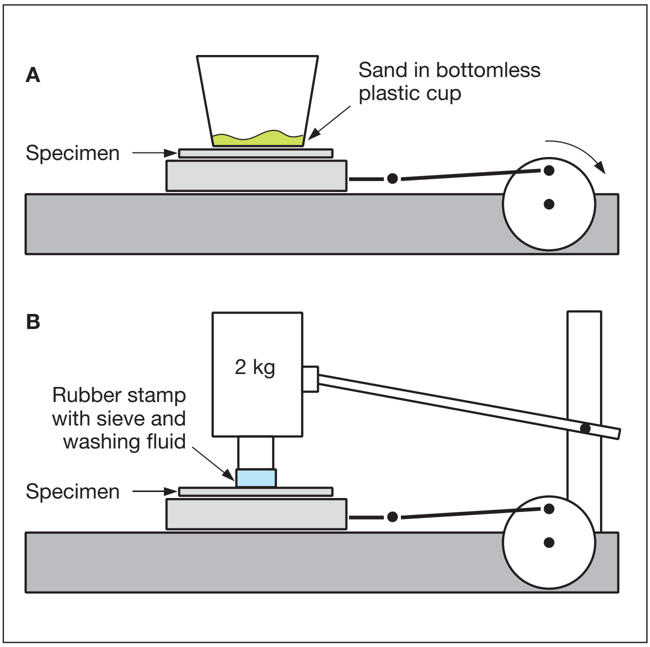


Fig. 3.2.89
Simple devices to determine scratch resistance on test panels

3.2.5.5 Other Tests

Apart from the visual and traditional functional properties such as adhesion, elasticity and hardness, surface properties are being increasingly specified which indicate not only visual attractiveness and physical functionality but also "tactile" effects.

So-called soft-feel coatings are designed to create a soft, pleasing feel when touched. This property known by the term haptics is aimed at imparting upon coatings the feeling of velvet and leather when viewed and felt. Soft-feel coatings are being used increasingly in the automotive, audio and computer industries.

Haptics is therefore an area of tribology, the theory of friction. Tribotechnical terms are described in DIN 50 323-2. They include the contact characteristics of surfaces moving in relation to one another, i.e. interactions of solid surfaces in the molecular range, influences exerted by the surface texture and deformation behaviour. In the case of haptics one of the interacting surfaces is the human hand, in which contact effects are transformed into a sensory impression by sensory cells.

The field is too new for any absolutely reliable test methods. Measurements of the **coefficient of friction**, also standardized in DIN 53 375 and ISO 8295 for plastic films, of scratch resistance, of gloss and simply the feeling when touching or running over with a fingernail are combined in the assessment of haptics and assessed more or less subjectively. With regard to objective quality assessment of this property complex there is plenty of development work to be done in the future.

Another important feature of good long term resistance is the freedom of coatings from **internal stresses and strains** [3.4.52]. Owing to excessively rapid shrinkage during the film forming process thermodynamically instable molecular structures can be frozen inside. On account of external stresses or other mechanical or chemical influences they can become apparent later in the form of cracks.

One simple method of visualising internal stresses and strains is to apply paint to thin substrates. If during film formation the coatings are subjected to internal stresses and strains, the substrates yield and become deformed.
A more elegant but also more elaborate method of detecting stresses and strains in polymers is to apply measuring techniques that use stress optics. Studying double refractions of polarized light is an important aid in investigating stresses and strains in polymeric films [3.4.53].

3.2.6 Summary

Coatings of commodities have to meet many different requirements which can be grouped under the terms of function and color. To meet the requirements of users with regard to all criteria it is necessary first of all to apply uniform, defect freel layers of sufficient thickness. Film thickness measurements are therefore an integral part of the fundamental tasks when characterizing coatings. Depending on the substrate and importance for the coated item, film thicknesses are measured, without making contact with the surface and without damaging it, using a considerable amount of sophisticated instrumentation in fractions of seconds.
The coating itself not only has to comply with visual properties such as gloss, color and effect but also has to meet physical and technological requirements. These include good adhesion, elasticity and hardness. When conducting tests to determine the mechanical properties a distinction must be drawn between short-time stress and continuous stress. The normal test methods of quantitatively describing the properties of coatings either simulate practical stresses and are therefore performance tests or they provide defined physical indicators allowing a statement which is of only limited reliability for assessment in practical situations.
For accurate monitoring of color and gloss a sophisticated measuring technique enables objective determination of color and visual effects. To describe gloss not only are optical methods used but also mechanical scanning processes to characterize surface texture.

3.3 Durability of Coatings

3.3.1 Fundamental Features of Ageing

The quality of coatings is chiefly determined by film forming agents. Pigments, extenders, additives, their fine distribution by dispersion and application are crucial factors that determine quality. The properties do not occur by chance though. They are always the result of usefully combining experience with scientific knowledge.
The aim of coating technology is to not only create quality but, in the same way, to also ensure that the degree of protection and visual attractiveness of the coating remain intact for the agreed periods of time. The influences on the coating to be scrutinized may vary enormously: sunlight with aggressive ultraviolet radiation in conjunction with atmospheric oxygen, heat, cold, moisture in the form of water vapour, rain, due, frost or snow with and without salty impurities, all in virtually any combination, alternating or in the form of continuous stress. Paint-damaging chemicals from industrial plants such as SO_2, volatile organic acids or alkalis in some regions are also worth listing in this

context. Nor should one forget natural active substances such as bird droppings, tree resins, bacteria and fungus. Contaminations of the coating of vehicles by road tar, overflowing fuels and battery acid are also active substances worth mentioning. All these influencing factors combine with mechanical strains acting on the coated items such as vibrations, deformations due to pull, pressure, compression and shear and thus lead to a wide variety of stresses for the coating. The physical, chemical and biological influences, with the exception of mechanical ones, will be grouped under the term of atmospheric influences. In accordance with DIN standards 50010-1 and -2 the term climate covers all the atmospheric conditions occurring at a location, including daily and seasonal changes.

Impact by Climate	Results
• Photochemical reactions • Hydrolytic degradation • Thermal degradation • Volume change by swelling • Volume change by temperature	• Molecular degradation • Crosslinking • Evaporation of cleavaged products • Extraction of cleavaged products

Fig. 3.3.1
List of factors and impacts on coatings

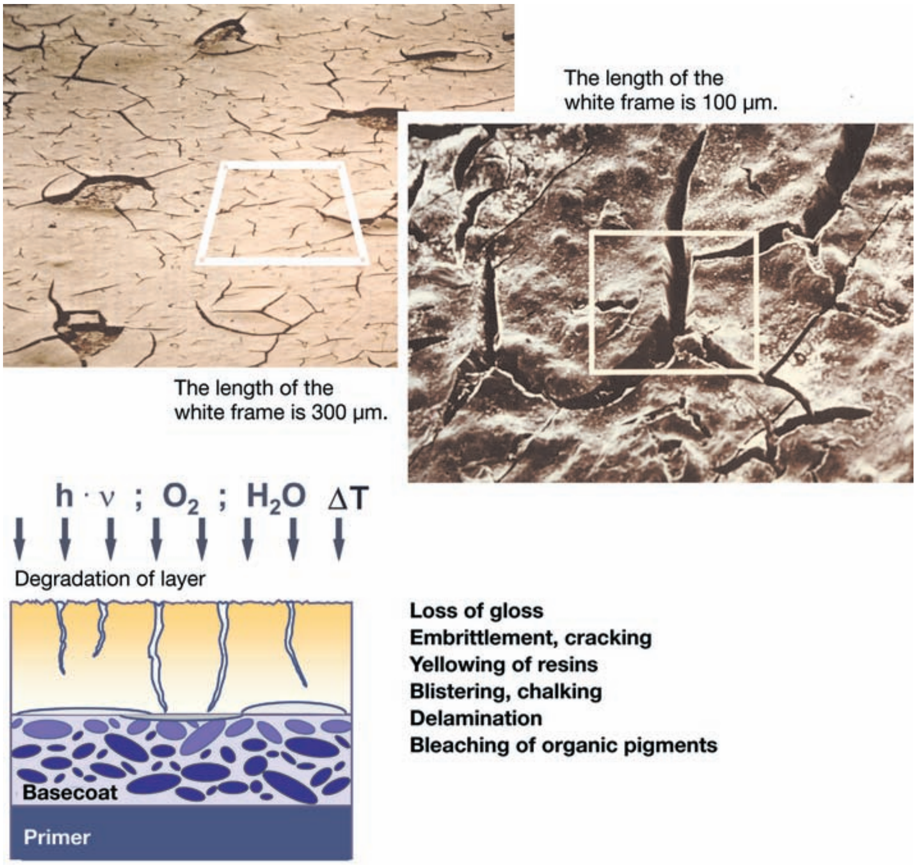


Fig. 3.3.2
Photochemical and chemical impact on coatings and typical results

The climate can, depending on its nature, cause changes to the coatings. These are photochemical reactions, initiated by ultraviolet light, hydrolytic degradation due to aqueous agents, thermal degradation by pyrolysis as well as swelling and shrinkage due to periodic influences exerted by moisture and temperature. Depending on the intensity of the influences and the type of polymers more or less rapid impairments occur in performance. Shorter chains brought about by ultraviolet light on the one hand and subsequent crosslinking on the other lead to an impairment of elasticity [3.4.54] whilst internal resistance declines at the same time. If there are changes in temperature and

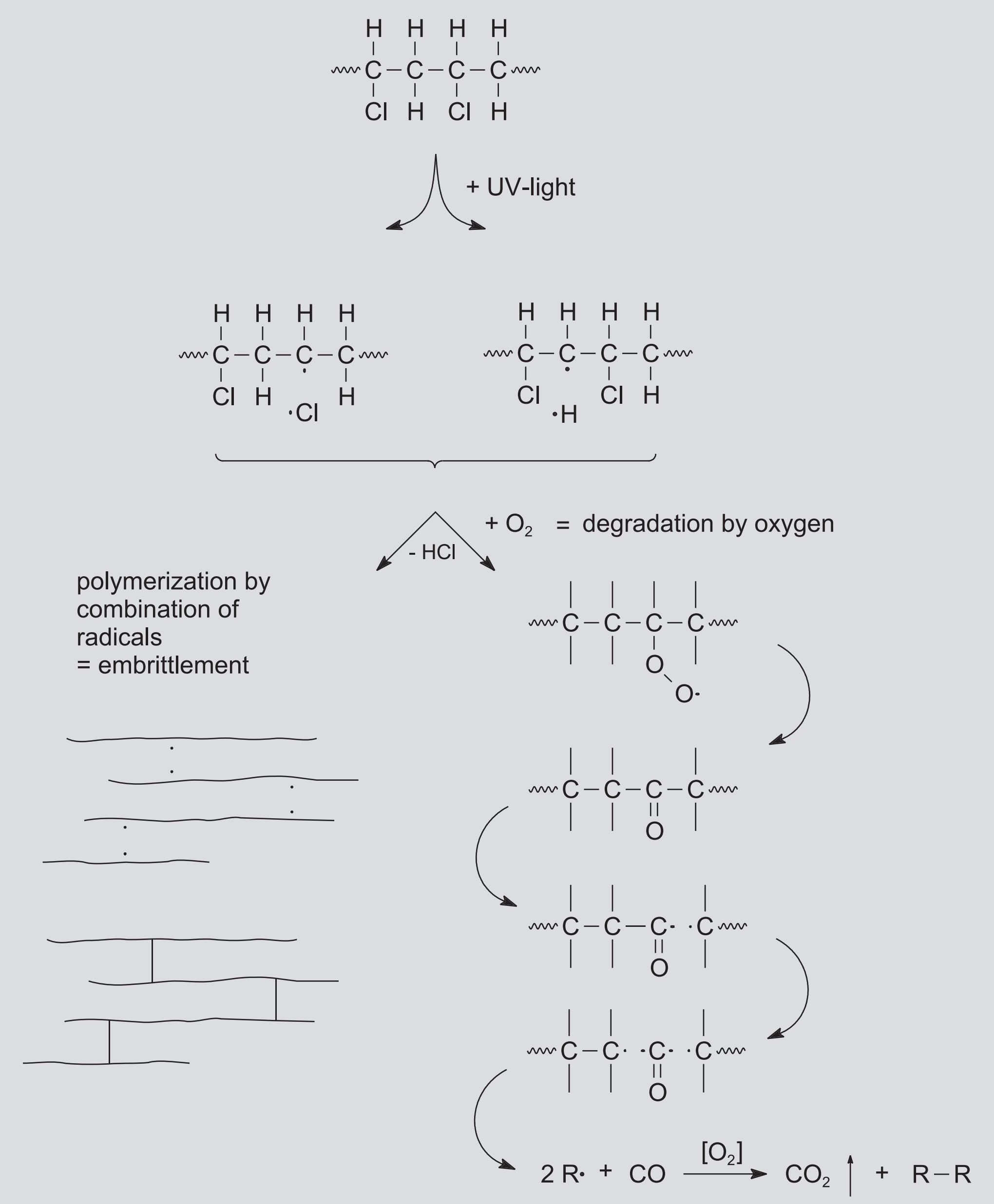


Fig. 3.3.3
Photochemical degradation of Polyvinylchlorid (PVC)

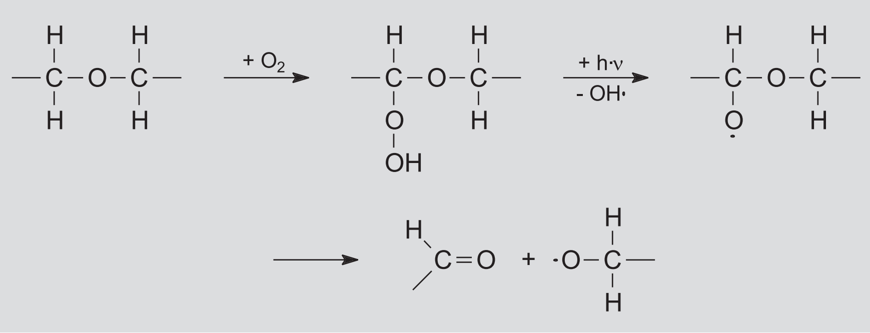


Fig. 3.3.4
Photochemical degradation of polymers with ether groups influenced by oxygen

humidity, increasing stresses and strains then lead to physical destruction of the coating. This becomes apparent first of all in the gloss-reducing degradation, accompanied by cracking, and, under extreme circumstances, the entire coating flakes off. That in turn destroys protection of the surface completely.

The chemical reactions responsible for the individual stages of ageing through to complete degradation of the coating vary enormously. Degradation by ultraviolet light,

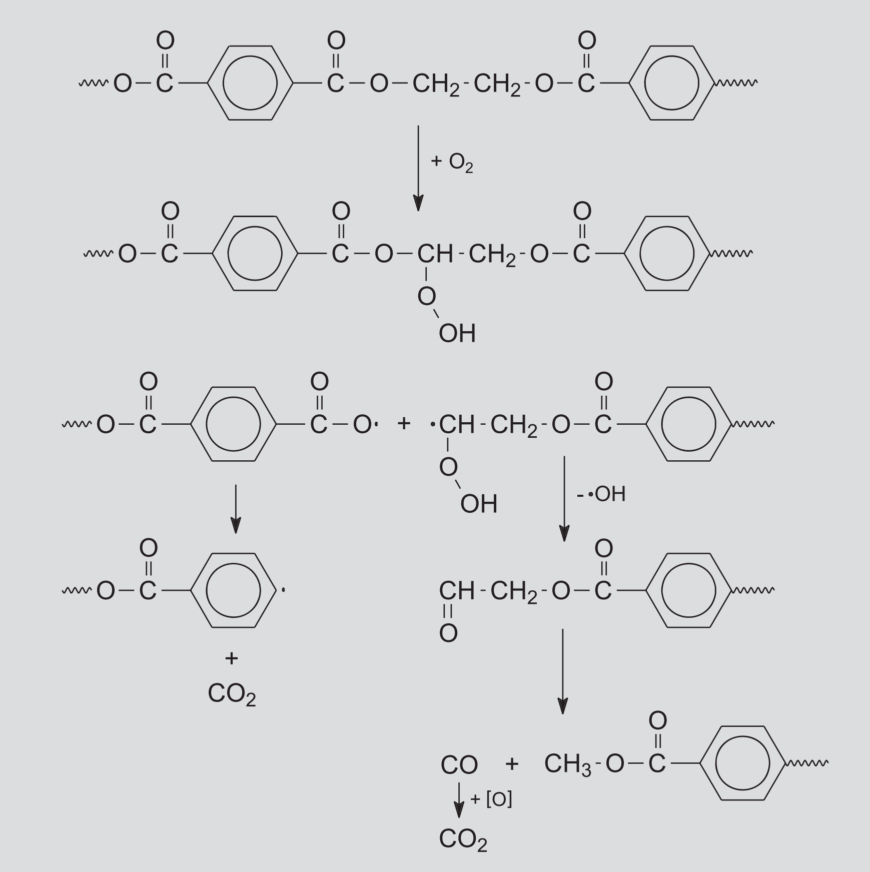


Fig. 3.3.5
Degradation of polyesters influenced by light and oxygen

hydrolysis and thermolysis, always under the additional influence of atmospheric oxygen lead to a wide variety of changes in all the constituents of the coating. For maintaining surface protection the focus must without doubt be on macromolecular film forming agents. Below we will therefore be presenting the most important ageing reactions of paint-specific polymers, quoting different examples.

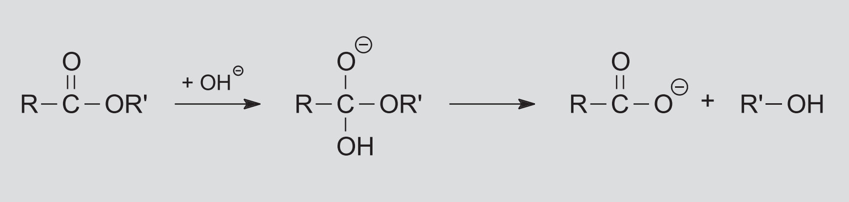


Fig. 3.3.6
Chemical degradation of polyesters by alkaline saponification

Homolytic cleavage of chemical bonds initiated by ultraviolet rays under the influence of atmospheric oxygen can create consecutive products with shorter chains on the PVC. On the other hand, new crosslinks occur via the intermediate stage of peroxides. Crosslinking and simultaneous chain reduction are hence the cause of embrittlement and a weakening of internal resistance.

Formation of radicals is the starting point in the ageing process and it ultimately leads to the formation of hydrochloric acid and CO_2.

Degradation of ether groups in polyethers or epoxy resins takes place via the intermediate stage of peroxides, which then suffer cleavage in the molecular chains on account of ultraviolet light.

Although under extreme exposure to ultraviolet light even saturated polyesters known to be stable in light are attacked to a much lesser extent but in a similar manner.

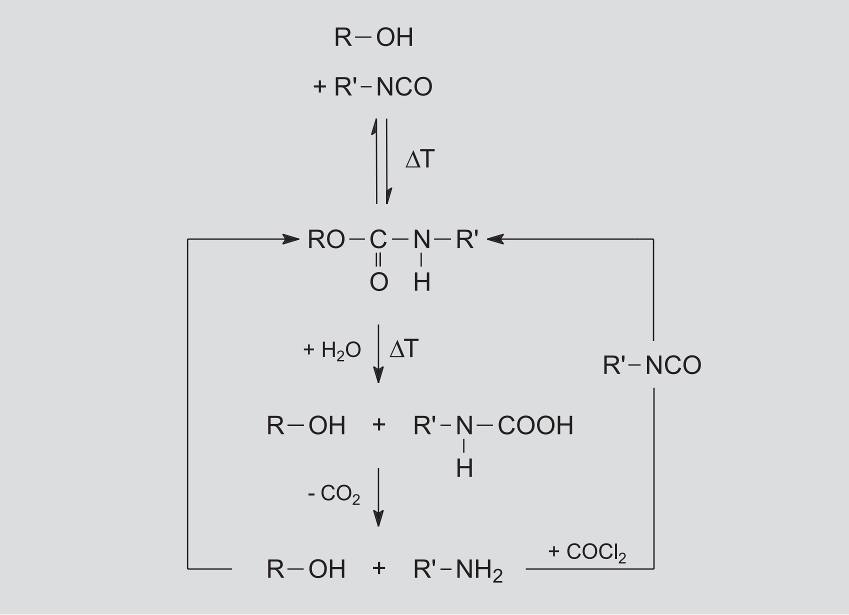


Fig. 3.3.7
Thermal hydrolysis of pulyurethanes

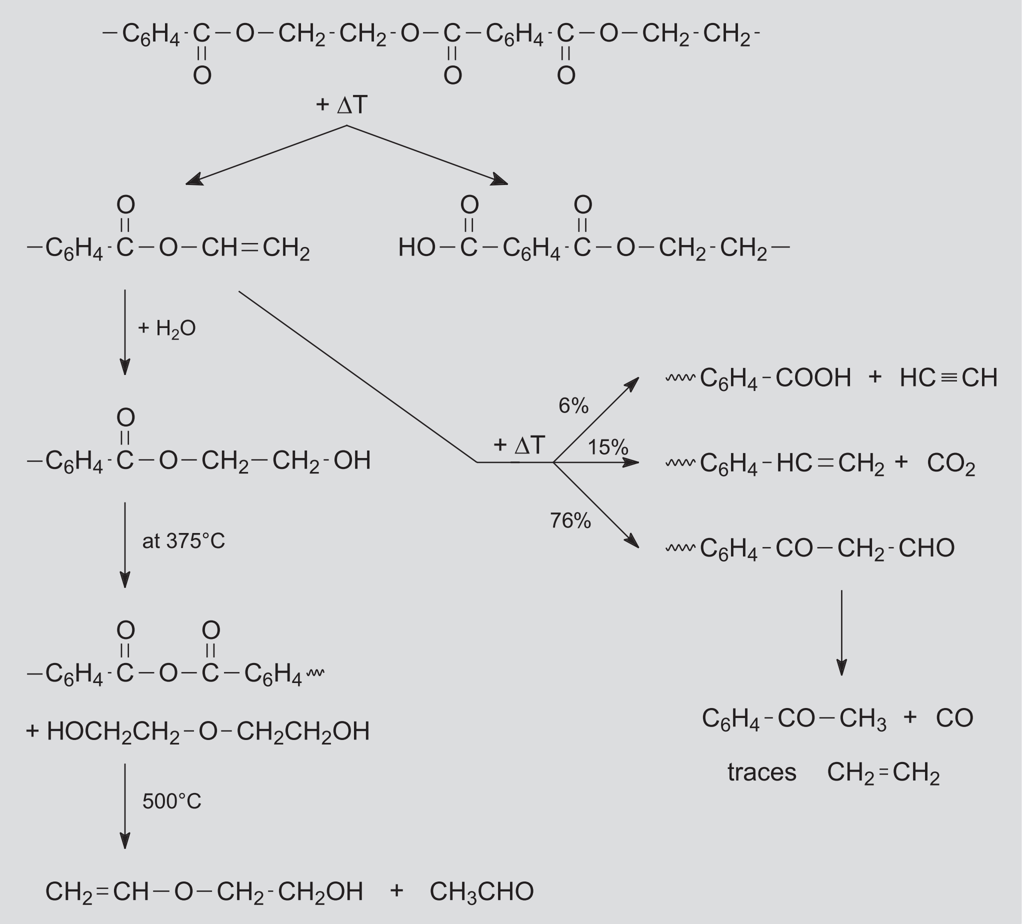


Fig. 3.3.8
Thermolysis of polyesters

Hydroperoxide formation, chain cleavage and partially oxidative degradation through to CO_2 can be detected if the intensity and duration of radiation are sufficient.

Apart from radiation-induced degradation reactions the atmospheric influences also include liquid chemical degradation processes in the form of saponification reactions. Polyesters and alkyd resins are examples of film forming agents which, when subjected to prolonged intensive interaction with acid or alkaline electrolytes, may react by chain degradation depending on the type and intensity of the resulting acid.

Apart from degradation of the macromolecules by photochemical, oxidative or hydrolytic cleavages thermal influences also have to be taken into account if there is such exposure. These frequently lead to consecutive reactions and therefore make ageing processes extremely complex. Consequently, by increasing temperature it is possible to detect not only the expected accelerations of esterification and oxidation reactions but also direct cleavage due to depolymerization and statistically distributed opening of the base chain.

One example of a distinct thermal cleavage, which is desirable in this case, accompanied by consecutive reactions and subsequent reprocessing, is the thermolysis of polyurethanes.

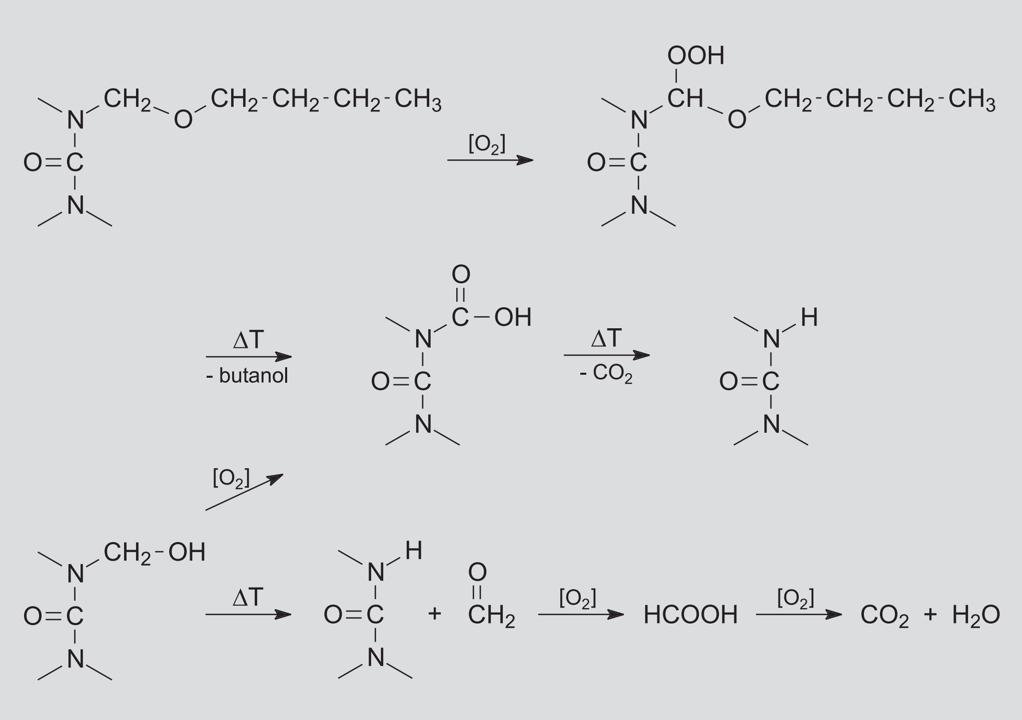


Fig. 3.3.9
Thermal degradation of urea resins

The situation with polycondensates is more complex. Normal film forming agents such as alkyd resins, amino resins, phenolic resins and polyamides lead to a whole host of consecutive products. The most important degradation reactions will be illustrated by taking a linear saturated polyester and a urea resin as an example.

In the case of polyester resins the chain is reduced and double bonds occur which continue to react in a variety of ways.

In the case of urea resins free carbamic acid derivatives occur on the hydroxymethylene group, which, after decarboxylation, are transformed into urea groups via peroxide formation.

Thermal degradation of polymers is fundamentally simpler. The next figures show the most important ageing reactions of thermoplastic acrylic resins with ultraviolet light involvement.

Side chains are cleaved homolytically by the ultraviolet light of the sun. Various radicals occur on account of the opening of C–C and C–O bonds, which stabilise owing to hydrogen abstraction or combination with other radicals. The connecting of new bonds involves crosslinking. Embrittlement of the coating is the result.

The ultraviolet rays are also capable of cleaving base chains. Taking acrylic resins containing methacrylic acid esters as an example it is demonstrated that radicals cleaved from the side chains cause a break in the base chain, forming double bonds and simultaneously transferring hydrogen.

A role is also played by thermal degradation in the ageing of film forming agents. Polymethacrylic acid esters split up on side and base chains, influencing each other, as

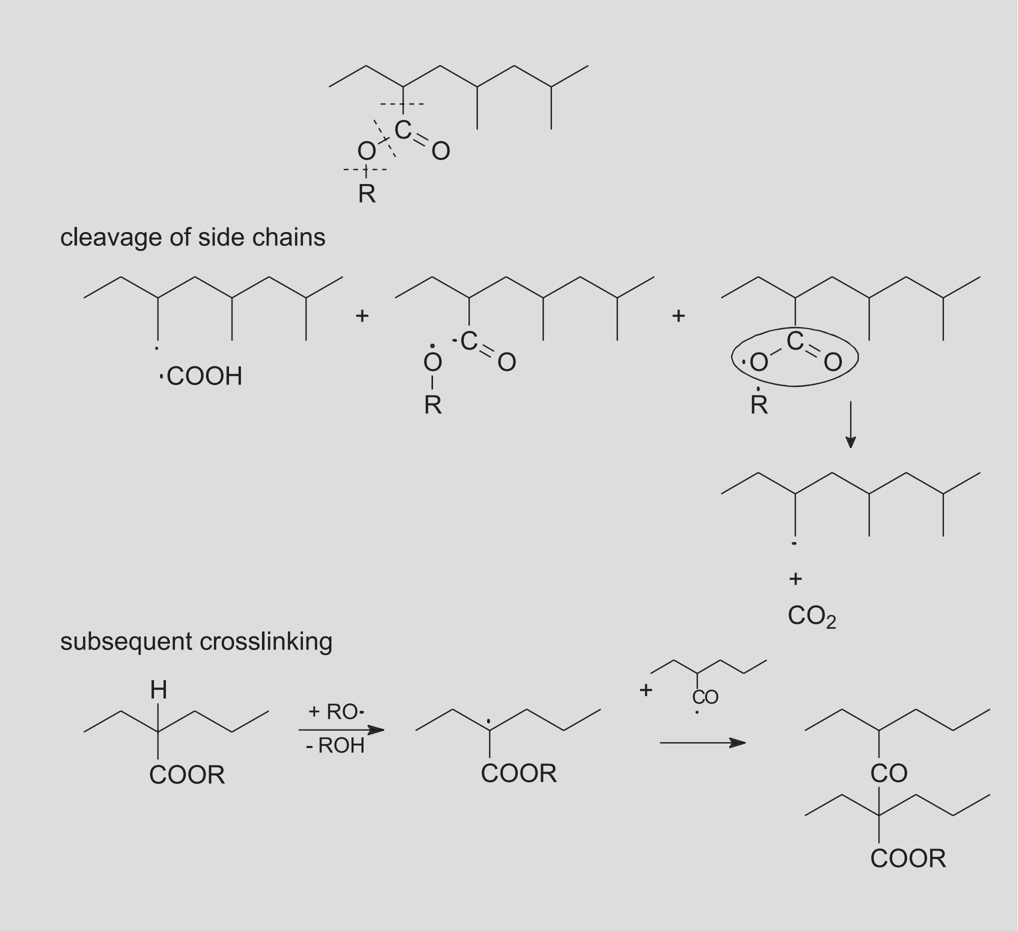


Fig. 3.3.10
UV induced crosslinking of polyacrylic resins

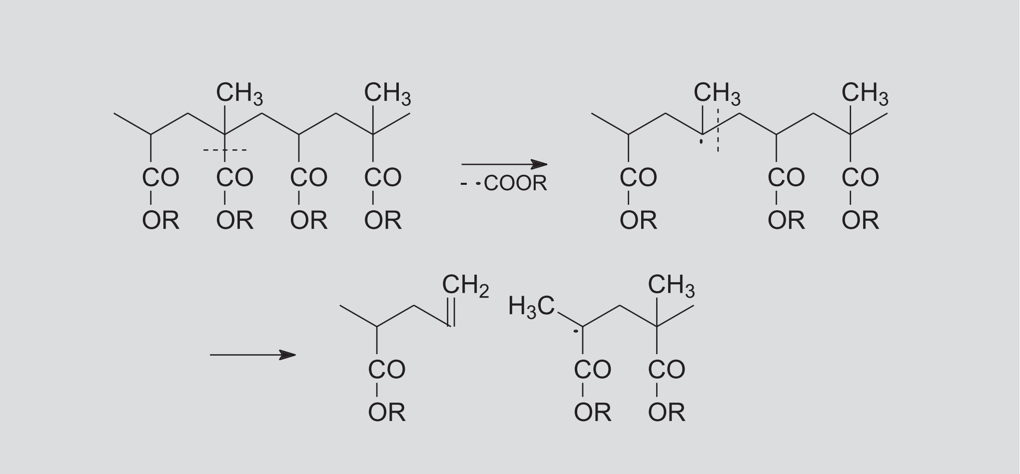


Fig. 3.3.11
UV induced cleavage of base chains of acrylic resins

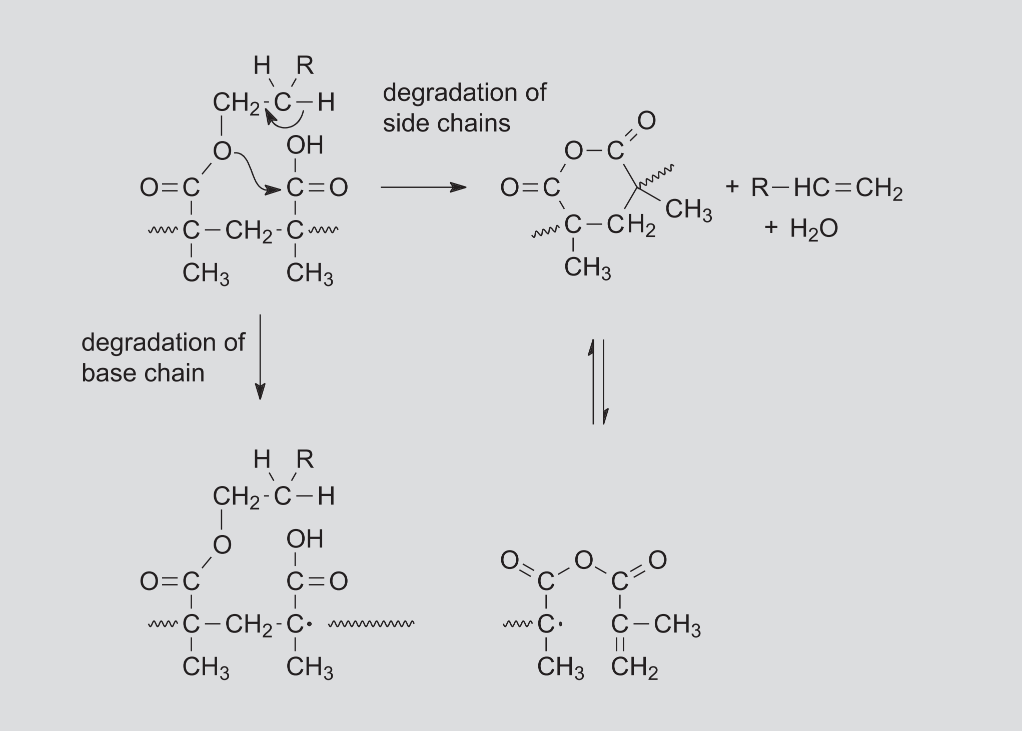


Fig. 3.3.12
Thermal degradation of polymethacrylic resins

is illustrated in figure 3.3.12. It also involves a reduction in molecular weight and hence the internal resistance of the coating [3.4.55].

The paint-damaging influences are not restricted to the degradation and embrittlement of polymeric film forming agents. The pigments, extenders and additives are also involved in the ageing process. On account of ultraviolet light or chemical influence color changes can occur, and even a pigment-induced degradation of the polymer matrix [3.4.56]. Comprehensive investigations on multilayer coatings have the target to help early indicating the long time durability of top coats [3.4.57]. New methods like the atomic force microscopy (AFM) will help further for deeper understandings [3.4.58].

3.3.2 Ageing Tests

The described ageing processes of coatings lead to two different types of damage. The first type comprises color shifts, reduced gloss, chalking, i.e. surface changes which are detrimental to visual attractiveness. The second type comprises reductions in protection due to blistering and cracking or complete delamination with subsequent damage to the substrate.

The first category of property changes is normally covered in testing by determining the weatherproofness and lightproofness as well as lightfastness whilst the second category is dealt with by special tests for the protective function under the influence of damaging agents such as salts, alkalis, acids and natural substances such as tree resin or bird excrements. Many tests combine the two types of stress.

3.3.2.1 *Test Methods for Surface Durability*

Weather resistance

It has already been pointed out that weather is determined by sunlight, atmospheric oxygen, humidity, changes in moisture and temperature as well as all the natural and anthropogenic atmospheric features. These influencing factors exert various influences on coatings depending on the geographic location. Temporary sunshine at the coast in conjunction with salt spray has a different impact on a coating from extreme, long-lasting exposure to light in the desert with substantial changes in temperature. The conditions in an industrial atmosphere are virtually incomparable with those in the mountains or in the tropics. There can be no standard test for simulating all variables

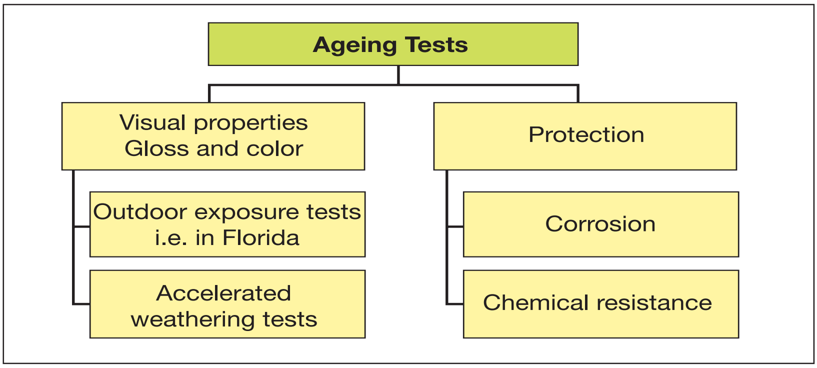


Fig. 3.3.13
Classification of durability tests

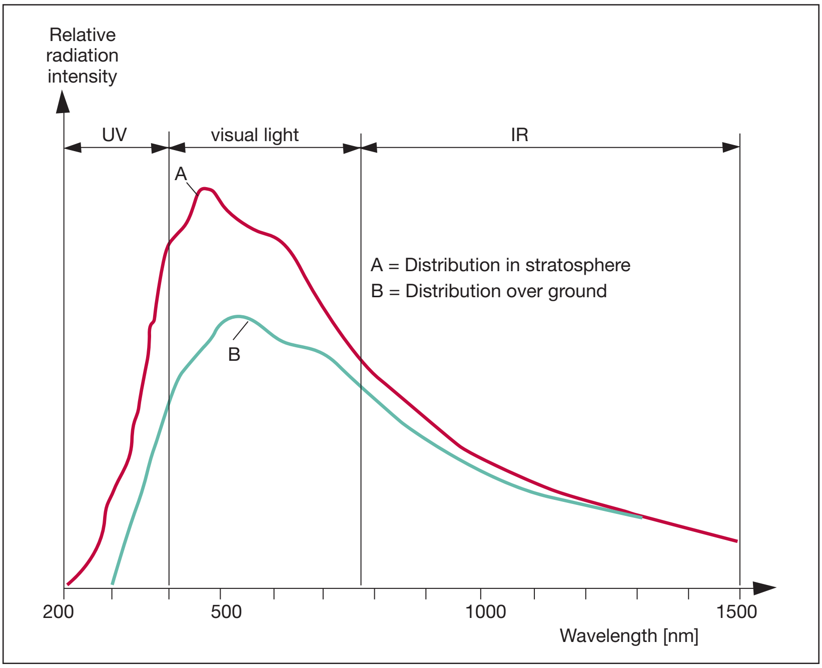


Fig. 3.3.14
Difference in the spectrum of light before and after passing the atmosphere

under the influence of natural ambient parameters as natural weathering. Either different tests have to be performed in different climatic zones or artificial climatic conditions must be created in which all the influences can be simulated. The former tests are known as natural weathering tests whilst the latter are known as accelerated weathering tests. So if one wishes to make forecasts about the long term behaviour of coatings based on testing, two requirements have to be met first:

1. There must be highly accurate knowledge of the conditions in the individual climatic zones.
2. For an informative quality inspection the test must be measurable and proportionable in order to then correlate the test result with the change in quality under practical stress conditions in an absolutely reliable manner.

Natural weathering tests nevertheless play an important role in testing the long term resistance of many coatings. One must bear in mind that the weather is a factor which is subject to considerable fluctuations depending on time and place. Solar radiation is particularly sensitive For the paint and raw material manufacturer the intensity and distribution of radiation are therefore important starting points when forecasting the ageing behaviour of coatings.

The sun with a surface temperature of 5,900 K emits a continuous spectrum of electromagnetic waves from 200 nm in the short-wave ultraviolet range to several centimetres in the infrared range (A). When passing through the earth's atmosphere components in the ultraviolet and infrared ranges are removed from the radiation selectively by ozone and water vapour (see figure 3.3.14). The spectrum particularly loses radiation up to 300 nm in the short-wave range on account of the influence exerted by the ozone belt. Selective weakening of radiation in the longer-wave range is caused by the excitation of molecular vibrations. In addition to water vapour, atmospheric oxygen and, to a lesser extent, carbon dioxide also play a role. At the same time one can also observe declines in intensity over the entire spectrum on account of the scatter and absorption of

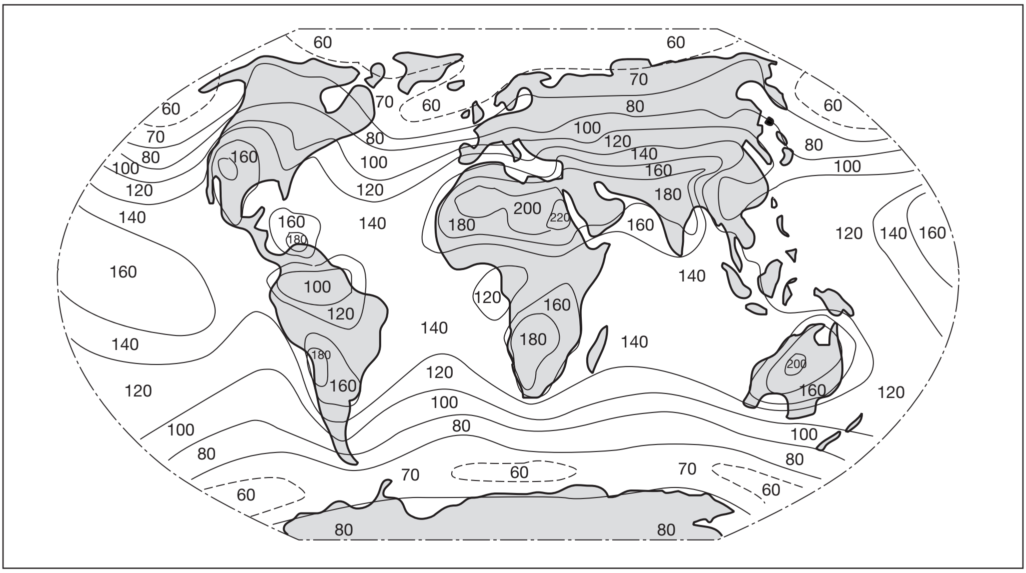


Fig. 3.3.15
Map of the world and lines of same light intensity in 1000 Langley

atmospheric aerosols such as smoke and dust particles. This phenomenon, which is known as *Rayleigh* scatter and *Mie* scatter, ultimately means that the remaining radiation intensity, naturally depending on time and place, has lost approximately 50% of the energy originally being emitted (B), 0.7 kW/m^2 on average.

Owing to the differences in radiation distribution due to time and place is may be necessary in individual instances to conduct accurate measurements of radiation distribution in order to be able to interpret weathering results. Pyrheliometers are suitable devices for this. However, they only record the total radiation and are therefore unable to provide information on radiation distribution. The principle of measurement is the different warming of white and black coated test panels under the influence of sunlight. Both panels are provided with thermocouples which record any difference in temperature depending on the intensity of solar radiation.

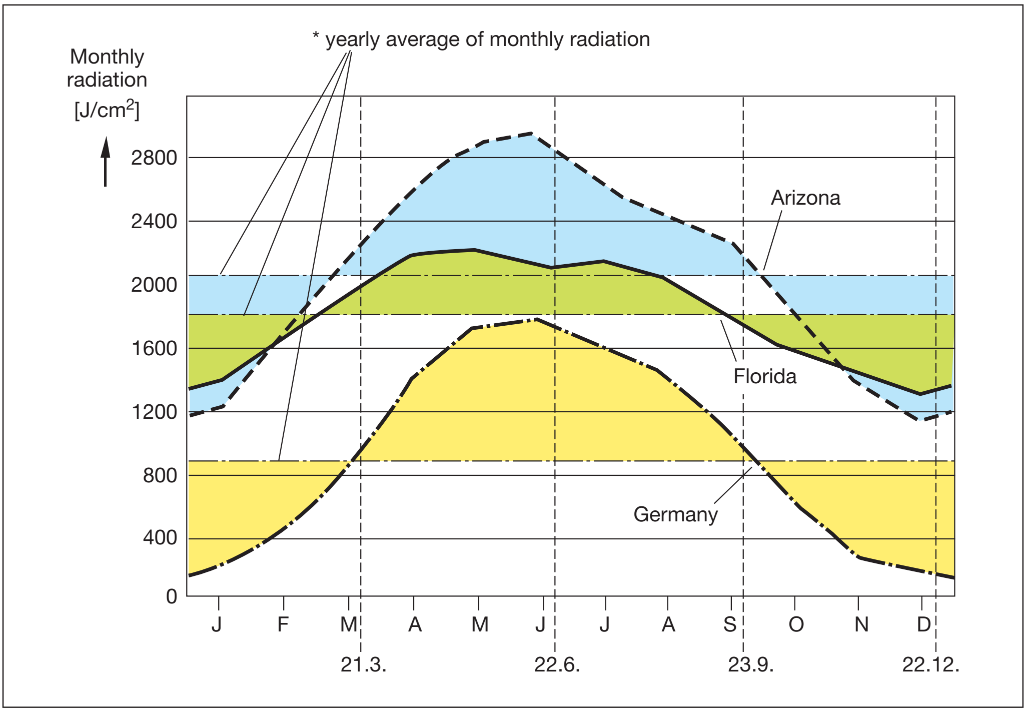


Fig. 3.3.16
Average monthly light intensity of different regions in J/cm^2

The total intensity measured on the ground with vertical solar radiation without clouds is, as already mentioned, 0.7 kW/m^2 or 0.07 W/cm^2. As a result the energy for a solar minute is 4.2 Ws/cm^2 or 4.2 J/cm^2. This measured variable has become established as a customary unit of measure for the area-related radiation energy in accordance with *Langley*.

The following figure provides information about the annual area-related global total radiation for different regions of the world, stated in *Langley*.

The highest values of over 200,000 *Langley* are only recorded in desert regions. Nevertheless, weathering tests are not only conducted in such regions. The reason for this is that the ageing of coatings is not only of a photochemical nature. Degradation

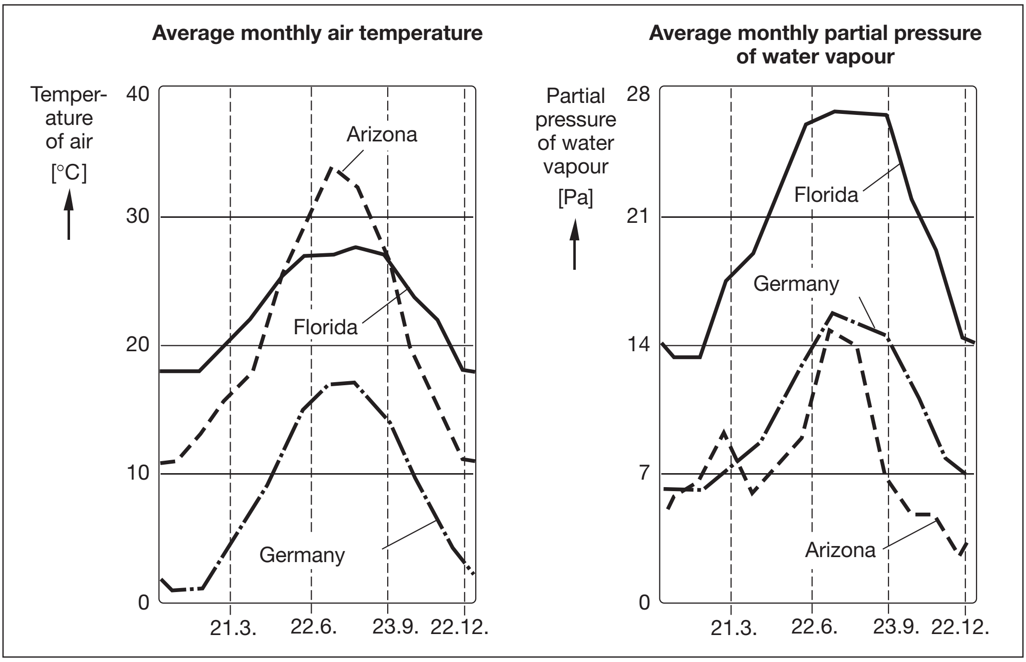


Fig. 3.3.17
Local and timely variation of air temperature and relative humidity in Florida, Arizona and Germany

processes are also accelerated by moisture and heat. Consequently it is understandable that regions with a high level of solar radiation such as North Africa, Arizona or Australia do not rank among the most aggressive regions in the world for coatings because of the lack of moisture. Regions with high humidity are far more damaging to coatings. The simultaneous action of radiation, moisture and temperature changes leads to chemical and physical ageing processes in the coating which, depending on the chemical structure of the film forming agent and the pigmentation, cause more or less rapid changes in the visual and physical/technological properties. Florida and Arizona are therefore reliable regions for conducting natural weathering tests. Especially Florida is characterized by a high level of moisture in comparison with Arizona and Germany. This is easily seen from the partial pressures of natural water vapour as illustrated in figure 3.3.17.

In order to conduct tests and evaluate the test results broad guidelines have been laid down in DIN 53166 and ISO 2810. According to these the term ‘long term outdoor exposure’ includes all changes to the coatings which are caused by the interaction of all the physical and chemical factors contained in the weather. Testing for long term outdoor exposure by natural weathering therefore means stress with exposure to light, water and temperature as well as all types of industrial exhaust emissions and atmospheric features such as salt, soot, etc. The test covers the entire change in the coating.

The paint systems to be tested in **Florida** are laid out at the weathering stations either on rigid racks with a consistent exposure angle or on swivelling sample supports. The exposure angle can thus be adjusted accordingly for the position of the sun. On account of the latitude 25° N and the hence high position of the sun the test panels are chiefly exposed to the weather at an angle of 5°. However, the slight angle of such a rack prevents particles of dirt from being washed off by natural rainfall. Therefore the test panels also have to be cleaned at regular intervals. The 5° southern exposure is particularly specified by vehicle manufacturers.

Since solar radiation is more intense than in Germany, humidity is higher, the quantities of precipitation are relatively large and the average temperature in Florida is much higher, the ageing processes start after a much shorter time and take place more quickly than in the Central European climate. Films reach peak temperatures of 60 °C depending on the color. The testing time up to about the same degree of damage is approx. 50% of Germany.

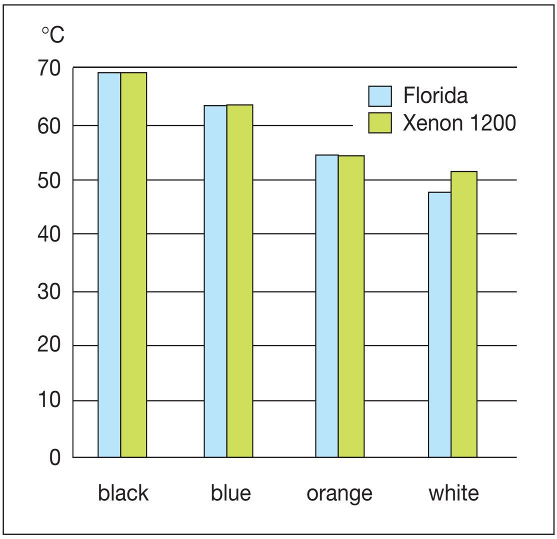


Fig. 3.3.18
Peak temperatures of test panels in Florida and their relation to color at 5° angle of exposure

For more intensive stress the test panels are exposed to the weather in “black boxes”. They are placed on a sheet metal box painted black. The only opening in the top is covered with test panels. The black boxes heated up by solar radiation warm the test panels in addition and speed up ageing at a faster rate than on exposed open racks.

The “heated black box” (HBB) is also provided with a heater, a thermostat and a fan. As a result a uniform temperature of 50 °C – 55 °C is achieved in the wall of the box, even if solar radiation is obscured by clouds.

Weathering stations have also been set up in the desert climate of **Arizona**. Regardless of the lack of moisture special devices have been developed called EMMA (Equatorial Mount with Mirrors for Acceleration) which increase the already high radiation intensity again by a factor of 8 using aluminium mirrors. The sample supports are always pointed towards the sun with the aid of a motors and appropriate sensors.

Fig. 3.3.19
Weather station in Florida (top) and blackbox HBB

Sample warming is limited by fan cooling. EMMA devices are only suitable for testing the lightfastness of pigments on account of the lack of moisture. Weak pigments become

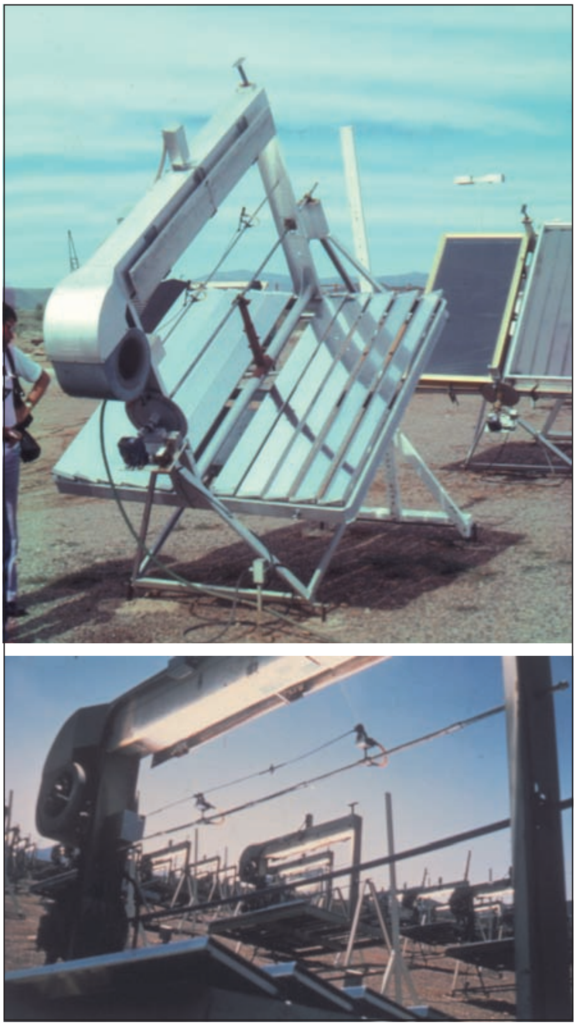


Fig. 3.3.20
EMMAQUA equipment for accelerated weather tests in Arizona

apparent after only a few months in the form of color changes and changes in color intensity.

Owing to the high exposure to radiation there have been plenty of experiments to convert these devices so that they can also be used for long term outdoor exposure tests. The test devices known by the name of EMMAQUA were therefore equipped with spraying apparatus for moistening the test panels artificially.

Since the test panels in these devices remain hot despite the cooling system, the water sprayed onto the panels evaporates very quickly. The influence of water necessary for film degradation is less compared with Florida.

Weathering tests are also performed **in the Central European region**. Since the sun is in a different position, the test panels are arranged at an angle of 45° facing south. The reduced testing time in relation to the service life of the coating is only marginal.

Owing to the still relatively longer exposure time of several years in climatically extreme regions one is endeavouring to shorten the testing time even further by conducting **accelerated weathering tests** using artificial light sources with a high light intensity, large temperature fluctuations and shorter intervals between moistening and drying.

By means of suitable sources of light such as carbon arc lamps and xenon lamps, water spraying as artificial rain and adjustment to a specified black panel temperature used for verification, natural conditions can be simulated to a large extent. Black panel temperature is the temperature of a black reference panel which adjusts under the accelerated weathering conditions in the tester.

The spectral distribution of the radiation sources is of fundamental importance as far as the usability of test results is concerned. For every radiation source there are sets of filters which, on the one hand, reproduce the intensity distribution of sunlight and, on the other essentially eliminate the short-wave ultraviolet components of light sources which are not present in the solar spectrum.

The most well-known devices and ones which are used most frequently in the paint and coatings industry are Weather-o-meters (WOM) manufactured by Atlas and the Xenon tester 1200 made by Original Hanau. In principle the method of operation of these devices is the same. There is a lamp fitted to the centre of an enclosed test chamber. At a fixed distance from it there is a sample drum rotating through 360° once a minute. Between the radiation source and the sample drum there are one or more spraying units, with which the test samples are sprayed with distilled water at certain intervals. Radiation sources in the Weather-o-meter devices can be carbon arc lamps, also referred to as sunshine lamps, or xenon high-pressure lamps. The carbon arc lamps are surrounded by a filter frame which serves as an air duct and as a support for 8 filter glasses. Since during continuous operation the permeability of the filters to light declines quickly below the wavelength of 350 nm, the filter glasses are cleaned once a day and replaced every 2,000 operating hours. The xenon high-pressure lamps are generally surrounded by borosilicate (Pyrex) filters. The highly aggressive ultraviolet radiation below 290 nm is filtered out because it is not present in sunlight close to the earth. By using different filters and combinations of filters it is thus possible to alter the spectral distribution of energy in the artificial radiation and thus adapt to the test conditions required.

The Xenon tester 1200 is fitted with 3 xenon high-pressure lamps. To ensure that the radiation energy applied to the test samples is as uniform as possible, each lamp is replaced in turn every 500 hours. In the first row of filters the xenon lamps are surrounded by a common quartz cylinder. That is followed by Pyrex filters, consisting of three 1/3 dishes. The dissipation of excessive heat from the Weather-o-meter is achieved by air and water cooling. The test chamber is also provided with a test drum, which can be run synchronously with samples on one side only or asynchronously with samples on both sides, whereby the sample supports are then rotated when they have passed through 180°.

Since the presence of water plays an important role for accelerated degradation, the test panels are sprayed with double-distilled water in certain cycles with all types of equipment. Minute impurities in the water due to silicates would cover the test panels

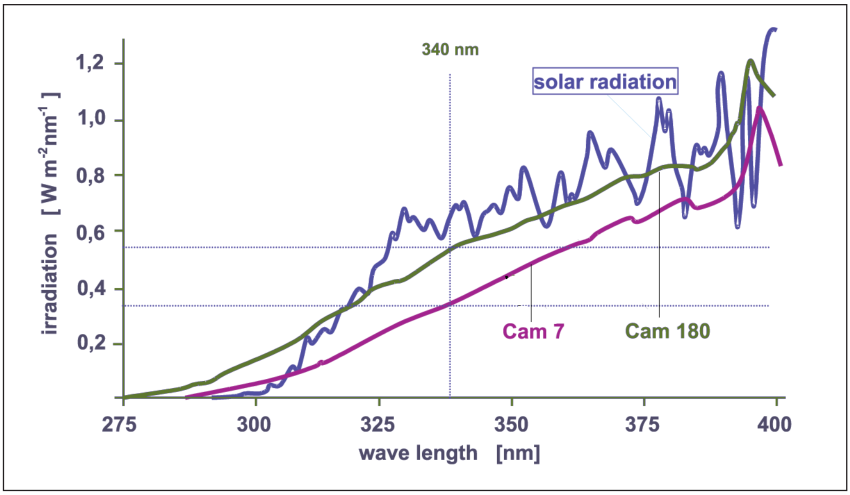


Fig. 3.3.21
Spectral distribution of emitted light in weather-o-meter test equipment

with a UV-absorbent protective layer in the course of time and thus impair the damaging effect of radiation in an uncontrolled manner.

Cam 180	Cam 7
• Quartz- and borosilicate filters • 2 h exposure • 1 h darkness with artificial rain	• Pyrex filters • 2 h exposure including 18 min artificial rain
recommended by VDA	
• examination on cracking	• examination of weather resistance (durability)

Fig. 3.3.22
Test cycles and test chamber of weather-o-meter equipment

The proven and therefore now customary test cycles of the Weather-o-meter are summarized in figure 3.3.22.

Under the names of UV-con and Q-Panel the market offers further useful weathering devices which are also inexpensive on account of their design. They were developed using new lamps and are based on the fact that it is ultimately only the short-wave ultraviolet component which is responsible for the light-induced ageing processes. Their use is preferred wherever intense solar radiation has to be simulated, i.e. North America and Asia.

Figure 3.3.23 shows a cross section through the UV-con device. The fixed samples are exposed to radiation from light emitted by eight fluorescent tubes. The manufacturers offer lamps with varying radiation distribution.

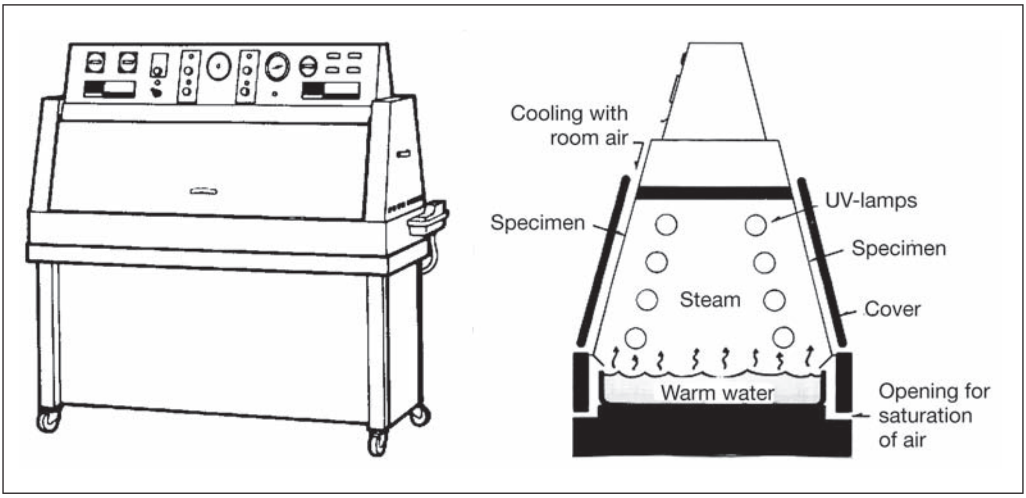


Fig. 3.3.23
Schemes of total view and of test room of UV-con equipment

The UV-con A lamp starts at 300 nm and is approximately equivalent to the short-wave component of sunlight whilst the UV-con B lamp at 280 nm emits a much more energy-rich radiation.

As opposed to the spraying units in the Atlas and Hanau equipment the moistening necessary to speed up ageing is performed not by spraying but by evaporation and subsequent condensation on the sample plates, which are cooler than the sample chamber. This prevents UV-absorbent silicates from being deposited. The entire test cycle takes 12 hours and includes 8 hours of exposure to radiation at 70 °C, followed by a 4-hour condensation phase at 50 °C also exposed to radiation. Assessment of the test result is normally conducted after stressing time of 2,000 hours.

The experience gained so far with the UV-con units indicates that the light resistance of plain-colored coatings does not correlate very well with the results of long term weathering in Florida but the cracking tendency of 2-layer metallic coatings correlates very well.

The assessment and evaluation of weathering results assumes an accurate test method with all items agreed. Depending on the field of application of the coating materials the test samples are treated differently for evaluation purposes. Coatings for façade elements are assessed visually without any further sample preparation. Automotive coatings, on the other hand, are washed in some cases or even polished and assessed at the points treated in that way. Depending on the problem at hand the test panels are examined for gloss retention, chalking and color resistance. Other changes in the coatings such as cracking and blistering, surface and edge corrosion, adhesive strength and flaking are normally assessed visually in addition. All the data is recorded in chronological sequence so that it is also possible to make statements about the dynamism of the degradation reactions.

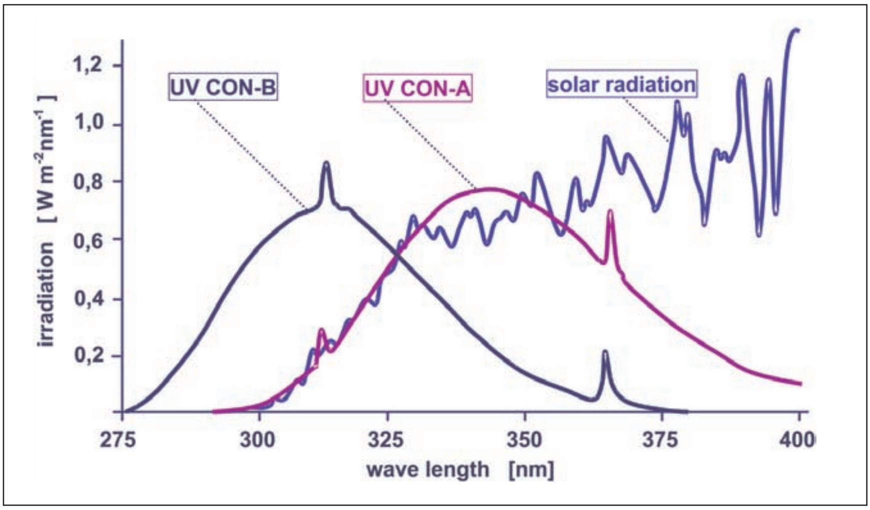


Fig. 3.3.24
Spectra of UV-con A and UV-con B lamps compared to sun light

When developing accelerated weathering tests one must bear in mind that although unrealistic conditions for the parameters are able to achieve shorter testing times, the reliability for a forecast of the behaviour in practice is considerably impaired.

Experience available to date resulting from the comparison of Florida weathering with the accelerated tests indicates an acceleration factor of approx. 5 – 6. Consequently the testing time of accelerated weathering tests for automotive coatings is approx. four to six months at minimum.

3.3.2.2 *Corrosion Protection Tests*

Functional tests, i.e. the special tests for certain protection values of the coating, can be based on natural weathering and accelerated tests, as was the case with weathering tests. In this context changes due to ageing are regarded not so much as relevant to attractiveness but rather related to function.

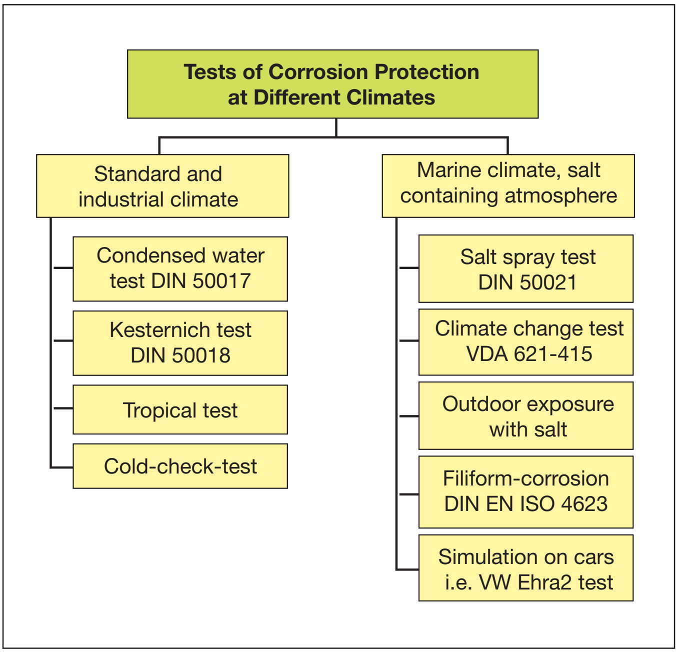


Fig. 3.3.25
Classification of corrosion protection test methods

In effect this means considering the resistance of the coating to temperature and moisture as well as changes in temperature and moisture in relation to a wide variety of salts and chemicals in the form of gases and liquids. It is primarily damage in the form of blisters and delamination which are assessed, but also consequential damage resulting from damage to the coatings.

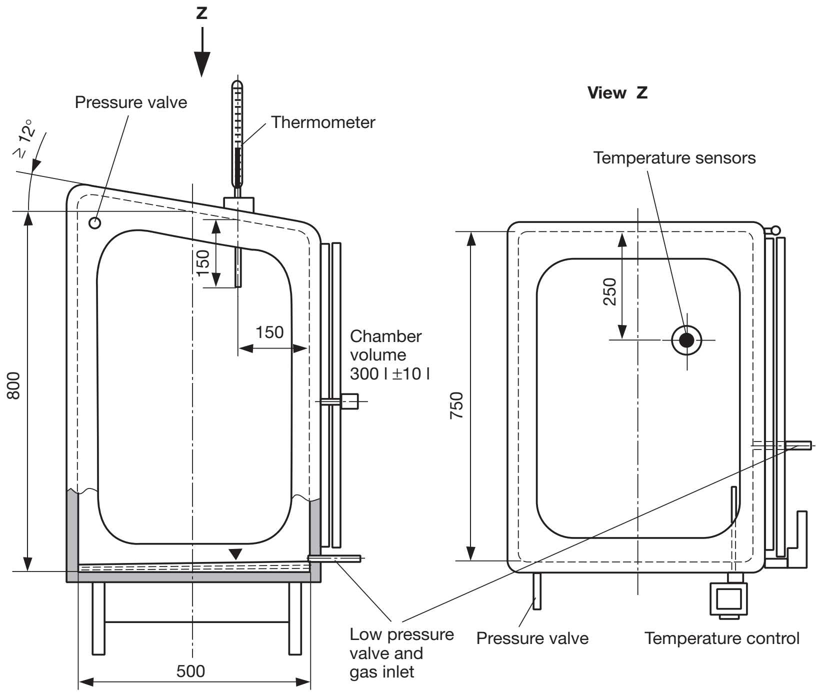
One of the chief economic tasks of coatings on metal substrates is to protect against corrosion. Despite enormous efforts, according to estimates by experts 3% – 5% of the gross national product of the industrialized nations is lost every year on account of corrosion. Protection against corrosion is therefore an important economic goal.

The term corrosion is used below as per DIN EN ISO 12944-1 to cover all the changes in the metal coated object caused by the influence of oxygen, water and catalytic electrolytes. From a chemical point of view it concerns the emission of electrons from the metal materials involving water. The result is the formation of an insoluble metal oxide layer (see chapter 4.1).

The rust formed on iron is porous so it is not capable of decelerating the progress of metal destruction. Effective protection against corrosion is therefore necessary. This can be achieved with organic coatings, for example, frequently in conjunction with corrosion-inhibiting pigments.

Standard reference atmosphere and industrial atmosphere

To simulate the specific conditions in tropical regions, but also in moist rooms such as indoor swimming baths, cold stores or kitchens the tests are characterized by the fact that high humidity in conjunction with temperature and/or changes in temperature either ensure consistently high or alternating water vapour concentration in the so-called **condensed water alternating climate tests** and **condensed water constant climate tests**. In all cases the samples in the test apparatuses are exposed to the test conditions defined in detail in the standards.



Type	Idiom	Duration of cycle	Duration of phases	Temperature in chamber °C	relative humidity %
		Hours			
Condensed water changed climate	SFW	24	8 including preheating	40±3°	100
			16 including cooling (chamber open)	room temperature [2]	unter 75
	STW	24 [1]	8 including preheating	40±3°	100
			16 including cooling	room temperature [2]	100
Condensed water constant climate	SK	–	from preheating until finished test	40±3°	100

[1] Standard cycle time, see 2.2

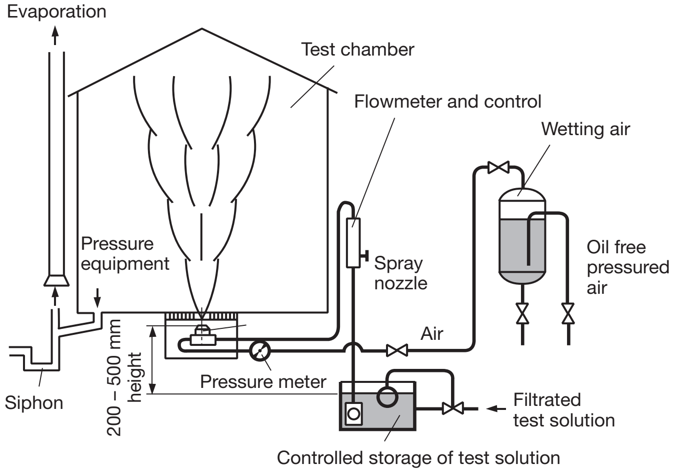
[2] Definition of room temperature : see DIN 50 014

Fig. 3.3.26
Test chamber and test conditions of condensed water tests according to DIN 50017

DIN 50017 contains all the relevant information required for conducting the tests. The standard distinguishes between three versions of the test:

- condensed water, moisture (and temperature) alternating climate (KFW)
- condensed water, temperature alternating climate (KTW)
- condensed water constant climate (KK)

One version of the condensed water tests which is now rarely specified is the alternating 'KFW' test using SO_2 atmosphere. Depending on agreement, either 0.2 litre or 2 litres of SO_2 gas are admitted to the 300 litre test chamber in order to simulate industrial atmosphere conditions. This test, which is standardized under DIN 50 018 and known by the name of the "*Kesternich* test" is unrealistic on account of the large spread of results and much too high a concentration of SO_2 compared with the stress in practice so it is only used for very specific test objectives. The individual test conditions are all listed in figure 3.3.25. The test is ended when the testing time agreed with the customer has elapsed or when visible changes occur such as disappearance of gloss, blistering or corrosion.



	Type Control	Salt spray test SS DIN 50 021
Spray solution	Natriumchloride in g/l	50±10
	other additions	no
collected solution	Natriumchloride in g/l	50±10
	pH-value	6,5 until 7,2 at 25 °C ±2°
	Temperature in test chamber	35 °C ±2°

Fig. 3.3.27
Test conditions and scheme of a test chamber for salt spray tests according to DIN 50021, ASTM B 117 and ISO 9227

Apart from the tests standardized in DIN standards there are numerous special-purpose tests which are agreed between customers and suppliers. The simulation of high but also substantially fluctuating temperatures in the tropics and the appropriately low but also substantially fluctuating temperatures in arctic regions should also be mentioned: the **tropics test** and the **cold check test**.

Marine climate

The most widespread corrosion protection test is the salt spray test as per DIN 50 021, ASTM B117 or ISO 9227. It is designed to simulate the corrosive atmosphere of coastal regions and the effects of road salt. At a test chamber temperature of 35°C a 5% sodium chloride solution is continuously sprayed with the aid of pre-warmed, humidified compressed air. Before exposure the test panels are damaged with a scorer parallel to the narrow edge down to the substrate. Completion of testing is followed by assessment of the width of creepback originating from the score as well as corrosion at the edges and on the surface.

The test is conducted in test chambers with capacities of 300 litres to several cubic metres, in which it is possible to test entire vehicle bodies (see figure 3.3.27).

Preparation of the test panels and evaluation of the corrosion pattern are conducted in accordance with DIN EN ISO 7253. There are images of standard damage to help make evaluation more objective. The pictures shown in DIN standards are regarded as a basis for a scale of grades from 0 to 5. By comparing the sample with the standards it is possible to establish the degree of damage. If blisters form, according to DIN 53 209 the number m and size g are evaluated and if extensive corrosion occurs it is the corroded area as per DIN 53 210 or ISO 4628-1. The letter Ri stands for the degree of corrosion internationally and in conjunction with a grade from 0 to 5 it indicates the degree of extensive corrosion. Despite widespread use of the salt spray test special care must be taken when applying the test results to long tern

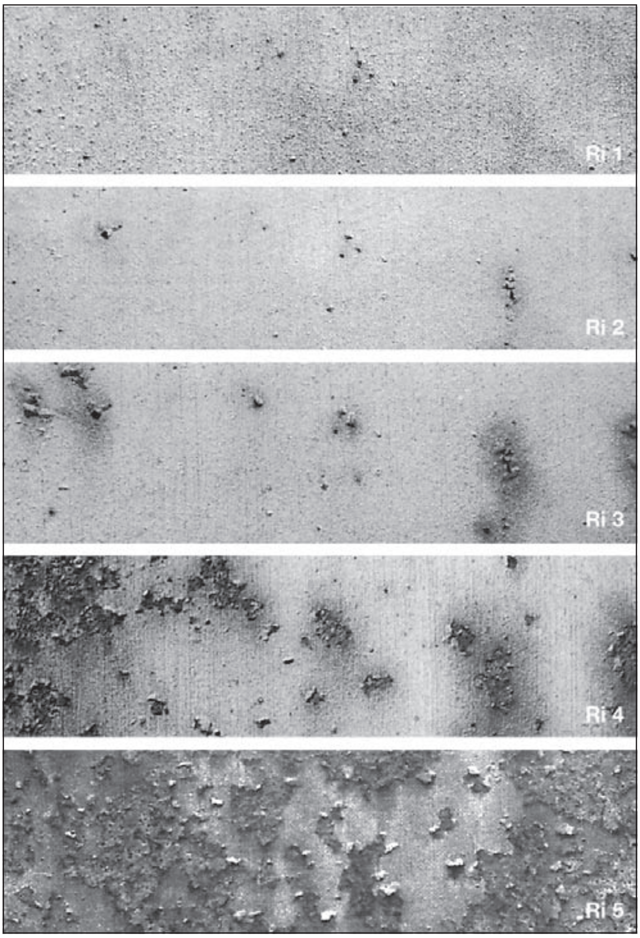


Fig. 3.3.28
Standards for objective evaluation of surface corrosion

corrosion protection. In the literature there are more and more critical voices which compare the accuracy of the salt spray test with the speculations of an experienced shepherd concerning development of the weather. Even the information content of comparative tests with known corrosion protection systems is questioned. Such opinions are confirmed when analyzing the corrosion pattern created by the salt spray test. Despite the loss of all protection, areas of serious delamination often manifest no damage due to corrosion as opposed to corrosion by the weather. Especially on galvanized steel it is impossible to make any reliable statements about behaviour under practical conditions [3.4.59]

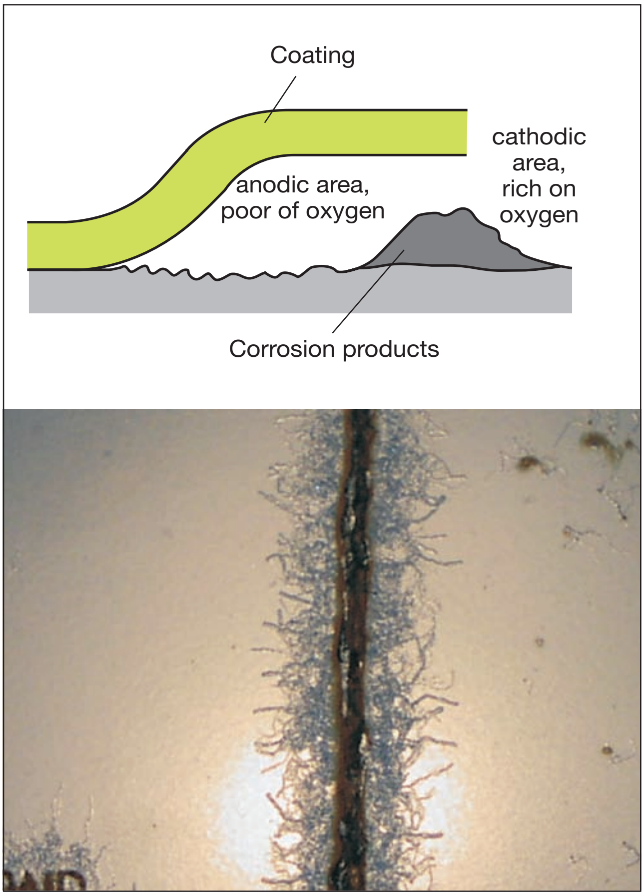


Fig. 3.3.29
Mechanism and example of filiform corrosion

One example of a type of corrosion which cannot be simulated by the salt spray test is filiform corrosion, which is found not so much in the European climate but more frequently in tropical regions. Originating in mechanical damage to the coating this type of corrosion takes the form of thread-shaped creepback. Since this form of corrosion cannot be simulated in a salt spray test, different tests have been developed specially for filiform corrosion, e.g. DIN EN ISO 4623. The procedure consists of immersing the panels prepared for the salt spray test in 0.1% sodium chloride solution for 30 – 60 s, drying them and then exposing them to 40 °C and 80% relative humidity in a climatic test cabinet. Any channel-shaped corrosion creepback forming is caused by the formation of so-called oxygen cells. On account of the higher O_2 concentration at the exit of the resulting channels cathodic and anodic areas develop together with the creepback areas which have less O_2. For aluminium one applies the DIN EN 3665 standard, which uses a different type of scoring and evaluation from that of the method described.

Owing to the uncertain reliability of the salt spray test efforts have been undertaken to develop better corrosion protection tests. The need for absolutely reliable forecasts of long term corrosion protection was quite urgent, especially in the automotive industry. Various tests, usually combinations of test methods which were already known but, on their own, were not very informative, were checked for correlation with practical conditions [3.4.60, 3.4.61].

The **climate change test** described in VDA 621-415 [3.4.62] is of major importance because it is recognized by the automotive industry. This test is a combination of the salt spray atmospheric test and the condensed water atmospheric test. The corrosion media used are a 5% saline solution and deionized water alternating. A cycle lasts one week and consists of 24 hours of salt spray test, 96 hours of condensed water humidity

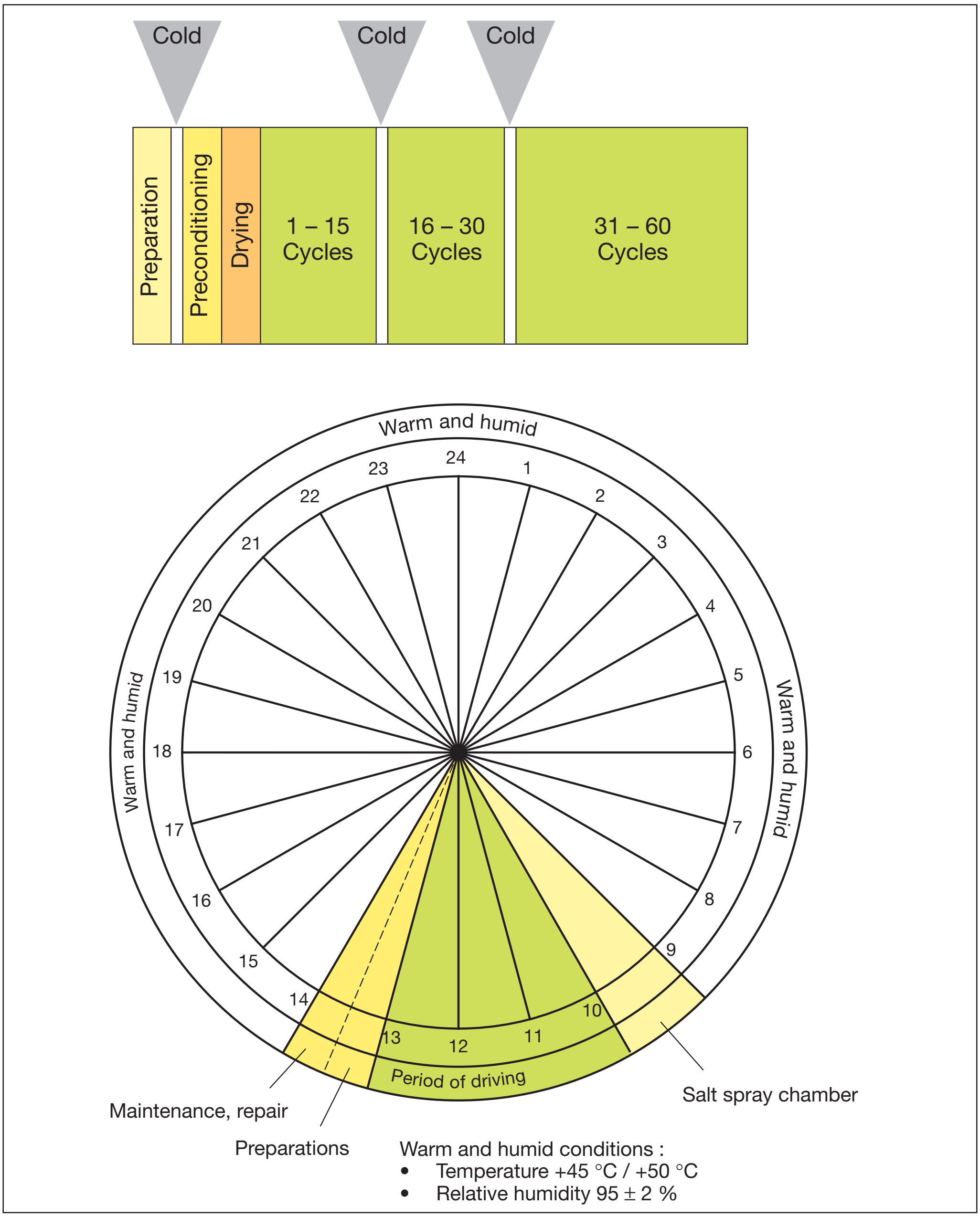


Fig. 3.3.30
Cycles of corrosion protection test on total cars according to VW Ehra2-test

alternating atmosphere (KFW) and 48 hours regeneration time at room temperature and a humidity of < 75%. The total testing time is 10 or 12 weeks and is roughly equivalent to natural weathering using artificial salt stress lasting 1 year (see below). As with the salt spray test as per DIN 50 021, ASTM B 117 and ISO 9227 the coated test panels are damaged with a scorer down to the bare metal before subjecting to stress.

Whilst with the pure salt spray test there is only corrosion creepback and hence a loss of adhesion, with the alternating atmospheric test corrosion products develop which are identical to corrosion pattern in reality. If the corrosion resistance of the coating is inferior, perforation occurs as observed in practice after a testing time of > 12 cycles, depending on the type and thickness of the metal substrate.

The **natural weathering with salt** already mentioned is also a method of accelerated testing for corrosion resistance. With this test the test panels, which are oriented southwards at angles of 5° and 45° to the horizontal, are usually positioned on sites in the paint-manufacturing industry or user industries and exposed to weathering over a period of 6 months or more. As opposed to normal weathering the test panels are sprayed with a 3% saline solution once a week in order to accelerate the corrosion process. In this test as well the test bodies are scored or damaged by firing steel chippings at them prior to exposure. Compared with normal weathering the rate of corrosion increases by a factor of 3 to 4.

Fig. 3.3.31
Weathering station in Münster, D

Despite a considerable improvement in correlation between the test result and corrosion pattern with the findings from practical stressing in the alternating atmosphere test vehicle manufacturers have developed more test methods, some of which are elaborate. Procedure consists of exposing entire cars according to fixed, detailed test cycles. Let us take a look at one example, the VW Ehra2 test (see figure 3.3.30):

Sample cars are selected from normal production. First of all they are cooled down to –35 °C in cold chambers and subjected to torsion by means of car jacks in accordance with mechanical stress due to driving. Any resulting cracks in the coating of the cavities would thus lead to weak points in the corrosion protection. For further preconditioning the test car is driven on road chippings and salty sludge road sections for 4 days. After cleaning and seven days of storage the corrosion test proper can begin. Over a total of 60 cycles with two interruptions for repeating the torsional stress in the cold chamber and subsequent salty sludge treatment the test cars are subjected to a damp heat chamber at 45 °C and 95% relative humidity every 24 hours, initially for 19 hours. That is followed by a one-hour salt spray test, then a three-hour driving stage, maintenance and possibly repair work, and finally repetition of this cycle another 59 times.

Corrosion protection tests with an extremely corrosive environment are not useful for all substrates in the same way. For example the salt spray test is not able to foresee the corrosion protection performance on galvanized steel [3.4.63].

Apart from the applicational corrosion protection tests by which damage due to corrosion is caused in a highly corrosive environment, there are other indirect test methods which are designed to provide information about corrosion and corrosion protection by analyzing the electrochemical processes taking place. Unfortunately the enormous reduction in testing time and the advantage of obtaining physical indicators are partially offset by insufficient correlations with behaviour in practice.

Out of the large number of tests described in the literature it is worth drawing attention to impedance spectroscopy [3.4.64]. Impedance, the alternating current resistance of stressed and nonstressed coating depending on the measuring frequency, supplies data which provides information about the level of protection against corrosion. However, there is no doubt that experience gained so far is not sufficient to set-up a quality assurance system based on it [3.4.65]. The measurement of dielectric constants, corrosion potentials and the plotting of polarization curves are examples of corrosion protection tests whose application is chiefly limited to comparative testing for development purposes.

Very interesting in this respect is the use of a *Kelvin*-probe for early indication of adhesion losses of organic layers on steel [3.4.66]

3.3.2.3 Chemical Resistance

The tests for chemical resistance are aimed at obtaining an overall performance profile, consisting of visual properties and protective functions. It has already been pointed out that ageing processes are accelerated by aggressive gases and liquids. Sulphur dioxide is at the top of the list of paint-damaging agents exposed to stress by outdoor weathering. It exerts a highly reducing effect and can therefore damage pigments and film forming agents in the same way. Apart from SO_2 there are also other pollutants in industrial regions. Depending on the type of industry and the region the pH values of the rain are influenced by acids, to a significant extent in some cases. This is called ”environmental etching” and plays an important role in North America and Asia for the automotive OEM paints, so that special development work has been initiated for testing methods [3.4.67] and coatings [3.4.68]. All in all, the problems due to emissions caused by industry have being alleviated considerably as a result of numerous measures such as desulphurization at power stations and catalytic converters on vehicles.

In addition to the gaseous and liquid anthropogenic pollutants, nature also makes its contribution in the production of paint-damaging substances. Bird droppings and tree resins do not harm the entire surface of a coated object but they are able to cause considerable spot damage to the coating. Physical swelling, chemical reactions of an inorganic, organic and even enzymatic nature can take place simultaneously or successively and destroy the coating. By swelling we are referring to the absorption of liquids due to diffusion, which then leads to an increase in volume and softening of the surface. It also involves a reduction in adhesion and resistance. Such purely physical processes are reversible if the active substance is sufficiently volatile. High-boiling terpenes and natural resins, as occur in conifers, are withheld in the film of paint owing to inadequate volatility. Regeneration of the damaged area is then no longer possible. One absolutely irreversible process is chemical attack by reactive natural substances. There are numerous natural resins and solvents which, on account of their reactive functional groups, not only penetrate the coating but also initiate degradation processes in polymers. Salts dissolved in the substances described are also damaging in that they penetrate the coating along with the water and remain in the film after its evaporation. It is rarely possible to divide the effect of paint-damaging atmospheric features into physical and chemical influences.

There is a whole host of test substances available in the furniture industry, in the can coating sector and in coil coating. Substances such as Coca Cola, coffee, tomato juice, etc. can attack and discolor unsuitable coatings seriously.

For tests relevant to practical situations it is necessary to select the appropriate active substances suited to the particular application. These are applied in droplets using a pipette in order to create an effect on the coating within a specified time. To achieve maximum reliability in such a test the test panels are hardened in gradient bar oven (see chapter 3.1.5). By setting a certain temperature gradient it is possible in this way to create inadequate and excessive crosslinking on a test panel in a reproducible manner. In addition, the gradient bar makes it possible to conduct tests on identically baked test panels under various temperature conditions. In the case of temperatures below and above glass temperature the breadth of information produced by the test results is extended.

The test and evaluation of the results should take place in accordance with DIN EN ISO 2812-1 in conjunction with agreements on the selection of test chemicals between paint manufacturers and paint users. Important test solutions are fuels, lubricants, brake fluids, antifreeze, cold cleaners, preservatives and aqueous substances such as hydrochloric acid, sulphuric acid, sodium hydroxide solution, but also oil soot from furnaces. Even water is used as a test substance. In certain industries the use of special test substances such as tar solutions, tar removers, insect juices, bird excrement, tree resins, etc. is common. Household chemicals and foods are also used for testing the surfaces of furnitures. By suitably combining the test substances and test conditions most of the damage encountered in practice such as discoloration, swelling and etching, can be simulated. In the test for microorganisms the coating substances are exposed to certain fungus or algae cultures under various environmental and atmospheric conditions.

To be able to test coatings for oil carbon resistance, samples of soot from furnaces were taken initially and used as test substances. The discovery that the damaging agents are mainly of an acid nature has prompted the VDA to recommend a list of substances. In the test procedure the test solution is applied to the coating, which is then covered with a clock glass. The test piece is then exposed to stress for either 1 hour at 70 °C or 48 hours at 23 °C.

The standards specially developed for the furniture industry, DIN EN 12720 and particularly DIN 68861-1, describe classification of coatings according to their stress categories 1 A to 1 F: 26 testing agents, including acetic acid, alcohol, white wine, red wine, Coca Cola, coffee, mustard and ballpoint pen paste, are specified as test substances.

3.3.3 Summary

Coatings, which are compositions of polymeric film forming agents, pigments and additives, can be exposed to considerable stresses during the service life of the substrate. The ultraviolet light of the sun, temperature fluctuations and water in all aggregate states and chemicals of various composition are the most important active factors influencing quality. Depending on the chemical structure of the individual constituents of the coating they lead to more or less rapid ageing reactions. On account of chain cleavage and subsequent connection of new crosslinking points the internal resistance and elasticity of the protective film are impaired. This can involve a direct attack on the substrate. In the case of metal materials the loss of protection is manifested in the formation of corrosion products. Ageing reactions are not restricted to the polymeric film forming agents. With pigments they result in more or less serious color shifts and reduced gloss and in many cases they lead to unacceptable changes in visual properties.

For absolutely reliable forecasts of the long term behaviour of coatings tests are conducted under stringent conditions. This is achieved by placing sample panels in regions with an extreme climate or in weathering apparatus with defined aggressive atmospheric conditions. To predict the protective functions coatings are subjected to special tests using common salt or other chemicals. To improve correlation with the results from practical applications elaborate systematic empirical tests are performed, particularly in the automotive industry.

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4 Coating Technology

The term ”coating technology” is intended to cover all the engineering processes which are necessary to transform the paint described in the previous chapter 5 into a functional coating. The stages of pretreatment, application and drying or curing with their peripheral equipment in the form of air, energy and material supply systems, conveyors and systems for disposal or the recovery of overspray and gaseous emissions from the waste air together with paint-removal systems for grilles, skids and conveyor chains are the major system requirements.

The design of the coating technology and the desired quality of the coating can only yield the optimum result if the specific properties of the substrate are taken into account. The chemical nature and the morphology of the material surface are as important in this respect as the design, joining method and construction of the object to be protected. The object to be painted, its pretreatment and the actual painting process itself have to be optimally coordinated with each other. Coordination does not refer here to a coating technology relating to an already specified object to be painted, but rather to a concept in which the issues of pretreatment and construction such as sharp edges, panel overlaps and difficult-to-access cavities are appropriately addressed.

The industrial objects to be coated pass through a correspondingly high number of units en route to achieving a permanently decorative and protective skin. Firstly, suitable pretreatment methods must be applied to the originally manufactured products to make them capable of being painted. The associated process stages focus on physical and chemical cleaning methods, on smoothing processes and on the application of thin, inorganic conversion layers.

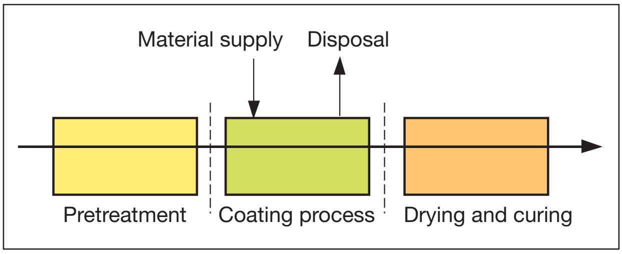


Fig. 4.1
Process steps of coating lines

The pretreatment line is followed by the processes of application, drying and curing of the coating material. The application lines consist of units which are charged with conditioned fresh air and material in order that the liquid or, in the case of powder coatings, solid coating material can be transformed there into a uniformly thin, mechanically strong film. This can take the form of brush, roller, dip, flood, curtain or spray coating. The overspray and the gaseous solvents which occur or escape during spray coating must be extracted from the waste air.

The process-engineering operations in the oven concentrate on removing escaping solvents, on the one hand, and initiating or accelerating chemical crosslinking reactions, on the other.

All the individual processes mentioned, such as paint and air supply, application, drying, curing, but also conveying and all the environment-related supplementary measures of exhaust gas, waste water and overspray processing together with the necessary

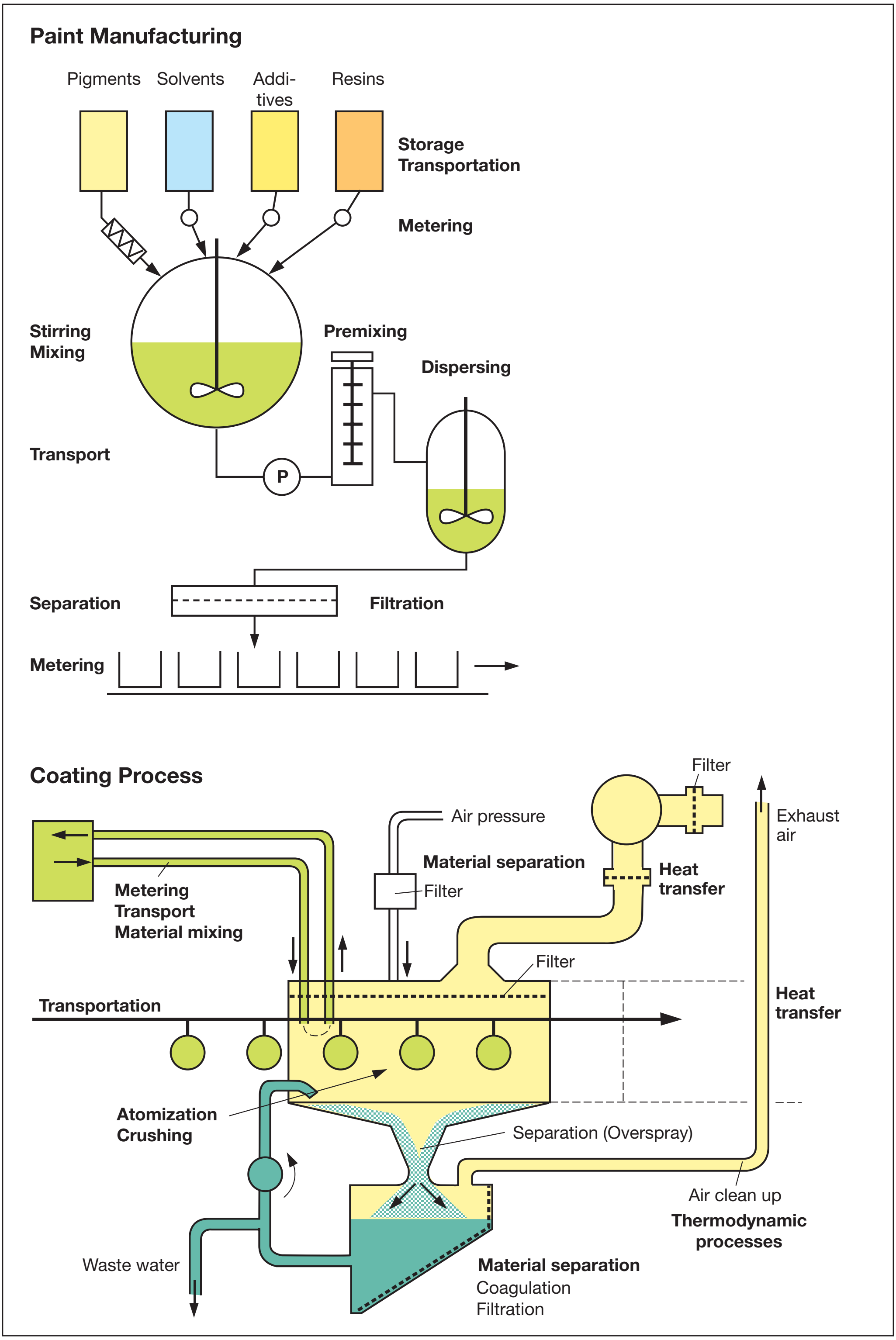


Fig. 4.2
Basic operations for paint manufacturing and spray coating process

process control can be broken down into individual elements corresponding to fundamental process-engineering operations. This then enables all the complex processes to be assembled for specific individual cases merely by connecting together a relatively small number of basic operations (individual modules).

The major basic processes which are of importance to coating technology are:

- Mass transfer
- Heat transfer
- Dispensing (metering)
- Material mixing
- Crushing
- Material separation
- Thermodynamic processes

The large number of different systems is therefore the consequence of the linking of individual modules in different ways. This also applies to paint production and is illustrated in figure 4.2 in comparison with paint processing.

4.1 Substrate Impact

With regard to the surface quality to be achieved, therefore, the coating material and the processing method play an important role. Paintability and design are still very closely linked together and should never be discussed independently of each other.

The aim of the following section is to examine the influences of the substrate to ensure that these are given due consideration when designing a painting process.

One main category of substrates is represented by natural materials subdivided into inorganic materials, such as concrete and mortar, and organic materials, such as wood,

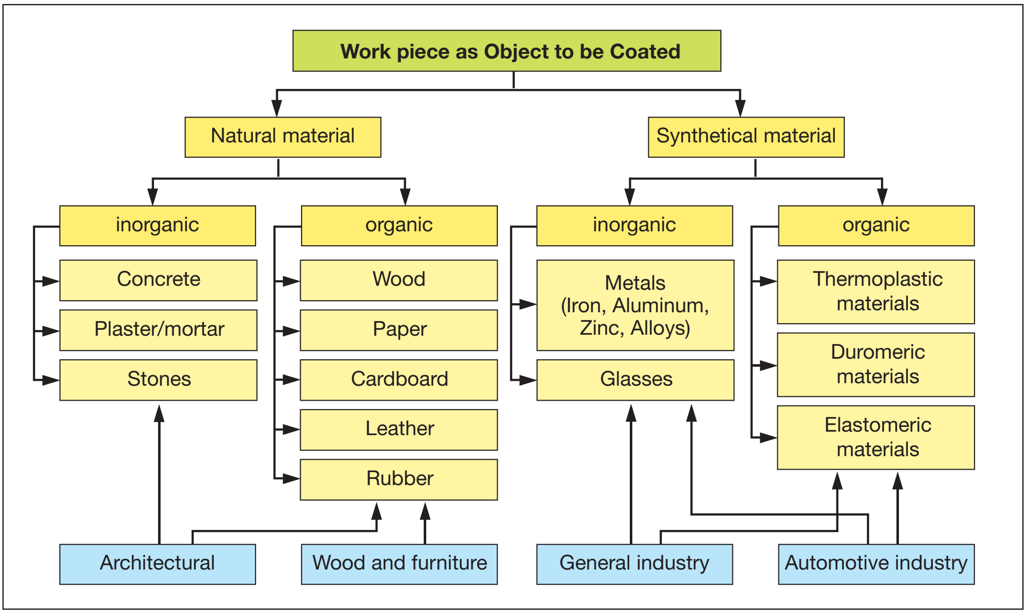


Fig. 4.1.1
Important substrates for coating processes and their applications

paper, cardboard, leather and rubber. Synthetically manufactured materials, the other main category, also have to be coated. Metals, such as iron, aluminium, zinc, magnesium and their alloys, as well as glass, ceramics and thermoplastic, duromeric and elastomeric organic plastics also deserve mention. Of these, metals are thermally stable yet subject to corrosion, while wood, by contrast, is unaffected by corrosion but can be damaged by micro-organisms.
The materials can be soft, such as leather and rubber, but also extremely hard. Their surfaces can be rough or smooth, neutral or alkaline. All this results in huge variety of properties which all have to be taken appropriately into account when selecting the material and process for surface treatment and coating.

4.1.1 Wood and Wood Materials

4.1.1.1 Wood as a Material

Wood, as the main constituent of the trunks, branches and roots of plants, is a complex organic material made of cells and therefore has a range of special features. Because of the way it has grown it exhibits nonhomogeneous structures. Wooden items sawn from the trunks, such as planks or boards are therefore nonhomogeneous as far as their expansion properties are concerned. Wood can absorb up to 30% water, depending on the relative humidity of the ambient air. And depending on the type of wood, the volume can increase by up to 10%. Lightweight wood which has grown quickly absorbs greater volumes of water more quickly, whereas the hard, slowly growing types also have a correspondingly slower water exchange process. Because of the different alignment of the cells, swelling caused by water absorption is not the same in every direction. Wood swells and contracts 10 times more in a radial direction and 17 times more in a tangential direction than longitudinally. The swelling therefore increases linearly by 0.2% vol/vol per percentage point increase in moisture. At the relative humidity of approx. 50%, which is the mean for central European climatic conditions, the moisture content in wood reaches equilibrium at 8 – 10%. Painting processes should ideally take place under these conditions [4.4.1].

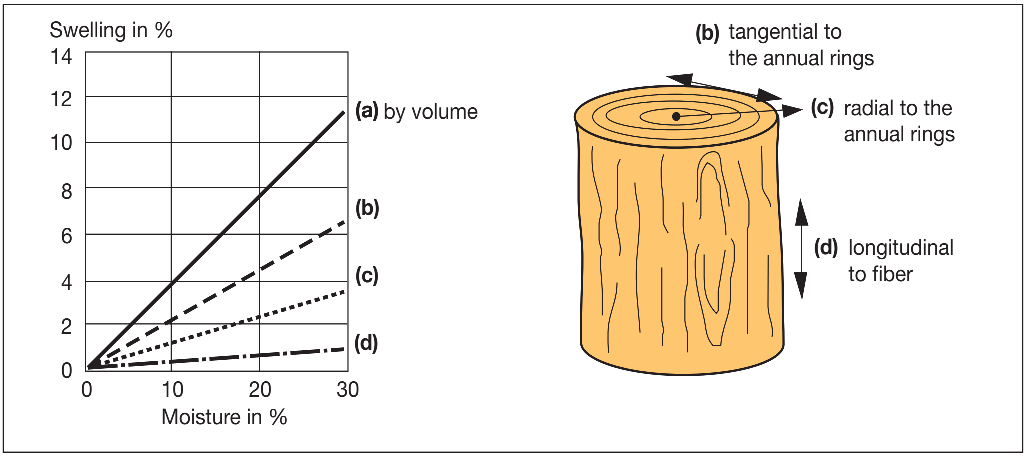


Fig. 4.1.2
Swelling properties of wood

At the same time the influence of water brings about a significant change in the density and hardness. Completely dry, compressed wood can have a density of up to 1.56 g/cm^3. The hardness can increase three-fold during this process.

Sawn timber also has a characteristic surface structure. It is composed of the annual rings, medullary rays, i.e. areas of different-sized cells and pores. The annual rings comprise two different elements, the lighter, outer, still living parts which are softer, known as the sap wood, and the darker heart wood or duramen, which consists of the dead cells. The latter performs merely mechanical support functions. It is protected against oxidative decomposition by tannic acid.

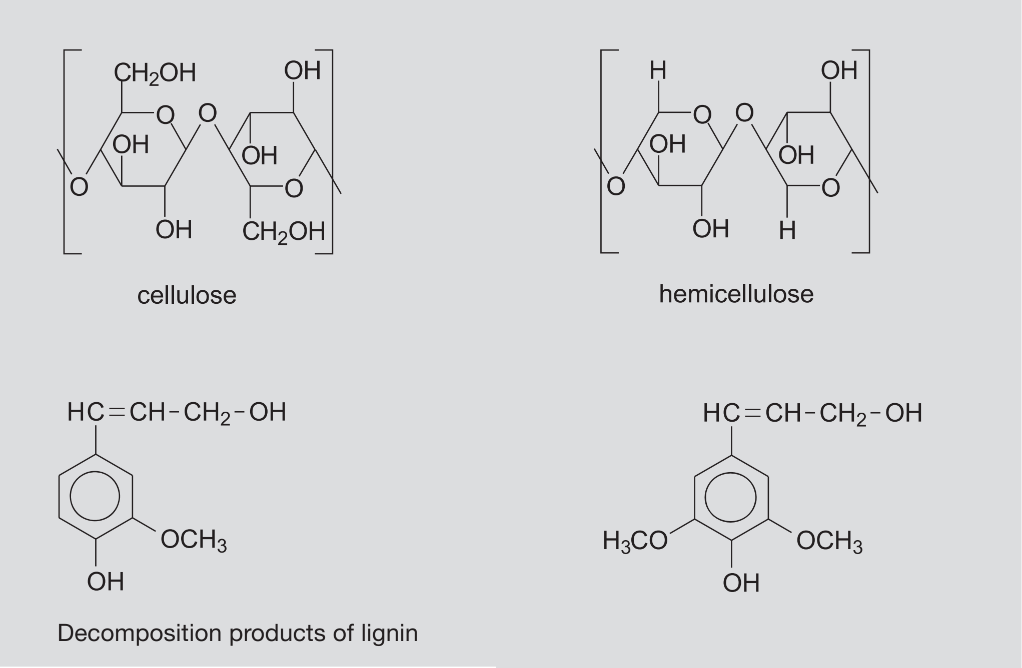


Fig. 4.1.3
Chemical components and decomposition products of wood

As a result of their cell structure, i.e. of chemical secondary and tertiary structures, as already mentioned, all wood types are nonhomogeneous in terms of their properties and are therefore anisotropic materials.

The chemical structure is also complex. Cellulose, which makes up 40 – 50%, is the main constituent of wood (see chapter 2.1.1). Although in the form of 1,4-β-D-polyglucosan it swells in water, it is completely insoluble and therefore represents the fundamental provider of mechanical strength and resistance to external influences. Hemicellulose deposits, which represent 15 – 20%, are responsible for elasticization (xylan), and lignin at 20 – 25% operates as a supplementary stabilizer.

Whereas hemicelluloses such as cellulose are oligomeric sugar derivatives (main constituent: xylose), the lignin cells have a completely different chemical structure. The decomposition products reveal that polyvalent phenol bodies, in some cases etherified with methanol, are present in a complex link with allyl alcohol.

In addition to the basic substances specified above, wood also sometimes contains soluble substances in a very wide variety of types and quantities. Mono- and diterpenes, waxes and oils are present, together with wood-specific substances which can cause problems for surface treatment because of their solubility in paint solvents [4.4.2].

Paper and cardboard are also cellulose-containing materials and therefore wood derivatives. These are flat leaf- or foil-like flexible materials for writing or printing on and for packaging. They mainly consist of plant fibres which are felted, pressed and bonded together. The fibrous materials are derived almost exclusively from wood. The purely mechanical processing of the wood yields wood pulp, a short-fibred mixture of cellulose and lignin. The combined mechanico-chemical disintegration of wood, in which the less resistant lignin is largely decomposed while the cellulose fibres remain intact, results in the longer-fibred chemical pulp which consists of up to 85 – 95% cellulose.

The use of recycled paper is playing a growing role in lower-quality papers. Apart from the fibre materials, fillers such as kaolin, barium sulphate, calcium and magnesium carbonate, talcum and titanium dioxide are important as basic materials. The inclusion of fillers produces smoother surfaces and brighter colors. The addition of natural soaps (colophony) reduces the paper’s absorbability with regard to writing and printing inks. Synthetic-resin glues and waxes increase the wet strength, starch and starch derivatives the tensile and folding strength, and water glass the hardness.

4.1.1.2 Wood as a Workpiece

The simplest form of woodworking involves the production of solid sawn timber in the form of laths, planks and beams. Solid timber is mainly processed in the construction and window industries. In the furniture industry the use of solid timber requires highly developed craft skills and is one of the most interesting forms of joinery. Wall-mounted shelving, mouldings and furniture built using frames and panels are made of planks and boards. Up to 90% solid timber is used in the manufacture of chairs and tables.

The natural work of the solid timber as a result of shrinkage, swelling and the associated cracking and warping makes special demands on subsequently applied coatings. Solid timber therefore requires very careful processing.

Because of changes in and warping of solid timber as a result of anisotropic swelling and shrinking numerous actions are carried out to give solid wood better dimensional stability. The wood is made hydrophobic and thus rendered largely unaffected by water in the environment by means of mechanical compression, on the one hand, but also by chemical means, including impregnation with polymerizing monomers in pressure chambers and subsequent polymerization.

The property profiles of veneers, which are only fractions of a millimetre thick, are similar to those of solid wood from a coating technology perspective. They are obtained from the solid wood by peeling (rotary-cut veneers) or cutting (sliced veneers) after the solid wood has been made appropriately soft and elastic by the application of steam. Because they are so thin, they require a suitable substrate to stabilize them. During the production process the possibility of the substrate or the glue having an effect on the painting process because of pores or flaws which go right through to the substrate cannot be ruled out. Pretreatment stages are therefore often necessary (see below).

Rotary-cut veneers are mainly used as cross-band veneers. Sliced veneers are used for deco-rative purposes on surfaces. To this end, high-grade decorative wood types such as walnut, mahogany, oak, elm, ash or rosewood are used. Wood core plywood, plywood, chipboard and hardboard panels can be used as the substrate.

If battens cut in different directions from solid wood and then bonded to form panels with different thicknesses of covers are chosen as the substrate, these are termed plywood or wood core plywood.

Wood core plywood panels are plywood panels which consist of a centre ply and at least one veneer ply on each side. Depending on the type of centre ply, these may be termed laminboard, blockboard or battenboard. Wood-based core plywood panels manufactured in this way are better able than planks or boards to withstand the effects of moisture. The danger of warping, distortion and cracking is minimized. The centre plies of wood-based core plywood panels are usually made of pine, fir and obeche. The cross-band and face veneers are bonded to the battens on both sides at right angles to the grain of the wood.

Another method of achieving wood materials with isotropic properties which is now in widespread use for furniture manufacturing consists of compressing comminuted wood particles. A wide variety of fibreboard and chipboard (also known as particleboard) products are now used. Fibred or grated wood in an

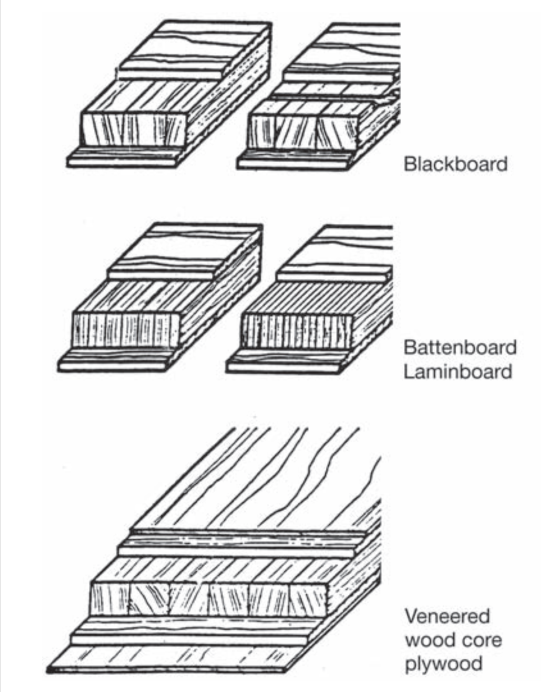


Fig. 4.1.4
Types of plywood as wood work pieces for furnitures

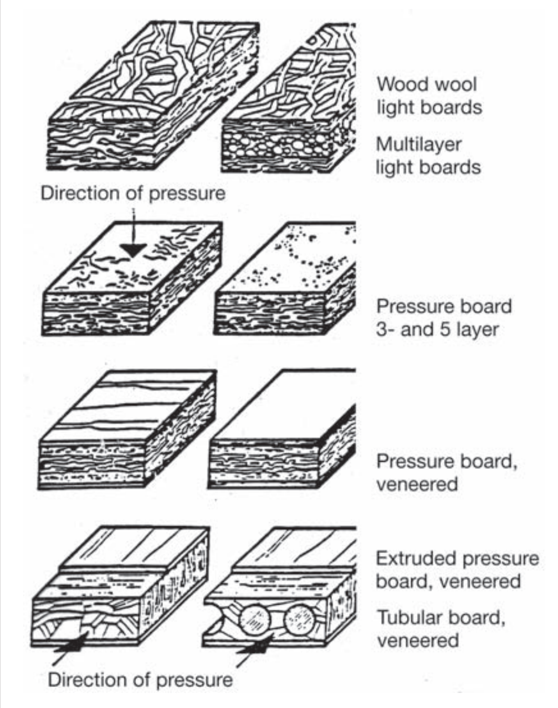


Fig. 4.1.5
Types of fibreboards and chipboards

extremely wide variety of sizes and shapes is compressed with urea, melamine or phenol resins and thermally cured. Depending on the pressure of up to 600 N/m^2 these boards are classified as softboard, medium-density fibreboard (MDF) and hardboard. These in turn are used in furniture manufacturing with and without veneer, depending on the particular requirements.

These materials can be compressed in all three directions. Because of their high strength, special tubular panels are also manufactured which feature a low weight and are relatively inexpensive.

4.1.1.3 Pretreatment of Wood

Before solid wood or wood materials can be subjected to surface treatment to form a surface layer, the workpiece must pass through a number of pretreatment stages. The most important stages before the actual painting process are wetting, cleaning, sanding, deresinification, removal of adhesive bleed-through and, if appropriate, bleaching and staining.

In craft processes the woodworking machines often leave behind visible pressure or drag marks which impair the attractiveness of the surfaces. To eliminate these, the parts are treated in warm water before then being dried for 1 to 2 days at 18 – 20°C.

Cleaning of the surface in the direction of the grain using short double planes or scrapers which used to be carried out before the sanding process has largely been superseded by the use of sanding machines. Sanding as the prerequisite for a perfect surface to which to apply paint must be precisely adapted to the individual types of wood. During wet sanding, solvents, unlike water, do not change the volume of the wood, a fact which should be borne in mind when sanding wood. Whereas water enlarges the cells through osmotic effects and aligns the fibres of the cut surfaces, such an effect does not occur when, for example, gasoline is used. Only thorough sanding creates the preconditions for a uniform application of the coating materials.

Corundum or silicon carbide particles of different levels of coarseness are used as abrasives. The individual abrasive types are attached to a backing fabric with synthetic resins, usually phenol resins, and nonstick coatings. The additional antistatic treatment prevents clogging with dust, and therefore ensures that no problems occur when using sanding belts.

The sanding process itself is nowadays electronically controlled using appropriate machines. Infinitely variable pressure control is provided by means of a computer, thereby enabling uniform sanding even at the edges of the workpieces. By combining several sanding processes, the optimum conditions can be generated for the subsequent surface treatment. With wood, too, the time and effort spent on preparing the surface pay dividends in the quality of the paint finish [4.4.3].

Should it be necessary to remove any resins or glues from the surface to be coated, this can be done using solvents or soft soap in conjunction with ammonia. With light-colored woods oxalic acid or a 30% H_2O_2 solution is used. The wood should be scrubbed in the direction of the grain until all the glue residues have been removed.

The bleaching which occurs as a side effect of the treatment with H_2O_2 is specifically carried out with certain wood types to achieve a uniform lightening. Beech, oak, but also wood types which discolor in daylight such as maple, birch or pear, are brightened using concentrated ammonia and subsequent treatment with a 30% H_2O_2 solution. The oxygen-containing foam which forms on the surface is spread with a brush and then removed by thorough rinsing.

The character of the wood can be enhanced by exploiting the different properties of the sap wood and heart wood sections, i.e. by dyeing them differently. Dyes dissolved in water or solvents, smoke mordants or metal salt or double stains should be used. Metal complex dyes are dissolved in alcohols as spirit stains, soluble anionic azo dyes in water and conventional azo dyes in gasoline or waxes as wax or gloss stains. The metal complex dyes feature good fastness to light. Although the browning of the heart wood which is achieved by smoking with ammonia in enclosed smoke chambers is smudge-proof and optically attractive, it is unfortunately not waterproof and light-resistant.

Metal stains are better because they are more durable. Wood containing tannic acid forms color complexes with various metal salts such as iron, cobalt or copper salts. If there is no tannic acid in the wood to be treated, the same effect can be achieved by prior soaking of the wood in solutions of tannin, pyrogallol or hydroquinone and subsequent treatment with metal salts using so-called double staining. The stains are applied with a brush or sponge and spread at right angles to the grain. Stains should be protected with a clearcoat to improve their resistance.

As the residue of a former living organism, wood is subject to attack by micro-organisms which decompose wood unless appropriate protective action is taken. Depending on the degree and type of protection necessary, biocidal agents are dissolved in solvents in the form of impregnations or in film forming primers or transparent paints. Fungicidal, bactericidal, insecticidal or algicidal active ingredients should be used, as required (see chapter 2.1.4).

To combat the cellulosis degrading brown rot and the lignin degrading white rot both of which are caused by fungi, organo-metallic compounds or halogenated phenol bodies were previously used effectively as generally acting biocides. However, the potential danger to humans as a result of the sometimes high dose and the cumulative effect in the environment have resulted in the withdrawal of these substances and their replacement today by modern wood preservatives which act specifically on the micro-organisms' metabolisms (see chapter 2.1.4 and 5).

4.1.1.4 Surface Refinement of Wood Panels

The desire to give chipboard, which is widely used for furniture production and other applications, the appearance of a high-quality natural wood, despite the shortage of and price increase in face veneers, has resulted in the development of the grain-printing process and other surface-refinement methods. Grain printing enables an image very closely resembling natural wood to be printed in any color onto chipboard, hardboard, paper and other materials. Before being printed, the panels must be properly filled, ideally using filler-spreading machines which smooth in the opposite direction. Printing itself is generally conducted in a combined rotogravure/offset process using printing rollers. The inclusion of pore images with a paint-repelling printing ink results in open-pore effects when the panel is later coated (synchronized pores).

The printing images are produced photochemically. This involves photographing a well prepared face veneer which is as flawless as possible. The image is adapted to the roller so that it is endless on the roller, generating a continuous pattern which is not interrupted at any point when printed.

Impregnated papers are also in use in the furniture and wood panel industry. The shortage of and price increase in genuine veneers has significantly contributed to the greater use of such paper foils. A clearcoat must be applied to the foils after they have been pressed onto the chipboard and hardboard panels as their surface protection is inadequate otherwise.

Moves to simplify the production sequence have resulted in finish foils. These are impregnated or printed paper foils to which a clearcoat is applied by the foil manufacturer. After pressing these onto panels, the processor of such foils has surfaces which require no further coating. Endless edges, which are used as roll stock in the furniture and wood panel industry for the continuous coating of edges, are also given this finished surface by the foil manufacturer.

The manufacture of such finish foils and endless edges is carried out in special impregnation-coating systems. The original paper foils are mainly impregnated with urea and melamine resins, but also with acrylic and polyester resins and thereby so hardened that they do not delaminate or crack during later furniture production, i.e. during sawing, drilling and milling of the foil-coated panel. Drying of the impregnated papers is carried out in float driers. Further treatment of the dried paper foils to produce the finish foil takes place either directly following the impregnation process or in a separate stage. Directly linking the impregnation process with the application of the topcoat after an interim drying stage avoids wasting time and material which otherwise occurs if material has to be rolled up and unrolled again.

The manufacturing process for the production of endless edges is analogous to that used for the production of finish foils. The papers used in edge production must be substantially heavier than those used for the panel faces to ensure that the chipboard edge, particularly the relatively uncompacted chipboard centre ply, can be satisfactorily bridged.

White or natural base papers are used for producing decorative edges, depending on the desired color of the edges. The papers are provided by the manufacturer with a smooth surface on one side so that little material and just one work stage are required when applying the topcoat (see chapter 7.10).

4.1.2 Metallic Materials

4.1.2.1 Properties of Metals

Despite the development of numerous attractive high-performance plastics, most consumer goods are still made of metallic materials. The most important materials are iron, aluminium, zinc, magnesium and their alloys.

These metals are chemical elements which, with the exception of rare meteorite finds, do not occur naturally since they are in a thermodynamically unstable state as metals. They therefore occur as oxides, hydroxides, carbonates or other stable compounds.

The oxidation process of the pure metals results often in oxide layers which are either porous or closed, depending on the particular type. Whereas zinc and aluminium form stable, closed oxide skins in certain pH ranges and are therefore passivated against further action by atmospheric oxygen, porous layers occur when iron is oxidized. Because of their permeability to oxygen and water they do not offer any protection to the metal. Since the metals described are not present as chemical elements in nature, they must be artificially manufactured and later protected against decomposition by means of protective coatings. Their properties depend to a great degree on the composition of the metals. They vary in their susceptibility to corrosion, depending on their order in galvanic serie and their degree of purity. The melting points can be influenced by combining different metals in the form of alloys.

The surface properties of metals, which influence the painting process and thus the quality of the coating surfaces, are of particular interest. The surfaces are affected in different chemical and mechanical ways by rolling or casting, depending on the type of manufacture of the workpieces. These include mill scale and the roughness of the material surfaces which vary according to the manufacturing process. Even traces of corrosion products can significantly impair the protective effect of coatings. It is therefore absolutely essential to remove all corrosion products completely from the coating. This is the only way to guarantee effective anticorrosive protection. Beneficial features with regard to surface treatment methods are the complete insolubility of metals in all organic solvents and their high melting temperatures. The baking temperature of coating materials is not limited by metallic materials. Certain alloys, e.g. soft solder, whose melting points of approx. 180 °C may well lie within the range of the baking temperatures of industrial paints, are exceptions to this. Some aluminium alloys are also sensitive to such baking temperatures.

Anticorrosive protection by means of coatings in order to maintain value is at the same time a means of protecting resources, saving energy and thus environmental protection. Every effort should therefore be made to avoid this type of material destruction more effectively. It is estimated that about one-fifth of all steel manufactured is lost as a result of corrosion. By corrosion is meant attacks on the materials as a result of a reaction with the environment and the subsequent change in the material properties. The term corrosion, which is derived from the Latin “corrodere” = to gnaw, relates to both the process and the damage caused by it.

Metal	Melting point
Iron	1530 °C
Copper	1083 °C
Aluminum	658 °C
Magnesium	650 °C
Zinc	419 °C
Tin	232 °C

Fig. 4.1.6
Melting points of coating relevant metals

The causes of corrosion lie in the formation of electrochemical potentials caused by unequal charge distributions in the material. These can be the result of inhomogeneities in the material itself as local cells or of different surface states arising from the external action of oxygen. This gives rise to cathodic and anodic areas which then result in the corrosion products in the presence of water and oxygen when the iron discharges electrons which are then absorbed by the oxygen. The size of this potential difference between the anodic and cathodic areas can be quantified using the *Nernst* equation. This describes the correlation between the individual potential φ of a metal electrode and the activity of the cations a in the solution. F represents the *Faraday* constant and φ_0 the reference potential.

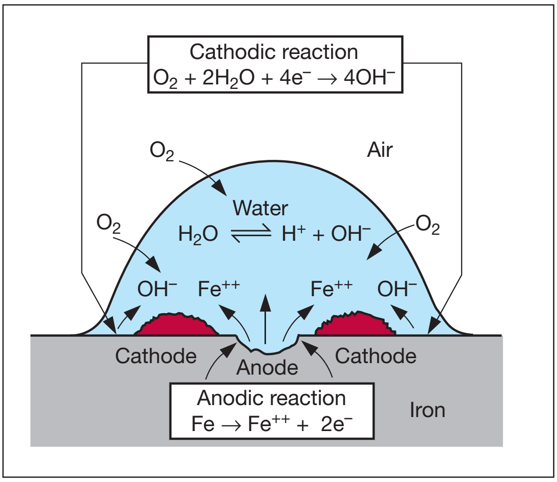
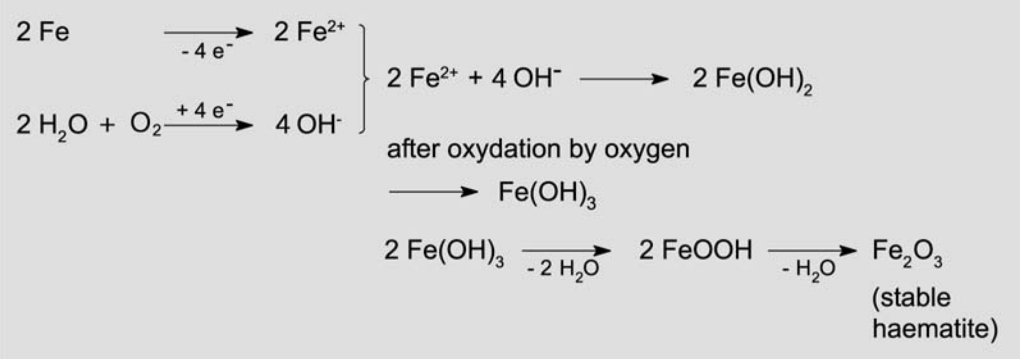


Fig. 4.1.7
Corrosion reactions under a water droplet

$$\varphi = \varphi_0 + \frac{RT}{nF} \cdot \ln a$$

The formation of corrosion products will be described in detail taking the example of a water droplet. The potential here is defined by the differential concentration of the oxygen dissolved in water.

Whereas the iron in the low-oxygen area goes into solution anodically, OH ions are generated in the cathodic area from H_2O, oxygen and the electrons emitted by the iron. These initially form insoluble iron(II)hydroxide at the edge of the water drop. The oxygen dissolved in the water then oxidizes the iron(II)hydroxide to hydrated iron(III)oxide which dehydrates to become stable haematite.



$$2\,Fe \xrightarrow[-4\,e^-]{} 2\,Fe^{2+}$$
$$2\,H_2O + O_2 \xrightarrow{+4\,e^-} 4\,OH^-$$
$$2\,Fe^{2+} + 4\,OH^- \longrightarrow 2\,Fe(OH)_2$$

after oxydation by oxygen

$$\longrightarrow Fe(OH)_3$$
$$2\,Fe(OH)_3 \xrightarrow[-2\,H_2O]{} 2\,FeOOH \xrightarrow[-H_2O]{} Fe_2O_3$$

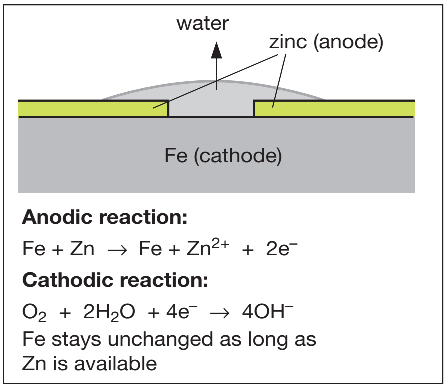
(stable haematite)

Corrosion products are formed in this way over the entire surface of the metal. As the corrosion products are formed, the atmospheric oxygen is increasingly prevented from passing through them, with the result that the rate of corrosion slows down. The critical relative humidity for triggering corrosion is around 60%, meaning that corrosion products cannot form at a lower relative humidity and in the absence of water in the liquid state. In dry areas, such as desert regions, corrosion problems are therefore almost unknown. Factors such as airborne pollutants and the pH value of the environment also play a decisive role. Airborne pollutants such as sulphur dioxide significantly catalyze the corrosion process. Salty sea air or acidic soot deposits can also promote the formation of contact elements and thus corrosion. Oxidative decomposition occurs particularly quickly in the acid range, and slows down with increasing pH value. The corrosion of iron decreases more and more between pH 4 and pH 10.5, before practically coming to a halt above 10.5, a fact that has to be particularly borne in mind with reference to the stability of steel in alkaline concrete. In the absence of local cells if the product is particularly pure, there is also little tendency to form corrosion products.

The situation with the amphoteric elements aluminium and zinc is different, however. Unlike iron, they are passivated in the mid-pH range because of the formation of a closed oxide layer, but are susceptible to corrosion in the acid and alkali ranges because the protective layer dissolves.

They are being increasingly used as metallic materials because of their passivation in the neutral range: zinc primarily as a coating on steel, and aluminium in numerous alloys as uniform materials.

Despite its more basic character compared with iron, zinc has proved successful as a protective coating for iron. The protection is still provided by electrochemical processes even if the coatings are mechanically damaged locally. As a result of its more basic character, zinc provides protection in that the formation of iron ions is prevented during a corrosive attack by electrons being transferred from the zinc to the iron. The zinc acts as an anode and consequently offers the steel cathodic protection. The damaged location is filled with zinc oxide, also known as white rust. The still intact zinc protects the steel against corrosion with its entire surface area until it has been completely used up.



Anodic reaction:

$Fe + Zn \rightarrow Fe + Zn^{2+} + 2e^-$

Cathodic reaction:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Fe stays unchanged as long as
Zn is available

Fig. 4.1.8
Zinc for cathodic protection of iron

The zinc coatings which are necessary to protect the steel can be applied in various ways. The important processes include hot galvanizing, in which the objects or coils are immersed in a zinc bath heated to 450 °C. The disadvantages of this process are the very thick coatings which it produces and the structures, known as flowers of zinc or zinc bloom, which occur during cooling. Because of variations in the configuration of the crystalline matrix irregularities occur which are difficult to cover from visual detection by coating. As far as the attractiveness of the coating is concerned, hot galvanizing modified by a roller method (Sendzimir galvanizing), spray-galvanizing or electrochemical galvanizing are much more suitable processes. Spray galvanizing in the flame descaling method involves melting zinc and spraying it onto the surface as a liquid with compressed air. Galvanizing by means of the electrolytic separation of zinc salts yields even more uniform and at the same time extremely thin (2 to 10 µm) coatings.

Sheradizing is an effective method of galvanizing small components. The objects are cleaned with acids and are then maintained at a temperature of 400 °C in contact with zinc and sand in rotating drums.

Another method of providing cathodic protection for steel by zinc is achieved by applying zinc-rich paints. A high concentration of zinc powder is distributed in organic film forming agent solutions such that the individual zinc particles touch each other after application on the substrate to be protected and subsequent drying. However, the protection they offer is not as good as that provided by closed zinc layers.

The straightforward zinc-rich paints were unsuitable at first for the use of precoated sheets in the coil coating process, which are then converted into stampings, because of the soiling of the press tools. The breakthrough for sheets coated with zinc-rich paints in the coil coating field came when the sheets were also coated with a clearcoat with a low coefficient of friction (see chapter 7.4).

Another metal frequently used in the production of goods is aluminium. It is extremely base. Despite this, aluminium is highly resistant to atmospheric oxygen because of its oxide skin which prevents the passage of oxygen. As mentioned above, however, the oxide layers are not stable in acid and alkaline environments. The oxide layer also offers no protection against chloride ions as it then dissolves to form chloro-complexes. The stable passivation range depends to a large extent on the purity of the metal.

Purity	Amount of dissolution in g/m^2/day
99,999 %	6
99,990 %	112
99,970 %	6500
99,880 %	36000

Fig. 4.1.9
Resistance of Aluminum against corrosive impact depending on its purity

Of the sometimes very thick oxide coatings the skin which forms the oxygen barrier directly on the metal surface is extremely thin at 0.005 µm. The rest is porous and impairs electrical conductivity and the adhesion of coatings, and it is therefore essential to remove it. Oxide skins created by electrochemical oxidation and known as anodized coatings are therefore used to promote the stability of aluminium. Aluminium is highly valued as a material because of its low density of 2.70 g/cm^3 and its excellent physical properties, but is only rarely used as a pure metal. It is alloyed with magnesium, silicon, copper and zinc to increase its dimensional stability and hardness.

A distinction is drawn in the manufacture of aluminium materials between wrought alloys and cast materials, depending on the processing conditions and the delivery form. Wrought alloys are poured to make ingots, drawn by rolling and then converted into coils, while cast materials are processed to manufacture pressure die castings, gravity die castings or sand castings.

When forming alloys with aluminium, magnesium promotes strength and corrosion resistance, silicon lowers the coefficient of thermal expansion and reduces density, and other alloying metals such as copper and zinc increase its strength. Either aluminium/zinc/magnesium/copper or aluminium/silicon alloys are successfully used, therefore, depending on the particular requirements. The compositions and designation of important alloys are specified in DIN EN 576 and DIN EN 573-1 and -4 or ASTM B 881-989.

The first stage in manufacturing aluminium coils and sheets is to cast aluminium ingots. These are rolled to a certain interim thickness at 400 – 500 °C and then finish-rolled to the required final thickness under cold conditions. As with rolled steel, crack products in the form of carbon can accumulate and adversely affect the corrosion resistance at the interface as a result of the thermal removal of drawing greases.

In recent years magnesium-containing materials have also gained increasing prominence, particularly for automotive engineering applications. Magnesium is self-passivating in similar fashion to aluminium, but is also unstable at low and high pH values and when subjected to the influence of chloride and similar ions. Although it has excellent deformation properties as a pure material, it is often unable to meet all requirements as a material because of its inadequate hardness. Like aluminium it has to be alloyed with other metals. By comparison with aluminium, whose density is only 1/3 that of steel, magnesium at 1/4 is an even better material with regard to potential weight reductions, provided the same strength can be achieved as with steel. The use of magnesium in carmaking with a quantity of 5 kg/body is still modest, whereas no less than 100 kg aluminium is now used in each car body (see figure 7.1.6). However, the increased use of magnesium also depends on its paintability. Pretreatment methods which permit painting are still being actively sought as this book goes to press.

The low-iron, -copper and -nickel or iron-, copper- and nickel-free alloys which have been developed recently feature improved corrosion resistance, and so an increase in the proportion of magnesium used as a material in future can be expected.

The specific properties of the metallic materials have resulted in several different materials often being combined in order to meet the broad property profile specified for consumer goods. It should be borne in mind in this connection that, where a conductive link is established between different metals, local cells form which significantly accelerate oxidative decomposition through galvanic corrosion. In metal-processing industries, such as in the production of cars, buses or commercial vehicles, galvanized components are often combined with aluminium and steel components. With such a mixed construction sustained anticorrosive protection is only achieved in design terms if the different metals are separated from each other by nonconductors. In the case of unavoidable contact the baser anodic areas should be as small as possible by comparison with the cathodic areas since the corrosion current density depends on the relative sizes of the parts in contact. The practical implication, therefore, is that sheet steel should never be attached using aluminium screws.

4.1.2.2 From the Material to the Workpiece

Apart from the chemical features of the material the surface structure of the workpiece also affects the optical and functional properties of the coating which is later applied. The surfaces have a more or less pronounced structure as a result of the manufacturing process used for the material and the specifications relating to deformability. To this

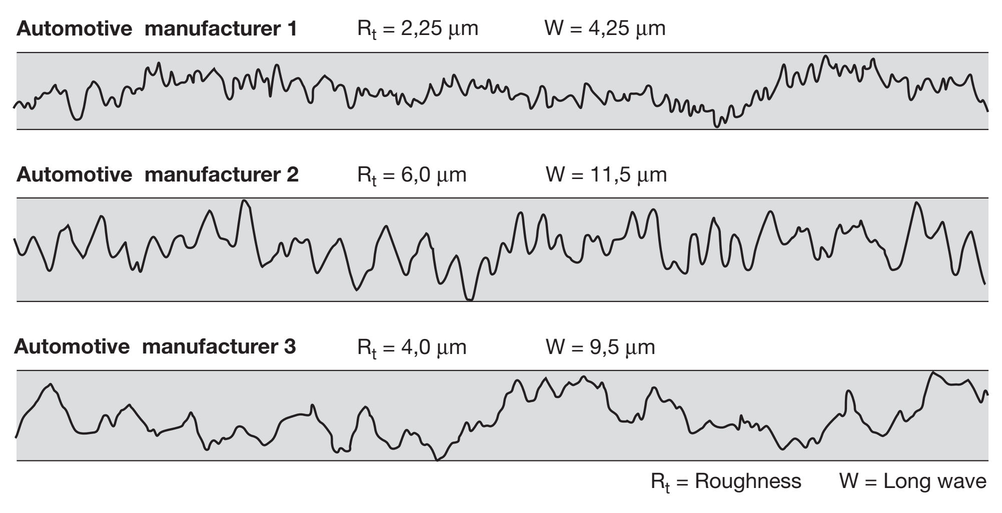


Fig. 4.1.10
Surface profiles of body steels

must be added changes in the surface roughness during the earlier cleaning process involving brushing, sanding or blasting with sand or steel shot. For example, steel castings and sheet steel surface-treated using shot-blasting can have very rough surfaces with roughnesses of 15 – 30 µm (see chapter 3.2.4). Bodywork panels, on the other hand, have peak-to-valley heights R_t of only a few micrometres, depending on the degree of necessary deformation in the stamping presses.
Since the optical attractiveness and the protective effect of the coating to be applied later depend on the way in which the surface structure, the paint system and the application process are matched, the mean peak-to-valley height R_a and difference in height between the highest and lowest peaks R_t must be measured and taken into account when specifying the substrate.

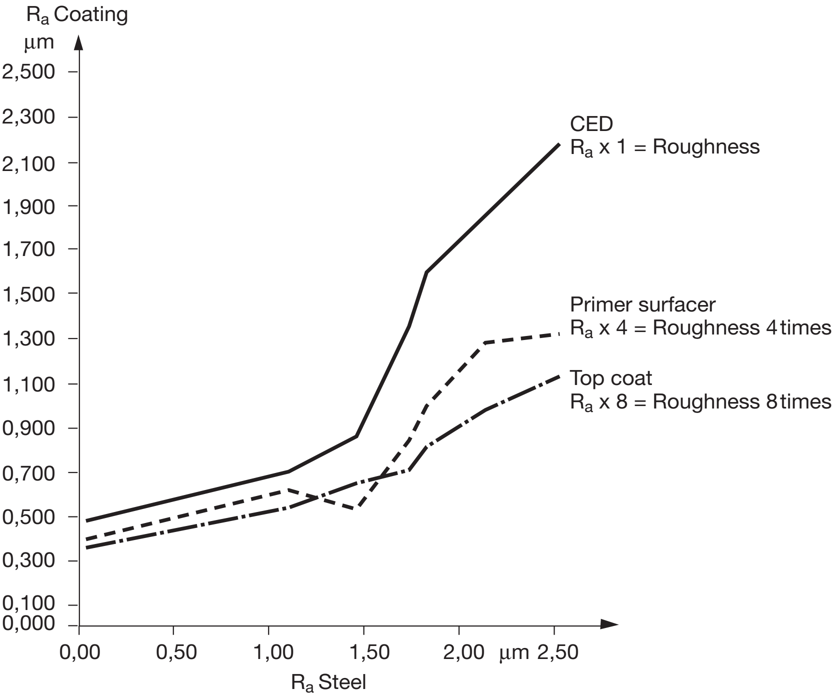


Fig. 4.1.11
Correlation of R_a of the substrate and a multilayer coating

As the roughness of the substrate increases, so the mean peak-to-valley height of the coating also increases. The influence of the substrate can still be seen in the topcoat even when several coats are applied.

4.1.2.3 Pretreatments

Because of the greater or lesser speed with which oxide coatings form, bare sheets are coated with anticorrosive oils immediately after manufacture to provide temporary anticorrosive protection. Depending on the nature of the metallic objects to be painted, therefore, different cleaning and pretreatment processes must be carried out before the actual painting process. Impurities arising from the production process such as mill scale, tinder and oxide layers or anticorrosive oils from the manufacturing process for steel coils and drawing greases from the deforming process must be removed when installing the untreated objects. Mechanical cleaning by means of brushing, sanding or blasting is often carried out. It is essential to remove organic impurities from technical surfaces using solvents or tenside-containing aqueous agents. By contrast with these physical methods it is expedient to carry out chemical pretreatment by pickling or, in the case of coatings subject to severe stresses, to carry out a film forming pretreatment before the actual painting process. Phosphating or chromating optimize the structure and conductivity of the surface and thus the anticorrosive protection in various ways.

Physical methods

Mechanical cleaning processes enable new surfaces with a changed roughness profile to be produced by removing impurities. **Brushing and sanding** are cleaning techniques which remove corrosion products, impurities or old coatings by means of the oscillating or rotating movements of grinding heads. Inevitably some of the metallic substrate may also be removed. The changes in the roughness profile vary depending on the type of abrasive, the brush design and the amount of pressure exerted. When pretreating heavily textured surfaces sanding tools which work only horizontally are less suitable. Rotating brushes which oscillate vertically in addition to their horizontal movements ensure a much better cleaning outcome.

A range of sanding tools which are operated electrically or via compressed air and which also work wet or dry and with rotating or vibrating discs are also available for mechanical rust removal and cleaning. Synthetic mats coated with silicon carbide or corundum are used as abrasives.

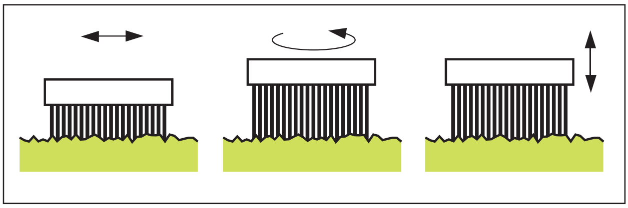


Fig. 4.1.12
Brushes for mechanical cleaning of metal surfaces

Blasting is an effective method of removing all impurities such as rust, mill scale, tinder and old coatings from metallic surfaces. The operating principle consists of projecting sharp quartz sand, corundum (Al_2O_3), glass beads or steel shot of varying sizes against the surface to be cleaned by air under pressure using a blower. The surface is also removed in part by the particles which impact with a high degree of kinetic energy. This causes a rise in roughness at the same time which increases the adhesion of the coating to be applied. If the roughness rises too far, however, peaks of the substrate can rise above the coating, thereby causing weaknesses of corrosion protection in the coating. Soft metals are therefore not suitable for sand blasting.

Because of the partial removal of the metallic substrate the blasting medium is contaminated with metal particles. When treating different metallic materials, therefore, traces of metals can be transferred from the blasting medium to the surface. The consequence is the formation of local cells which cause an increasing susceptibility to corrosion. The latter applies in particular when steel shot of a different chemical composition is used as the blasting medium. Such problems do not occur of the blasting medium and the substrate are chemically identical.

Application

The cryo-clean process to DIN 8200 works with no problems whatever with regard to galvanic corrosion and also does not removing any metal.

This process involves using solid carbon dioxide at temperatures below –78 °C as the blasting medium. In addition to the mechanical effect, the object is also cooled down. This results in embrittlement and the formation of cracks in the layer to be removed with partial separation of the surface coating. CO_2 which penetrates the cracks and then evaporates blasts off impurities without attacking the metallic surface. Furthermore, no blasting medium waste is created [4.4.4]. Bridges and steel structures are among the objects which are suitable for this process. The substrate treated in this way forms an excellent basis for the subsequent coating.

General industrial companies and the automotive industry also make use of sand or steel-shot blasting if surfaces capable of being painted or phosphated have to be created on castings and other heavy-section steel components. However, the components must be thoroughly cleaned and degreased prior to blasting or else the blasting would press the contamination into the substrate.

Process	**Application**	**Parameter**	**Process Data**		
			Removal of material after 40 s	**Change of roughness R_t before**	**after**
Wet blasting with Al_2O_3	Removal of rust from surfaces, preparing for coating with mild metal grating	Particle diameter d = 90–150 µm/H_2O pressure 300–600 kPa	4 µm	3,0	5,5
Wet blasting with glass pearls	Removal of thin layers, cleaning and polishing with mildest metal grating	Particle diameter d = 150–200 µm/H_2O pressure 300–600 kPa	2 µm	0,9	1,7
Dry blasting with Al_2O_3	Removal of corrosion products, increase roughness for better coating adhesion	Particle diameter d = 50–150 µm pressure 50–600 kPa	≈ 50 µm	4,5	7,5
Dry blasting with steel	Removal of rust tinder and old coatings with significant metal grating	Coarse steel particles d = 600–1000 µm pressure 200–300 kPa	≈ 25 µm	3,5	8,5

Fig. 4.1.13
Application and operating parameters of blasting processes

Even better cleaning can be achieved with steam or wet blasting processes with the supplementary use of alumina or silicon carbide particles, pumice powder or glass beads. These must be mixed with the water in advance and blasted onto the workpiece with steam or water which is under high pressure. Because the mechanical blasting is highly effective, this process is mainly used with solidly attached scale and firmly adhered old coatings.

In practice the machines operate using various particle-acceleration principles. In addition to shot-blasting wheels compressed-air systems are also used. In shot-blasting wheels the medium is accelerated by throw-shovels, and in compression systems by compressed air.

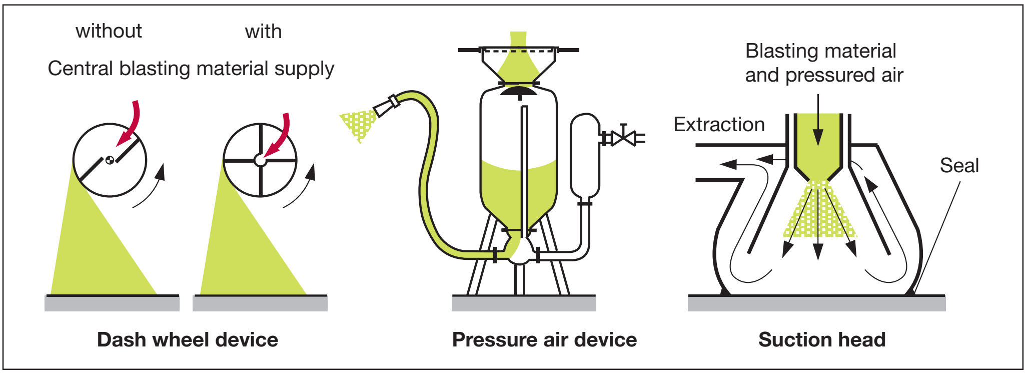


Fig. 4.1.14
Schemes of equipments for surface cleaning by blasting operation

These systems cause environmental pollution with the blasting agent. If they are also fitted with an additional suction head to collect the blasting agent, and removed material, this reduces the environmental pollution while at the same time permitting the reuse of the blasting medium. Since the suction head has to be positioned close to the surface of the workpiece, suction-head systems are ineffective with components of complex shapes.

There has been no shortage of attempts made to provide immediate protection against corrosion for bare metallic surfaces produced by blasting. The object can be sealed during the cleaning process itself with an organic paint coat by means of paint-impregnated blasting media or by the simultaneous spray-coating of a primer in accordance with the Gritcote method.

Rust, all impurities and even old coatings can be removed in a single stage using **flame-cleaning blowers**. Bare metal surfaces can be produced using an appropriately operated hot oxy-acetylene flame set for reduction and then coated with a primer while still warm and, with a high degree of reliability, dry.

Physical cleaning with liquid agents serves to remove surface dirt and organic, artificially applied anticorrosive oils and drawing greases.

Modern solutions of **aqueous detergents** contain tensides, builders and complex

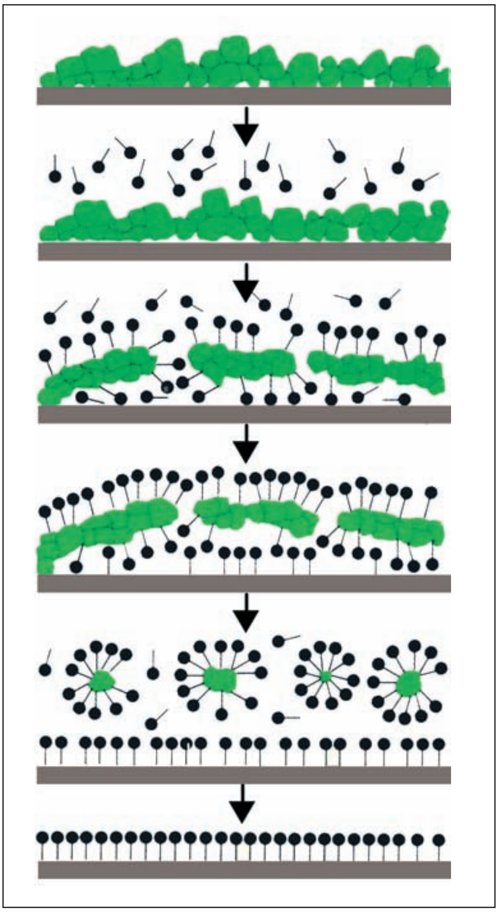


Fig. 4.1.15
Mechanism of waterbased tensides for surface cleaning

agents. Apart from the classic anionic types based on carboxylates and esters of sulphuric acid the tensides in use also include sulphonates. Cationic and nonionic products are also taking on an increasingly prominent role (see chapter 2.1.4). Their task is to wet and emulsify the hydrophobic oils. Tensides are either alkaline, acidic or neutral in accordance with their chemical structure. Alkaline cleaning agents have pH values between 9 and 12. They are particularly active and initiate an additional pickling action in conjunction with phosphates when cleaning aluminium. The acidic cleaning agents contain acidic phosphates in addition to tensides, with the result that a thin phosphate film is formed when pickling steel. The mildest cleaning agents are the neutral agents with pH values of 4 to 10. They are therefore equally suitable for the physical cleaning of steel, aluminium and zinc. All tensides have a polar and thus hydrophilic element and a nonpolar, hydrophobic element. They therefore link the aqueous phase with the surface of the nonpolar greases and oils and promote emulsification with appropriate artificial agitation of the liquid. So tensides and builders enclose dirt and oil particles and stabilize them by forming repelling forces.

Classification	pH	Components	Application
Strong alkaline	10,5–13	• Alkaline • Silicates • Phosphates • Complex formers • Surfactants	• Steel • Heavy soil • High cleaning requirements
Weak alkaline	8–10	• Phosphates • Borates • Carbonates • Activating compounds	• Steel, Zinc, Aluminum and alloys • High cleaning requirements • Suitable for spray application
Neutral	7–9,5	• Surfactants • Corrosion inhibitors • Phosphates • Solvents	• Steel and zinc • Precleaning and preliminary corrosion protection
Weak acidic	3,5–5,5	• Acidic phosphates • Surfactants • Accelerators	• Cleaning and pretreatment of steel and zinc • Cleaning of aluminum

Fig. 4.1.16
Compositions and application of waterbased cleaners

Builders are inorganic compounds which help tensides in emulsifying the greases to be removed. They are so strongly alkaline that they promote the saponification process of the greases and oils and therefore improve their emulsifiability. However, their use is limited to steel. They attack the amphoteric aluminium and zinc too strongly. Phosphates, borates or carbonates are then more useful. In order not to impede the effect of anionic tensides, complexing agents must be used to inactivate the interfering cations of calcium and magnesium.

The degree and speed of cleaning depend on the appropriate selection of the tensides, complexing agents and builders, but also on the temperature, duration and circulation of the cleaning solution.

Because of the high salt concentration, surfaces treated with aqueous detergents must be thoroughly rinsed afterwards with deionized water. Rinsing zones in spray processes offer advantages in respect of the emulsification rate. However, if cavities in complex-shaped components have to be protected, it is better to use the slower dip coating method with them. In smaller systems ultrasound has an accelerating effect.

Environmental and occupational health and safety legislation has substantially restricted the range of permitted solvents and thus the importance of **solvent degreasing**. The chlorinated hydrocarbons such as 1,1,1-trichloroethane, trichloroethylene or perchloroethylene, which were successfully used in the past for degreasing tasks, may now either not be used at all or only in emission-free, fully closed systems and subject to special conditions. They are being used less and less in coating processes and they are therefore not described further.

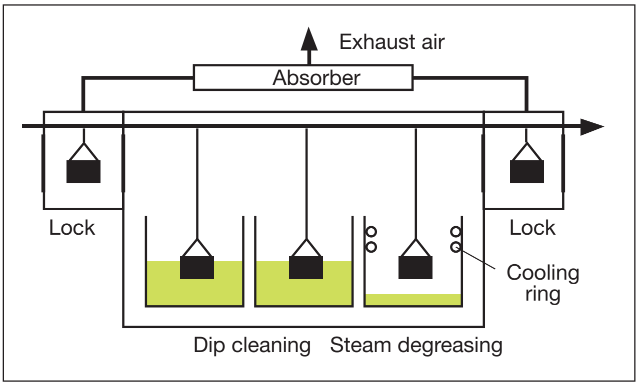


Fig. 4.1.17
Process flow of combined dip and steam degreasing

Hydrocarbons, alcohols, ketones, esters and glycol ethers such as methoxypropanol (PM) and dipropylene glycol monomethylether (DPM) are still used because of their cost-effectiveness, though only under stringent occupational health and safety and environmental conditions. The solvent power of hydrocarbons depends on their aromatic content. Because of restrictions relating to aromatic hydrocarbons, low-aromatic or aromatic-free hydrocarbons are mixed with esters or ethers to increase their solvent power (see chapter 2.1.2).

Hydrocarbons with narrow boiling ranges prevent high-boiling residues from being left on the objects to be cleaned. Among the oxygen-containing detergents, esters of lactic or succinic acids are of increasing interest in addition to the alkoxypropanols mentioned. Both classes of substances have relatively high flashpoints and a good solubilization power for oils and greases.

The solvents are recirculated during cleaning for environmental and economic reasons. It is important to ensure that no dirt particles remain on the surfaces. For this reason the solvents have to be periodically reprocessed by means of distillation before they are reused. By contrast with the aqueous detergents, organic solvents are generally used in dip or immersion systems. The individual sub-units must be enclosed in booths and equipped with air locks.

Because of the danger of an explosion spray processes may only be used with inert gas and are therefore only seldom encountered.

The cleaning process for raw metallic components is made all the more difficult in that microscopic cracks can occur in the surface during deformation in the stamping presses, into which drawing greases can be pressed by the high stamping forces. To this must be added the fact that anticorrosive oils containing carbon double bonds resinify when stored for extended periods, which makes degreasing more difficult.

Chemical pretreatment

The chemical pretreatment methods can be divided into film forming and non-film forming processes. The first group contains the already mentioned flame cleaning as a method of thermal reduction of oxides and the pickling of metal surfaces with acids and bases. The second group includes the processes which form inorganic conversion layers. By this is meant the various methods of phosphating, chromating and conversion processes based on titanium and zirconium compounds.

Pickling solutions are active substances dissolved in water which chemically attack the oxide and the material from the surface to remove or dissolve them. Depending on the material to be cleaned, pickling solutions are acidic or alkaline. Proven acids for cleaning metals include sulphuric acid, hydrochloric acid and phosphoric acid. Caustic soda in pickling baths has proved effective for the alkaline cleaning of amphoteric materials such as aluminium.

The objects to be painted are pickled by immersing them in the aqueous solutions of the acids or bases. The baths are heated to 65 – 80 °C to accelerate the pickling process with the exception of hydrochloric acid solutions. The formation of hydrogen caused by the pickling action and the associated embrittlement of the metal can be controlled by organic inhibitors such as quinoline, thioaldehyde or pyridine.

The film forming phosphating and chromating processes are incorporated after cleaning and before coating, especially where stringent requirements relating to anticorrosive protection have been specified. Such processes have been used very successfully for many decades. Even before 1930 phosphating was a familiar means of improving anticorrosive protection under the trade names Parker, Bonder or Granodine processes. The chemical processes, which ran very slowly at that time, have been accelerated by means of catalysts and optimization measures, and their quality has been improved very much.

The prerequisite for a closed inorganic conversion layer is thorough preliminary cleaning and the complete removal of all oxidic and organic residues.

The simplest method of forming a protective coating for steel is to form an iron phosphate coating. This involves treating the objects, after appropriate preliminary cleaning, with an acidic sodium phosphate solution in a spray or dip method. This results in the release of hydrogen and the formation first of acidic iron hydrogen phosphate in a pickling reaction, which is then converted into insoluble, neutral iron phosphate with atmospheric oxygen.

$$\mathrm{Fe} + 4\,\mathrm{NaH_2PO_4} \longrightarrow \mathrm{Fe(H_2PO_4)_2} + 2\,\mathrm{Na_2HPO_4} + \mathrm{H_2}\uparrow$$

$$2\,\mathrm{Fe(H_2PO_4)_2} + 2\,\mathrm{Na_2HPO_4} + {}^{1}\!/_{2}\,\mathrm{O_2} \longrightarrow 2\,\mathrm{FePO_4}\downarrow + 4\,\mathrm{NaH_2PO_4} + \mathrm{H_2O}$$

The resulting coating is extremely thin (coating weight of 0.3 – 1.0 g/m^2 or less than 1 µm film thickness) which is beneficial when the product is subjected to tough loading. Because of the formation of iron phosphate, the term ”iron phosphating” is used for this type of conversion coat. The term ”alkali phosphating” is also used synonymously because of the acidic alkali phosphate as the active substance. However the term ”non-film forming phosphating” is misleading since measurable film thicknesses are demonstrably produced. The explanation for this confusing formulation is that the layers are substantially thinner than in other phosphating processes and the fact that part of the film comes from the iron substrate.

The anticorrosive protection is clearly exceeded by other zinc phosphate coatings which take longer to carry out and are more expensive because of the higher material consumption. There are numerous variants of the zinc phosphating process nowadays because of the necessary adaptation of the phosphating solutions to the different substrates, substrate mixtures and mixed construction methods. After degreasing, zinc phosphating is carried out using spray or dip coating, depending on the object and specifications. Combined spray and dip coating have proved successful in carmaking because of the improved anticorrosive protection for the cavities (see chapter 7.1). The phosphating bath consists of an aqueous solution of phosphoric acid, acidic zinc phosphates and special additives. At equilibrium there is a fixed ratio between water-soluble hydrogen phosphates of the zinc and insoluble tertiary zinc phosphate.

$$3\,Zn^{2+} + 6\,H_2PO_4^- \longrightarrow Zn_3(PO_4)_2\downarrow + 4\,H_3PO_4$$

Phosphoric acid is consumed during phosphating and therefore the balance in the above equation is shifted to the right. More and more tertiary zinc phosphate occurs and is precipitated as a fine crystalline protective coating on the metal which was etched to bare metal and roughened in the preceding acid action. Unfortunately the hydrogen gas formed by the pickling action has an inhibiting effect on the formation of the phosphate coating.

$$Fe + 2\,H^+ \longrightarrow Fe^{2+} + H_2\uparrow$$

Sodium nitrate and nitrite or chlorate, but also hydrogen peroxide or hydroxylamine, are added to the phosphating solution as accelerators to eliminate the hydrogen. These oxidize the iron to trivalent iron ions while forming water at the same time.

The accelerators are also used in combination. They permit dense fine-crystalline phosphate coatings with film weights of 1 – 3 g/m^2 to be produced within 60 – 180 seconds. Without accelerating additives the phosphating times would be considerably longer, i.e. 30 – 60 minutes at bath temperatures of 90 – 95 °C.

$$3\,Fe + NaClO_3 + 6\,H^+ \longrightarrow 3\,Fe^{2+} + NaCl + 3\,H_2O$$
$$6\,Fe^{2+} + NaClO_3 + 6\,H^+ \longrightarrow 6\,Fe^{3+} + NaCl + 3\,H_2O$$

The iron(III) ions contained in the phosphating solution combine with phosphate ions to form iron phosphate which is very difficult to dissolve. This is removed by sedimentation. The precipitation of the iron ions is necessary since large quantities of iron ions would impair the anticorrosive properties of the zinc phosphate coating by forming mixed crystals.

In addition to pure zinc phosphate coatings phosphating treatments using several cations are also proving increasingly successful. Zinc-calcium or zinc-manganese phosphates may be cited as examples. The microcrystalline, firmly anchored mixed crystals offer excellent anticorrosive protection. Low-zinc phosphate treatments have also been specially developed for cathodic electrocoating. The baths have a high phosphoric acid level. This enables iron ions formed by the pickling reaction to be incorporated specifically in the phosphate coating. The resulting phosphophyllite exhibits good anticorrosive protection properties when combined with cathodically deposited primers. Furthermore, in the case of items made of a mixture of steel and zinc both materials are provided with an equal level of protection because of the more powerful pickling action of the low-zinc process. While the iron-containing phosphophyllite is formed on steel, tertiary zinc phosphate is deposited on the zinc as hopeite. The phosphophyllite-forming low-zinc process was then modified to improve the anticorrosive protection still further. Additives of manganese or nickel ions are incorporated in the phosphate coating as in the zinc-calcium phosphating process.

$Zn_2Fe(PO_4)_3 \cdot 4\ H_2O$ phosphophyllite

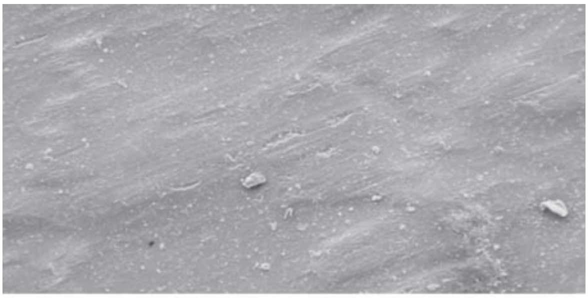
$Zn_3(PO_4)_2 \cdot 4\ H_2O$ hopeite

$Zn_2Mn(PO_4)_2 \cdot 4\ H_2O$	manganese containing hopeite	trikation phosphatation
$Zn_2Ni(PO_4)_2 \cdot 4\ H_2O$	nickel containing hopeite	
$Zn_2Ca(PO_4)_2 \cdot 4\ H_2O$	scholzite	

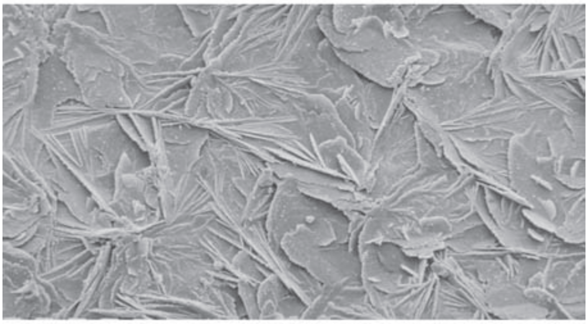
The uniformity of the film forming process is promoted by pretreatment with titanium phosphate dispersions. The manganese ions support the pickling action and therefore contribute to the uniformity of the film forming process. Nickel is becoming less important because of physiological reservations.

Apart from steel and zinc, aluminium has an important role to play as a material. If aluminium is the only material in use, chromating is the usual pretreatment process like in the aircraft industry (see chapter 7.11.3). If, however, a phosphate coat is to be applied to aluminium, the classic methods cannot be used because of excessively powerful pickling action and the formation of soluble aluminium ions. In order to eliminate the interference of the soluble aluminium ions in the equilibrium reaction, they must be transfered to cryolite complexes using sodium fluoride. Silicates act as inhibitors to ensure a moderate pickling action. In this way it is possible to achieve a uniform conversion layer when steel, zinc and aluminium are used together [4.4.5].

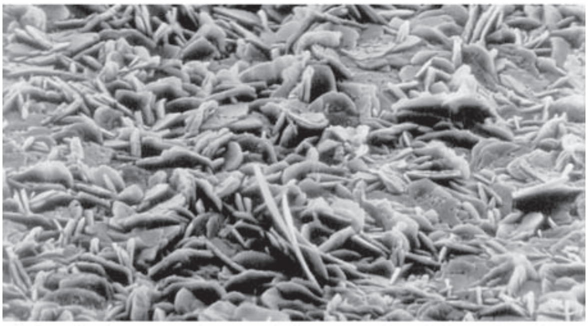
The quality of the phosphating process also depends on the size and shape of the crystals which are firmly attached to the substrate. Because of their porous structure, coarse crystalline layers not only impair the anticorrosive protection, they also have a negative effect on the quality of the topcoat. Activators influence the fineness and thus the closed structure of the crystal matrix. The positive effect of manganese ions and titanium activators has also already been mentioned above.



Automotive steel, degreased



Automotive steel, degreased and phosphated



Galvanized automotive steel, degreased and phosphated

Fig. 4.1.18
Scanning electron microscopic (SEM) pictures of degreased and phosphated surfaces of automotive body steels

It is possible, in order to improve the quality of phosphating coats, to use rinsing solutions to compact the coat, which reinforces passivation. The treatment with chromic acid which was successfully used in the past has been superseded by alternatives because of the hazard it causes to watercourses and because of the carcinogenicity of chromium (6) ions demonstrated in laboratory animals. Zirconium fluoride and titanates have shown themselves to be particularly effective. Polyphosphates also seal the pores of the still free steel surface and therefore prevent the formation of microscopic local cells [4.4.6]. The corrosion rate at damaged locations or pores is also a function of the solubility of the cations which have an inhibiting effect. OH-ion concentration decreases with increasing numbers of manganese ions particularly in the alkaline surroundings of the areas acting as cathodes, and with it the progress of the corrosion.

The influence of the surface structure of the metallic substrate on the uniformity of the phosphate coat should also be noted. Appropriate roughness profiles of rolled sheets for automotive engineering are therefore selected or they are generated by post-treatment with laser beams with defined abrading properties. This profile is significantly changed by the phosphate coat. An example is shown in figure 4.1.19. Although the roughness profile does not increase in terms of peak-to-valley depth compared with the untreated sheet, it does increase in terms of the number of peaks. This is also associated with an

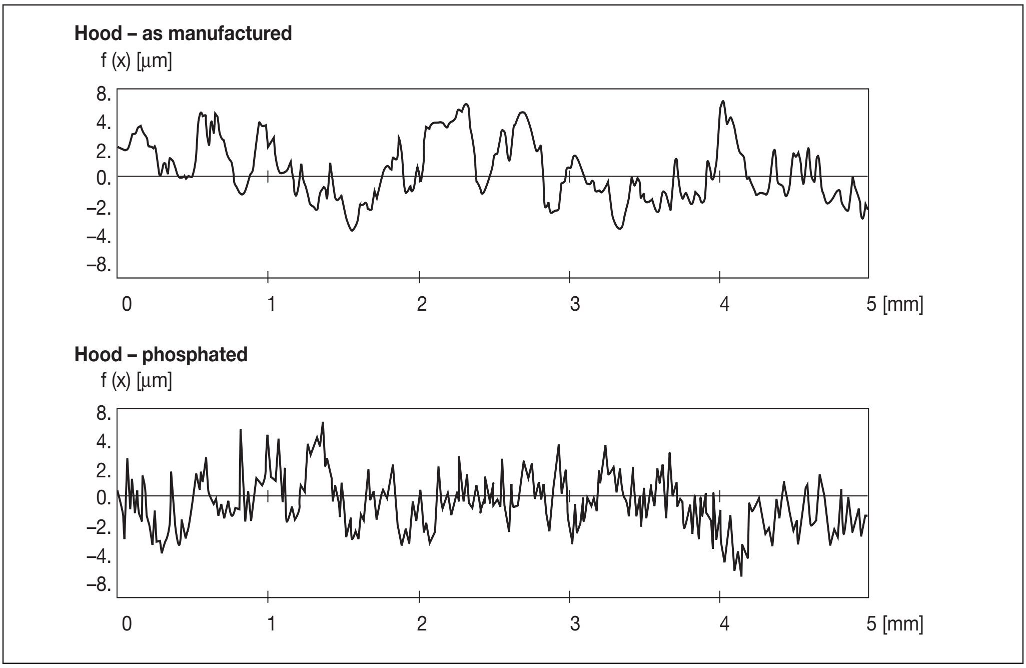


Fig. 4.1.19
Changes in surface roughness of steel surfaces by phosphatation

improvement in wetting and, because of the increase in the surface area, the mechanical fixation and thus the adhesion of the primers.

The film thickness also has a decisive impact on the quality of the phosphate layer. Excessive film thicknesses impair the elasticity and thus all the mechanical/technical properties. On the other hand phosphate layers are electrical insulators and thus chemical inhibitors which slow down the action of corrosive agents on the metal.

One issue which is frequently discussed, but to which a generally applicable and binding answer is never given, is the question of the purpose or effect of subsequent drying of nonpassivated phosphate layers. The results of a large number of trials show that the effects on the anticorrosive protection are system-dependent and a decision therefore has to be taken on the merits of individual cases as to whether drying is meaningful or not.

The pretreatment systems which are commonly used in industry vary in accordance with the requirements on the quality of the conversion coat. Irrespective of whether the system is being operated as a spray or dip system, they usually consist of at least five successive individual stations for cleaning, phosphating, recompacting and interim and final rinsing (see chapter 7.1). It is important to guarantee that all the bath contents have been removed from the workpieces after exiting the pretreatment systems. For the subsequent application of the coating, even traces of electrolytes result in a weakening of the longterm anticorrosive protection as a result of osmotic effects of the salts incorporated in the coating.

Pretreatment processes other than phosphating have also proved successful, especially for aluminium with its dense, firmly attached oxide skin which has poor electrical conductivity, but occasionally also for zinc and magnesium alloys. The chromating processes mentioned previously have the greatest practical significance. A distinction is drawn between green and yellow chromating, depending on the composition. Both pretreatment methods form excellent substrates for the subsequent coating within a few minutes in either spray or dip coating.

$$2\,Al + 4\,H_3PO_4 + 2\,CrO_3 \longrightarrow 2\,AlPO_4 + \underbrace{2\,CrPO_4}_{\text{green}} + 6\,H_2O$$

The main constituents of green-chromating baths for the pretreatment of aluminium are chromic acid or chromates plus fluorides and phosphates. When zinc surfaces are being treated, chlorides and sulphates should also be used to supplement the main constituents.

Aluminium and chromium phosphates form on the surface of the aluminium. As in phosphating, the fluoride serves as a complexing agent for the aluminium ions. The green coloration comes from the trivalent chromium in the chromium phosphate. Although hexavalent chromium is present in the bath, green chromating is free of hexavalent chromium. Solutions of chromic acid or chromates with fluorides are also used in yellow chromating. The first stage in forming a layer is a pickling reaction in which aluminium ions pass into solution. At the same time hexavalent chromate is reduced proportionately to chromium(III)cations by the hydrogen which is formed. As a result cover coatings consisting essentially of oxides and hydrated oxides of chromium and aluminium are formed on the aluminium. In addition to chromium(III)compounds, changing quantities of the yellow chromate are also incorporated in this layer.

$$2\,Al + 3\,CrO_3 + 6\,H_2O \longrightarrow 2\,Al(OH)_3 + Cr(OH)_3 + \underbrace{Cr(OH)CrO_4 \cdot H_2O}_{\text{yellow}}$$

The coating, which is initially still jelly-like in its softness, must be solidified by heat action. Since the temperature resistance is limited to 150 °C, the chromate layers should only be heated to 70 °C, though to 100 °C in the event of a subsequent paint coating. This helps to avoid cracking or chipping. The specific weights of the chromate coats are in the range 0.1 to 0.5 g/m^2.

Because of the toxicity of hexavalent chromium compounds attempts have long been made to find chromium-free **alternatives**. The ever more stringent environmental protection provisions are also adding to the demand for chromium-free pretreatment methods for aluminium.

The formation of chromium-free layers based on titanium-, zinc- or zirconium-containing compounds is achieved by means of a pickling reaction of the phosphoric acid-containing baths which are set to be acidic with simultaneous sequestration of the aluminium ions with sodium fluoride. After that the titanium and zirconium compounds are deposited in the form of phosphates or oxides. The coatings, with a film weight of

only 0.01 to 0.02 g/m^2 are extremely thin. Nonetheless, the protective effect in combination with a subsequent coating is equivalent to that of chromate coats.
The tried-and-tested method of electrochemical oxidation is an alternative to the titanium and zirconium pretreatment. In this process, which is known as anodization, the aluminium components are immersed in dilute sulphuric acid and, as the anode, are coated with a thin, but pore-free barrier layer using a direct voltage of 20 volts.
The parts treated in this way, painted or unpainted, offer a varying level of anticorrosive protection, depending on the type and quantity of alloying components. Unfortunately the process is more expensive than chromating because of the electrical energy required.

4.1.3 Plastics

4.1.3.1 Plastic Types and Properties

Plastics are synthetically manufactured polymers. They can be obtained by synthesising low-molecular structural components or by modifying natural polymer materials. Their manufacture uses the processes of polycondensation, polyaddition or polymerization (see chapter 2.1.1) [4.4.7]. Depending on the functionality of the basic structural elements or the form of the molecules, the materials are sub-divided into thermoplastic, duromeric and elastomeric products. Thermoplastics consist of long linear or branched molecular chains which occur as internally looped individuals. It is a specific property of this class of substances to become liquid on heating because of the increasing mobility of molecules, to solidify on cooling down again, and to pass into solution reversibly in interaction with appropriate solvents.
If, en route from monomers to the solid plastic, crosslinking of the forming polymer molecules is induced, the materials can no longer liquefy with heat action nor be dissolved by solvents. Such materials remain viscoelastic even under extreme conditions (see chapter 3.2.5). They are, therefore, the suitable materials where resistance to solvents and heat are specified.
Elastomers, which are only slightly crosslinked and consist at the same time of movable basic chains, have a very specific property profile. They should always be considered potential solutions when there are extreme demands relating to expandability or reversible deformability. Elastic sealing compounds for joining nondimensionally-stable objects, e.g. for window or concrete frames, or energy-absorbing front and tail components on cars are just two examples of the importance of highly elastic plastics.
Despite a relatively low number of monomer structural elements, the number of technically relevant plastics is extraordinarily high. The reasons for this lie in the fact that, apart from the many molecular shapes and sizes, there is the possibility of combining several monomers during manufacturing in the form of copolymers and the physical mixture of already finished polymers as blends. If it is also mentioned that the configuration of the monomers in copolymerization can be designed to be random, alternating or in block form, it is easy to see why the range of plastic types is so great.
In order to modify their mechanical properties plastics are often modified with fillers, to influence their hardness, or fibres, to enhance their cohesion. The embedding of reinforcing materials in the polymer matrix significantly improves the tensile and breaking strengths and the impact and notch impact strengths. Glass fibres are the most widely

used reinforcing materials. If the specification is to design high-strength, high-performance plastics with a low weight and low thermal expansion, carbon fibres are also suitable auxiliary materials.

Ongoing improvements in plastics are taking over more and more new application fields, both for everyday products and also for industrial purposes. Their specific properties such as low weight, deformability, corrosion resistance, toughness and elasticity on the one hand, but also hardness and internal strength, on the other hand, and their high resistance to the action of solvents and chemicals are the major benefits of plastics over many other materials.

In addition to their traditional use in large areas of the packaging and construction industries and in electrical engineering, they are now also being used increasingly in automotive engineering, the latter primarily because their ability to adapt to specific requirements such as design options, weight reduction, non-corrosive properties, impact elasticity, and not least their price.

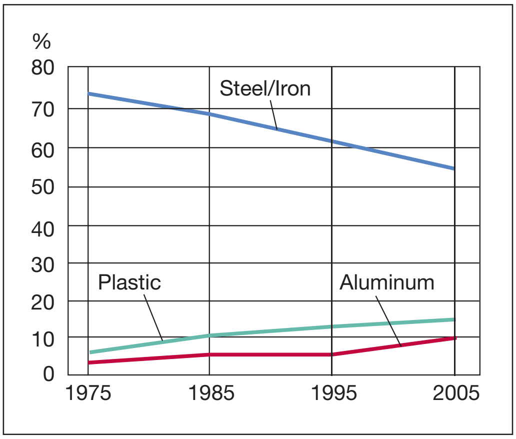


Fig. 4.1.20
Development of plastic usage in weight percent in automotive construction

It may sound paradoxical but plastics, made from crude oil, become cheaper compared with metallic materials when the energy price rises. It is often forgotten in comparative studies that large amounts of energy are also needed to manufacture metallic materials from their oxides and to convert them into the workpiece by melting or by drawing and pressing processes. For example, 1 kg plastic is manufactured from 2.5 kg crude oil, taking account of energy and material losses, whereas 4 kg crude oil equivalents are needed in the manufacture of steel, 12 kg for copper and as much as 15 kg for aluminium. These figures do not contain the energy for deformation processes required in the manufacture of the workpieces.

To this must also be added the simpler manufacturing process for complex-shaped parts and components without lavish welding and joining methods. Solid or expanded-plastic components, which are lighter and therefore being increasingly used in aerospace and automotive engineering, can be manufactured quickly and economically using injection-moulding or extrusion methods. In similar fashion liquid base materials can be converted in chemical reactions into duromeric plastics and closed- or open-cell foam plastics in every hardness grade and density variant. One well-known method is the proven reaction-injection-moulding process (RIM) for polyurethane plastics and unsaturated polyester resins. This involves injecting the reaction mixture into a mould, where the materials react with each other to produce a solid or foam material. Where fibres are added for reinforcement purposes the process is termed reinforced reaction-injection-moulding (RRIM). Another method of producing duromer mouldings is the compression moulding of semi-finished product, known as prepregs. These are fibre laminates impregnated with synthetic resin, generally unsaturated polyester resins (UP),

Type of plastic	Short form/ abbreviation	Application
Polyurethane	PUR	
	• PUR hard foam	Window frames
	• PUR medium hard foam	Spoiler, bumpers, steering wheels
	• PUR soft foam	Spoiler, head sets
Polycarbonate	PC	
	• Pure	Crash helmet, lamps, bottles, windows
	• Modified	Front spoiler, bumpers, front ends
Polyamide	PA	Wheel covers, front spoiler, garden furniture, pipes
Polyethylene terephthalate	PET	Cooling grids, front ends, gasoline covers, bottles
Polypropylene-ethylene-diene moulding	PP-EPDM	Bumpers, front and rear spoilers
Acrylnitrile-butadiene-styrene copolymers	ABS	Cooling grids, rear spoiler, toys, computer housing
Polyphenylene oxide	PPO	Instrument panels, television, pipes, containers
Polystyrene	PS	Flower pots, television, audio equipment, computer housing, toys, household goods
Polyvinylchloride	PVC	Pipes, foils, window frames, toys, balcony balustrades
Polymethylmethacrylate	PMMA	Rear lamps, windows, household goods, audio equipment
Glass fiber reinforced unsaturated polyester	UP-GFR	Front spoiler, bumpers, sun roofs, boats, skiers
Epoxy	EP	Rackets, gliders

Fig. 4.1.21
List of platics usually being painted

which are only cured once they have been moulded into a workpiece in a die. This process is known as sheet moulding compound (SMC).

The selection of the plastic is therefore determined by the specific requirements it has to meet. The mechanical, chemical, thermal and electrical properties have an important role to play, as do factors such as transparency or pigmentability, resistance to longterm outdoor exposure, processibility and the price.

Figure 4.1.21 shows an overview of the thermoplastic and duromer products commonly used for general industrial purposes together with their abbreviations to DIN EN ISO 1043-1.

Because of their naturally smooth and relatively resistant surfaces plastics and plastic objects can certainly be used in unpainted form. Since most plastics can be pigmented during their manufacture, the desire for color can be satisfied without the need for a painting process which involves both time and costs. Despite the inherent benefits of pigmented plastics, the process of painting plastics has nonetheless proved itself in many applications. The reasons for this may be of a cosmetic or functional nature. Improved resistance to light by means of UV-protective coatings, improved resistance to longterm outdoor exposure, waterproofing, solvent or chemical resistance through the use of saponifying, solid, highly crosslinked protective coats merit special mention. Effects on flame retardance, electrical conductivity, abrasion resistance or cleanability are further important arguments with regard to the functionality of the polymer workpiece.

From an economic perspective, effect coatings should be particularly borne in mind. A coating with a thin colored polymer skin consisting of expensive effect materials and pigments is often more cost-effective than the complete pigmentation of what are sometimes very large components, despite the additional surface treatment involved. Where mixed materials are used, it should be noted that it is not possible to achieve an optically identical appearance for the pigmented plastics and the painted metal components. The different surface structures of metal and plastic surfaces require surface treatment with paint to achieve a visual match.

Sometimes plastic elements such as dashboard components and trim strips on motor vehicles are required to have a metallic appearance. This is achieved by vapour-deposition of metals such as aluminium, copper, silver or even gold. Since plastic surfaces are generally not smooth enough to permit the production of a perfect metal level they must first be painted with a primer before metallization. Furthermore, the vapour-deposited metal layer has to be coated to protect it against mechanical damage and corrosive influences.

If plastics are to be painted successfully, it is important to have precise information on the specific properties of the materials and workpieces. Thermal properties, solubilities, structure and polarity, but also production-induced properties such as frozen-in strain, nonhomogeneous discharge of additives, release agents, sink marks, bond lines, blisters below the surface, visible or even projecting glass fibres, impurities from the tools or dies, electrostatic charges and particularly wetting and adhesion problems are the major causes of coating problems to mention in this context.

4.1.3.2 Pretreatment

The quality of coatings on plastics depends to a considerable degree on the correct selection of the paint system and the state-of-the-art preparation of the surface. The adhesion which is necessary for lasting protection can generally only be achieved by applying a material-specific pretreatment. The pretreatment includes the removal of release agent residues and soiling, the dissipation of electric charges and the elimination or levelling of production flaws.

During the manufacture of plastic components by means of injection-moulding of thermoplastic materials, compression-moulding of duromers or reaction-injection-moulding of polyurethanes the surfaces come into contact with release agents which facilitate remove of the moulding. Such release agents generally consist of oils, wax-like substances or metal soaps. Silicone-containing release agents should not be used because of the difficulties removing them and the associated high risk of contamination of the coating. Greasy soiling marks caused in transit, sweat from hands and dust, which also impair the adhesion and often in addition the appearance of the paint coating, have just as adverse an effect as release agent residues.

Wiping down with dry woolen and synthetic fibre cloths is not recommended because this generates a static charge in the plastic components. Because of the low conductivity the electrical charges remain where they were generated and attract dust particles of the opposite charge to them. This effect can be prevent or lessened by increasing the conductivity. Thus plastics can either be antistatically equipped during their manufacture or subsequently treated with antistatic agents. However, these antistatic agents only reach their full effectiveness above a certain relative humidity. Furthermore, they have a certain level of volatility, as a result of which their effect gradually diminishes. One method which has proved successful, therefore, is to blast the component to be painted with ionized air directly before coating it. The alternating-current ionizer first neutralizes the fixed electric charges and then blows the adhering dust from the surface using an adjustable air current.

Relatively simple processes such as washing with tenside-containing aqueous domestic or industrial detergents are often suitable means of thorough direct cleaning. The effect can be substantially enhanced by heating to approx. 50 °C and using high pressure (“power wash”). The use of organic solvents for cleaning purposes must be very carefully matched to the plastic to be coated in order to avoid damage to the surface of the plastic. Furthermore, solvents can result in weakening of the internal strength because of their ability to penetrate the plastics.

Excessively rapid cooling of the plastic workpieces during manufacture results in tensions or strain being frozen in, and these can cause cracks with the action of solvents. With many thermoplastics, therefore, particularly polystyrene, polycarbonate and polymethyl methacrylate, a few minutes of tempering should always be interposed before the painting process. This should involve heating the materials to just below their softening point. The internal tensions are cancelled out thanks to the increased mobility of the molecular segments, and the macromolecules occupy their thermodynamically ideal location.

In order to achieve good adhesion the mechanical pretreatment operations which may be considered include roughening (satinizing) and sanding. Regrettably blasting and sanding processes are difficult to automate and therefore costly. Care must be taken not to use excessively coarse abrasives or shot, or to sand too hard, particularly with glass-fibre-reinforced materials, as new problems will be created thereby because of surface faults. For these reasons mechanical processes are little used.

Where no reliable adhesion between the cleaned plastic surface and the coating can be provided by special bonding agents or as a result of slight dissolving or swelling of the primer because of solvents, oxidizing chemical processes are used. This include the action of fluorine or flame-treatment with gas burners adjusted to ensure oxidation. Surface treatment with plasma has proved particularly effective. Gas discharges are induced in vacuum chambers at pressures of approx. 1 mbar by connecting a high direct voltage to two electrodes. This results in ionization of the gas molecules. The plasma is then introduced into the test chamber where it acts on the surface of the plastic parts and chemically changes them. Plasma of oxygen or of oxygen/nitrogen mixtures is particularly suitable. However, the effectiveness of the process must be weighed against the cost of the equipment.

A process operating under normal pressure uses high-frequency alternating voltages to generate free electrons which are also capable of chemically changing the surface of the plastic. The process is based on a gas discharge caused by electrodes designed as contact elements with an alternating voltage of 10 – 20 kV at 20 – 40 kHz. The corona discharges give rise to atomic oxygen and the extremely reactive atomic nitrogen. Both gases are adsorptively bound to the workpiece to polarize the surface. The polarization then results in an increase in the surface tension. This improves the wettability, but also the intercoat adhesion [4.4.8]. The volumes of ozone generated during operation of the systems (0.05 ppm up to limit values of 0.1 ppm) are within the permissible range for

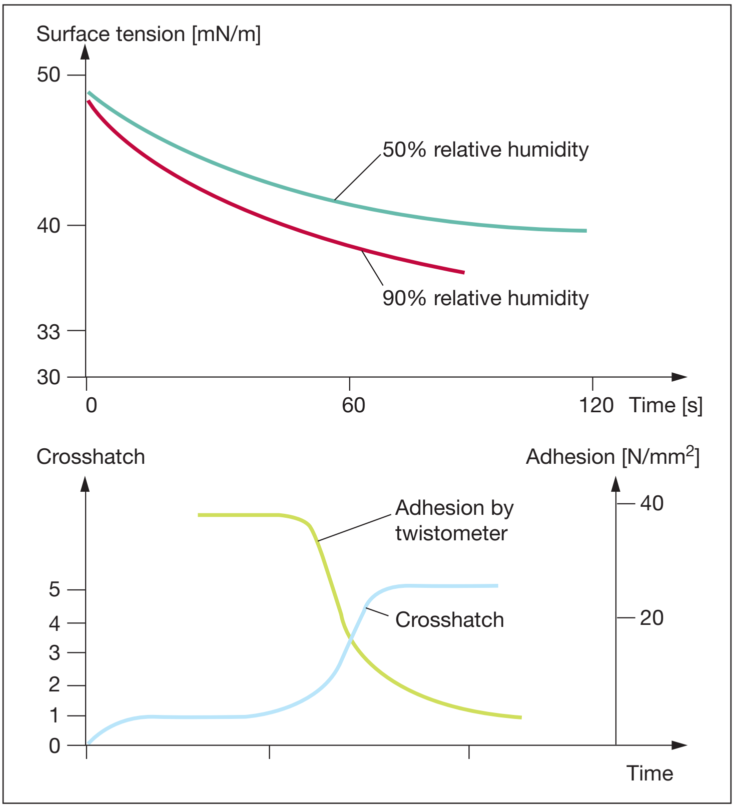


Fig. 4.1.22
Changes of surface tensions and adhesion values of plastic corona treated surfaces by time

manual application. Infrared spectroscopy can identify generated peroxides and polar products, such as aldehydes, ketones, carboxylic acids and hydroxyl groups on the surface of the plastics. Compared with the untreated plastic, the surface tensions can be increased temporarily by more than 10 mN/m.

This effect gradually diminishes again as a function of the relative humidity of the air. Some of the generated polar groups are evidently only physically bound. It is important, therefore, to apply the subsequent paint coating within one hour if possible when using corona-discharge equipment with a high relative humidity.

If the recommended times are observed, constantly good intercoat adhesion is achieved. However, the process only works with components of simple geometric shape because of the very short range (only half a centimetre) of the activated gases.

Pretreatment also includes eradicating defects on the objects to be coated. Even under the most careful production conditions surface defects can occur in plastic components which seriously impair the outcome of painting operations. Flow lines, joint lines (”bond line readouts”) [4.4.9] or differences in gloss levels can only be eradicated with a high input involving polishing or buffing. A simple process is available specifically for the joint lines. Sprayable joint line liquids can be used to treat parts made of impact-resistant polystyrene (PS), styrene acrylonitrile (SAN), acrylonitrile-butadiene-styrene (ABS) or polycarbonate (PC). These joint line liquids are solvents which are matched to the plastic under treatment. They cause slight swelling and separation of the thin polymer skins without damaging the solid plastic. They not only cover the production faults, they also improve the general usability properties and the antistatic effect of the plastics.

Concealed blisters are a particular problem. The air inclusions in the liquid plastic of the reaction materials in the closed moulds or the gases which occur during processing enter the interface between the plastic component and the mould. A thin polymer film then often remains between the blister and the mould wall.

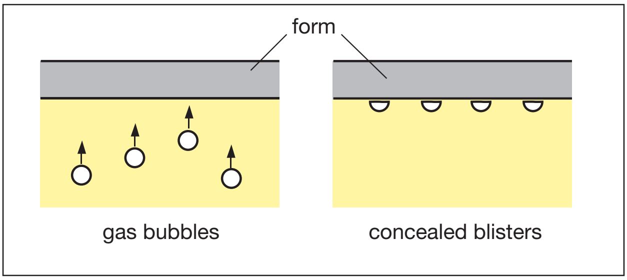


Fig. 4.1.23
Concealed blisters before and after coating of plastics

After release from the mould these flaws are initially not visible to the eye. During the subsequent painting the covering skins are destroyed either by solvents or thermal expansion in the oven, as a result of which the coating material can penetrate the blisters. This causes significant faults in the painted surface. In such cases it is sensible to puncture the blisters deliberately by thermal pretreatment and then level the resulting indentations with filler.

The pretreatment methods described thus far do not increase the poor electrical conductivity of usual plastics sufficiently to permit the electrostatically assisted application of paints to be carried out. This would require the electrical surface resistance to be reduced from its original 10^{12} to 10^{14} Ωcm by several powers of ten. This can be done by adding conductive carbon blacks to the plastic material during compounding or by coating already manufactured components with electrically conductive paints.

One process which is specially designed for the plastic coating is the application of a primer or single-coat finish to components while they are still in the mould. In this process, known as inmould coating (IMC), the mould in which the plastic is pressed or cured in conventional methods is opened by a few millimetres to permit the primer material to be injected. When the mould is closed, this material is uniformly distributed over the surface of the plastic and then pressed and cured.

Because of the low resistance of thermoplastics to heat and solvents the standard plastic paints are either waterbased, air-curing dispersions, oxidatively curing alkyd systems or force-dried 2-component polyurethane paints (see chapter 7.3) [4.4.10, 4.4.11].

4.1.4 Mineral Substrates

4.1.4.1 Concrete, Mortar, Plaster

Concrete is one of the most important construction materials. It is used in civil engineering projects including the building of roads, bridges, industrial buildings and houses. According to DIN 1045 concrete is a synthetically manufactured stone material made of a mixture of cement, aggregates such as gravel and sand, other additives and water. It is sub-divided into reinforced concrete, prestressed concrete and simple concrete. Set concrete is classified according to its density as lightweight concrete with a maximum density of 2000 kg/m^3, normal concrete with values of 2000 – 2800 kg/m^3 and heavy concrete with a density above 2800 kg/m^3.

Concrete is extremely resistant to ageing and normally requires no further protection for it to withstand the influence of the weather in the long term without suffering damage. For that reason it was not usual in the past to apply a surface protection to concrete as a matter of course. Coatings were applied solely for cosmetic purposes. At the latest at the time of the collapse of the prestressed concrete roof of the congress hall building in Berlin, however, it became clear that, as a result of the carbonatization of the alkaline concrete, the pH value can fall below 10, which means that the reinforcement steel, which is being used more and more, is subject to corrosion, even if it is fully enclosed by concrete. Since then, CO_2-barrier coatings have become usual for functional reasons to protect reinforced concrete structures. It should be noted that concrete is an absorbent substance to a greater or lesser degree, depending on its density, which requires pretreatment, depending on the admixtures and additives used.

The surface roughness of concrete varies as a function of the raw material mixture, its processing and the smoothness of the moulds or formwork. This results in a greater or lesser ability to absorb water via cavities. To this must be added the influences of the varied additives and release agents. These include special tensides to influence the rheological properties of the fresh concrete just as much as hydrophobic compaction agents to increase its impermeability to water. Additives which retard or accelerate the setting process are also important formulation components in this context.

The requirements on the concrete surface are specified in detail in DIN 18217. It should be solid and free from loose layers and bloom. It can be recommended that the concrete surface be pretreated by sand-blasting before applying an organic coating. Any cracks present should be sealed using a resilient filler.

The release agents used between the formwork and the concrete surface must also be taken into account in any later surface treatment or pretreatment. Mineral oils, water/oil or oil/water emulsions and waxes are used as release agents. Before concrete can be painted, any residues of these release agents must be removed. Otherwise patches will form on the coating or the coating will peel off. Such removal is not easy in essence precisely because release agents are required to be water-insoluble and to remain effective over an extended period. Under no circumstances may organic solvents be used to remove release agents as these can penetrate the concrete.

A concrete coating must have a high diffusion resistance to CO_2, so that it can effectively prevent the carbonatization mentioned above. Since concrete is always alkaline, longterm protection can only be provided by coatings which are resistant to saponification. Aqueous acrylic resin dispersions or styrene copolymers such as butadiene-styrene or acrylonitrile-butadiene-styrene, organically dissolved epoxy resins or moisture-curing polyurethanes are established paint systems. Chlorinated and cyclorubber paints as modified natural materials are also well suited to the protection of alkaline mineral substrates [4.4.12].

The numerous types of mortar and plaster offer similar conditions for coating materials to those of concrete. Plaster on external or internal walls or ceilings is a special mortar layer applied in a particular thickness. Whereas concrete is used solely as a base material, mortar is used to provide the joints in masonry, and plaster to provide cosmetic cover on walls and ceilings. Unlike concrete, mortar and plaster contain various additives plus lime and, in special cases, even gypsum (calcium sulphate). Curing with water is supplemented by the slow conversion of the lime with CO_2 to calcium carbonate which takes several weeks.

Because of their alkalinity, the same rules apply to the surface treatment of plastered masonry surfaces as for concrete surfaces. The amount of preparatory cleaning work is lower because of the lack of contamination by release agents. It should be noted that H_2O is formed during the curing of the lime component, as a result of which plastered surfaces release water for several months and therefore only coatings which are permeable to water vapour may be used.

4.1.4.2 Glass

Glass is an amorphous mixture of glass-forming substances such as SiO_2, B_2O_3 and P_2O_5, alkali metal salts to lower the melting point and stabilizers such as carbonates of calcium, barium, lead or zinc. As an inorganic transparent material with a softening point of approx. 1500 °C, glass is seldom surface-treated. If, however, an inscription is to be made or a particularly decorative appearance needs to be achieved, glass products are also provided with organic coatings.

Glass is a poor conductor of heat and electricity. As a result it quickly generates internal tensions when heated. Glass is not absorbent and is extremely smooth. Coatings with a good finish quality are therefore easily achieved. Consequently, attention is directed mainly towards good adhesion between the coating and the surface of the glass.

Glass which is to be coated should be thoroughly prepared using aqueous or organic detergents and, if necessary, also etched with aggressive acids, such as hydrofluoric acid, in order to create the ideal conditions. The paints are then selected in response to the requirements of the particular product.

4.1.5 Other Substrates

4.1.5.1 Rubber

The raw material for the production of rubber is obtained from hevea plants as 1,4-cis-polyisoprene, or caoutchouc, in the form of a latex dispersion. The elastomeric rubber is produced by macroporous crosslinking with sulphur bridges.

The hydrophobic effect of aqueous dispersions of caoutchouc has been known for centuries. South American Indians impregnated their clothing with the extract from the hevea plant. Only later was the method for crosslinking crude rubber by means of vulcanization discovered. The experience of *Goodyear* and *Parker* enabled car tyres to be made permanently resilient and wear-resistant. Rubber is a versatile material nowadays. Rubber soles, shoes, boots, balls, countless robust parts in consumer goods and resilient sealers are based on this material.

Because of its special material properties rubber as an object to be painted places particular demands on the coating materials. To prepare rubber articles for coating, any impurities on the surface, particularly release agents from the manufacturing process, have to be removed. This is done by simple washing with solvents such as gasoline, alcohols or alkaline aqueous detergents.

Consumer goods made of rubber require correspondingly elastic coatings because of their huge expandability. Oil paints and alkyd resins used in the past because of their good adhesion, often applied before vulcanization to create a better bond, suffered from the disadvantage of embrittlement and therefore had only a limited lifetime.

More suitable coating materials are based on solutions and dispersions of elastic chloroprenes or chlorosulphonated polyethylene products, silicone resins and resilient polyurethanes. Because of their resistance, low wear and longterm resilience polyurethanes have now become the most important coating materials for elastomers. This use is not only limited to the classic natural rubber but also extends in the same way to numerous synthetic elastomers such as EPDM.

4.1.5.2 Leather

Leather is processed animal skins which have been bated and tanned to make them supple and stable. The leather which consists of proteins is treated to this end with tanning agents and inorganic complexing agents.

Only in rare cases is a color-imparting surface treatment not carried out. Measures to affect the appearance and the properties represent two different goals. By this is meant the color, gloss and effect of the leather, on the one hand, but also protection against water, improved cleaning properties and constant elasticity, on the other. Apart from impregnations to make the leather hydrophobic, primers are applied which have a levelling effect if the leather has a pronounced grain. Finally, leather paints are applied for decorative purposes. These can be pigmented opaque materials or also transparent products. The coating materials used include conventional, solvent-containing and water-soluble or water-dilutable materials.

Solvent-containing leather paints contain cellulose nitrate, cellulose acetobutyrate and cellulose acetate, but also polyurethanes and acrylic resin dispersions. Because of the demanding elasticity specifications, elastic polyurethanes and cellulose derivatives appropriately regulated with plasticizers should be used.

4.1.6 Work Piece Design and Coatability

In addition to the properties of the material, its specific surface structures and its pretreatment, the impact of the design and joining method on processes when painting and on the coating quality which can be achieved should not be underestimated. Designers of consumer goods have to bear certain basic rules in mind if the desired quality expectations of the object to be painted are to be met in the long term. Specific design-related factors have to be addressed for the most commonly used materials today, i.e. wood and composite materials, steel or other metals, and plastics.

In particular, measures have to be taken for finished components made of wooden materials to avoid stresses arising from longterm moisture action. Furthermore, conditions have to be created in the design which enable a coating to be uniformly applied.

The correlation between design and durability of the coating is especially evident with windows. When designing the frame profile, it should be ensured that water can drain off. All joints should be as flush as possible, using tenon-and-slot mortises or double tenons. All edges should be rounded to reduce the effect of paint running away from the

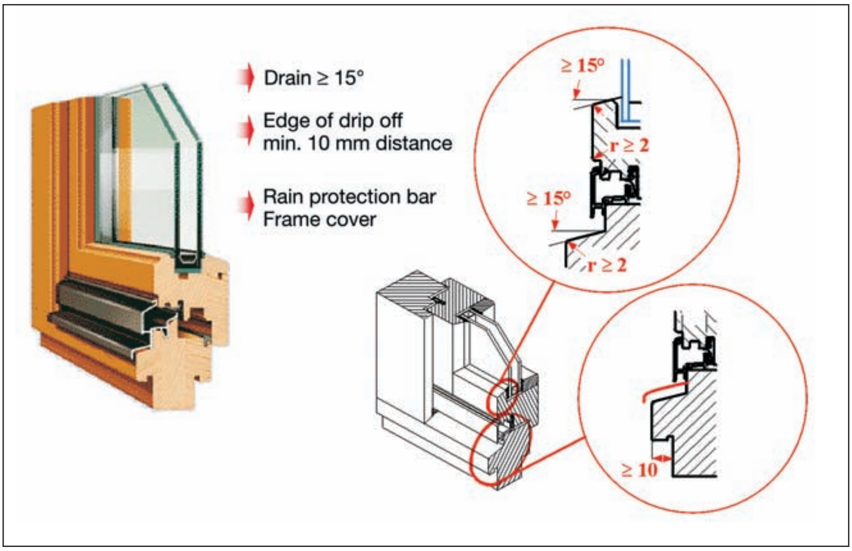


Fig. 4.1.24
Example of a well coatable window

edge and thus to guarantee an adequate film thickness in all areas of the coating. Effective seals must be provided between the casements and the frame. These seals must have sufficient longterm elasticity because of the permanent tensile, compressive and shear loads. This is the only way in which the necessary protection can be guaranteed at all connecting points of the window with glass and masonry [4.4.13].

Leaving aside the coating of planar endless coils in the coil coating process, metallic objects which have to be painted are often of extremely complex shape and include welded and riveted joints or bonded connections with cavities to stabilize the products. Beads and sharp cut edges make the geometry of the object to be coated even more complex. Cavities which are closed or are difficult to access must either be effectively and permanently sealed or made accessible for coating materials; then, however, good ventilation of the cavities must be provided, and with it the necessary conditions for longterm anticorrosive protection. Capillaries, narrow gaps and large overlaps must be avoided. When using dip coating it is important to avoid having scoop-like parts in the object. The rounding of cut edges and dispensing with sharp-edged beads are further sensible requirements. The burr on edges causes the still liquid material of fresh coatings to run away from the edges. Sharp edges should therefore be rounded or protected by means of PVC strips after beading.

Places where water can accumulate must also be avoided. In addition, numerous conditions relating to welding must be observed: sheet metal overlaps should only touch at the welds. There must be an adequate gap between all other areas so that they can be coated (fish mouth design; see figure 4.1.25).

Other potential weak points must be eradicated by the design. For example, the front of a car is particularly at risk from stone-chipping. Raked shapes reduce the problems.

A passive measure which can be implemented is to select the right material. Often, therefore, corrosion-resistant metals, precoated sheets or plastic parts are integrated in the otherwise steel workpiece. Using a mixture of materials enables the individual parts of the object to be better adapted to practical requirements. When using different metals the avoidance of local cells is of primary importance for good corrosion protection.

The fundamental rules are: avoid permanent moist spots by ensuring that water can drain properly, do not create areas which are inaccessible for paint as a result of punched holes or similar measures. Furthermore, sharp edges should be eliminated by rounding them, metal beads should be protected by plastic strips, suitable materials should be selected, and galvanic corrosion caused by contact between different metallic materials should be avoided.

4.1.7 Summary

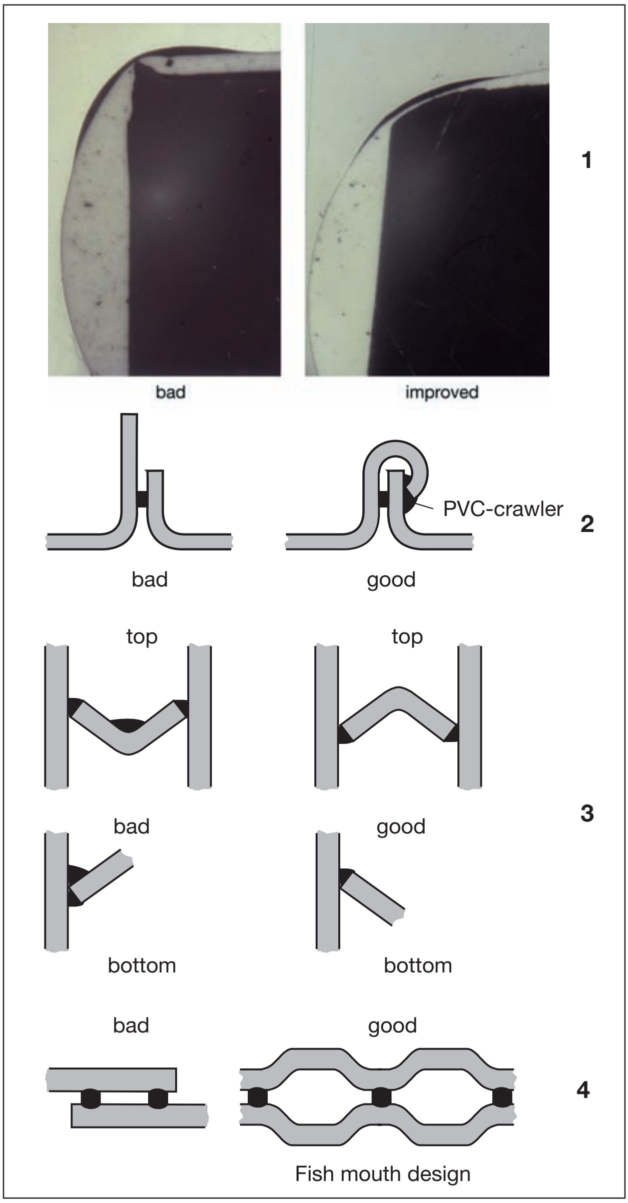


Fig. 4.1.25
Example of well coatable construction elements (1-4) in form of different cross sections

The vast majority of all commodities and consumer goods need to be painted for protection. Due account must be taken of the specific material properties of the objects to be painted. Wood, plastics, metals, mineral substrates and natural materials such as leather and rubber are different materials in many respects. Thermally stable metals feature only minor expandability, but are susceptible to corrosion. Wood is a thermally unstable, absorbent material which degrades with longterm outdoor exposure and exhibits different properties during the painting process from plastics which are sensitive to solvents and are often thermally unstable.

Other factors which influence the selection of and processing method for the coating material are the design and construction of the workpieces. Cavities in which moisture accumulates, edges from which the paint runs or overlaps of sheets which cannot be reached by the coating materials are weaknesses when it comes to producing a lasting coating.

In all cases a perfect coating is only possible if the surfaces have been pretreated in an appropriate manner for the subsequent painting process. This involves removing all impurities such as dirt, corrosion products, oils or drawing greases from the surface. Supplementary chemical operations are often necessary, such as film forming phosphating or chromating in the case of metal objects to be painted or, when dealing with plastics, oxidation reactions to increase the polarity and prepare the surface for good wetting and adhesion strength. Only when pretreatment which is appropriate to the process and has been adapted to the material or workpiece has been carried out have all the conditions been met for a lasting coating.

4.2 Paint Processing

A very wide range of processes is available to convert the paint into the end product, the coating. The associated process stages must, if they are to be successfully implemented, on the one hand be matched to the nature, size, shape and number of objects to be painted per unit time and, on the other hand, take due account of the properties of the paint to be used and the painting sequence of a multicoat paint system.

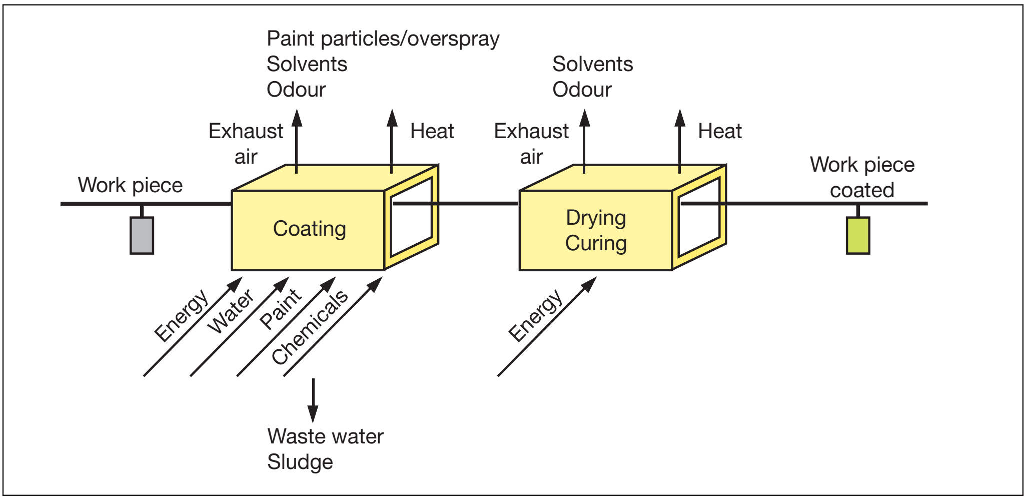


Fig. 4.2.1
Application, drying and hardening of paints

All industrial painting processes have a division into two successive sub-stages in common.
In the first process stage, application, a generally organic coating material is applied to the pretreated surfaces (see figure 4.2.1). The paint-application process ranges from manual processes, which require craft skills and ability on the part of the user, to large-scale systems with high-output process-controlled automatic systems and robots.
The aim of the second process stage, drying and curing, is to convert the applied paints into the usable coating. During this, physical processes of solvent release overlap with chemical crosslinking processes. The energy required for this is transmitted by convective heat exchange, by infrared radiation, microwaves, or UV or electron radiation (see chapter 3.1 and 4.3).

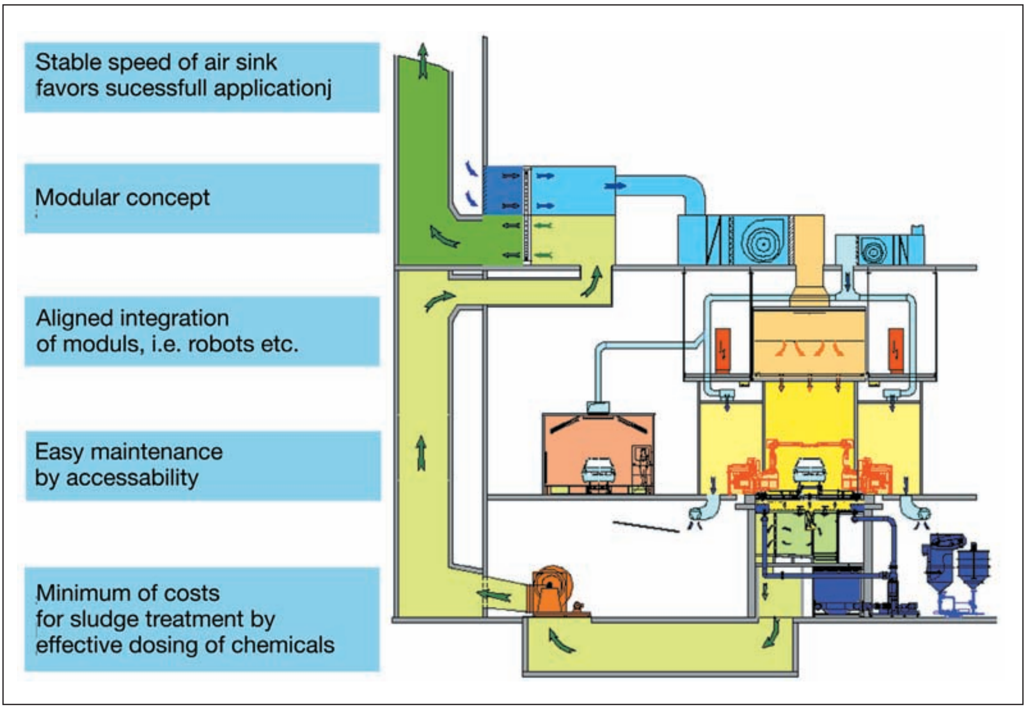


Fig. 4.2.2
Cross section of a paint shop for spray application process of mass products

4.2.1 Processing of Wet Paints

Figure 4.2.3 shows a simple and clear system for classifying painting processes.
In conventional dip coating processes or those assisted by electrochemical coagulation the object is transported to the coating material. Such processes also include fluidized-bed coating for processing powder coatings.
In all other processing methods the coating material is taken to the object to be painted. This can be done directly by means of manual or mechanical roller, curtain or flood coating with only low material spill or indirectly by means of atomization and spray coating, albeit with at times considerably lower material yields. Despite this disadvantage the latter processes are the most commonly used industrial application techniques. The tried-and-tested application methods include pneumatic spray application using the high pressure method, the hydraulic airless spraying method or purely electrostatic and electrostatically assisted methods such as high rotation atomization.

Object to Paint	**Paint to Object**
Conventional dipping • Solventborne paints • Waterborne paints	**Direct processes** • brushing • scrolling, rolling • flooding, pouring
Electrodeposition • anodic • cathodic	**Indirect processes** • High pressure atomization • Airless atomization • High rotation bell application • Electrostatical atomization

Fig. 4.2.3
Important coating processes

4.2.1.1 Dip Coating (Object Taken to Paint)

Conventional dip coating

Dip coating is one of the simplest and oldest methods of painting industrial goods. It is easy to automate, has a much higher material yield when compared with spray coating and low capital costs. The process makes use of the adhesion properties of viscous paints on the objects to be painted. Its disadvantages are the lack of processing window with regard to film thicknesses and the defects associated with it, such as runs and blisters, the costs and the need for special precautionary measures to avoid explosions or fires when using solventborne paints. As a result of these dangers and corresponding incidents practically only waterbased dip coats are now used in the few still operating conventional systems.

Attempts to replace water by trichloroethylene did not succeed in overcoming all the difficulties associated with the process. Even though, the tendency to run was reduced and a greater uniformity of film thickness was achieved, there was the question of the fire risk, and thus it was the already mentioned occupational health and safety reasons which ensured that this very useful and sometimes successful process was relegated to secondary importance again.

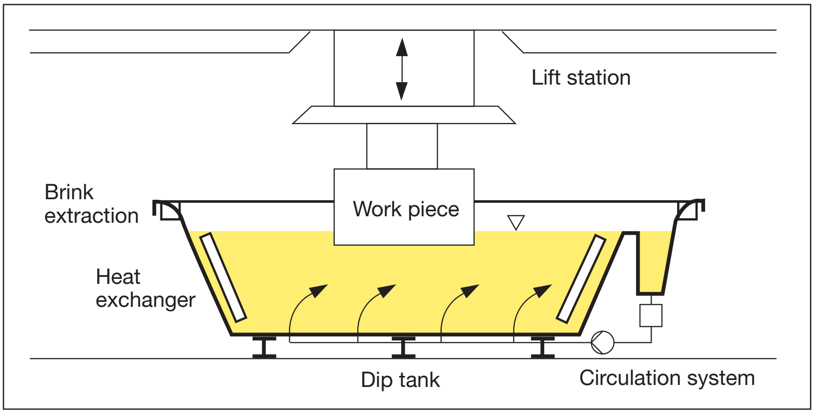


Fig. 4.2.4
Process scheme of conventional dip coating

In dip coating the workpiece is immersed, either in a batch or continuous process, in the relatively low viscous paint, removed and, after passing through a draining section, conveyed to the oven. Draining, combined with evaporation of the solvents, has to last long enough to ensure that no surface defects in the form of blisters, pinholing or runs occur. With waterbased dip paints a sufficiently long blow-drying zone, which is usually heated in addition, must also be installed.

Despite all the optimizations implemented, it is not possible to achieve uniform film thicknesses on every part of the object. Furthermore, the paint still tends to run, especially away from edges, and these are further specific drawbacks of conventional dip coating with waterbased paints.

The disadvantages of conventional dip coating become particularly apparent with complex objects which include cavities. During the evaporation phase and the subsequent heating in the oven a saturated vapour atmosphere can build up in the cavities through which air cannot pass. As a result it is possible for the fresh paint film to be washed off again by condensation because of the slower heating of the cooler parts of the object. The consequence of this is an incalculable weakening of the cavity protection which is impossible to monitor.

Electrocoating

More uniform coatings in all parts of complex objects without the risk of being washed out of cavities can be achieved on electrically conductive substrates if ionic, aqueous dispersions are deposited electrochemically. If a direct voltage is connected between two electrodes, the charged paint micelles or dispersion particles in a diffusion-controlled interface move to the electrode with the opposite charge where they are deposited because of the change in pH value as a result of the electrolytic decomposition of the water. If the surface charge of the dispersion particles is positive, deposition takes place at the cathode, if it is negative, at the anode.

Following a great deal of studies and patents at the start of the 20th century on the subject of coating metals with resins, the intensive development of commercially used electrocoat paints started at the end of the 1950s at Ford with anodically deposited paints. The first plant for coating car bodies went on-stream in 1963 in the US, followed a short time later by one in Europe [4.4.14].

The development of cathodically deposited paints started in the mid-1960s [4.4.15]. They quickly turned out to be high-quality primers and took over from anodic electrocoat paints in the mid-1970s, first in the US and later also in Europe and the rest of the world. Nowadays this system is in sole use on automotive paint lines and is widely used for other industrial applications.

The advantages over the various processes used previously such as spraying and dip coating are the environmental compatibility because of its low emissions and, following the introduction of ultrafiltration, also the high material efficiency of > 99% [4.4.16]. In addition, thanks to its good throwing power, the uniform coating of even complex components outside and inside and the high reliability of the process are unbeatable factors. The worldwide market for electrocoat paints in 2006 is estimated at 1000 kt. About 300 kt is consumed by the automotive manufacturers.

Physico-chemical principles

Electrocoat paints are aqueous compositions made up of film forming agents, additives, pigments and extenders. The dispersion, which is made of typical paint ingredients, is used to deposit an organic paint film by means of a direct current on a conductive, generally metallic substrate. Dispersions stabilized by a negative charge coagulate at the anode (anodic electrocoating or electrodeposition, AED). If the particles are stabilized with a positive charge, they are deposited correspondingly at the cathode (cathodic electrocoating or electrodeposition, CED). To enable the paint to be deposited, the object to be painted is connected as an electrode and is dipped into the aqueous coating material with the counter-electrode. The paint is circulated to keep it in motion in order to guarantee a continued supply of material for the interface, to dissipate the heat generated by the flow of current and ultimately also to prevent the generally pigmented dispersions from settling.

Figure 4.2.5 shows the chemical equations necessary for electrocoat dispersion in water and for precipitation. For anodically deposited electrocoat paints the anionic carboxylic acid groups and their reaction with amines or other bases are necessary, and for cathodically deposited electrocoat paints the cationic groups such as amino groups and their reaction with acids are necessary. Film forming agents with different functional groups such as the sulphonium or phosphonium groups are used only occasionally [4.4.17].

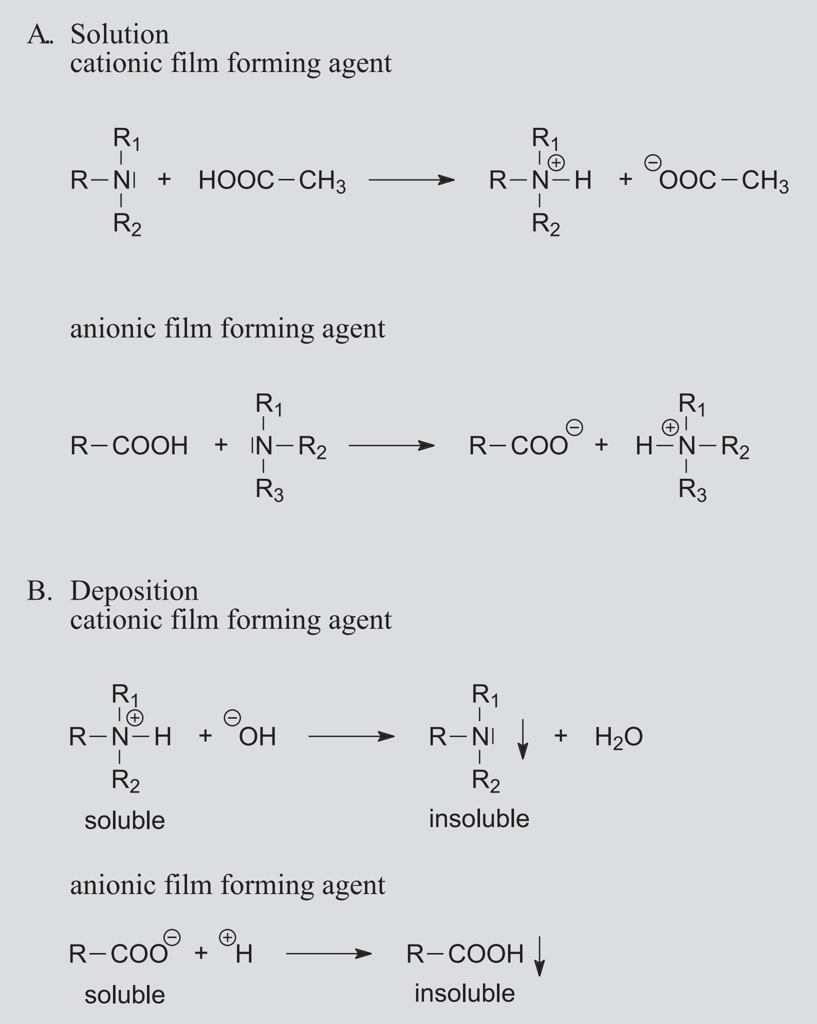


Fig. 4.2.5
Solution and deposition reactions of resins for electrodepostion process

In accordance with the chemical reactions precipitation of the electrocoat paint takes place by means of deprotonation for cathodic deposition and protonation for anodic deposition. This occurs under the physical conditions of electrolysis of water in a diffusion-controlled interface on the substrate which is to be coated.

The presence and necessity of a diffusion-controlled interface for successful deposition was demonstrated by *Beck* in experiments with rotating disc electrodes [4.4.18]. Depending on the paint system it is possible to identify a rotational speed at which no deposition of the electrocoat paint takes place any longer, despite the voltage and current flow. To view it a different way, precipitation or deposition takes place as a result of the forced migration of the paint dispersion particles into an area of greatly changed pH value, as shown in figure 4.2.6 (A). In the event of coagulation the concentration curve of H^+ ions changes as shown in the schematic (B).

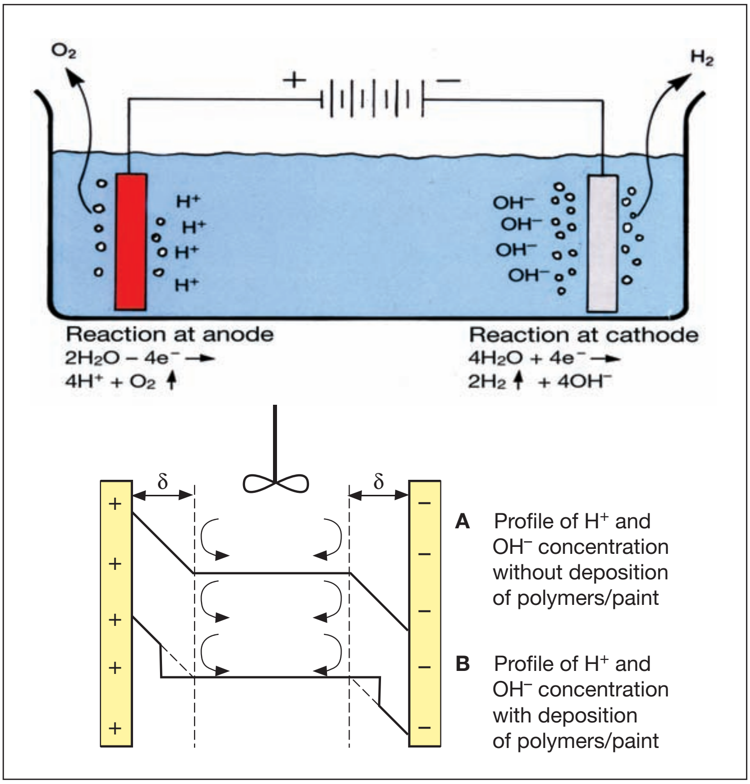


Fig. 4.2.6
Processes at electrodes during electrodeposition

The pH values at the electrodes can be estimated with the aid of simple assessments based on diffusion constants and the electrical current density in accordance with the *Sand* or *Cottrell* equations [4.4.19]:

$$C_{0_{H^+}} = \frac{j \cdot \delta}{2 \cdot D \cdot F}$$

j = current density (A cm^{-2})
D = diffusion constant of H^+-ions
F = Faraday constant
δ = thickness of diffusion controlled layer

If appropriate data is entered for the technical processes, this shows pH values at the electrode surface of 2 for anodic and 12 for cathodic deposition.

The dispersion particles of the electrocoat paint migrate as charge carriers in the electrical field (electrophoresis) of the diffusion-controlled interface as a result of the interaction of electrical attraction and retarding friction at a uniform rate in the direction of the substrate surface. Because of the film of water adhering to the surface of the migrating particles, which contains some of the free moving and retarding counter-ions, the charges of the film forming agent particles are partially screened. The still effective residual potential, known as the ζ-potential (see chapter 2.2.3), generates a migration rate u of $10^{-4} – 10^{-5}$ m/s. This is independent of the particle size and sufficient, with a correspondingly low viscosity,

$$u = \frac{\varepsilon \cdot \zeta \cdot E}{k \cdot \eta}$$

E = dielectrical field
η = viscosity
ε = dielectrical constant
k = constant

to generate film thicknesses of 15 – 20 µm in 1 minute. Because of the insulating effect of the film which is being deposited, the connected deposition potential is shifted to this film. Electrical fields of approx. 10^5 V/cm form inside the deposited film because of the low film thickness [4.4.20].

Electro-osmosis

The dispersion particles are neutralized even before they reach the electrodes and are thus precipitated. Accordingly, there is no direct transfer of charges at the electrodes.

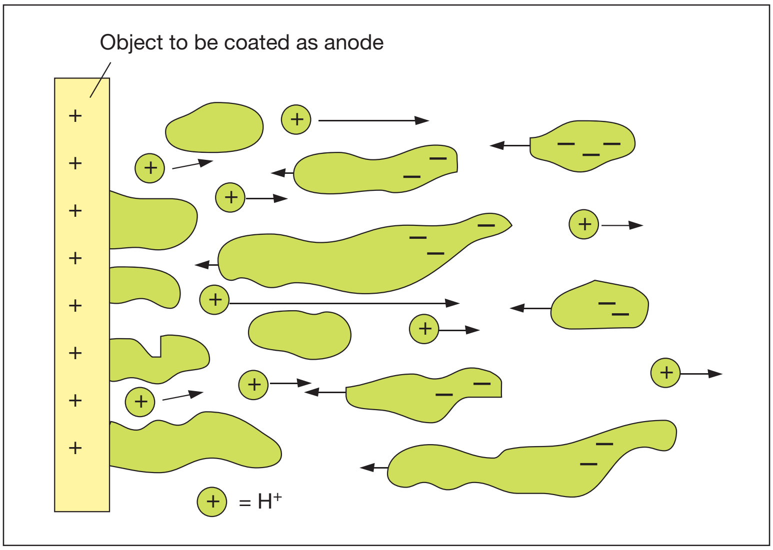


Fig. 4.2.7
Dewatering of the electrodeposited coating by electro-osmosis

The originally mobile particles halt when they encounter the object to be painted. Because of the electromotive force acting in the electrical field, movement of the water is induced, with the result that dewatering and thus a solids content in the film of more than 90% is achieved directly at the substrate surface at the transition from electrophoresis to electro-osmosis. As already mentioned, the film resistance is increased as a result and the growth in film thickness is reduced.

The resulting film adheres firmly to the substrate, can no longer be washed off and has a characteristic morphology which is initially marked by blisters and pores. The nature of this morphology is very characteristic for electrocoat formulations and depends to a large degree on the viscosity properties [4.4.21].

Cathodically deposited films in particular exhibit these structures since gas development at the cathode is twice as much as at the anode.

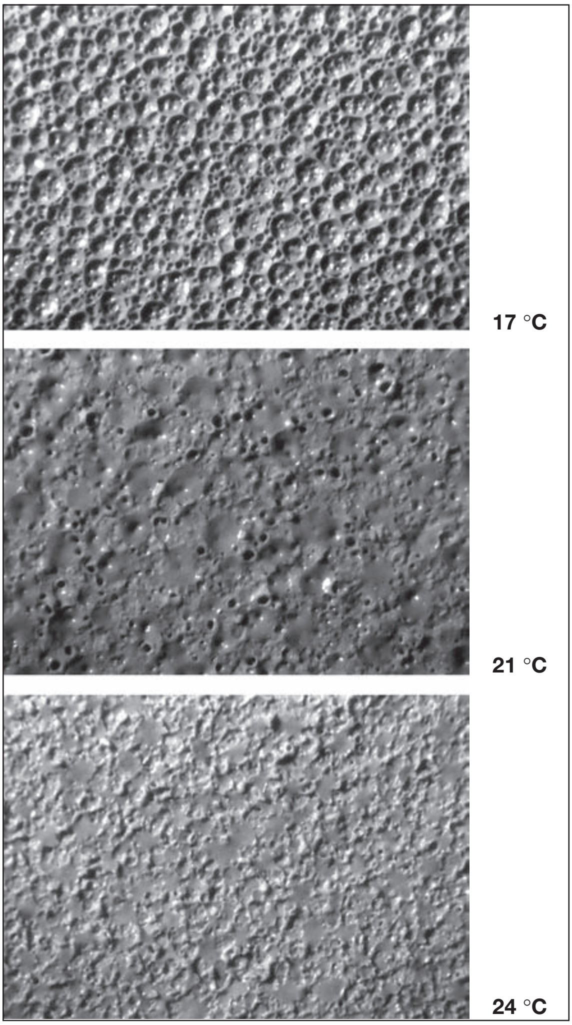


Fig. 4.2.8
Morphology of catholic deposited coatings at different bath temperatures

Side reactions

A few secondary reactions take place at the electrodes during the electrochemical deposition of the polymer ions, and it is necessary to know what these are in order to resolve practical problems when operating electrocoat tanks.

One electrode reaction worth noting is the dissolving of metals at the anode. Both the deposition of iron ions and the dissolving of amphoteric metals such as aluminium take place at the cathode, depending on the substrate material.

If metallic objects made of iron are being coated in the anodic process, it must therefore be anticipated that the object which is temporarily in the dipping bath will partially dissolve. The incorporation of metal ions in the paint film has been demonstrated. On the other hand, the counter-electrode (anode) which is now permanently in the bath must be prevented from dissolving in the case of cathodic deposition. It has, however, also been shown that measurable quantities of aluminium or zinc can pass into solution as anions in the strongly alkaline region of the cathode. But the concentrations are significantly lower than those of the dissolved iron ions during anodic deposition [4.4.22].

$$\begin{array}{lll} \text{anode:} & Fe \; - 2\,e^- \longrightarrow & Fe^{2+} \\ \text{cathode:} & Fe^{2+} + 2\,e^- \longrightarrow & Fe\downarrow \end{array}$$

Mathematical models of deposition and growth in film thickness

The dynamics of deposition are sufficiently well known as to permit mathematical models to be developed with which the deposition properties of electrocoat paints can be calculated, even on complex substrates [4.4.23, 4.4.24].

A certain time t_i passes until the OH^- concentration is reached at which coagulation of the electrocoat paint starts. The product of the current density j and the square root of this time t_i is the specific paint constant k:

$$k = j \cdot \sqrt{t_i}$$

This results in the following condition for the start of the coating:

$$t_i = \frac{k^2}{j^2}$$

The phase of film thickness growth ΔS_D which then starts can be calculated using the following equation:

$$\Delta S_D = \frac{1}{Ä} \cdot (j_t - j_d) \cdot \Delta t$$

ΔS_D = film thickness (µm)
j_t = current density at the time t ($A \cdot cm^{-2}$)
j_d = lowest current density ($A \cdot cm^{-2}$)
Ä = electrochemical equivalence ($A \cdot s \cdot cm^{-3}$)
t = time (s)

If the current density j_t falls because of the increasing resistance of the depositing film to values of less than j_d, no further deposition takes place.

$$\frac{\Delta S_D}{\Delta t} = 0 \quad \text{at} \quad j_t < j_d$$

The current density j_t can be expressed using *Ohm*'s Law

$$j_t = (\kappa \cdot E)_t$$

where E = electrical field strength in V/cm and κ = specific conductivity in S/cm. This yields a general formula for the growth in film thickness of

$$\int \frac{dS}{dt} = \frac{1}{Ä} \cdot ((\kappa \cdot E)_t - j_d)$$

In this equation the specific conductivity is composed of the conductivities of the bath and the film which is forming. Whereas the first is constant and easy to measure, the conductivity of the film is included as a function of the film thickness and the current density j_t. For calculations this is usually determined by measurements [4.4.23].
Another approach to calculating the growth in film thickness after *Machu* [4.4.25] is based on the assumption that the reduction in the free surface area dA is associated with the electric charge dQ. The quotient a of the surface area and electric charge is defined by *Machu* as the ”electrophoretic equivalent”.

$$a = -\frac{dA}{dQ} \quad \left[\frac{cm^2}{A \cdot s}\right]$$

Since dQ = I dt and, according to *Ohm's* Law U = I·R and R = ρ ·l ist, it follows that:

$$\frac{dA}{dt} = -a \cdot \frac{U \cdot A}{\rho \cdot \ell}$$

$$\int_{A_0}^{A} \frac{dA}{A} = -\frac{a \cdot U}{\rho \cdot \ell} \int_0^t dt$$

ρ = specific film resistance
ℓ = distance of electrodes

Because of the proportionality of the current I and the area A follows for the solution of this differential equation :

$$I = I_0 \cdot e^{-\frac{a \cdot U}{\rho \cdot \ell} \cdot t}$$

The current/time curve relation determined in this way for the deposition of an electrocoat paint only applies to monomolecular films, but includes the major variables which determine film thickness, viz. film resistance, voltage and electric charge.

Physical characteristics of electrocoatings

Standard deposition experiments are monitored in the laboratory with the current/time curve. Integral characteristics are determined from this. Schematically speaking, all depositions follow the dynamic more or less as shown in figure 4.2.9.
The rise in the resistance associated with the creation of the film and the reduction in the current flow mean that relatively uniform film thicknesses of electrocoat paints can be achieved even on objects of complex shape. The ratio of the film thicknesses of the internal and external areas of complex bodies is termed the throwing power. The throwing power properties are tested in special test configurations [4.4.26] such as the BMW throwing power system to VDA 621-180.

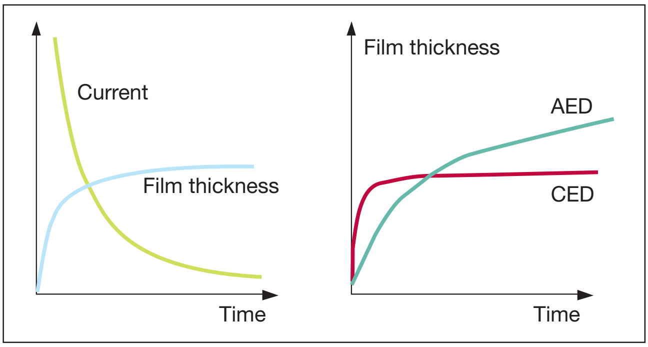


Fig. 4.2.9
Schematic current/time and filmthickness/time curves of cathodic and anodic deposition coatings

The electrochemical equivalence Ä' is determined as a guideline electrochemical characteristic in an electrical measuring system by establishing a relation between the consumed electric charge and the deposited quantity of the electrocoat paint:

$$Ä' = \frac{Q}{m} \quad \left[\frac{A \cdot s}{g}\right]$$

It is possible to calculate the electrical energy W, for example for coating a car body, from the electrochemical equivalence together with the electrical conditions. Usual val-

ues for the voltage U are 350 V, for the mass of the electrocoat film m = 2000 g and for the electrochemical equivalence Ä' = 40 C/g.
The following applies:

$$W = U \cdot I \cdot t \quad \text{if} \quad \ddot{A}' = \frac{I \cdot t}{m} \quad \text{follows} \quad W = U \cdot \ddot{A}' \cdot m \quad [\text{kWh}]$$

If the specified values are inserted, a number of 7.8 kWh is obtained. This provides a good fit with the practical experience of 5 – 8 kWh/body in most coating lines.
From the previously described laboratory-scale experiments the film resistance is determined at the end of the deposition process by inserting the measured bath resistance ρ_b into the corresponding formula as described from *Ohm*'s Law:

$$I_E = \frac{U_E}{(\rho_b + \rho_s) \cdot S}$$

The specific resistance ρ_s of the coating S of the baked film gives an indication of the potential throwing power of the electrocoat paints.

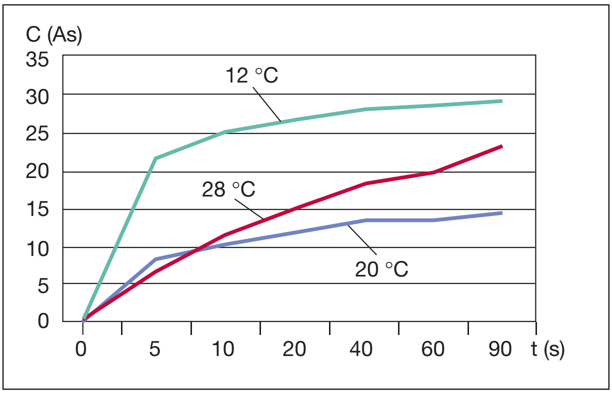


Fig. 4.2.10
Coulomb/time curve on an example of cathodic electrodeposition coating in relation to the bath temperature

The most important physical parameters in controlling the deposition properties of electrocoat paints, apart from the voltage applied and the current density, are the bath temperature and the solid content. As far as the voltage and the current density are concerned, there are limit values at which depositions no longer occur homogeneously over the entire surface area of the object but instead breakthroughs occur in the forming film as a result of the high temperature generated. These breakthroughs have negative consequences in the form of coagulates and destruction of the dispersion particles for the state of the electrocoat paint, with the result that deposition does not yield usable films. Experience shows that voltages determined in the laboratory should be lower by 20% in practical operations since faults in the form of the defects just described can otherwise occur. The dependence of the coating properties on the bath temperature is very high [4.4.21]. The example in figure 4.2.10 shows the dependence of the electric charge in coulombs on the coating time at different temperatures. The consumed charge C is proportional to the growth in film thickness. In the above example the optimum bath temperature is around 20 °C: below this, the film thickness is too high; above it, the throwing power becomes worse. The specific paint formulation is responsible for this. Recent studies confirm that the glass transition temperature Tg of the relevant resin (see chapter 3.2) plays an important role in the deposition mechanism of cathodically deposited electrocoat paints [4.4.27].

Apart from the process-engineering variables, the composition of the electrocoat bath also plays an important role in the deposition properties. This includes the solid content, the neutralization level of the dispersion, the specific bath conductivity and the solvent content.

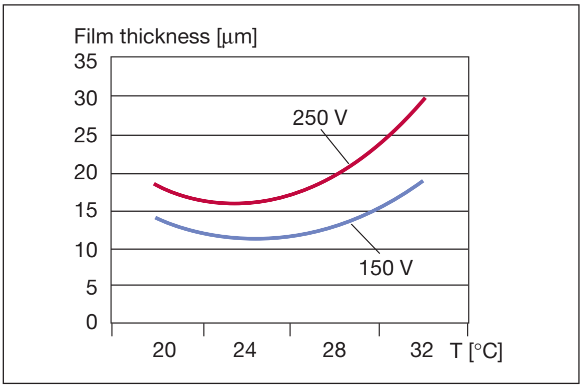


Fig. 4.2.11
Development of film thickness versus solid content of a cathodic electrodeposition coating

Electrocoat paints with a low solvent content show the dependence of the growth in film thickness on the solid content only to a minor extent. The throwing power is always improved by the increase in the bath conductivity. Limitations in the increase in the solids content are provided in that the ultrafiltration performance of all commercial membranes reacts negatively in a very sensitive way to excessive solid contents in terms of both output and service life.

By raising only the neutralization level of the electrocoat paints, the film thickness is reduced for the same application voltage [4.4.28]. The voltage that therefore has to be raised to achieve the standard film thickness increases the throwing power. The higher bath conductivity also contributes to this. A limiting factor in this case is the increase in gas and heat development which can lead to electrical breakthroughs and a lower electrochemical yield, which is indicated by the increase in the deposition equivalent Ä in C/cm^3.

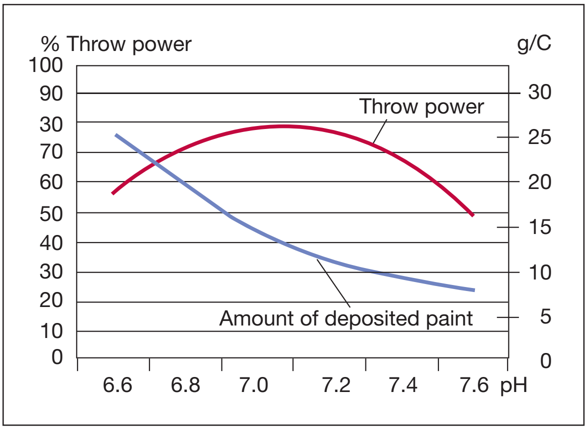


Fig. 4.2.12
Development of deposited mass in g/C and the throwing power versus degree of neutralization (pH) of an anionic deposition coating

While only single-component paints were used in the early stages of anodic electrocoating technology, today's electrocoating systems, which mainly deposit cathodically, work with two refilling (feeding) components. In order to maintain a uniform coating result it is necessary to replace the paint material consumed in coating the object by supplying new material.

There are two processes in principle:

- Refilling with generally one-component, underneutralized electrocoat paint
- Refilling with generally two-component, neutralized electrocoat paint

In the first case the refill material is dispersed in an adequately large premixing vessel using dispersers in the electrocoat paint. The excess neutralizing agent from the bath is generally sufficient to achieve this. The disadvantage of this process is that there is no simple quality control method for the dispersion stage of the refill material. This refill

Parameter	**CED**	**AED**
Solid content (2 h/130 °C) %	15 – 22	8 – 15
Pigment content (450 °C) %	1 – 5	2 – 7
Solvent content %	0.5 – 3.0	4 – 10
pH	5 – 7	7 – 9
Spec. conductivity (20 °C) mS/cm	1.5 – 2.5	2 – 3

Fig. 4.2.13
Typical bath parameter of electrocoatings : CED = cathodic, AED = anodic

method can only run trouble-free by maintaining the empirically determined process conditions.
The second refill method permits a considerably more stable and defined state to be achieved in the electrocoat tanks. This involves adding a completely neutralized binder dispersion and a paste dispersion to the bath separately at an appropriate place, without requiring a dispersion stage. This offers a number of advantages: only very minor fluctuations in the state of the bath since already predispersed material is added, and automatic, continuous dispensing as a function of power con-

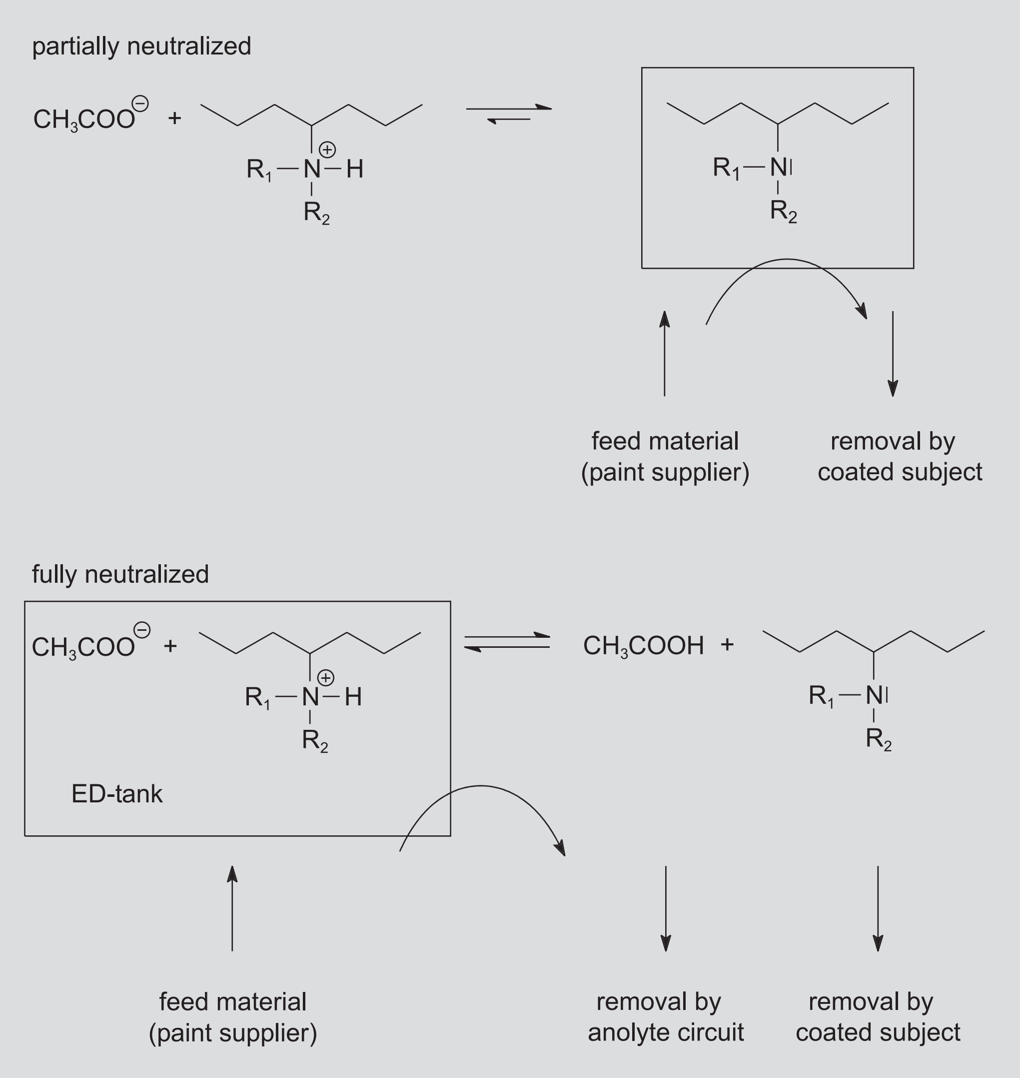


Fig. 4.2.14
Acid-base-balance of different refilling (feeding) processes

sumption. Furthermore, a low-solvent refill material can be added which has only approx. 20% of the usual solvents of 1-component refill materials.

However, the refill method using fully neutralized material requires a further circuit to extract the excess neutralizing agent occurring during deposition from the paint system. This circuit is known as the anolyte circuit for cathodically deposited and catholyte circuit for anodically deposited electrocoat paints. Furthermore, the process involving refilling with fully neutralized material requires the supply of large volumes of material. Depending on the volumes consumed, transport and delivery are carried out in road tankers or, as is usual in the case of automotive paint lines, in 1 t special steel vessels or 200 l drums. Delivery by tanker requires the provision of correspondingly large storage tanks at the electrocoating lines.

Plant engineering

Electrocoat paints are used in tank sizes ranging from 0.1 to 500 m^3 in volume. The largest tanks are found in the commercial vehicle industry, the smallest at job coaters or companies which have to coat small components and quantities using manual systems. The largest tanks are continuous systems which guarantee the greatest productivity of up to 70 bodies per hour (see chapter 7.1). Batch systems, on the other hand, achieve about 15 units per hour, though are only approx. 30% of the tank size.

Fig. 4.2.15
Examples of industrially by electrodeposition process coated products

The tank size plays an important role in the replacement rate of the bath material with refill material. One single theoretical material replacement is termed a turnover. For CED this should not be substantially longer than 12 months since the quality of the coating is no longer guaranteed for reasons of reducing stability. With anodically deposited paints this time is usually shorter.

The materials used in the system are special steel or plastics for CED systems. Cold roll steel can be used with the slightly alkaline anodic electrocoat paints.

Apart from the tank made of plastic-coated steel and the paint-discharge vessel an electrocoating system for cathodic deposition requires the following other plant elements:

- Power supply
- Heat exchanger
- Ultrafiltration system
- Filters
- Paint-dispensing (refill) system
- Anolyte circuit
- Rinsing zones

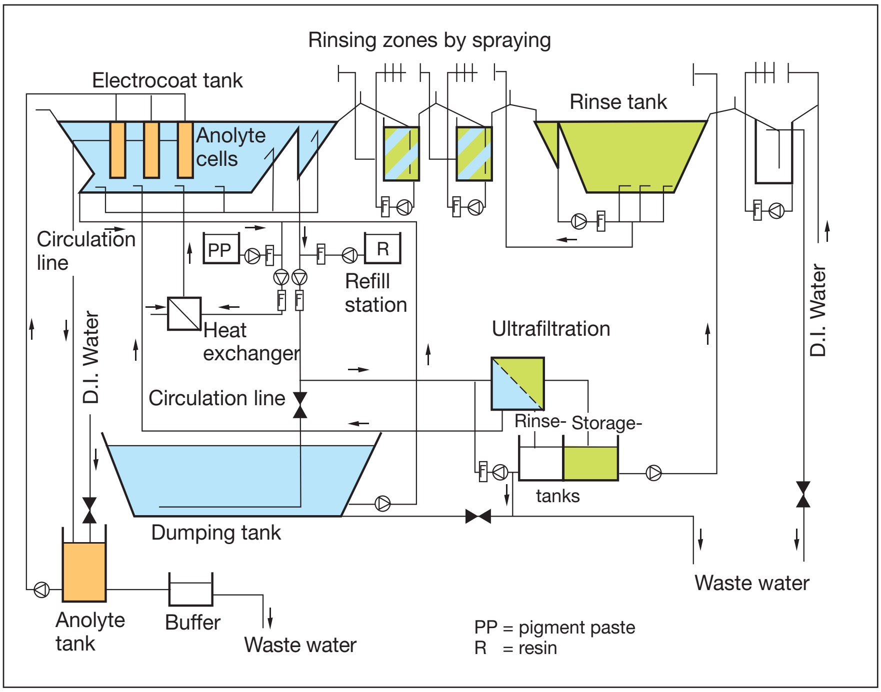


Fig. 4.2.16
Process scheme of the cathodic electrodeposition process

Rectified **electric current** is required for the deposition of electrocoat paints. A voltage program is run to avoid excessive current densities which can cause coating defects and can even ruin the paint (see chapter 6.2.2). The purpose of this is to reduce the current peaks at the start of the deposition process by setting the voltage to a lower level than in the later stages of the coating process. In batch systems this can easily be achieved by setting a voltage program in one rectifier. Continuous systems, where there are several objects in electrocoat tanks at the same time, require at least a second rectifier. This enables the variable setting of a separate voltage progam for the entry area. In less demanding processes it is possible to work with one rectifier and electrode-free entry zones since the voltage peaks can be reduced as a result of the greater bath resistance which can be achieved in this way.

In the case of cathodic electrocoating the workpiece is connected as the cathode and is at zero potential in example A in figure 4.2.17, i.e. it is grounded, while the anodes are connected to the plus potential. The voltage progam with at least 2, generally 3 rectifiers is run via the anode potential. Example B shows a sectionalized rail where the voltage is generated via the cathode potential.

The direct current is usually supplied in industrial systems by thyristor rectifiers. To achieve a good coating result, the residual ripple of the generated direct voltage should not exceed 5% of the complete plant conditions. The coating voltages are between 300 and 450 V for a coating time of between 2 and 4 minutes. The temperatures of the bath contents are between 25 and 35 °C (see figure 7.1.7).

Several circuits with pumps are set up to operate the **heat exchanger**, the ultrafiltration system and the filters. These pumps maintain flow in the bath at the same time which

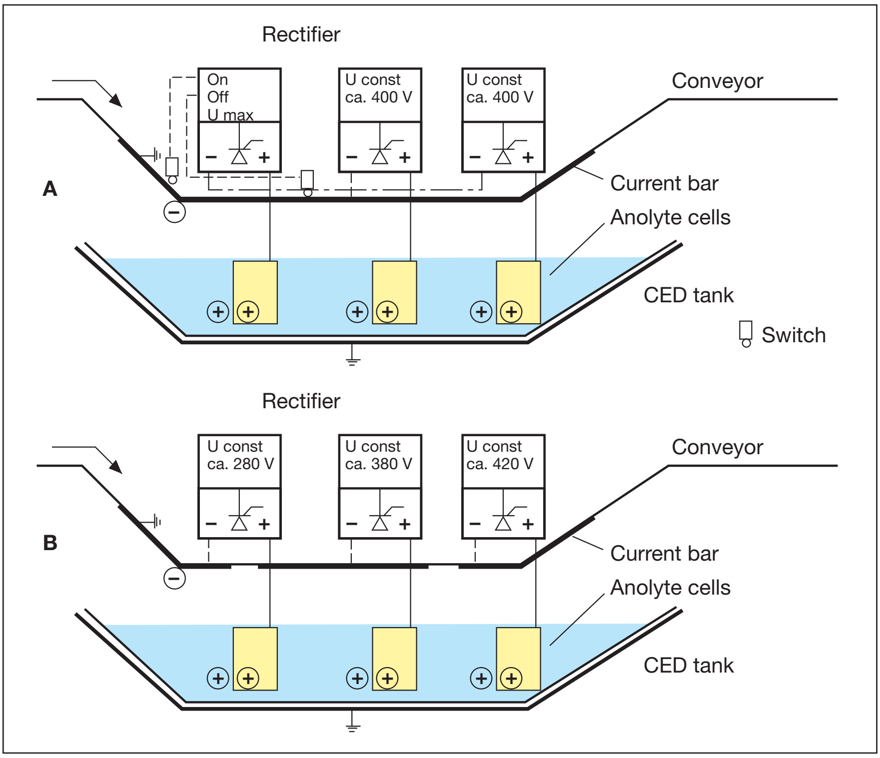


Fig. 4.2.17
Principles of electric circuits for continuous conveyor systems in case of cathodic electrodeposition coatings

ensures that sedimentation of the electrocoat paint is avoided. To this end jet nozzles are configured in the bath such that no flow dead spots occur. The mean flow rate relative to the free cross section of the bath should not be less than 0.3 m/s. This means that the tank volume is circulated about 4 – 6 times per hour. Normally the direction of flow at the surface of the bath is in the direction in which the objects to be coated pass through the bath. The bath level may not be less than 20 cm above the objects in order to guarantee the necessary current. The flow rate in pipes, as in the bath, should not be less than 0.3 m/s.

The pumps for conveying the paint should be fitted with double-acting mechanical seals which are operated with the ultrafiltrate (see below) generated from the paint as the sealing liquid. Immersion pumps can also be used. Tungsten carbide/tungsten carbide is suitable as the material combination for the seal surfaces. Filters should be installed upstream of the pumps in all paint circuits.

Effective filtration includes the careful selection of the extraction locations in the electrocoat tanks. It is definitely recommended that a partial flow be extracted from the contaminated entry area.

The bath temperature (see above) plays an important role in the application process. The bath quickly heats up because of the electrical energy input during the deposition process and the frictional heat of the circulating pumps and therefore has to be cooled down. Deviations by more than 1°C from the standard temperature specified by the paint manufacturer have an impact on the film thickness and the surface quality of the baked film. The tempering system must be designed such that the recommended bath temperature can be maintained even under the most unfavourable conditions of a hot summer's day and also in winter.

The high material yields of the electrocoating process are achieved by **ultrafiltration**. This is a separation process in which low-molecular constituents are removed from a dispersion or colloidal solution. With electrocoat paints these constituents are, of course, water, organic solvents, electrolytes and low-molecular fractions of the binder. The process involves having the electrocoat paint pass a suitable membrane at high speed. The concentration gradient between the inside and outside and a pressure gradient of several thousand hPa are responsible for causing this separation at the ultrafiltration module membrane. Depending on the membrane system, the separation threshold relative to the molecular weights of dissolved constituents and the binder dispersion lies between 0.0015 and 1.0 µm.

The liquid flow which passes the membrane is termed the permeate. The specific yield (or flux) is given in l/m^{2}h relative to the surface area and membrane. The flux rate is a function of the membrane surface area, pore size, flow rate at the membrane surface, concentration gradient and pressure differential.

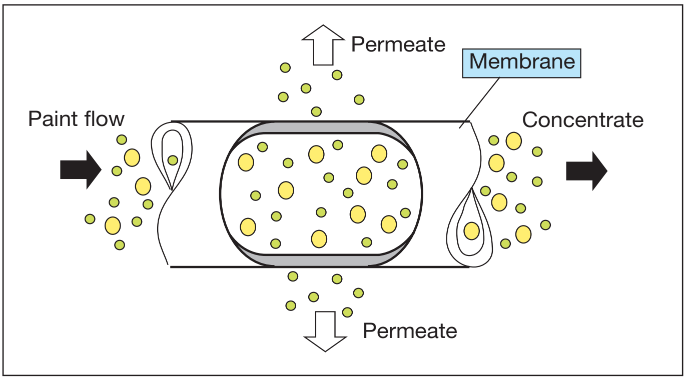


Fig. 4.2.18
Scheme of ultrafiltration process at pipe modules

The two most important variables for a high permeate yield are the membrane surface area and the flow rate of the electrocoat paint at the membrane surface. On the one hand, it maintains the concentration gradient at high throughputs and, on the other hand, it retards the formation of a diffusion-inhibiting interface at the membrane surface caused by paint deposits. As the membrane slowly becomes clogged with dirt, unstable dispersion particles and pigments, the process becomes less regular, and a reduction in the flux rate is normal. The performance can be returned almost to its original level by cleaning with a suitable rinsing agent.

The ultrafiltrate obtained in this way is fed to the last spray head or rinsing tank in the system as the rinsing agent using the countercurrent principle. The discharging rinsing agent is generally recirculated to the bath material via two three further rinsing zones. The efficiency of the paint depends, of course, on the amount of ultrafiltrate input into the rinsing zone. In rare cases, e.g. in the event of excessive contamination of the electrocoat paint by electrolytes, ultrafiltrate is discarded and replaced by demineralized water.

Ultrafiltration systems are developed with the aim of obtaining the largest volume of ultrafiltrate per hour from the largest possible membrane surface area in the smallest possible space and with the smallest possible quantities of paint. The membrane mod-

Value	Dimension	CED	Ultrafiltrate
Visual inspection		Opaque	Clear
Solid content (2h/180 °C)	%	18 – 20	0.3 – 0.6
Spec. conductivity (20 °C)	mS/cm	2.0	1.8

Fig. 4.2.19
Physical data of ultrafiltrate in comparison to the respective coating

ules play an important role in this. A distinction is drawn between simple tubular modules, hollow-fibre modules, spiral modules and plate modules. Tubular modules have a diameter of several centimetres. The permeate is collected between the membrane and a plastic housing and discharged to the outside. The advantages of such a module lie in their high flux rates and simple mechanical cleaning. Hollow-fibre modules consist of a bundle of thin, tube-like membranes, with up to 90 units located in a housing. The internal diameter of the tubes is only about 1.0 – 1.5 mm. Here, too, the resulting permeate is collected by a plastic sleeve and discharged to the outside. The advantages are a high membrane surface area per unit volume.

Spiral modules are designed such that two flat membranes are welded on three sides like an envelope. There is a porous medium between them to absorb the permeate. The end of this carrier material is fastened to a perforated manifold. The entire membrane/carrier system is wound up together with a spacer. The paint flows between the membranes which are separated by the spacers. The permeate passes through the membrane into the carrier material which drains tangentially into the perforated manifold. As with hollow-fibre modules, the advantages are a high membrane surface area per unit volume.

In the plate modules a stack of porous plates coated with a membrane are mounted in a frame. The paint flows through the interspaces, the permeate passes into the porous plates and is discharged from there to the outside. The advantages of this module are low replacement costs for the membranes and low maintenance costs.

The paint may not contain any impurities whose diameter is the same or greater than the film thickness if defect-free electrocoat surfaces are to be achieved with a film thickness of 20 – 25 µm. Since the paint ingredients are up to about 5 µm large, there are specifications for the size of the pores in the **filter** bags. These are usually of the order of 25 – 50 µm. The preferred filter material is polypropylene in a needle-felt finish. The filter bags are placed in special steel baskets, and these in turn are placed in special-steel filter vessels holding 2 to 8 such baskets. The electrocoat paint flows through the filter system from top to bottom. As a rule, all circuits are subject to filtration. The correct operation of the filters can be verified by monitoring the pressure differential between the input and output pressures of the filter vessels. This differential should not exceed 1.5 bar. A means of bypassing individual filter vessels is necessary as a pressure-relief system in the event of a sudden rise in pressure so that the filter bags do not split. These bypasses must be rinsable as the remaining electrocoat paint would sediment in the event of a fault. Under normal operating conditions a filter change should be carried out approximately weekly as part of the general maintenance schedule.

Causes of impurities in electrocoat paints can include :

- Entrainment of dirt from the unpainted body
- Dirt from the periphery of the CED system via air
- Abrasion and dirt from the conveyor system

- Dried-on paint from the hanger
- Coagulation and deposits of the electrocoat paint
- Electrical breakthroughs/high peak voltages
- Contaminated demineralized water
- Formation of coagulate through shear forces e.g. in defective pumps

Small quantities of special surface-active substances represent an extremely unpleasant type of contaminants. Depending on their hydrophobic character (HLB value) and the surface tension, silicone oils and perfluorinated hydrocarbons at a concentration of ppb to ppm are capable of causing either craters in the electrocoat film or later in the subsequent coating e.g. the primer surfacer. Special surface-active filters are used to remove these contaminants. Because of the weak hydrophobic interaction of the filter medium with the contaminants the greatest effectiveness is achieved with filtration using minimum pressure. Such filtration should be operated outside the normal circuit.

The installation of an **anolyte circuit** is necessary for cathodically deposited electrocoat paints and refilling with two-component neutralized refill material in order to remove the acid which is released during deposition from the paint bath. Otherwise the acid/base equilibrium would be lost. The resulting low pH value leads to poor deposition properties of the paint because of the rise in the specific electrical conductivity, and reduces the electrochemical efficiency.

There are two characteristic features in the anolyte circuit: firstly, the semi-permeable anion exchange membrane in front of the anode and, secondly, the water supply which is controlled via a conductivity measurement system.

The anion exchange membrane separates the box in which the anode is housed from the electrocoat. It ensures that only the anions necessary to ensure electrical neutrality can pass the membrane in the direction of the anode when current is flowing and the electrocoat paint is being deposited. If no voltage is connected, it acts as an electrolyte barrier.

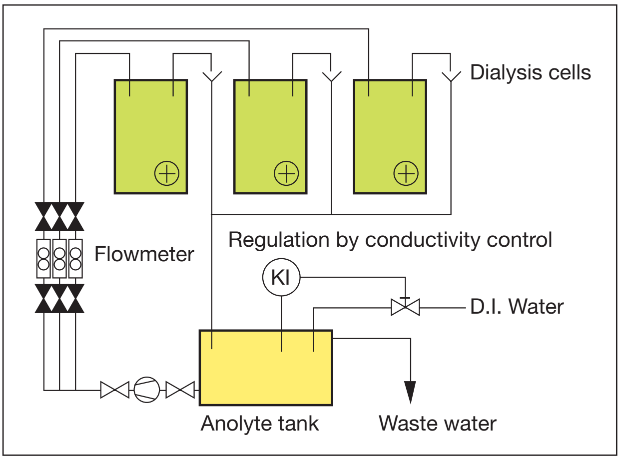


Fig. 4.2.20
Scheme of an anolyte circuit

The acid concentration is controlled by means of a conductivity measurement system and control system which reduces the level by feeding demineralized water to the anolyte tank. The concentrated acid is discharged via an overflow. In most cases this is acetic acid, occasionally lactic and formic acid which is treated for disposal by straightforward neutralization.

Because of the low pH value of the anolyte liquid, the anolyte circuit is made of plastic, usually PVC. The return flows of the anode cells should have a transparent section so that throughput can be checked. The circulation pump must be made of acid-resistant special steel, and the pipework must be earthed.

Property	Dimension	Value
pH		2.2 – 2.8
Spec. conductivity (20 °C)	mS/cm	0.3 – 2.0
Solid content (2 h/130 °C)	%	< 0.2
Relation cathode/anode area		4 – 6 : 1
Flow of cells	l/min	4 – 15

Fig. 4.2.21
Process data of an anolyte circuit

A special stainless steel type resistant to anodic dissolving in an acid and slightly chloride-containing medium is required for the anode panels within the anode cell. Special steels to DIN 1.4401 and DIN 1.4439 are suitable material types. A weight loss occurs at the anodes as a function of the electric charge passing. The usual service life in automotive systems is between two and four years, depending on the position in the bath. Iridium coated titan electrodes provide longer service life.

If leaks occur and paint therefore enters the anolyte circuit, material is deposited on the inside of the membrane which significantly impedes the current flow. This becomes apparent in a reduction first in the throwing power and then in the film thickness of the deposited film. It is then essential to halt production immediately, repair the leak and fit new membranes, which obviously causes serious production shortfalls. For this reason, the installation of turbidity sensors in the control circuit is necessary to increase operational reliability.

The electrocoat paint deposited on the object removed from the bath is firmly bonded to the substrate, has a marked texture and is porous (see above). On its surface is a liquid film consisting of bath material and entrained gas bubbles. If timely removal of this film is not ensured, serious surface defects occur after initial drying which cannot be eradicated during the baking process. Furthermore, in the event of the complete failure of a rinsing zone there would be a material loss of up to 60% (relative to the deposited electrocoat paint). The **rinsing zone** therefore serves to optimize the surface quality and the material-application efficiency and is fed with the ultrafiltrate in accordance with the countercurrent principle.

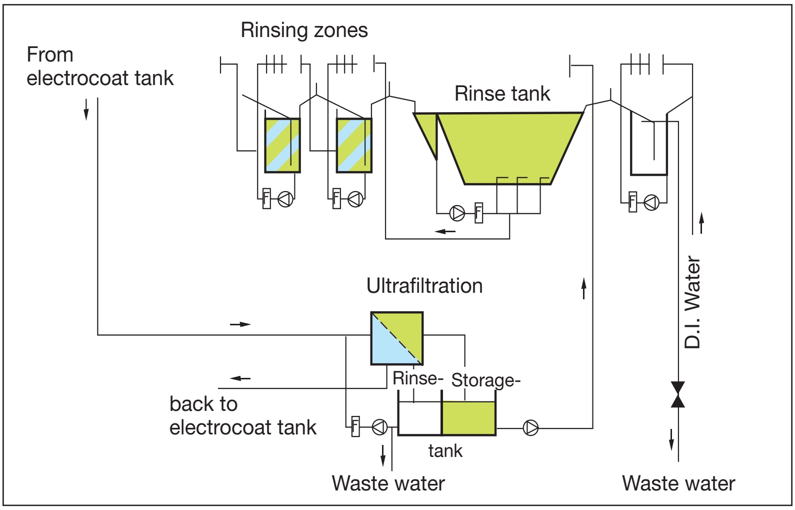


Fig. 4.2.22
Scheme of a rinsing zone with one dipping tank

The rinsing zone generally has 5 or 6 individual units:

1. Rinsing of the surface shortly after removal from the bath
2. Zone I – Spraying
3. Zone II – Spraying
4. Zone III – Dipping
5. Spraying with pure ultrafiltrate

Optional: 6. Spraying with demineralized water

The last unit, i.e. spraying with demineralized water which was still in use in the 1990s, has now largely been dispensed with since the ultrafiltrate quality has been improved such that it is very close to the state of demineralized water by optimization of the membranes and of the electrocoat paint constituents. This permits costs to be cut.

The spray process in unit 1 is important in ensuring a defect-free, smooth surface in the electrocoat paint. It must be carried out less than one minute after removal from the bath. This is done using spray nozzles which are installed above and to the sides of the objects to be painted when it is still above the outlet area of the ecoat bath.

There are then three rinsing zones which have different paint concentrations because of the input of electrocoat paint bonded to the object and are connected in a cascade towards the electrocoat bath.

The pure ultrafiltrate is fed into the last rinsing zone before the optional demineralized-water spray head. In some cases part of the pure ultrafiltrate is used for the first rinsing which takes place while the object is still above the electrocoat bath.

Depending on the quantity of ultrafiltrate supplied and the coating quantity, the solids content in rinsing zone I is usually approx. 1 – 2% and in rinsing zone III around 0.5 – 1.0%. The rule of thumb when designing the ultrafiltration system is that there should be about 0.8 to 1.5 l ultrafiltrate per m^2 surface to be coated. The contents of the individual rinsing stages are termed Recirculate I (Zone I) and Recirculate III (Zone III), depending on their position in the rinsing process.

The automotive industry uses dip tanks almost only for rinsing zones II and III because of its more complete rinsing system.

If a spray head or tank using demineralized water is installed as the last unit, this material is not fed to the electrocoat tank via the recirculate stages. It must be disposed of. This is generally carried out in the systems using precipitation agents.

The systems designed with such cascade rinsing units reach a material-application efficiency of greater than 98%.

Process parameters

Both analytical bath data and application figures are periodically determined to monitor the process. The cycle of different tests is specified depending on the paint quality and the throughput rate (see chapter 7.1).

The key analytical figures include the solid content, the binder/pigment ratio or the pigment concentration as an ash content, the pH value, the specific conductivity and the solvent content of the bath material. These figures are primarily used for quality control of the refill material. The measurement methods are usually derived from the relevant DIN-EN-ISO or ASTM standards (see chapter 2.3 and 8).

Daily checks on the bath contents are limited to the solid content, pH value and specific bath conductivity. The physical deposition data determined under defined physical conditions confirms the constancy of the bath state, on the one hand, and the deposition properties such as the throwing power, on the other. These figures are more sensitive to fluctuations in the bath state than the analytical data.

Overview of binders and paint formulations

To make it possible to deposit film forming agents **anodically**, it is necessary as described above, to incorporate negatively charged ionic groups in the matrix of the film forming agent. The carboxylic acid group is most frequently used for this. Conversion into the salt form using alkaline or amines (see figure 4.2.14) makes it possible to disperse the film forming agent in water. The desired properties of the coating such as anticorrosive protection, smooth surfaces and gloss are determined to a significant degree by the chemical structure of the film forming agent and the crosslinkers. Polyacrylics and polyesters are preferred as film forming agents for direct-gloss paints. Oils, alkyd resins, polybutadiene resins, phenol resins and epoxy resins are used as the base material for primers [4.4.29]. The first important anodically deposited electrocoat paints were unsaturated oils which were reacted with maleic anhydride (see chapter 2.1) [4.4.30, 4.4.31]. The main raw material used is linseed oil which is converted with approx. 10 – 30% maleic anhydride.

The modified resins used in electrocoat paints have molecular weights of 1,000 to 10,000 g/mol. They are crosslinked at temperatures of 140 – 200 °C. Esterification reactions with phenol resins or resins rich in OH groups are generally used for crosslinking. The polymerization of the carbon double bonds induced by oxygen for crosslinking the unsaturated film forming agents also plays a role. In the past this reaction was catalytically assisted by the addition of lead compounds. Crosslinking is reinforced with phenol resin precondensates to improve the anticorrosive protection [4.4.32].

Oligobutadienes, also termed polymer oils, superseded the natural raw materials in the mid-1970s. Their properties are easier to optimize for the desired applications by means of targeted synthesis processes, and they are saponification-resistant. The use of oligomers with cis double bonds is preferred because of their higher reactivity during maleinization [4.4.33]. In addition to 1.4-butadiene, copolymers of various dienes such as isoprene, cyclopentadiene and 1.3-pentadiene, sometimes in combination with natural oils, are also used to a lesser extent [4.4.34].

Unsaturated polyesters and alkyd resins can be made watersoluble through high acid values. They are only used to a small degree nowadays. Saturated, acid polyesters have a certain importance for the steel furniture industry as particularly smooth direct-gloss electrocoat paints. They are correspondingly easy to manufacture and crosslink with resins rich in OH groups [4.4.35].

Epoxy resins can be used as diols in the synthesis of polyesters or converted directly as difunctional epoxides with polyfunctional carboxylic acids. The carboxylic acid function is introduced by using unsaturated fatty acids which are converted with maleic anhydride [4.4.36]. Such resin based electrocoat paints offer good anticorrosive protection. They have therefore been in use in the automotive industry for some time

One simple means of synthesizing anodically deposited resins is the copolymerization of acrylate, methacrylate and styrene with free acrylic or methacrylic acid. The latter must be present in a proportion of 5 – 20% in the polymer. Crosslinking can be carried out via amino resins or phenol resin modification if OH groups are present in the acrylic resin chain. Alternatively, self-crosslinking systems can be formulated by incorporating methylol groups in the acrylic chain [4.4.37]. Transesterification is another important crosslinking mechanism [4.4.38].

In general acrylic resins are suitable as direct-gloss topcoats with acceptable fastness to light. Their anticorrosive protection is significantly weaker than that of electrocoat paints based on epoxy resins.

Anodically deposited electrocoat paints based on polyamides, polyimides and polyester imides are also described in the literature, though they have never achieved practical importance [4.4.39]

Cathodically deposited electrocoat paints are formulated on the basis of film forming agents which are modified by the incorporation of positively charged functional groups. The most important is the amino group which can be primary, secondary, tertiary and quaternary. In addition, phosphonium, isothiouronium and sulphonium groups have been investigated in resins. In principle they result in coating materials which are capable of being deposited. With the exception of the sulphonium group, however, they have not attained any practical prominence [4.4.40, 4.4.41].

Amine-modified epoxy resins, which deliver the best anticorrosive protection and excellent adhesion to metals, are important in practical applications. Over 90% of them are used as primers in the automotive industry [4.4.42]. The amino function can be achieved by converting free epoxy groups with amine or ammonium salts, starting from pure or polyester-modified epoxy resins [4.4.43]. The subsequent neutralization of the amino groups with organic acids such as formic, acetic or lactic acids makes the resins dispersible in water. The commercially important electrocoat paints manufactured on this basis contain dispersed crosslinking agents based on capped isocyanates [4.4.44]. For some time an epoxy-modified phenol resin which was converted into water-dispersible, self-crosslinking resins in a *Mannich* reaction with secondary amine and formaldehyde was of importance. The *Mannich* group separates thermally from the amino group at approx. 190 °C and thus results in crosslinking [4.4.45]. Such paints enable good anticorrosive protection on bare steel.

As with the anodically deposited paints based on acrylic resin, cathodically deposited acrylic resins can be manufactured by using acrylate monomers containing amino groups, e.g. dimethylaminoethyl methacrylate as polymerization components. In addition, monomers containing hydroxyl groups or epoxy groups can be modified. Crosslinking, mostly to form direct-gloss, relatively weather-resistant coatings, is generally achieved with capped, multifunctional isocyanates [4.4.46]. Binders based on alkyd resins can either be functionalized to epoxy groups using peroxides or can be made capable of cathodic deposition with diamines by conversion with maleic anhydride. These resins have not achieved industrial importance.

Variants on electrocoating

In addition to straightforward electrocoating, painting processes have been available since the 1970s in which electrocoating is used for a complete paint system. A rinsed, as yet unbaked electrocoating can have a second electrocoat applied, using the same or a different paint. This results in total film thickness of up to 60 µm. This process is used in some industrial-scale applications.

Baked CED films can also be coated a second time if they attain appropriate film conductivities by means of suitable pigmentation after baking [4.4.47]. Compared with the first variant, this is a more reliable process since it is not necessary to pay attention to the compatibility of the two paints. The second electrocoat paint can be specifically formulated to the requirements of the particular user. This has been investigated in the automotive industry for the application of primer surfacers [4.4.48]. Such coating processes have failed to gain acceptance to date for process-engineering reasons and because of the high capital costs and a loss of leeway with colors.

Further examples of special electrocoating processes include continuous systems for the electrophoretic coating of endless coils or wires and flood-coating systems for coating steel pipes. In the former case the dip bath is provided with openings at the side through which the coils to be coated can be fed. The paint which escapes through the openings is collected in an overflow tray and then returned to the coating bath.

Electrophoretic flood-coating systems for coating metal pipes work in similar fashion. The paint floods out of the opened perforated base of a storage vessel which is connected as an electrode and onto the rotating metal pipe which is connected as the anode. After filtration, the excess material is also returned to the feed bath so that it can then be recycled in the coating process.

Electro powder coating (EPC process) was developed as a specially designed electrocoating variant for the automotive sector with the specific aim of achieving high film thicknesses which render an additional primer surfacer superfluous [4.4.49].

The bath material consisted of suspensions of finely ground powder particles with particle sizes of < 5 µm in cathodic electrocoats.

Film formation was carried out in accordance with the same principles as already described for the electrocoat paints. The incorporation of paint-enclosed powder particles means that film thicknesses of more than 50 µm were achieved within short deposition times of 30 – 60 s.

The extremely poor throwing power was a disadvantage. In order to obtain the anticorrosive protection necessary for components of complex shape, nonetheless, it was essential to include a second coating tank so that the necessary cavity protection could be provided after interim drying at temperatures of approx. 110 °C. No aesthetic requirements were made of the material in the second bath as this was purely for cavity protection purposes.

The EPC process was unable to meet the expected optical quality requirements. In addition, with its need for an extra tank the EPC process was so costly in terms of plant and space requirements that it had to give best to the high film build electrocoating process, which was developed at the same time, before even having seen industrial-scale use. The high film build electrocoat can be deposited in one bath up to a film thickness of 35 µm and offers economic advantages.

Another electrocoat variant which no longer exists was the reverse process. In this the outer skin of the object to be painted was primed with a conventional wet paint or powder coating. After this first film had been baked onto the outer skin an electrocoat primer provided the necessary coating inside. The development of such coating materials was exclusively aimed at improving the anticorrosive protection. Although this process was used in the automotive industry for many years, it no longer has any practical importance.

Autophoresis

Autophoresis is a special dip-coating process variant. In this process the object to be painted is completely immersed either in a batch or a continuous tank, as in straightforward dip-coating processes. The aggressiveness of the acid and low-viscous autophoresis paint on steel results in coagulation of the aqueous dispersion onto the steel surface [4.4.50]. The iron ions formed by the action on the steel surface precipitate the paint. The film thickness deposited is mainly determined by the object's dwell time in the bath and the bath temperature. The adhering film still contains over 50% water and is therefore still very soft. The pre-drying stage which lasts 5 – 10 min at 100 °C solidifies the film sufficiently that it can be crosslinked at approx. 130 – 160 °C. The decomposition and embedding of the iron in the film limits the use of the process considerably. On the one hand, no light films can be produced and, on the other hand, the anticorrosive protection of such coatings is weak by comparison with electrocoat paint films.

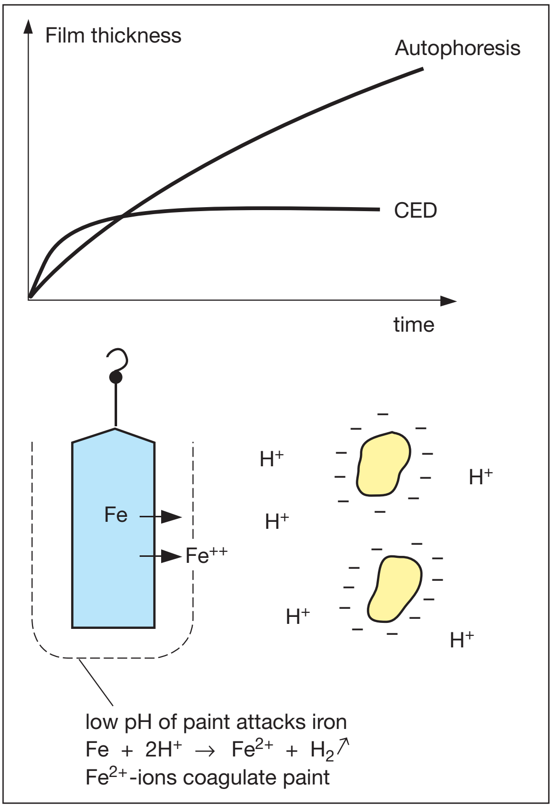


Fig. 4.2.23
Coagulation of paint suitable for autophoresis process

It is important to ensure a defect-free substrate surface by implementing appropriate process-engineering measures in order to obtain a reliable coating.

Until just a few years ago this process had failed to gain widespread acceptance and therefore remained a niche application. Recently, however, improved formulations have been introduced. The reasons for the renewed interest in this coating technology lie in the omission of any inorganic pretreatment (see chapter 4.1), as is usual for dip coating and electrocoating, the opportunity to dispense with electrical energy for the deposition process, and complete coating of inner sections [4.4.51]. An example of applications for which this process is used involves seat frames for car seats which are generally painted with a black coating. For such an object, where practically none of the surface is visible in the finished seat, the requirements relating to both anticorrosive protection and surface finish are low.

4.2.1.2 Brushing, Manual and Mechanical Roller, Flood and Curtain-Coating Methods (Paint Applied Directly to the Object)

If the coating is brought to the object, two fundamentally different processing principles are commonly applied.

The direct and technically straightforward processes include brushing, manual and mechanical roller, curtain or flood coating. In all cases the coating material is transferred from the application device to the object to be painted without any detours and with the advantage of a high material efficiency.

The other method is the indirect process in which the material is first broken down into tiny particles and only then transported to the object to be painted where it is converted into a closed film. This group of application methods results in very different material yields, depending on the different atomization methods. Whereas material yields of up to 98% are achieved with purely electrostatic spray coating, pneumatic atomization processes with application rates of sometimes less than 40% are far from being efficient.

Brushing, manual roller coating

The oldest processes, which are primarily used for housepainting, are brush and manual roller application. The advantages of applying paint by brush or manual roller are the universal usability on components of complex shape, the good and uniform wetting or distribution of the paint and the excellent material yield of practically 100%. The disadvantages are the low speed, the necessary skill and experience of the painter in producing smooth and uniformly thick coatings. Brush coating is not therefore used as an industrial-scale application method.

Mechanical roller, flood and curtain coating

The manual roller method can, however, be scaled up. The application of paint, albeit limited to planar surfaces, is possible if the lambswool or foam rubber roller is replaced by rubber rolls. Continuous, large-scale application is possible if the appropriate supplementary equipment and paint-supply systems are used. Automated roller-coating systems have been in operation in Germany since 1928 and are suitable and now proven paint-processing machines for coating planar workpieces such as wood panels, hardboard, plastic foils, cardboard, paper or metal coils.

The planar objects to be painted are transported underneath the fixed transfer roll by a conveyor, thereby enabling the roll to transfer the desired quantities of paint uniformly to the workpiece in accordance with the gap between the roll and the workpiece. To do so, the coating material is first taken from a storage tray by a rotating dispensing roll, known as the pick-up roll. The polished roll with its hardened surface transfers the paint to the transfer roll which is also rotating, so that the transfer roll can transfer the coating to the material to be painted. Three-roll systems also have a smoothing roll, the doctor roll, between the pick-up roll and the transfer roll. The purpose of the doctor roll is to help to provide better conditions to ensure a smooth film. Each roll is driven individually and can therefore be regulated independently of the speed of the other rollers.

The transfer roll, which consists of a metallic core with a rubber coating, can turn either in the same direction as the conveyor in a synchronous process or in the opposite direction in a reverse process. Because the amount which can be applied without trouble assuming smooth operation in one stage in the synchronous process is limited, rolls turning in opposite directions to the direction of movement of the object to be painted are used to achieve thick coats.

Such reverse-operation machines allow a greater range of film thicknesses to be achieved with higher material viscosities and thus lower solvent emissions at the same

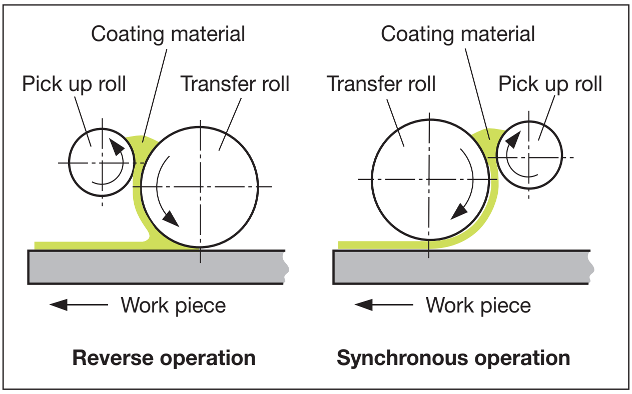


Fig. 4.2.24
Scheme of two-roll applicator for reverse and synchronous process

time. Texture-free films with a uniform film thickness profile can be produced with processing viscosities of up to 600 mPa·s and 100% material yield using roller-coating methods. Whereas coat thicknesses of only 10 – 15 µm can be applied with an adequate surface smoothness using the synchronous system, films of up to 100 µm in thickness can be applied using the reverse process. Strongly thixotropic paints can also be processed because of the forced distribution of the paint by the rolls. Direct transfer without the detour of the interim enlargement of the paint surface area via atomization and the short dwell time between application and the baking oven offers the environmental advantages of low solvent emissions during processing. The solvent component of the paint is mainly given off in the oven where it can be eliminated or reclaimed without difficulty using already available technology, viz. incineration or adsorption methods.

However, advanced systems running at line speeds of up to 200 m/min are not only environmentally sound, they also offer the most efficient processing methods from an economic perspective. A further technical advantage of the roller-coating process is that the planar objects to be painted can be coated on both sides with appropriate configuration of the rolls.

Certain special demands are made of the coating materials for this process. High baking temperatures are required because of the high line speeds in order to limit the length of the oven. Oil-free, thermally resistant, polyester-modified or silicone-resin-modified acrylic resins in conjunction with highly etherified HMMM resins have proved successful for this (see chapter 2.1).

The use of electron-beam-curable and UV paints is an obvious choice with the high-speed roller-coating method because of the short curing times. These systems are used as liquid coatings and now also as powder coatings and are cured in fractions of a second after melting by IR radiation.

Particular demands are placed on the solvents of roller-coated paints. Apart from having a high evaporation

Fig. 4.2.25
Picture of a roll coater

number and a good solvent power for the film forming agents, they must not cause the rubberized transfer rolls to swell. Good results have been achieved with rolls sheathed in butyl rubber by using solvents such as methyl glycol acetate, butyl glycol acetate or butyl diglycol acetate. Natural rubber jackets are the more suitable coverings for transfer rolls when aromatic-rich solvents are used.

A uniform coating result can only be guaranteed if the paint has adapted rheological properties in conjunction with a contact pressure which is appropriate to the line speed. The wet-film thicknesses must therefore be continuously measured and corrected, if necessary. In order to limit wastage, control actions must be implemented quickly because of the high line speed (see chapter 3.2.1).

The roller-coating units can be parts of continuously operated coating systems. The coil coating process refers to a process in which sheet metal coils are unrolled, degreased, pretreated, coated, cured and rewound in a continuous process. In order to ensure a continuous process, coil reserves are stored in loop towers, and these reserves are then used if a new coil has to be welded to the end of the previous one (see chapter 7.4). The sheets and coils coated in this way are then formed into a very wide range of consumer goods. Façade elements, garage doors, fridges, steel furniture, car body parts, cans and lighting fixtures are just some of the objects which are manufactured from these precoated coils.

This process will become increasingly prominent in future because of the cost-effectiveness of the coating systems, the low emissions in the application area, the good material efficiency and the coating’s excellent optical and mechanical/technical properties.

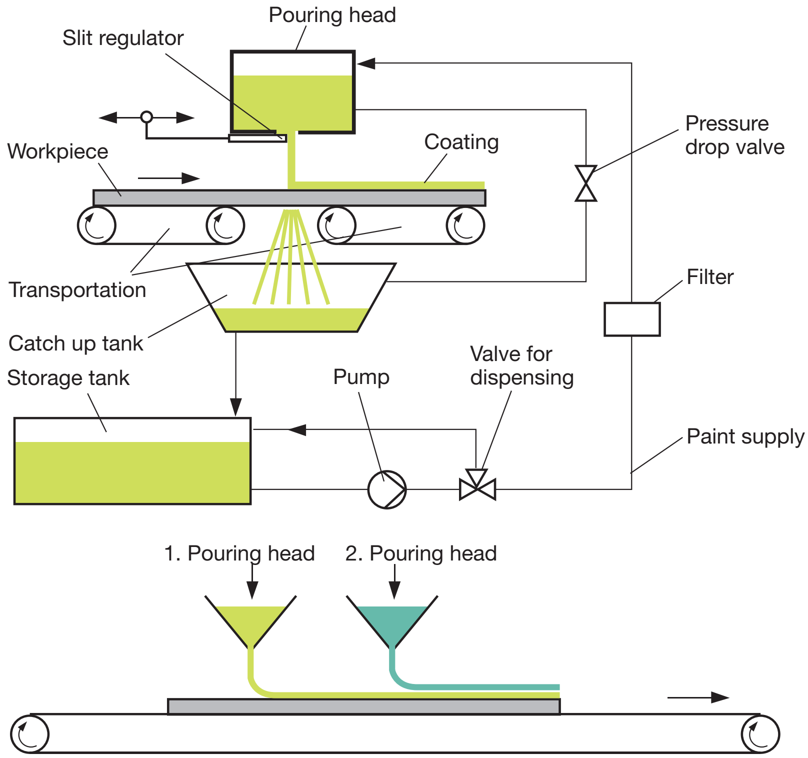
Another direct paint-processing method which is also suitable for planar components is **curtain coating.** The paint is applied to the objects to be painted as they move by on conveyor belts, in similar fashion to the roller-coating method described above. By contrast with the roller-coating method the liquid coating material is poured onto the object. To ensure a uniform coat, the coating material is converted into a permanently flowing ”paint curtain” from a pouring head. The pouring head consists of a storage reservoir with a slit.

The pouring heads can be open or closed at the top. In the latter case different pressures can be set which provide an additional variable for the discharged quantity and thus for the film thickness.

If the object to be coated passes through the flowing liquid paint curtain, the curtain uniformly covers the surface to be coated. The film thicknesses are defined by the viscosity of the paint, the width of the slit in the pouring head and the feed rate of the object.

If the curtain is wider than the object to be coated or if no objects are coated when the paint is flowing, the material is collected and returned to the pouring head after filtration (see figure 4.2.26). The material is not fed directly to the pouring head in order to avoid problems during the coating process. Air bubbles entrapped in the paint must be allowed to escape in a settling chamber. This is the only way to produce a continuous and uniformly discharging paint curtain.

To permit better maintenance and thus ensure trouble-free operation of curtain-coating systems, it must be possible to open the pouring head so that the discharge area can be cleaned properly.



Principle of wet on wet pouring process with 2 pouring heads

Fig. 4.2.26
Scheme and picture of a curtain coating machine

The process permits a coating of 50 – 500 g/m^2 to be applied and therefore, unlike the roller-coating process which can only apply 10 – 100 g/m^2, is particularly suitable for high-build coatings. Curtain-coating machines have proved particularly useful in the woodworking and furniture sectors as well as paper and packaging industry [4.4.52]. They are used in these industries equally widely for high-build coatings with unsaturated polyesters or polymerizable polyacrylates and for thin-film, open-pore coatings with cellulose nitrate lacquers.

The use of 2-component paints causes problems because of the limited pot life when the curtain-coating machines have only one pouring head. In such cases multihead machines are used which apply several individual curtains of the individual components to the object. Additional mixing is initiated by diffusion and flow in the wet film. Uniform curing is achieved as a consequence.

Further variants are possible when unsaturated polyesters are used. The unsaturated polyester, which is dissolved in a nonreactive solvent, is applied to the wood substrate together with peroxide. The substrate absorbs the solvent, with the result that the styrene-containing unsaturated polyester applied subsequently together with the primer accelerator is dissolved again so that chemical curing is initiated. In rare cases three-head curtain-coating machines are also used to ensure even better mixing of the components. The curtain-coating process is of particular interest when the sometimes very thick films are cured in seconds with UV or electron beams (see chapter 4.3.2).

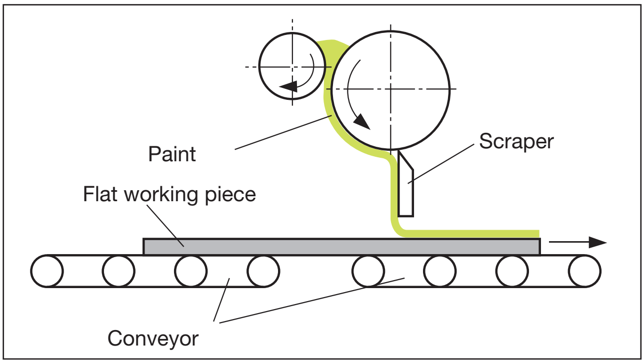


Fig. 4.2.27
Scheme of a roller/curtain equipment

The roller/curtain-coating method is a technical hybrid between curtain coating and roller coating. When processing low-solvent or solvent-free and highly viscous coating materials defined quantities of the film are transferred via a pick-up roll to a transfer roll. Here it is removed by an applicator (scraper or coating knife) and then poured onto the surface to be painted in a precisely metered quantity [4.4.53]. The roller/curtain coating method permits processing viscosities of up to 800 mPa·s with shear of 100 s^{-1}.

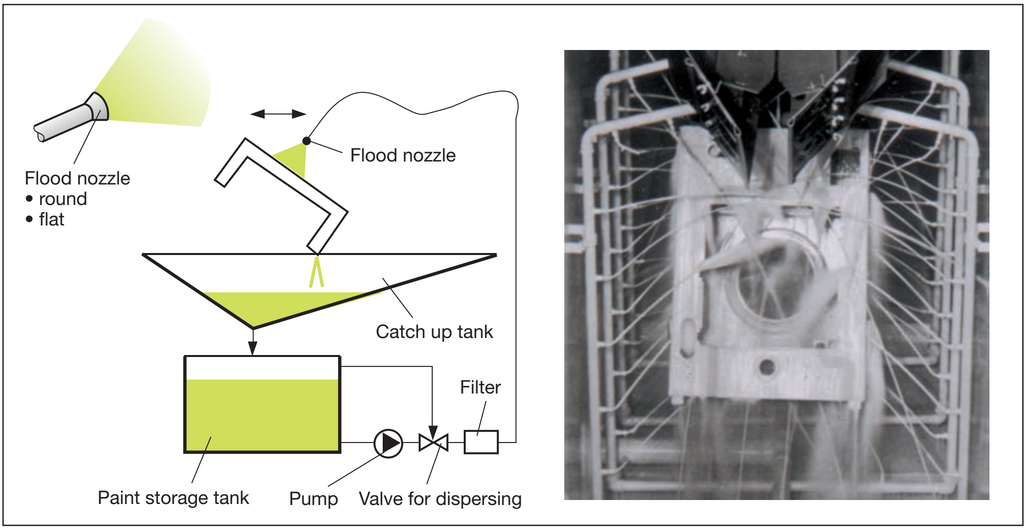


Fig. 4.2.28
Scheme and picture of a flood coating machine

Flood coating is similar to the dip-coating process already described. In this the paint is applied from nozzles to the workpieces as they pass by. The excess paint is collected in a collection tray and is fed back to the flood nozzle after filtration.

Flood processes have only limited use because of the nonuniform film thicknesses and the formation of unavoidable runs. The surfaces are not attractive even if the flood-coating systems are optimized and the components are also rotated during the painting process. Flood-coating processes have therefore only achieved a certain importance for coating engine blocks, central heating radiators, pipe racks or other bulky components for trucks or agricultural machinery. Because of the relatively high degree of solvent evaporation during flooding the materials used now in open systems are mainly limited to waterbased paints. They are going to be replaced by electrodeposition and other processes

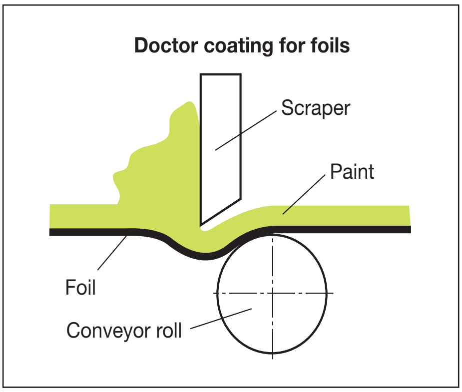


Fig. 4.2.29
Scheme for application of coatings by doctor coating for foils

Other direct processes are **drum coating, doctor coating and filling**. The first of these processes is useful for coating small components. Components are shaken or rotated in drums or cages together with the paint and then, after the excess paint has drained off, the films are dried or cured by heat action.

With doctor coating a coating knife (scraper) presses the highly viscous paste onto the paper or textile web as it runs through the machine, thereby guaranteeing uniform film thicknesses. Whereas doctor coating has gained acceptance as an industrial method for processing highly viscous paints in the textile and paper industries, filling with non-free-flowing coating materials is limited to manual paint processing.

4.2.1.3 Spray Processes (Paint Applied Indirectly to the Object)

Although indirect application processes are by far the most important for industrial paint processing, they give the most cause for concern at the same time from an environmental perspective (see figure 2.3.61). Despite the disadvantage of the sometimes extremely poor material yields with the simultaneous accumulation of paint waste, atomization methods for spraying are still dominant for industrial-scale coating technology when there are demanding specifications for the optical attractiveness of the coating. They enable a uniform coating with intricate parts of complex shape. If a wide range of colors is demanded and pronounced effects have to be achieved, there is practically no alternative to spray application.

The technical principle of this process involves the production of droplets which are converted back into a closed, smooth film after being transported to the object to be painted. To produce the droplets methods are in use today which use electrical forces, centrifugal forces, the energy of accelerated air or that of the highly accelerated paint itself in order to provide the necessary free surface energy. The transport to the object mostly is assisted by shaping air.

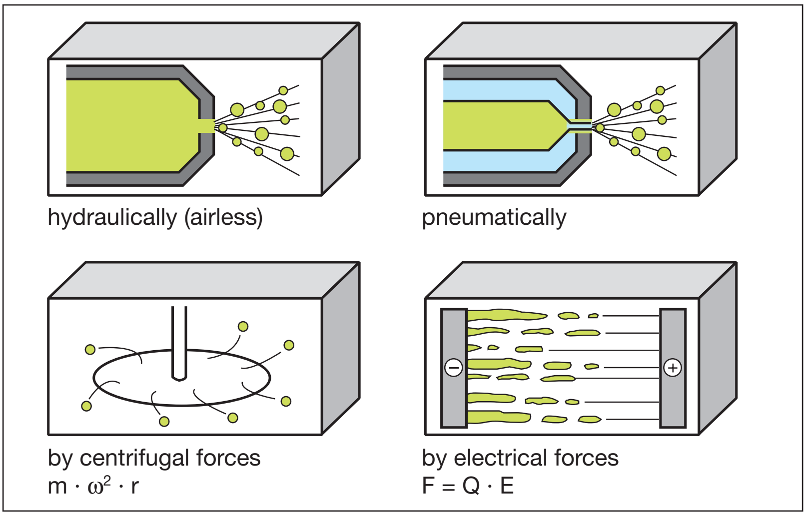


Fig. 4.2.30
Methods of atomizing

Spray processes require a booth in addition to the actual spray head itself. Spray booths must be provided with suitable inlet air, air-extraction, flushing and separation systems and paint-supply and conveying equipment because of the formation of overspray (see figure 4.2.2).

A specific droplet spectrum is required in order to achieve a particular coating result. For optically attractive, i.e. smooth and at the same time thin films and the reproduction of colors the droplet spectrum is decisive, though certain limit conditions have to be observed. If the droplets become too small, the material spill increases as a result of more overspray. This part of the spray cloud is not deposited on the object to be coated. In addition, more solvents evaporate because of the greater paint surface area. The consequence would be high emissions and paint waste from spray booths and poor viscosity-induced flow. On the other hand, excessively large droplets result in an unacceptable surface property profile (see chapter 3.1). Because of the contrary influences of the droplet size on the quality of the coating and environmental pollution the best compromise is usually for average droplet sizes ranging from 30 µm to 35 µm.

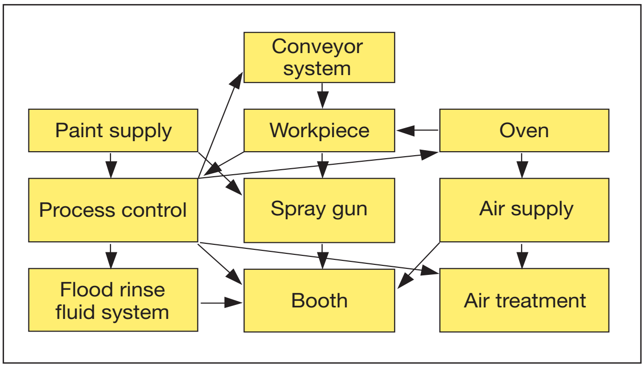


Fig. 4.2.31
Elements of a spray coating process

Atomization through nozzles

The free surface energy which has to be exerted to overcome the cohesive forces can be generated by flow in nozzles. A nozzle is a constriction at the end of a pipe for transferring hydrostatic pressure into kinetic energy for fluids. Single- and multicomponent nozzles are usual for the industrial-scale application of this principle. The former are used in hydraulic atomization. High material acceleration, caused by high material pressure and narrow nozzles, results in the accelerated coating material being broken down into tiny droplets after exiting the nozzle by interaction with the ambient air. Multicomponent nozzles cause atomization by the additional interaction of the exiting material with greatly accelerated air.

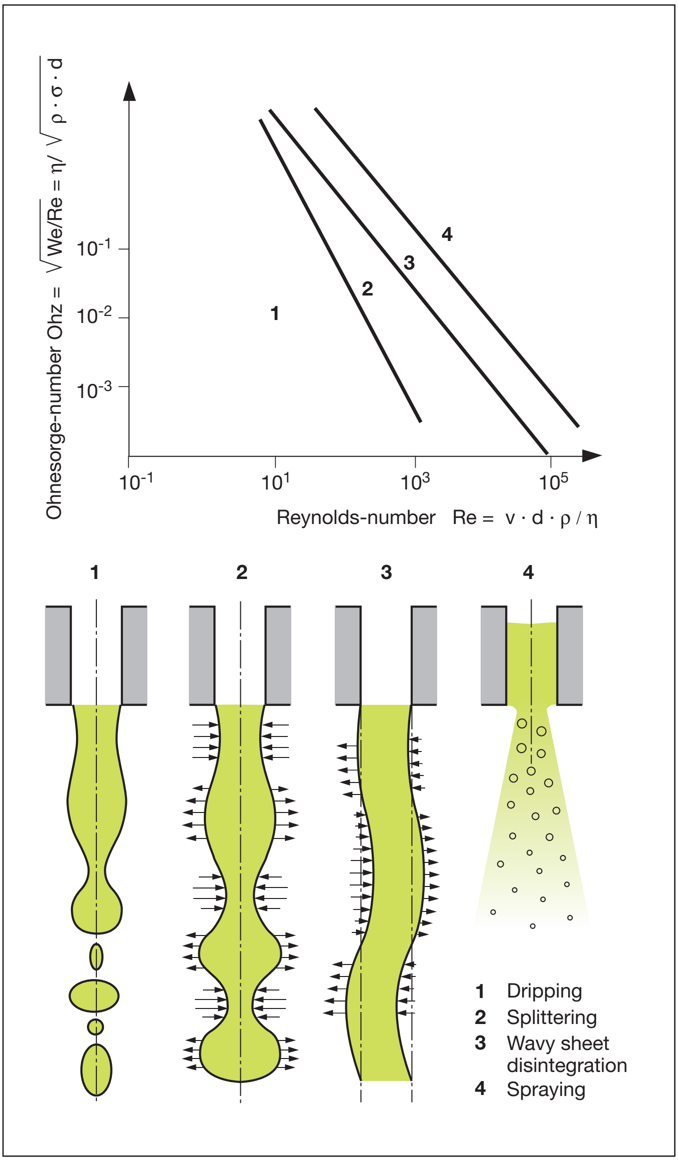


Fig. 4.2.32
Mechanism of droplet generation and working conditions for spraying process

Droplet formation by liquids after discharge from nozzles is influenced by their speed relative to the ambient air (see figure 4.2.32). Depending on the conditions at discharge dripping (1), splittering (2), wavy sheet disintegration (3) or the desired spraying (4) is achieved. If a liquid is forced only very slowly out of a nozzle, a continuous line of liquid is initially formed which is then constricted after a minimum length is reached, before attaining the thermodynamically most stable state of dripping when individual droplets are formed. Although, under the conditions outlined, monodisperse distributions with only a few large droplets are obtained.

If the discharge speed is increased, longitudinal oscillations are induced in the line of liquid as a result of friction with the ambient air which is at rest, with the result that areas of swelling and constrictions provide the conditions for droplet formation by splittering. The droplet spectrum is again uniform. The droplet size is a function of nozzle width, surface tension and density.

A further rise in the velocity results in an increase in the air friction and conversion of the line of liquid into transverse waves. Wavy sheet disintegration also produces large droplets with a narrow spectrum.

With even greater pressure such high exit speeds are reached that further secondary atomizations are added to the primary effects described as a result of the collisions between the primary droplets and the now significantly slower air. The primary droplets are deformed by the dynamic pressure of the ambient air, then constricted and divided. Further deformation results in ever smaller droplets until the deforming dynamic pressure is in equilibrium with the resisting cohesive pressure. This is the principle of hydraulic atomization in the form of airless atomization.

The generation of tiny droplets but now of very different sizes can also be achieved by pneumatic atomization using greatly accelerated air with a liquid which is moving slowly.

The operating ranges of the individual atomization types can be shown graphically if the variables which characterize the flow state such as density, flow rate, viscosity and surface tension are merged to form dimensionless numbers which are then plotted meaningfully against each other. The numbers relevant to the present case are the *Reynolds* number Re, the *Weber* number We and the *Ohnesorge* number Ohz as the quotient of the square root of the *Weber* number and the *Reynolds* number.

$$\mathrm{Re} = \frac{u \cdot d \cdot \rho}{\eta} \qquad \mathrm{We} = \frac{u^2 \cdot d \cdot \rho}{\sigma} \qquad \mathrm{Ohz} = \frac{\sqrt{\mathrm{We}}}{\mathrm{Re}}$$

If a liquid is in the operating range of an atomizer for long enough, the droplet size will, as described above, be reduced further and further until the cohesive pressure corresponds to the deforming dynamic pressure. Where there are no other variables influencing this size-reduction process, the droplet size can be calculated for the stationary state. According to *Bernoulli* the following applies for the dynamic pressure p_{St}:

$$p_{St} = \frac{\rho}{2} \cdot u^2$$

The cohesive pressure p_{Ko} in droplets is given by:

$$p_{Ko} = \frac{2 \cdot \sigma}{r}$$

Size reduction therefore always takes place when

$$\frac{\rho}{2} \cdot u^2 > \frac{2 \cdot \sigma}{r} \quad \text{respective} \quad \frac{4 \cdot \sigma}{d}$$

or, resolved differently

$$\frac{\rho \cdot u^2 \cdot d}{\sigma} > 8 \qquad \text{because of} \qquad \frac{\rho \cdot u^2 \cdot d}{\sigma} = \mathrm{We} \qquad \text{follows}$$

atomization if

$$\mathrm{We} > 8$$

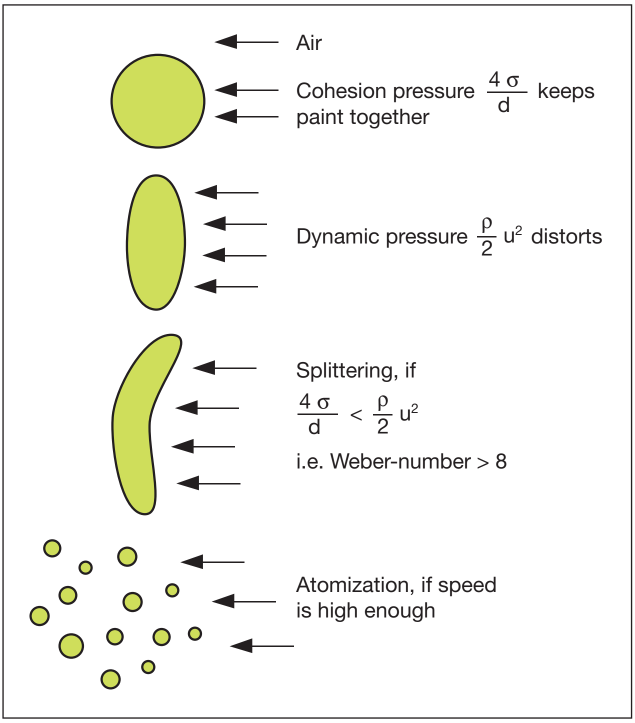


Fig. 4.2.33
Mechanism of generating secondary droplets during atomization

Consequently the conditions for conversion into finer droplets are always right if the *Weber* number > 8. This shows an excellent fit for liquids such as water. With coating materials with higher-molecular polymer solutions, however, it requires a certain supplementation and correction.

Various methods are in use to achieve the high speed differentials between the substances to be sprayed and air. In the pneumatic process the atomising air supply must reach a high speed, as explained above. The air meets the material either, in the case of an internal mixture, before exiting the atomization device or, in the case of an external mixture, which is the usual method in coating technology, only after leaving the nozzle. With an external mixture, therefore, the paint droplets are generated not inside but outside the spray head.

Since the external mixture is of far greater importance for pneumatic processing in coating technology, the following descriptions concentrate on this technology.

Pneumatic atomization is sub-divided according to the effective air pressure into low-pressure (0.5 to 1 bar) and high-pressure atomization (4 – 8 bar), with the latter the more important variant in industrial processing. As a result of the high air pressure the exiting air attains high air speeds. Provided there is a sufficient quantity of air, up to 1 litre of paint per minute can be atomized which meets the needs of high-performance industrial processes.

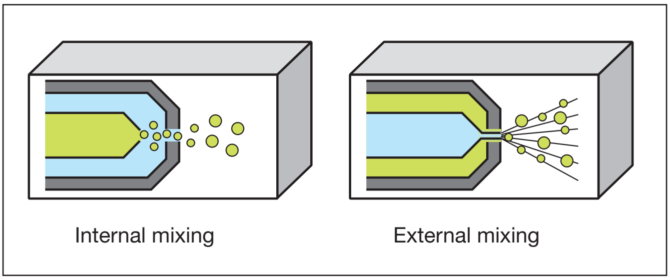


Fig. 4.2.34
Pneumatic spraying with inner and outer air mixing

The spray heads or guns are based on the invention by the Dutch doctor *DeVilbiss* who registered a patent for a process for manufacturing aerosols for medical purposes in 1887. The principle of such a gun, which has been constantly improved to the present day, is shown in the form of a sectional drawing in figure 4.2.35.

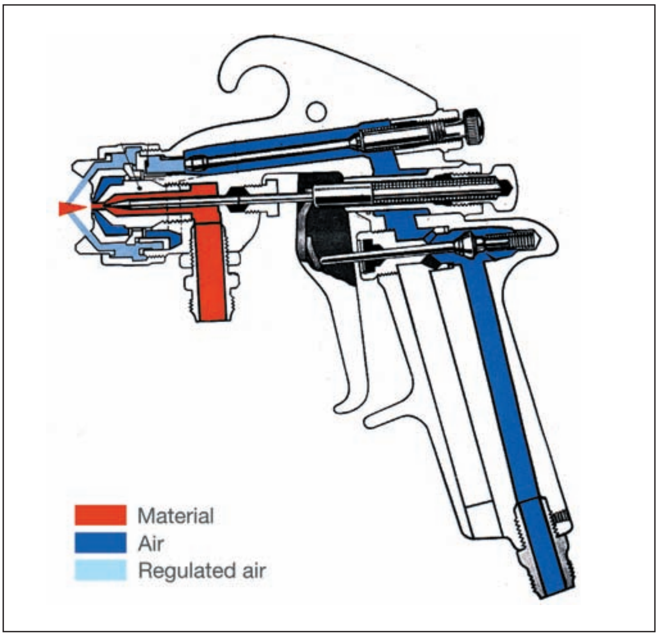


Fig. 4.2.35
Cross section of a spray gun

The paint which is fed to the nozzle is initially prevented from leaving the gun by the nozzle pin. Once the trigger guard has been opened, only the atomizing air which is under a pressure of 5 – 8 bar is discharged from an annular gap configured concentrically to the nozzle. As a result of the highly accelerated atomizing air an area of underpressure is created at the nozzle aperture. The coating material is consequently entrained once the nozzle has been opened before being deformed in the acceleration area of the spray air by the dynamic pressure acting there and ultimately converted into smaller droplets. The air speed can reach up to 400 m/s.

Different discharge rates are achieved, depending on the supply method for the paint. Siphon feed spray guns achieve only low material discharge rates. In more powerful spray guns, therefore, either gravity in the form of a gravity feed spray gun or additional material pressure ensures an effective increase in the material discharge rate. In the latter case the material supply is no longer provided by storage reservoirs attached to the gun. Separate pressure vessels or circulation systems handle the material supply.

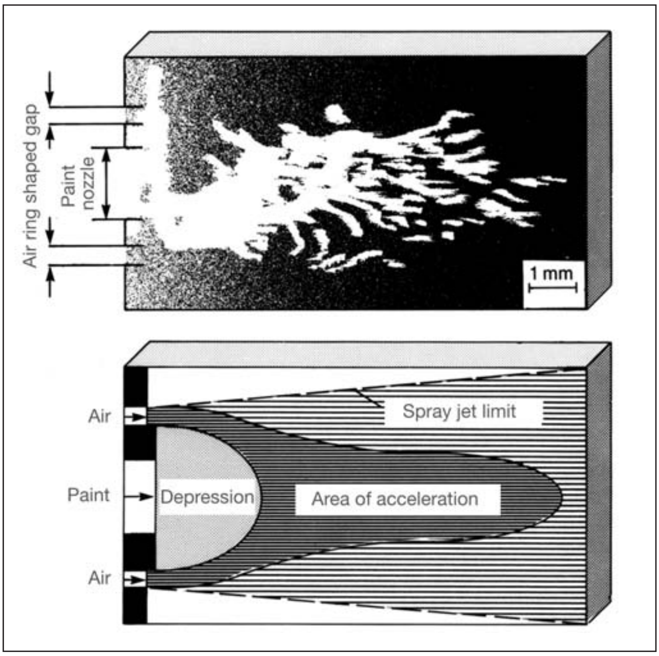


Fig. 4.2.36
Picture and scheme of atomization process

It should be noted that the resulting air speed does not rise linearly with increasing air pressure. It reaches a plateau at air pressures of less than 8 bar, with the result that any further rise

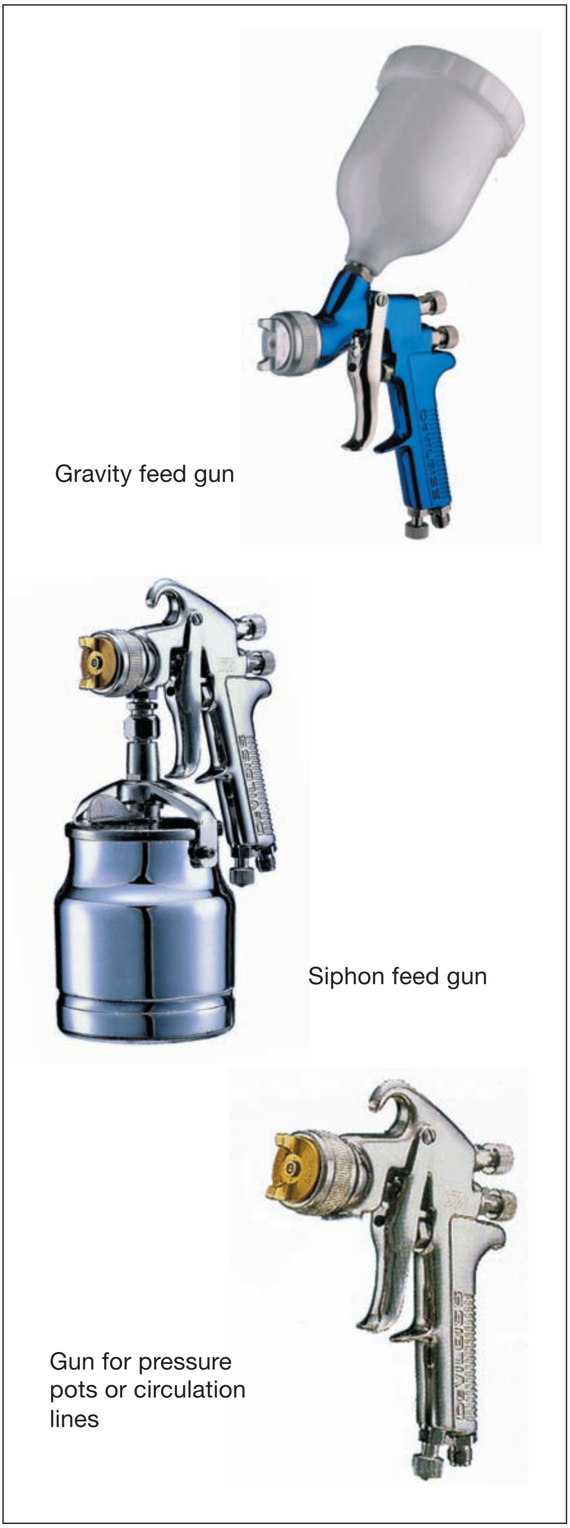


Fig. 4.2.37
Different types of material feed for pneumatic spray guns

merely increases air consumption without significantly influencing the droplet spectrum. Furthermore, an increasing air volume leads to excessive energy consumption and a deterioration in the material efficiency because of increased overspray. There can be up to 50% wastage of the material used. The causes of this lie in the large volumes of spray air moving at high speed which carry the small and less sluggish droplets past the object. The 1000 l accelerated air which are necessary to atomize 1000 g paint are routed past or reflected, depending on the shape of the object to be painted together with the spray cloud. This involves a rebound effect and an undesirable distribution of the spray cloud in the vicinity of the workpiece. If the droplet size has to be reduced nonetheless at high air pressures, other measures must be taken such as lowering the material output by reducing the material pressure or using smaller nozzles.

There are limits to the material discharge rates with pneumatic atomization. The droplets increase in size with increased material discharge. This is explained by the braking of the spray air when it interacts with the paint and the resulting decrease in dynamic pressure. It is therefore clear that the formation of the droplet spectra depends not only on the air speed, but also on the air volume. The latter is determined by the surface area of the annular gap in addition to the pressure of the spraying air. The influence of the spraying air pressure or air volume on droplet size is indirectly proportional to the

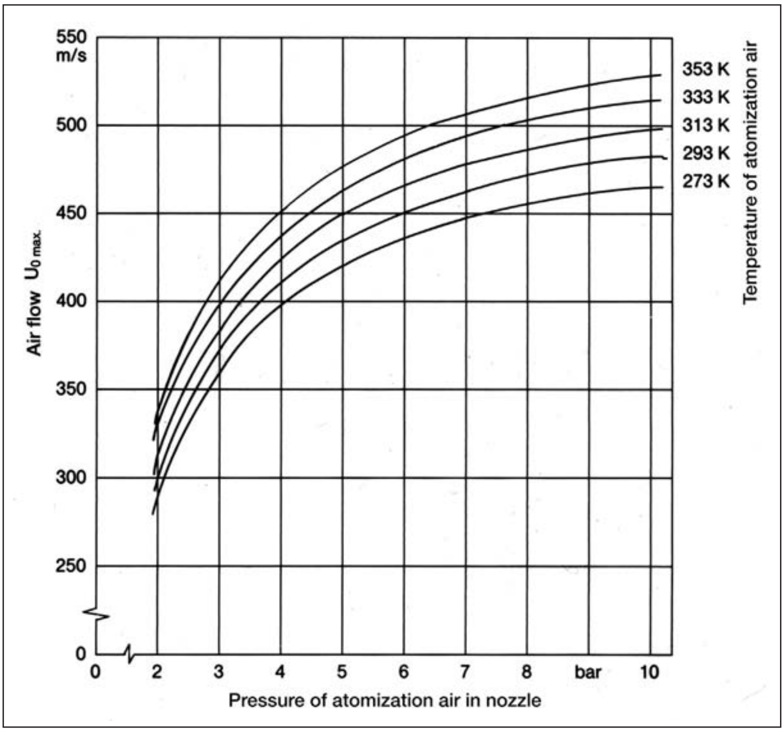


Fig. 4.2.38
Speed of atomization air depending on air pressure

material discharge rate and thus the material pressure with a constant specified nozzle surface area. If a constant spray pattern is demanded, changes in the material output always result in a corresponding effect on the volume and pressure of the spraying air. However, this is only meaningful if effective acceleration of the air is still possible (see figure 4.2.38).

The volumes of atomization air should be limited, if possible, for cost reasons. Approximately three-quarters of the total energy for droplet formation also has to be generated to accelerate the spraying air, while the rest, which is for friction and acceleration of the paint and the actual free surface energy, plays only a subordinate role [4.4.54].

There are other variables for influencing the droplet spectrum from the paint property side, of which the viscosity and rheological properties of the coating material to be atomized are the decisive ones. Assuming forced feed systems are not used for dispensing the material, the discharge rate is influenced in a directly proportional manner by the material pressure and in an indirectly proportional manner by the viscosity after the *Hagen-Poiseuille* equation (see also chapter 2.4). Since the viscosity of inherently viscous coating materials falls not only because of the shear load but also, as with all liquid materials, by approx. 5% per °C temperature increase, it is clear that fluctuating ambient or material temperatures will lead to fluctuating discharge rates. These in turn are reflected in different spray patterns and, associated with this, also in different film thicknesses, and will result ultimately in flow defects in the form of, for example, ”orange peel” or ”runs”. Temperature constancy of the material or forced delivery systems help avoid quality fluctuations.

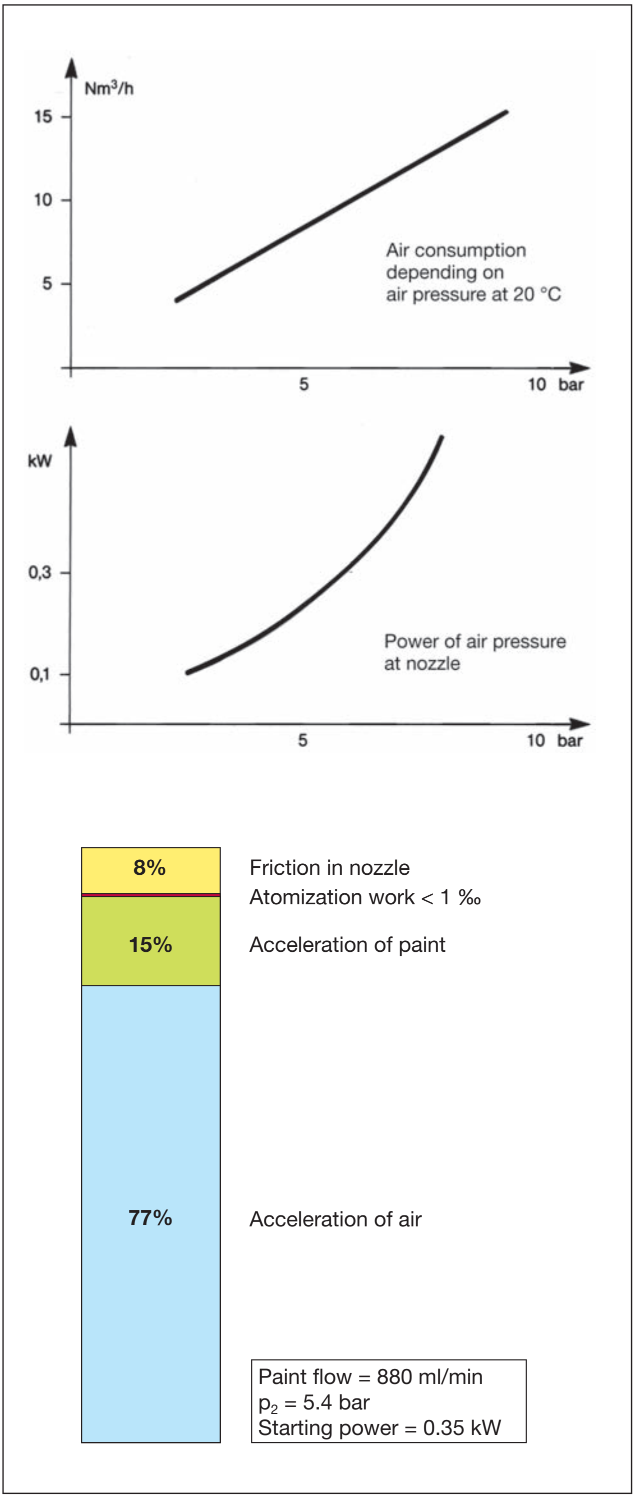


Fig. 4.2.39
Air consumption, power consumption and energies used for pneumatic spray application

Independently of the indirect influence of viscosity on the discharge rate and thus on the droplet spectrum, the rheological properties also have a direct impact on the droplet size and especially the droplet size distribution. Because of the relatively short period in the droplet-forming acceleration zone the elastic properties of the coating material also play a supplementary role, in addition to viscosity. Paint with a high elastic component requires a longer period in the shear zone to reach equilibrium. If it is also assumed that the dwell time in the shear zone for the onset of equilibrium is not the same for all droplets and if, furthermore, account is taken of the fact that the shear zone is not homogeneous either, this provides an explanation of the broad spectrum of droplet sizes.

Further physical paint variables which influence the droplet size are surface tension and density. Low surface tensions result in a smaller cohesive pressure in the droplets and thus facilitate atomization. High densities promote atomization, since the dynamic pressure decreases more slowly because of the higher inertia.

There are numerous references in the literature to pneumatic atomization and calculating droplet size [4.4.55, 4.4.56, 4.4.57, 4.4.58]. Of the

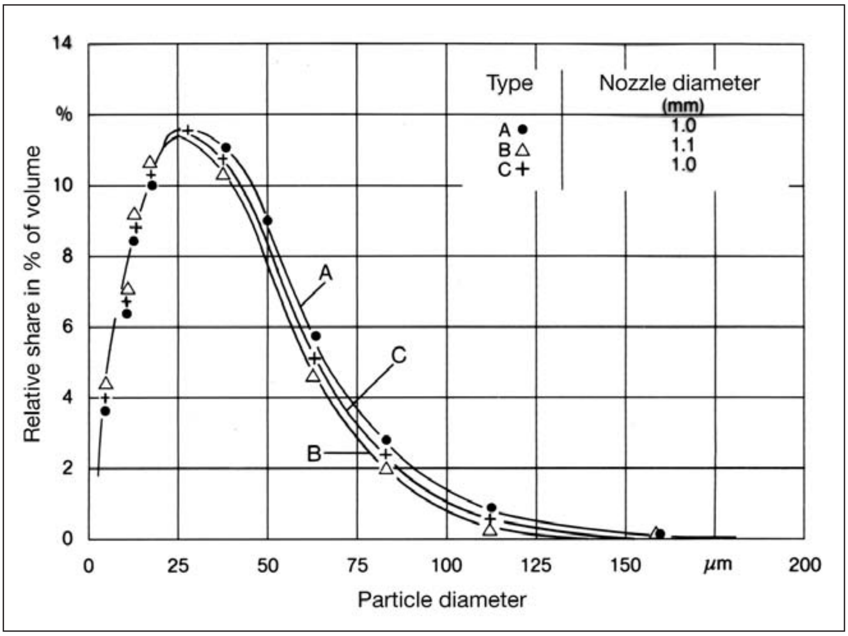


Fig. 4.2.40
Typical spectrum of droplet sizes at high pressure spray guns

many publications on calculating the droplet spectrum *Walzel*'s formula merits particular mention as a simple and thus straightforward formula [4.4.59].

$$d_{32} = 51 \cdot Re^{-0,39} \cdot We^{-0,18} \cdot \left[\frac{\dot{m}_{paint}}{\dot{m}_{air}}\right]^{0,29} \cdot d_D$$

In this d_{32} is the *Sauter* diameter as the mean droplet size (see chapter 2.3.3).
The *Reynold*s number Re and the *Weber* number We contain the relative speeds of air to paint droplets, viscosity, density and surface tension. These variables are supplemented by the ratio of the mass flow rates $\dot{m}_{paint}$ and $\dot{m}_{air}$ and by the diameter of the material nozzle d_D.
This mathematical relation enables the effects of specific changes in the variables on the droplet spectrum to be calculated with a good fit to measurements from practical applications.
Figure 4.2.41 shows the calculated effects of the material, equipment and process variables on the droplet spectrum. The influence on the spray pattern is greater, the steeper the individual curves. A positive incline represents an increase, and a negative incline a decrease in droplet size.
Consequently the fineness of the atomization deteriorates significantly with increasing paint throughput $\dot{m}_{paint}$ unless the air throughput $\dot{m}_{air}$ is increased correspondingly at the same time.
Calculations also show a higher sensitivity for viscosity compared with surface tension and density, which also fits with practical experience. Atomization is therefore defined far less by the gun type than by the gun setting or by the ratio of paint throughput to air

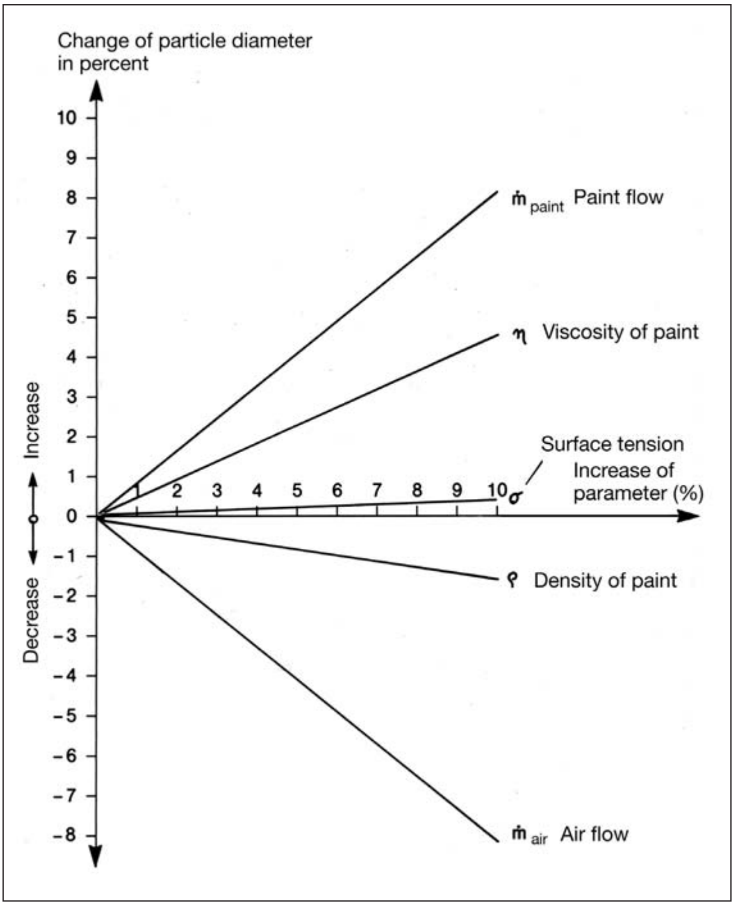


Fig. 4.2.41
Sensitivity diagram of the material and application parameters at spray coating process

speed. It should be noted in this regard that the same pressure gauge settings for air pressure with otherwise apparently the same conditions do not necessarily mean the same droplet size. Different cross sections and lengths of hoses result in different pressure drops in the gun, despite the same pressure gauge setting. If reliable forecasts of the spray pattern are required, such factors have to be taken into account or the pressure gauges have to be positioned as close as possible to the spray gun.

Absolute calculations of droplet sizes to evaluate flow properties are made more difficult by the fact that the individual droplets take on different speeds depending on their size. Collisions en route to the object cause droplet contaminations which change the primary droplet spectrum.

To this must be added the fact that the generated spectrum does not match the deposited droplets in that the finer particles are also less likely to be deposited on the object because of their greater mobility. They accumulate in the air carried past the object in the form of overspray and therefore change the deposited spectrum once more.

In order to improve the application window in which pneumatic high-pressure atomization can be used still further, supplementary devices are used on high-performance atomizers which permit the spray jet to be adapted to the shape of the objects to be painted and special effects to be set. Depending on the shape of the object to be painted it is advisable to adapt the spray pattern to the specific shape of the workpieces by expanding or constricting the spray cone. The normally round spray cone can be flattened to a greater or lesser extent by means of a separate supply of a partial flow of the atomizing air, the fan air, to the fan bores (see figure 4.2.43), depending on the particular task.

Pneumatically operated spray guns are fitted with supplementary air outlet bores around the annular gap to ensure that the underpressure in the vicinity of the atomizing nozzle does not cause any deposition of overspray in the atomizing area of the spray gun. This prevents return flow of the overspray and thus soiling of the gun.

The cross flows from the fan bores and the supplementary bores in the air cap therefore regulate the spray jet and prevent deposits but do not influence droplet formation since they only have an effect on the spray pattern after the formation of the droplet spectrum.

Pneumatic high-pressure atomization has become a complex process which can only be managed and used to reach an optimum coating result if all the variables are known to

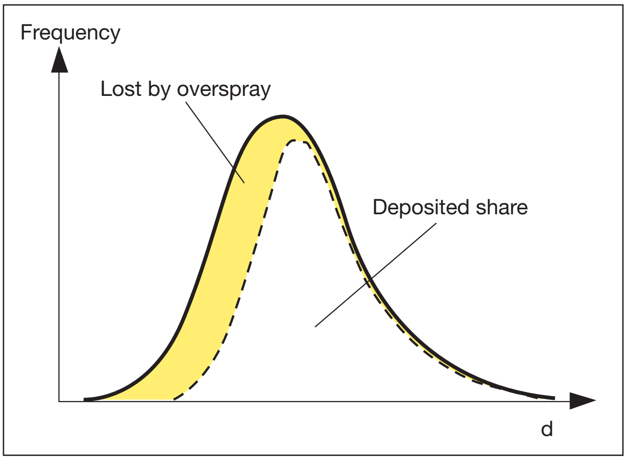


Fig. 4.2.42
Difference between the generated and deposited droplet size distribution at pneumatic spray application process

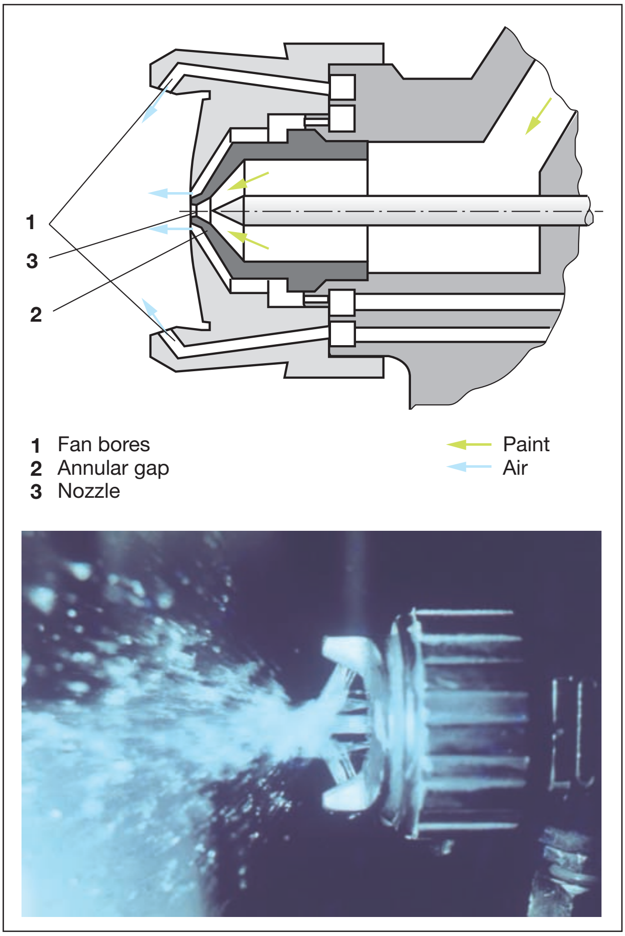


Fig. 4.2.43
Scheme and picture of the effect the fan bores

those involved and are correspondingly addressed when running the process (see figure 1.1.7). The viscosity, surface tension and density, but also the solid content are relevant material variables; nozzle, annular gap, air cap and fan bores represent the equipment parameters; and air and material pressure are the adjustable process-engineering variables. The viscosity affects atomization directly and also indirectly by influencing the discharge rate.

The air and object temperatures and especially the distance from the object are significant variables affecting product quality in terms of gloss, color, effect, flow and, in certain cases, even adhesion. The average time of the droplet flow and thus the solvent content of the resulting film are determined by the distance of the gun to the object. If the distance is only short, this results in wet and therefore low-viscous paint droplets. With greater distances, on the other hand, the droplets become too dry because they are in motion for too long. The outcomes of this are variations in flow or running, but also fluctuations in the formation of effects.

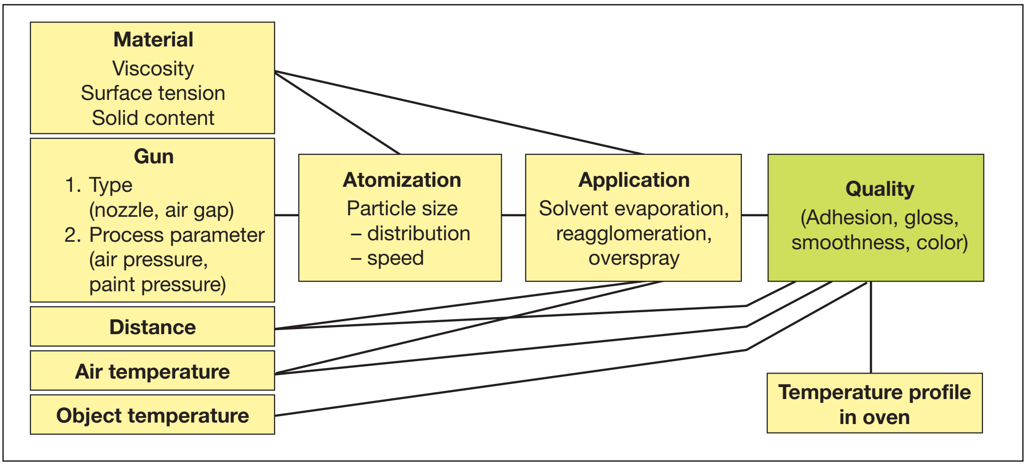


Fig. 4.2.44
Factors defining the coating quality for pneumatic high pressure spray application

The distance from the object generally used in practice of 25 – 30 cm is the best compromise, taking account of the evaporation properties and the rising amount of overspray with increasing distance. During manual application distances to the object are sometimes also consciously varied to compensate for varying ambient temperatures and to influence effect formation.

Hot application

During spray application it is possible to reduce emissions and overspray by heating the conventional coating material. The lowered viscosity as a result of the temperature increase opens up new means of influencing the processing method. Using hot application either the solid content can be raised or the spraying air pressure can be lowered. In the former case the higher viscosity resulting from the decision not to use solvents can be returned to its former level by means of heat action. In this way, despite the higher solid content, a similar spray pattern is obtained. On the other hand, with a lower viscosity the overspray can be reduced thanks to a lower spraying air pressure, without any deterioration in the spray pattern. The material consumption is reduced and thus also the emissions. Figure 4.2.45 shows the pronounced temperature dependency of viscosity using two paints as examples. It is known from practical applications that heating the material to 60 – 70 °C enables either the solid content to be increased by 4 – 6% or the spraying air pressure to be lowered by 1 – 1.5 bar. The latter is equivalent to a 10 – 15% reduction in overspray.

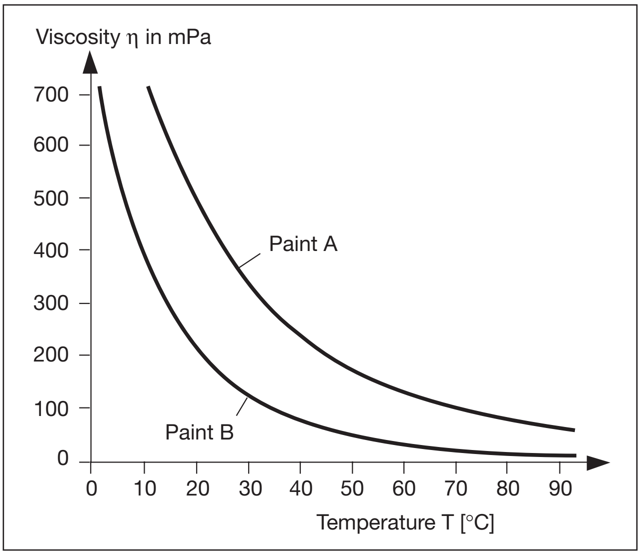


Fig. 4.2.45
Viscosity of paints in relation to paint temperature

The material is heated indirectly by means of heat exchange with a heat transfer liquid. Since the flash point of the solvents is generally exceeded in so doing, the systems must be designed to be explosion-proof. The energy required to heat the paints is more than compensated for by savings in the consumption of compressed air.

Low-pressure process

The classic low-pressure process is only of importance for the manual processing sector. Only small quantities of material can be atomized in this process because of the low pressure and therefore the low air volumes. Furthermore, it is not possible to achieve an optimum droplet fineness, as a result of which the coating result does not always meet the very demanding surface quality requirements.

Interest refocused on the low-pressure process in the US initially in response to more stringent environmental regulations. Because of the statutory requirement to reduce wastage during spray coating to less than 35% and reduce emission the low-pressure process has been further developed such that it now better meets the demands of industrial processing. This development has resulted in a low-overspray variant of pneumatic atomiza-

Fig. 4.2.46
Example of a High-Volume-Low-Pressure gun

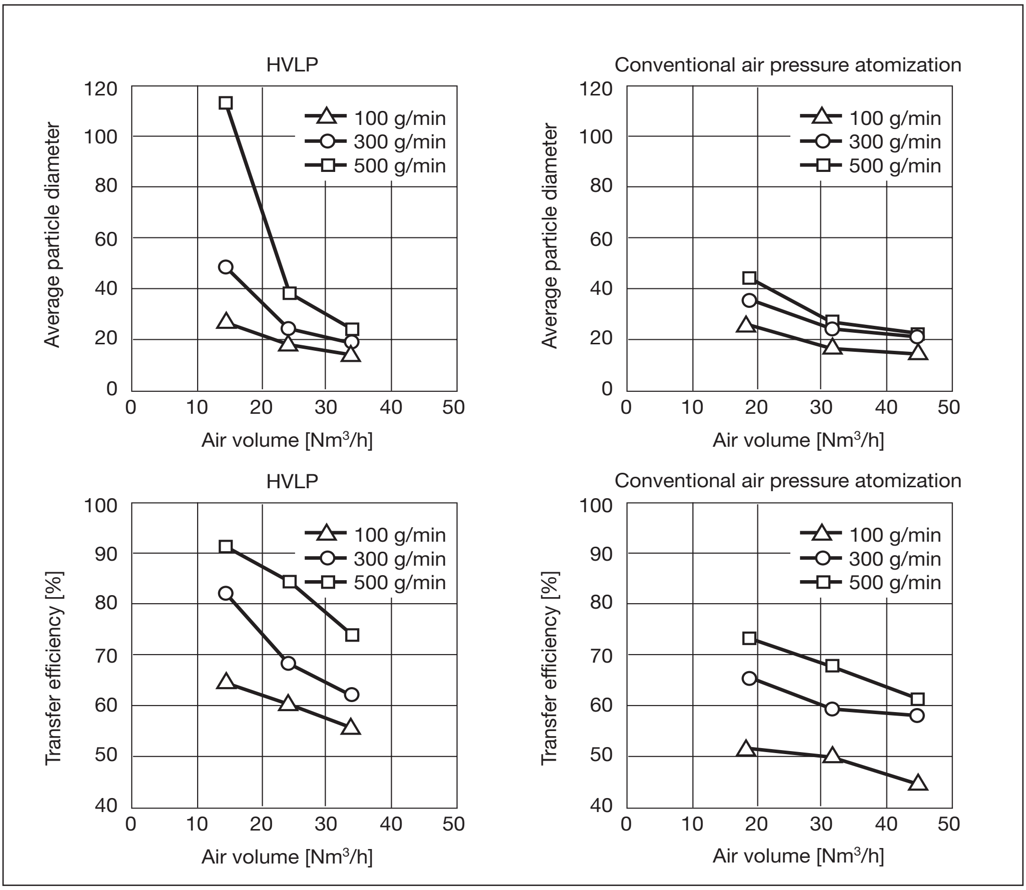


Fig. 4.2.47

Droplet sizes and transfer efficiencies of HVLP-process in comparison to standard spray application and their dependence on material flow and air flow (Nm^3 = standardized cubicmeter)

tion, known as the high-volume low-pressure (HVLP) process [4.4.60]. It permits a compromise between an optically attractive coating and reduced overspray formation. The atomization principle corresponds to that of the pneumatic process, though it reduces the air speed by means of a lower air pressure with a higher air volume and a wider annular gap at the same time.

This means that, despite the lower initial speed of the spraying air because of the significantly greater air volume available, the air is also retarded less during atomization. The positive side effect is a lower component of fine droplets in the droplet spectrum.

The optimum spraying air pressure of HVLP guns is only 0.8 bar and less, although the gun is initially supplied with a pressure of 5 bar. The lower air pressure is achieved by expanding the air before it leaves the gun, thereby greatly increasing its volume. Thus, with a reduced discharge rate of approx. 150 – 250 ml/min a droplet spectrum similar to that of the conventional atomization process is achieved with a simultaneous reduction in overspray by 15 to 20%.

Figure 4.2.47 shows the sensitive factor of the volume of material to be atomized on droplet formation in the low-pressure processes. Furthermore, the effect on the coating efficiency is also described.

Hydraulic or airless atomization

The hydraulic atomization process, also known as airless atomization, brings about particle formation of the liquid coating material purely by high material pressure. The energy required for droplet formation is provided by the material pressure of 50 – 400 bar. On discharge from the fine nozzles with a diameter < 0.5 mm the paint is accelerated to more than 150 m/s and atomized by its spontaneous expansion and additional interaction with the stationary ambient air. The paint flow disintegrates immediately after exiting the nozzle because of the high degree of turbulence which is well above the critical *Reynold*'s number of 2000. The discharge aperture can be designed in the form of a slit nozzle to produce a shaped flat spray. The degree of turbulence can be increased even further by means of special atomizing nozzles which form inlet and discharge eddies and thus produce even finer atomization.

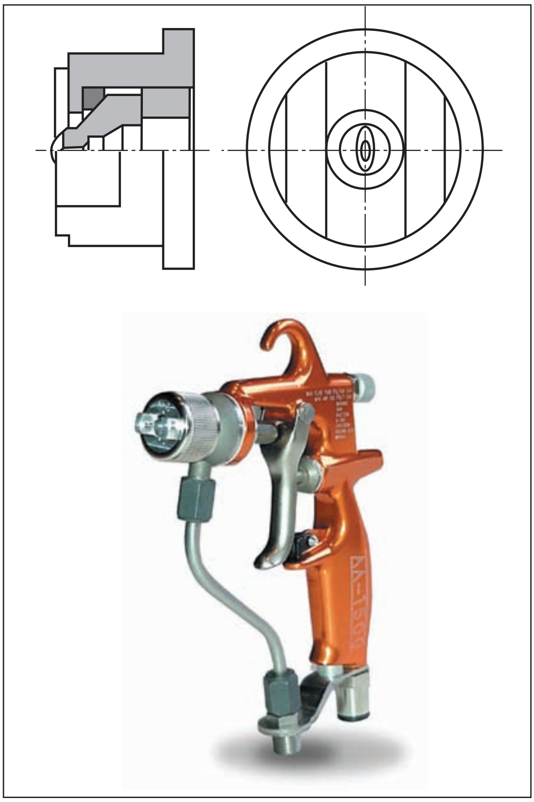


Fig. 4.2.48
Scheme of a nozzle and picture of an airless gun

The spray pattern variables can be summarized after *Walzel* in the following formula [4.4.61]:

$$d_{32} = We^{-0,5} \cdot \left[\frac{\rho_{paint}}{\rho_{air}}\right]^{-0,25} \cdot (1 + 3,3\ Ohz) \cdot d_D$$

A high particle speed, concealed in the *Weber* number We, results in a lower particle diameter. A higher viscosity, concealed in the *Weber* and *Ohnesorge* numbers, and a larger nozzle diameter d_D increase the droplet size. The discharge rate can be influenced by changing the material pressure or the nozzle diameter. It should be noted, when interpreting such data, that the paint speed u contained in the *Ohnesorge* and *Weber* numbers is defined by the material pressure and the nozzle width. Any change in d_D also results in a change in u. By contrast with the pneumatic process, the paint viscosity has only a minor influence, while the surface tension and density have a similar effect on the droplet spectrum. The sensitivity graph in figure 4.2.49 shows the characteristic dependencies in qualitative terms.

Hydraulically operated atomizers have no means of adjusting the paint quantities and are either open or closed. Any change in throughput would result in changes in the droplet formation.

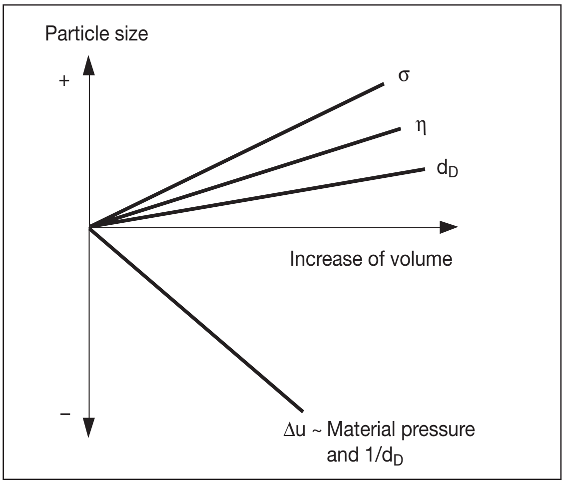


Fig. 4.2.49
Sensitivity graph on material and technical parameter for airless application

The marked stress to which the nozzles are exposed has a detrimental effect on trouble-free longterm operation. Because of the high relative speed of the paint to the inside of the nozzle, the material wear in the nozzle is high, especially when abrasive pigments are used. Even minor nozzle wear results in increased film thicknesses and thus runs and craters because of the discharge rate which increases to the power of four of the nozzle radius in accordance with the *Hagen-Poiseuille* equation. On the other hand, if hard metals are used as the materials for the nozzles there are also, of course, difficulties in producing fine bores. It only became possible to process hard nozzle materials satisfactorily once laser drilling had been invented.

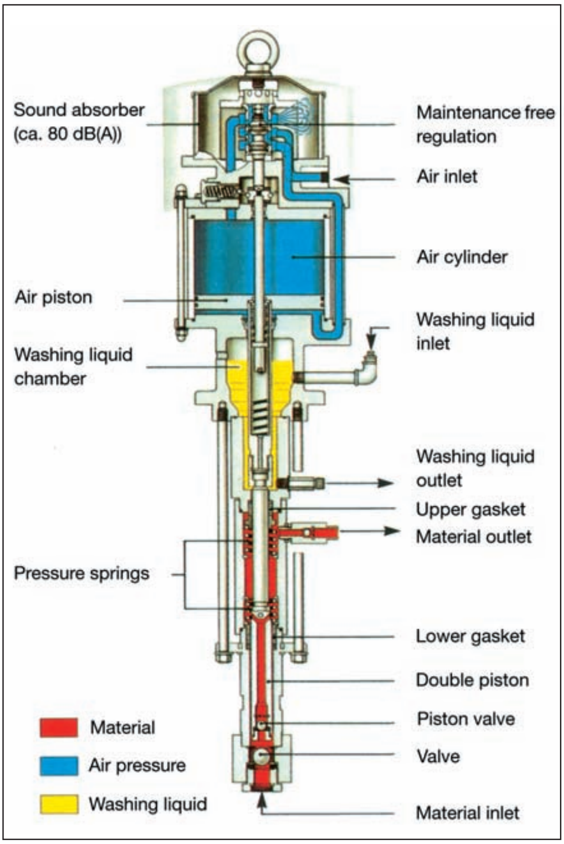


Fig. 4.2.50
Scheme of an airless pump

Apart from a gun, the nozzle and the necessary safety features, a hydraulic atomization system contains a means of generating the required paint pressure of up to 400 – 500 bar. This task is met by pumps operating with compressed air or electrically powered special piston pumps which are robust and work locally and trouble-free to produce the high material pressure. The special feature of the pneumatically operated double-piston pumps is that the required high pressures can be achieved merely by means of large differences in the cross sections of the pistons. A surface area ratio of 1:10 to 1:20 enables the normal output pressure of 12 bar to be raised without difficulty to 120 – 240 bar. Approx. 200 litres of air expanded to normal pressure are required per litre of paint to be atomized.

The airless process permits the atomization of relatively large volumes of paint of up to 2 l/min and is suitable for coating large surface areas. Airless atomization is therefore a proven process, particularly for coating large objects such as ships, cranes or industrial plant. A beneficial feature is its high material yield compared with the pneumatic process because it dispenses with the use of atomizing air.

Because of the lack of spraying air the rebound effect familiar from pneumatic atomization is absent. The consequence is lower overspray losses. Low overspray airless atomization therefore has advantages for paint spraying in enclosed spaces. The component of the solvents evaporating in the spray booth is also reduced because of the lower air volume, with the result that a major proportion of the emissions is transferred to the drier or oven.

The 0.1 – 0.5 mm fine nozzles with their extremely small free nozzle surface area do not permit effect paints to be processed since the large aluminium flakes block the fine nozzles (see chapter 3.2.3).

In order to make the use of airless guns more universal there has been no shortage of attempts at influencing the spray jet during the atomization process itself. Success was achieved in deforming the spray cone by means of additional air flow without any impact on the atomization process. Such air-assisted hydraulic guns are operated at material pressures of less than 200 bar and air pressures of 1 – 4 bar. They are also suitable for more difficult and complex components. Such processes are known by the name Airmix. They combine the benefits of pneumatic spraying with those of the hydraulic process.

When operating airless or Airmix systems the formation of relatively large quantities of overspray is occasionally observed which settles primarily on earthed parts in the vicinity. Tests have shown that –as a result of the high friction of the paints and solvents, which are poor conductors, in the nozzles of the airless guns – considerable quantities of charge are transferred to the paint. Unearthed or only poorly earthed parts are then relatively quickly charged during coating, as a result of which any subsequent paint with the same charge polarity is repelled and deposited in the vicinity [4.4.62]. With hydraulic atomization, therefore, it is recommended that the objects to be painted together with conveyors be earthed.

In closing, it may be noted that heated material can also be processed to optimize hydraulic paint atomization. This offers the corresponding advantages to those described under pneumatic application.

Electrostatic spray coating

The energy required for spray application of coating materials can also be electrical. If charged liquids with the charge Q are brought into an electrical field of strength E, a force F_1 acts on them. As a result the material is attracted by the electrode with the opposite charge.

$$F_1 = Q \cdot E$$

The electrical force is directly proportional to the charge of the liquid and the electrical field strength. Because of the frictional forces F_2 acting in the opposite direction

$$F_2 = 6 \cdot \pi \cdot \eta \cdot r \cdot u$$

a stationary state is soon established in accordance with *Stokes*' Law. The electrically charged material then moves at a speed of

$$u = \frac{Q \cdot E}{6 \cdot \pi \cdot \eta \cdot r}$$

along the field lines.

In order to exploit such electrical phenomena for coating purposes, equipment has to be designed which can transfer charges to the liquids to be atomized in order to create the conditions for droplet formation and the transport to the counter-electrode. To this end a sufficiently strong electrical field has to be generated by connecting a direct voltage between the atomizer and the object to be painted. The whole process of electrostatic paint application can therefore be broken down into the generation of an electrical field, the charging of the paint, the formation of paint droplets, the transport to the object and the discharging of the film as it forms.

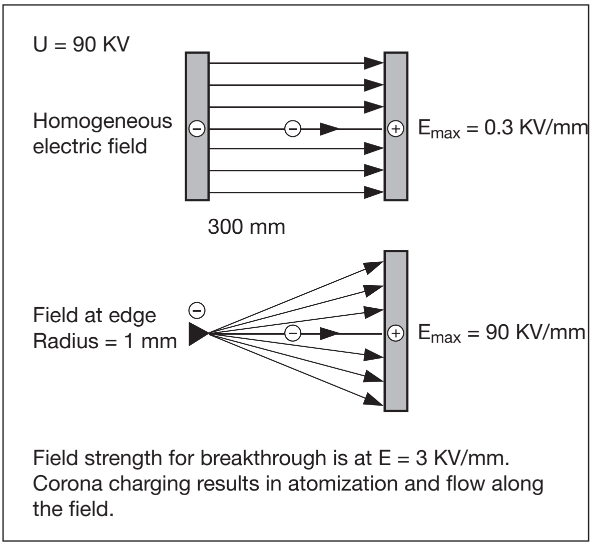


Fig. 4.2.51
Profile of homogeneous and nonhomogeneous electrical fields

An electrical field which is strong enough to transfer charges is created by generating a negative potential in an electrode with a pronounced curve and by the resulting increase in field density. The field strength E which can be reached in the range of such pointed electrodes can be approximately calculated by E = U/r, where r describes the real rounding of such points. Calculating the non-homogeneous field in the region of spray electrodes in the form of edges is somewhat more complicated. Here the field strength E(x) at the location x obeys the following rule:

$$E(x) = \frac{2 \cdot a \cdot U}{(a^2 - x^2) \cdot \ln \frac{2 \cdot a}{r}}$$

In this a is the distance between the two electrodes and r the radius of the edge. Thus the maximum field strength E_{max} of the nonhomogeneous field at the point x = a-r is:

$$E_{max} = \frac{U}{r \cdot \ln \frac{2 \cdot a}{r}}$$

With real spray edge radii of approx. 0.5 mm field strengths are already reached which exceed the breakdown field strength of approx. 3 kV/mm at usual voltages of 90 kV.

This enables the electrons of the metal in the spray edge to leave the metal and ionize the surrounding material.

If there is any paint in the region of the spray edge, this is usually charged negatively and is attracted by the object to be painted which is connected as the counter-electrode and thus separated to form threads. It is easy to estimate that the force F acting under the electrostatic atomization conditions described is capable of performing the necessary work to enlarge the surface area. It is influenced by the electrical field strength and also by the dielectric constant ε_{paint} (see below).

$$F = E^2 \cdot \frac{\varepsilon_{paint} - 1}{2 \cdot \varepsilon_{paint}}$$

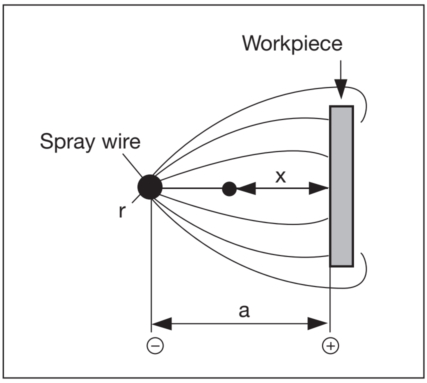


Fig. 4.2.52
Parameters for calculation of electrical field strength in the area of atomization

Once the threads reach a sufficient length (see figure 4.2.32 and 4.2.53), necking occurs because of the surface tension acting, and electrically charged droplets form. It has been demonstrated using high-speed photographic images of charged liquids exiting nozzles that the forming threads do not take the shortest path to the counter-electrode because of the surface charge which is the same and thus repels. Slowed down by the air resistance, wavy electrical counterforces which can be recognized by their meander shape overlap en route to the counter-electrode. The thread then becomes excessively extended and thus thinner [4.4.63].

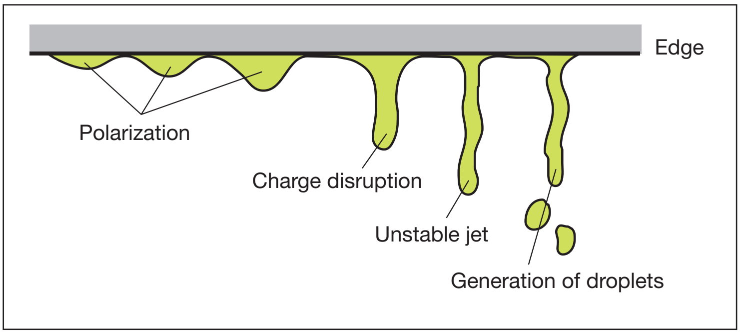


Fig. 4.2.53
Generation of droplets by electrical forces

The droplet size is estimated with electrostatic atomization in the same way that the droplet spectrum is calculated for pneumatic or hydraulic paint application. Particle formation is again influenced by two surface-related forces acting in opposite directions. In this case the repelling electrical forces act on the paint surface against the cohesive pressure p_{Ko} (see above).

$$p_{Ko} = \frac{2 \cdot \sigma}{r}$$

The electrical counterpressure p_{El} is calculated as

$$p_{El} = \frac{\pi}{2} \cdot \Psi^2 \cdot r$$

where Ψ represents the charge per unit area.
At equilibrium state both forces are equal so at $2r = d_m$

$$\frac{2 \cdot \sigma}{r} = \frac{\pi}{2} \cdot \Psi^2 \cdot r \quad \text{or} \quad d_m = k \cdot \sqrt{\frac{\sigma}{\Psi^2}}$$

Since the charge per unit area Ψ is a function of the conductivity λ, the voltage U, the dielectric constant ε and the resulting mass flow rate $\dot{m}$, which is determined by the design, the following is calculated for the charge per unit area which occurs during electrostatic spray coating:

$$\Psi = \frac{k_2 \cdot \lambda \cdot U}{\varepsilon \cdot \dot{m}}$$

The droplet d_m diameter is therefore given by:

$$d_m = \frac{k \cdot \sqrt{\sigma} \cdot \varepsilon \cdot \dot{m}}{\lambda \cdot U}$$

From this formula it is clear that with purely electrostatic atomization the droplet size is directly proportional to the material properties of surface tension and dielectric constant and indirectly proportional to the conductivity.
Technical equipment used for electrostatic atomization consists in its simplest form of a metal bar fitted with a sharp edge. The paint is supplied via an aperture in the area of the spray edge behind which the paint that is to be sprayed is passed when the equipment is in operation.

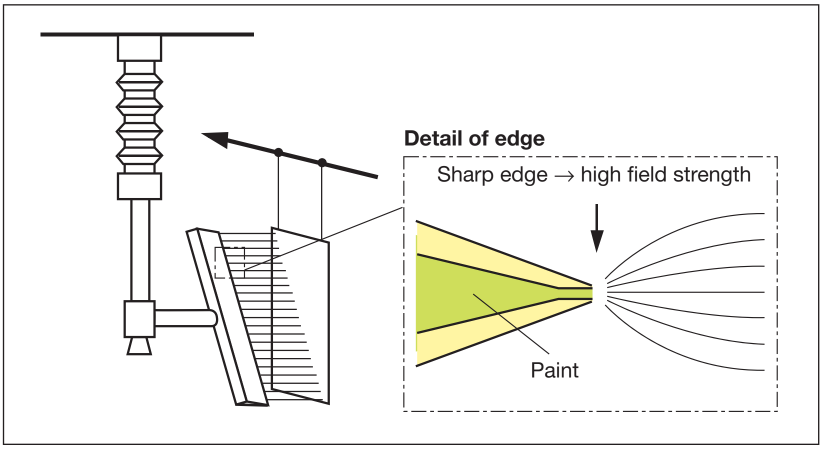


Fig. 4.2.54
Scheme of a spray gap for electrostatic paint application

The spray aperture (spray gap) shown in figure 4.2.54 is only suitable for stationary systems because of its large mass which is under a high voltage of up to 160 kV [4.4.64]. If an earthed workpiece is brought into the vicinity of the aperture on a conveyor, an electrical field is generated if a voltage is applied. The paint is then drawn out of the aperture, converted into droplets and transported along the field lines to the object to be painted.

A particular feature of this process is that, despite a permanently connected voltage, atomization only takes place if earthed objects, i.e. connected as a counter-electrode, pass close enough to the spray head. Since the paint is only transported along the field lines to the object, the material yield is extremely high at approx. 98%.

The painting width is essentially determined by the length of the spray aperture. Adjustable auxiliary electrodes are located at the ends of the aperture to optimize the spraying width. These enable the spray edge to be covered locally. Only a certain quantity of paint can be atomized in accordance with the set voltage for a specified spray aperture length. If this quantity of paint is insufficient for the desired film thickness, the aperture can be turned at a diagonal to shorten the coating width and thus increase the film thickness.

The film thickness distribution of the resulting film is determined by the field density. If this is the same at all points of the object, extraordinarily uniform film thicknesses are achieved. Pipes and balls, i.e. objects without corners and edges are optimally coated. Angular objects or those containing cavities cannot be satisfactorily painted using this process. Overlapping coatings take place on corners and edges which can result in faults in the form of runs during the subsequent film forming process. Cavities form *Faraday* cages, as a result of which no coating takes place at all because of the lack of field lines. It has already been shown that the droplet size is a function of the mass flow rate, the specific electrical properties of the paint and the voltage applied. A material which has already been set to optimum electrical conductivity will only be influenced by the voltage for mass flow. The influences of material fluctuations in the event of different ambient conditions of temperature or relative humidity can therefore only be compensated for with difficulty. A further disadvantage is the only moderate output performance with approx. 1.5 g/min per 1 cm edge length.

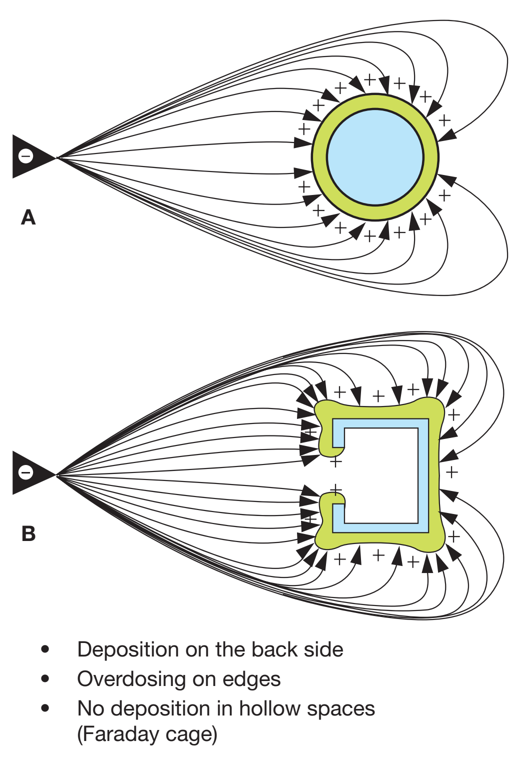


Fig. 4.2.55
Film thickness distribution of electrostatically coated parts

In order to utilize the advantages of the high paint yield at a higher material output, equipment was developed for the electrostatic processing of paints which permit proc-

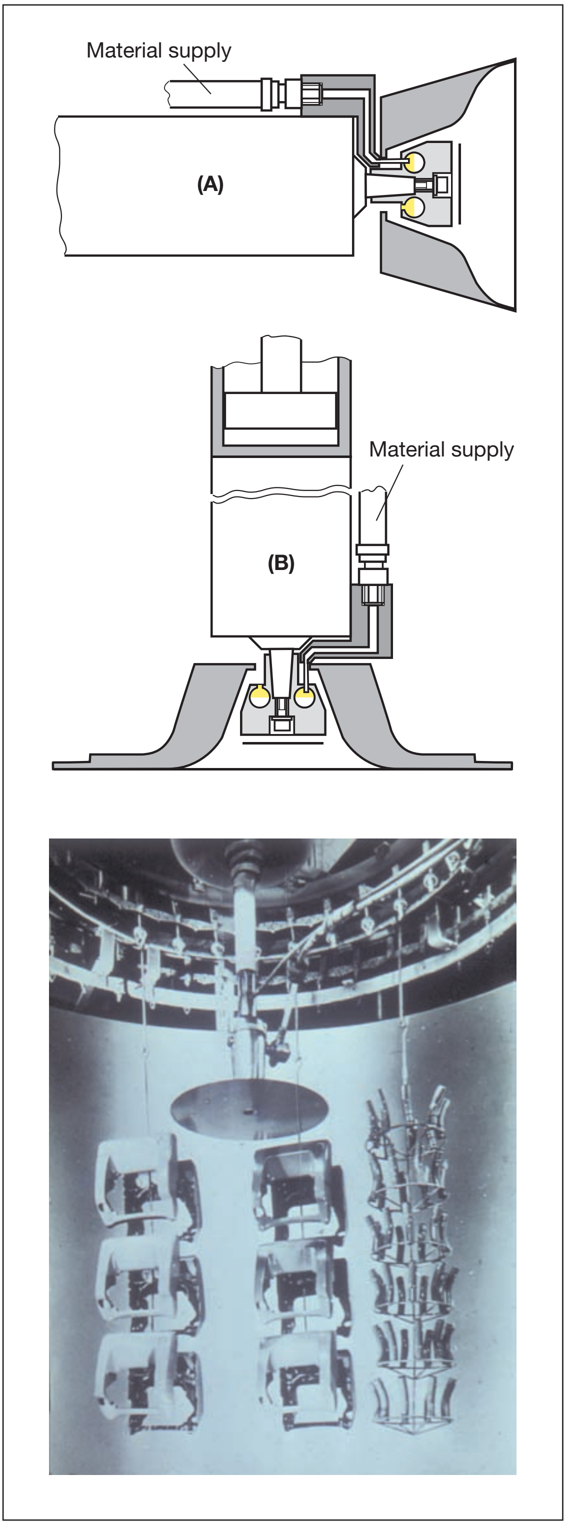


Fig. 4.2.56
Slow-running bells and discs

ess-regulating material dispensing. Slow-running spray bells, which also atomize purely by electrostatic means, are more adaptable and, at the same time, deliver better performance. At a speed of < 3000 rpm droplet formation occurs without mechanical assistance purely in accordance with the laws of electrostatics described above. The centrifugal forces which are also acting merely ensure an adequate, speed-dependent transport of the paint to the atomizing edge.

The discharge rates can be adjusted within certain limits by the speed of rotation. Feed and discharge at the edge must remain in equilibrium. The disc speed imparts additional kinetic energy to the droplets, with the result that *Faraday* cages become coatable to an extent.

Like the spray aperture, the spray bell, which runs at 900 – 2000 rpm at a voltage of 90 – 160 kV, is only suitable for automatic processing systems because of its design. Atomization of the paint occurs at the rotating, sharp bell edge which is under high voltage. The paint is fed to the centre of the bell on the inside, accelerated by the bell's rotation and transported to the edge of the bell by centrifugal forces. At the bell edge the paint forms a bead, from where it is then electrostatically entrained droplet by droplet. At approx. 3 g/min per cm edge length the maximum spray quantity is double that of the spray aperture.

The spray disc which, with diameters of 200 – 600 mm, is larger than the spray bell is an application device that is in widespread use for the electrostatic coating of mass-produced goods of simple shape. Atomization takes place, in similar fashion to the spray bell, at a rotating, sharp disc edge. Generally the paint is applied to the underside of the disc, accelerated and transported to the disc edge via centrifugal forces. The remainder of the atomization and paint droplet transport sequence is the same as that of the spray bell.

The advantages of this spray system come in useful when the workpieces travel around the horizontally configured disc in the form of an Ω (omega loop). Since the disc sprays in only one level, it must be moved vertically by a lifting cylinder to ensure a sufficiently uniform coating.

It has already been mentioned that electrostatic atomization is a function of the conductivity of the coating material. The electrical conductivity is responsible for the rapid charging during droplet formation and for a correspondingly rapid discharge during film formation. Only where rapid discharge is provided by means of good earthing can it be guaranteed that subsequent spray dust is deposited, thereby ensuring good flow. The latter feature is a fundamental problem when coating wood and plastics. If discharge is too slow, whether because of the insufficient conductivity of the paint or substrate, this leads inevitably to flow faults because of the presence of the same, and thus repelling, charges.

The optimum conditions for electrostatic processing and the relevant equipment obtain if the resistances of the coating material are between 10^6 and 10^{10} Ωcm or the conductivity is from 10^{-6} to 10^{-10} S/cm. Such values are easily achieved for solvent-containing paints e.g. by means of blends of xylene ($R = 10^{10}$ Ωcm) and butanol ($R = 10^6$ Ωcm). If polar solvents cannot be used in the necessary quantity, supplementary regulation of the conductivity is also possible through the use of appropriate additives (see chapter 2.1.4). Consequently, waterbased paints cannot be processed with this method because of their exaggerated high conductivity.

Electrostatically assisted spray processes

Pneumatic and hydraulic application

Because of the good material yield with the electrostatic application processes there has been no shortage of attempts to combine pneumatic and hydraulic atomization processes (see above) with electrostatic techniques. The achievable increase in the material yield has an impact on the total material flow in the spray booth, the evaporation zone and the oven. The following example provides detailed information on the advantages (see figure 4.2.57). To achieve a coating of 45 g solid content 150 g paint are required in the case of pneumatic atomization (A), whereas in the case of the electrostatically assisted coating process (B) only 105 g paint are required with the same solid content of 55%.

Two different types of charging process have been shown to be effective, depending on the paint. Charging takes place either before atomization by means of internal charging or only after exiting the spray head and once droplet formation is complete, by means of external charging, depending on the paint's conductivity. In the case of pneumatic application only the internal charging process is used in daily operations. In this the paint passes a high-voltage electrode in the electrically insulated gun attachment where it picks up the charges. Since the droplets which are later generated already carry a charge

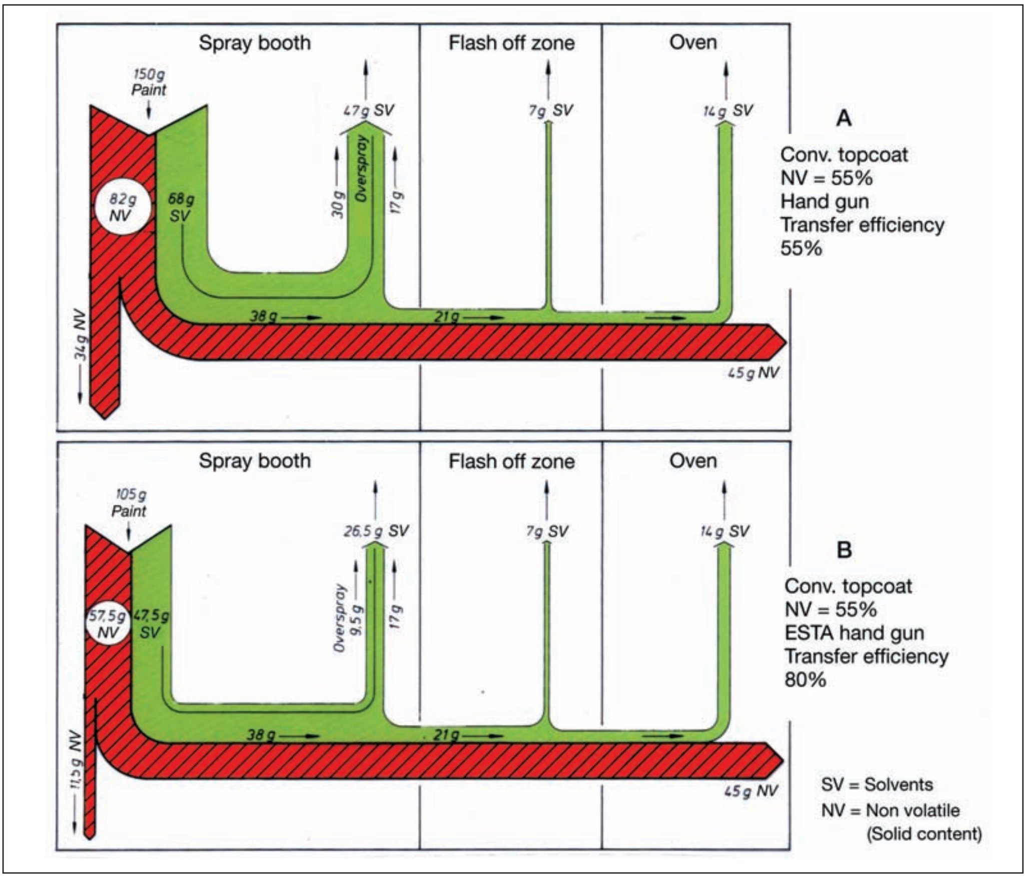


Fig. 4.2.57
Yield at conventional and electrostically supported high pressure atomization

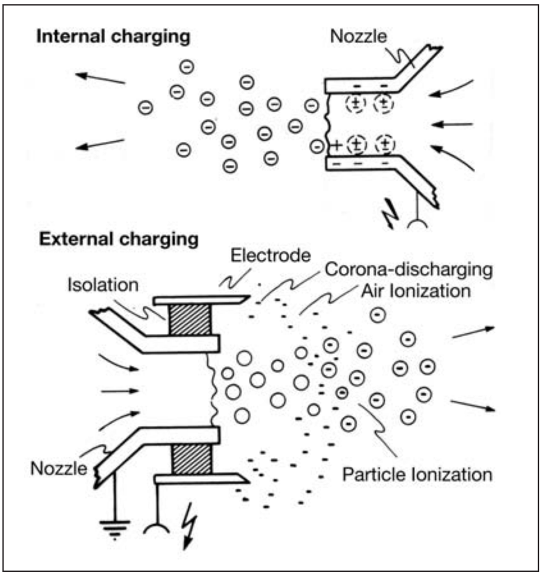


Fig. 4.2.58
Scheme of the two charging mechanism of spray guns

before they are formed, the current surface tension is reduced because of the repelling electrical forces. The outcome is better atomization. This means that atomization can be carried out with a higher spray viscosity or lower spraying air pressure. The first case results in even lower emissions because of the higher solid content, while the second leads to even lower material loss as a result of overspray. Under ideal conditions the material yield can be raised from 50% with conventional processing to 80%.

However, internal charging is only possible if the specific resistances of the coating material lie within the al-

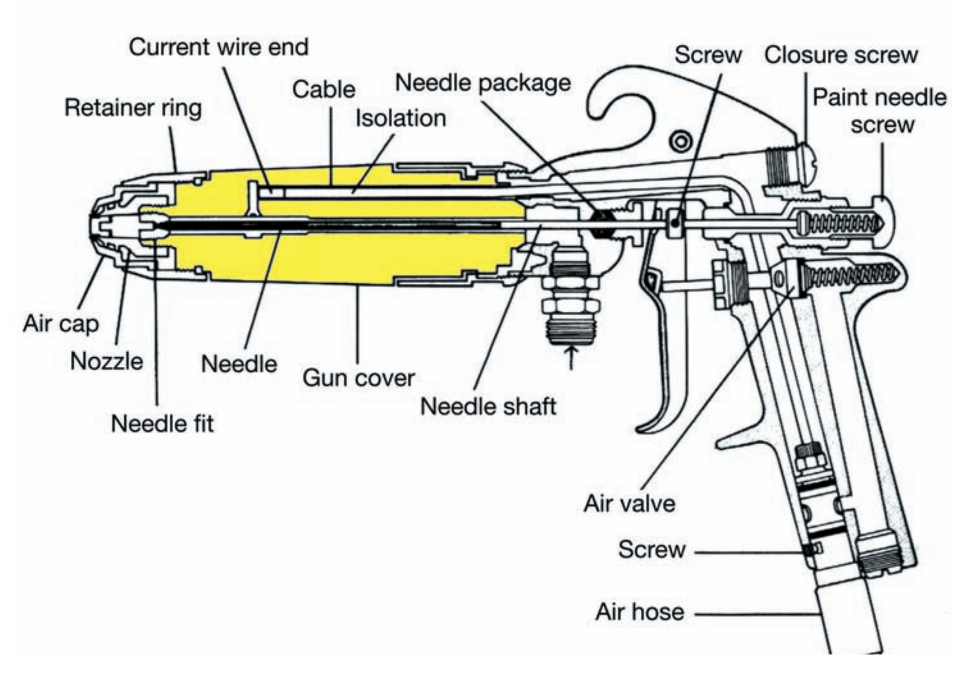
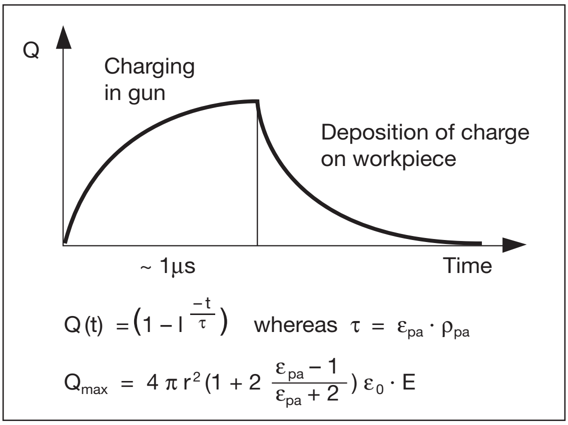


Fig. 4.2.59
Cross section of an internally charged high pressure gun

ready specified limits of $10^6 - 10^{10}$ Ωcm. Otherwise considerable expenditure would be required for safety reasons to insulate the paint-feed system. Furthermore, it should be noted that the charge rate depends directly on the dielectric constant ε_{pa} and the specific resistance δ_{pa} and therefore does not permit excessively high electrical resistances.



$$Q(t) = \left(1 - l^{\frac{-t}{\tau}}\right) \quad \text{whereas } \tau = \varepsilon_{pa} \cdot \rho_{pa}$$

$$Q_{max} = 4 \pi r^2 (1 + 2 \frac{\varepsilon_{pa} - 1}{\varepsilon_{pa} + 2}) \varepsilon_0 \cdot E$$

Fig. 5.2.60
Time depending charging and the charge maximum of coatings

High-rotation atomization

The most advanced and effective electrostatically assisted spray process is atomization with high-rotation bells. The bells used, which have diameters of 60 – 100 mm, rotate extremely fast at speeds of up to 80,000 rpm. Consequently the atomization mechanism is different from the slow-running bells and discs. Unlike the atomization process induced exclusively by electrostatic forces, high-rotation atomization is based solely on the effect of centrifugal forces. The supplementary electrostatic charge of droplets serves purely to aim the spray jet towards the earthed object and thus increase the material yield. This can reach extremely high levels of 85 – 90%.

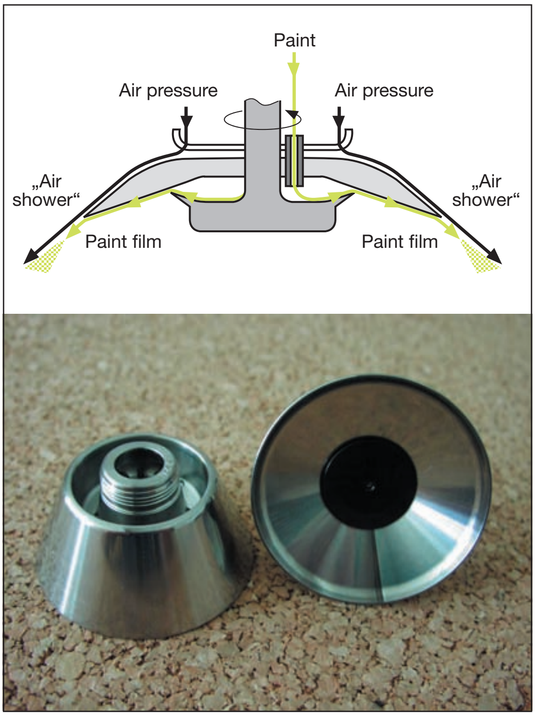


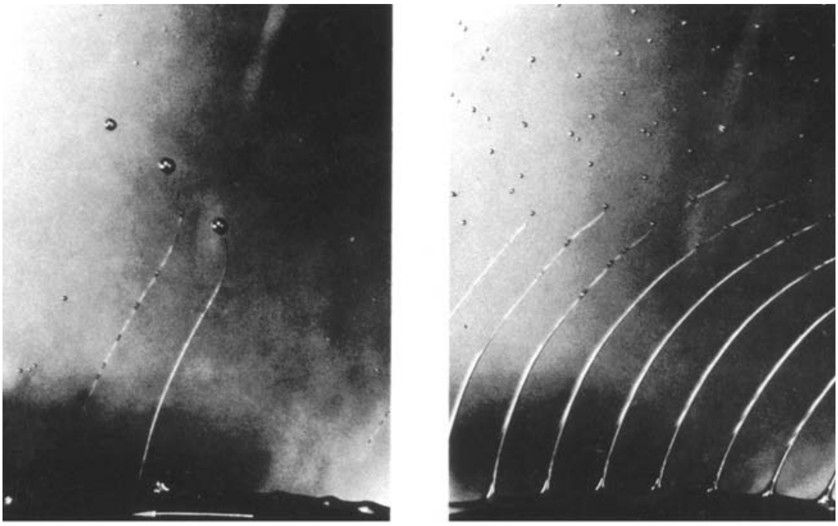
Fig. 4.2.61
Scheme and picture of high-rotation bells

Unlike spray discs, high-rotation bells do not spray the object radially as it passes by. The spray jet is diverted by 90° by means of additional shaping air and thus directed onto the object to be painted which is under the bell.

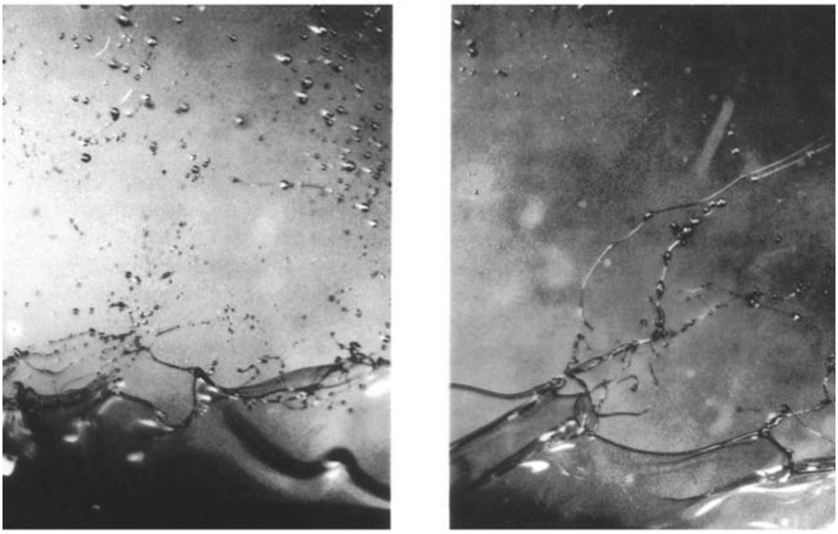
As a result of their high speed high-rotation bells with a material output of 15 – 20 g/min per cm edge length are much more productive than purely electrostatically operating bells. In addition, the droplet spectrum is tighter and easier to optimize in response to the particular requirement by means of machinery adjustments or settings. Because of the excellent visual quality of the coatings which can be achieved using this method, high-rotation systems are widely used.

After being fed to the inside of the bell, the coating material is transported to the bell edge by centrifugal forces and from there, depending on the operating conditions, it is atomized by means of various mechanisms [4.4.65]. If the material feed is low at normal speed, a bead forms at the bell edge from which individual threads are drawn because of the high centrifugal forces and then stabilize into droplets (see figure 4.2.62, A). With a higher material feed the number of threads increases. Once these reach a certain length, the particle formation results in a uniformly tight droplet spectrum of thread atomization (B) because of the effect of the surface tension and the electrical forces. This represents the best atomization method for many applications. In the event of any further increase the paint supply becomes so great that the threads are converted into lamellae. With aerodynamic lamellar atomization which occurs initially (C_1) the paint bead is extended without forming threads to a paint curtain which is made to oscillate by the ambient air. This process, which resembles a flag fluttering in the wind, also results in droplet formation in the second stage. The droplet spectrum generated by the lamellar atomization is considerably less regular and broader than that created by thread atomization. If the speed is increased, the lamellar motion changes to turbulence, with the result that regular disturbing fronts migrate from the edge to the end of the lamella where they have an impact on droplet formation (C_2). As a result of the high centrifugal forces an area of underpressure occurs in the region of the centre of the bell.

The plate edge is the most sensitive part of the bell in design terms with reference to the fineness of atomization. The bevel and texture (in the form of knurling) of the bell edge have an impact on the droplet spectrum and thus also on the quality of the coating. Since the aim is to achieve the tightest and finest possible droplet spectra with a high edge



A Atomization in droplets **B** Thread atomization



C1 Aerodynamic lamellar atomization **C2** Turbulent lamellar atomization

Fig. 4.2.62
High resolution pictures of droplet generation at high-rotation bells

cover and thus a high material output, the paint beads are converted into threads by the grooves in the bell edges (see figure 4.2.63).

The relevant atomization mechanism and thus also the droplet spectrum depend on the material feed $\dot{V}$, edge cover K_b, angular velocity ω, bell diameter D and coating material variables of surface tension σ, viscosity η and density ρ. The operating ranges just described can be represented graphically by calculating atomization coefficients. The most favourable conditions can be described by plotting $We_2^{1/2} \cdot Kb^{5/6} \cdot Ohz_2^{10/36}$ against Ohz.

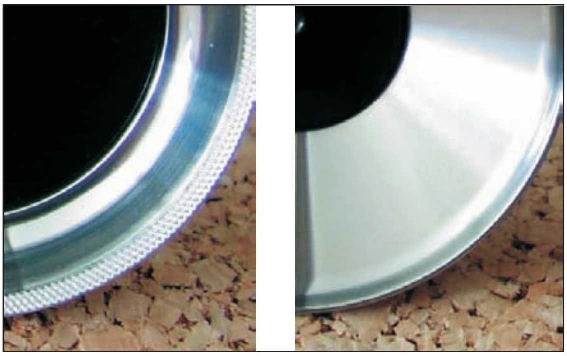


Fig. 4.2.63
Smooth and textured bell edges

$$We_2^{\frac{1}{2}} \cdot Kb^{\frac{5}{6}} \cdot Ohz_2^{\frac{10}{36}}$$

$$Ohz_2 = \frac{\eta}{\sqrt{\rho \cdot \sigma \cdot D}}$$

$$We_2 = \omega^2 \cdot D^3 \cdot \frac{\rho}{\sigma}$$

$$K_b = \dot{V}^2 \cdot \frac{\rho}{\sigma \cdot D^3}$$

The boundary lines in figure 4.2.64 indicate the changeover areas from one atomization mechanism to another. The relevant working area is marked as a hatched surface.

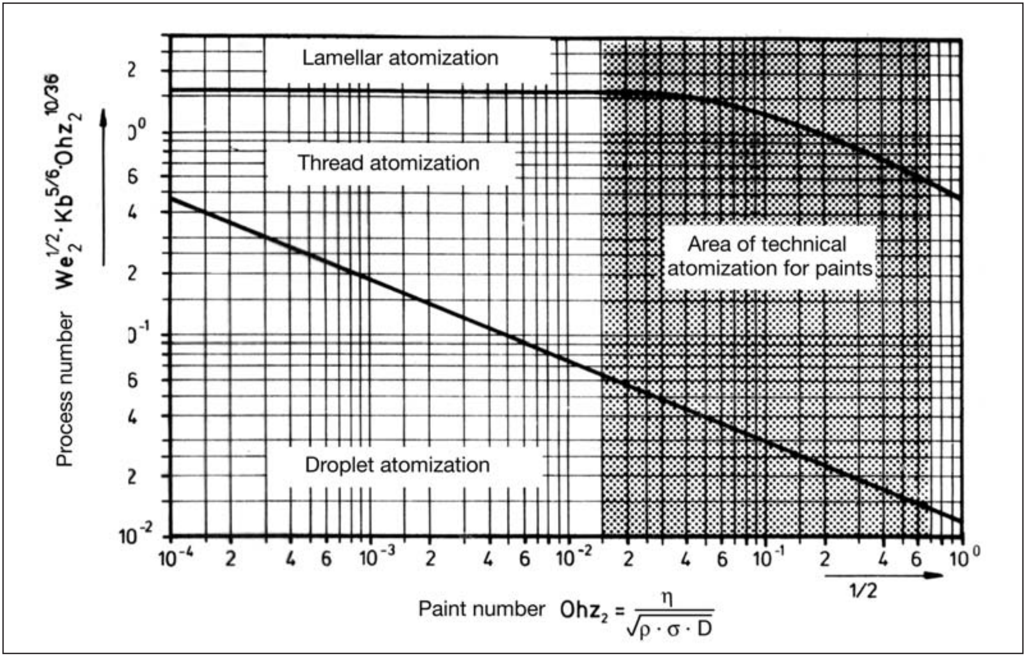


Fig. 4.2.64
Processing area for high-rotation atomization depending on We and Ohz

Forecasts of the anticipated droplet size with high-rotation atomization can be made in similar fashion to calculating the droplet sizes with pneumatic and hydraulic atomization. The results published in the literature do not give a consistent picture [4.4.66, 4.4.67]. The tests were carried out with different liquids. Water, glycerine or paints have different atomization properties and cannot therefore be described with a single mathematical formula either. A feature common to all the results, however, is the marked dependence of the droplet spectrum on the surface tension, angular velocity and thus rotational speed and size of the bell. The minor influence of the viscosity within large operating ranges is also worth noting. This fact is confirmed in practice.

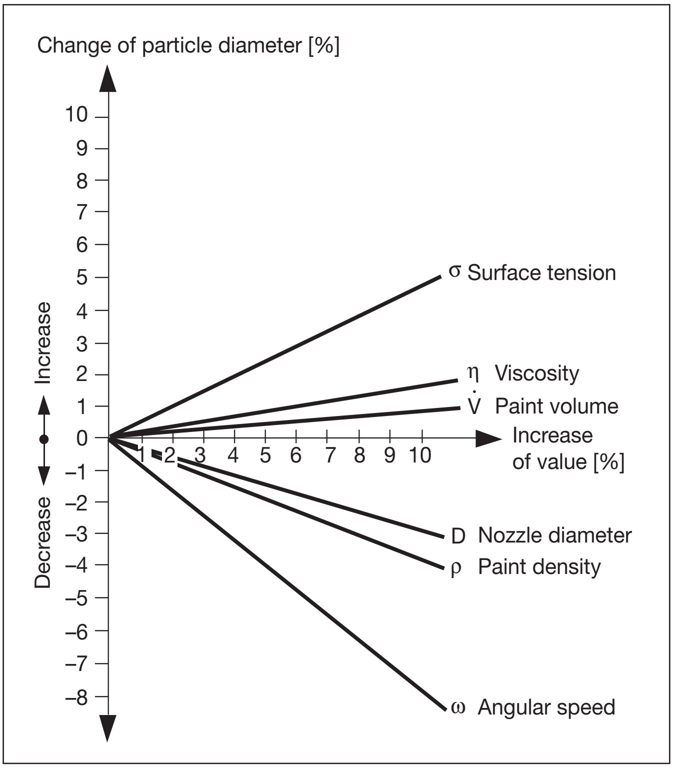


Fig. 4.2.65
Sensitivity diagram of high-rotation atomization

The great dependence of the atomization quality or droplet spectrum on the surface tension is a striking fact, particularly when processing waterbased paints. In comparison with solventborne paints speeds up to 1000 rpm higher have to be set if the coarser droplet spectrum of waterbased paints, caused by the high surface tension (see chapter 5.6.2), is to be brought to the fineness achieved with solventbased paints under the same conditions. The influence of the paint throughput is also lower than with pneumatic atomization.

The feed and distribution of the material on the bell also requires special attention. To avoid deposits of overspray on the bell plate the material flow can be split. While the major part of the material is discharged in the outer area of the plate, a smaller portion is fed to the bell plate through the centre bore. In this way overspray sucked back into the already mentioned area of underpressure at the bell cannot be deposited there and later result in quality defects on the object to be painted in the form of pinholing (see chapter 6.2).

Rapid color changes which are necessary for many painting tasks can be achieved with only little material loss by circulating a rinsing agent. The rinsing process including color change can be completed in just a few seconds.

When using the high-rotation bell, the coating material is charged by means of the material feed which is subject to a voltage, as with the internal charging for spray guns already described. This applies in particular to solvent-containing paints with sufficiently high electrical resistance (see above). When processing waterbased paints the entire system must be insulated. The paint-feed system in particular must be designed with reference to the insulation of working and top-up dispensing vessels such that no voltages or current flows can occur in any part of the circulation system (see figure 4.2.66). Color changes can be achieved with this system only with corresponding investment.

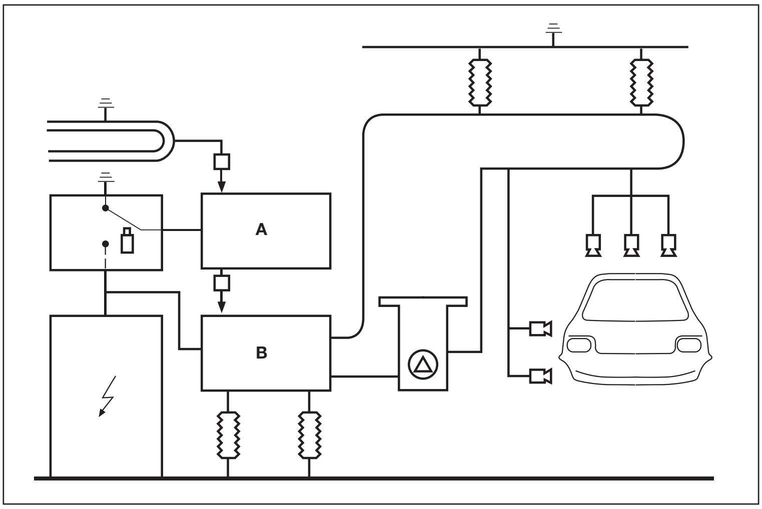


Fig. 4.2.66
Processing of waterbased paints with internal charging by two separated feed tanks

The already mentioned method of external charging is more important in practice. This can be used in principle with any type of paint. It results in charging of the already formed droplets and is easy to achieve in high-speed application processes. To bring external charging about, electrons have to be released which ionize the air molecules in the atomization area in front of the material nozzle. The freshly created droplets adsorb part of the charge carriers as they fly through this ion cloud and become electrically charged particles themselves in the process. The high atmospheric ion concentration, which screens the object to be painted and also results in a less uniform droplet charge compared with internal charging, is disadvantageous. Associated with this is the fact that material transfer is up to 5% lower than with internal charging.

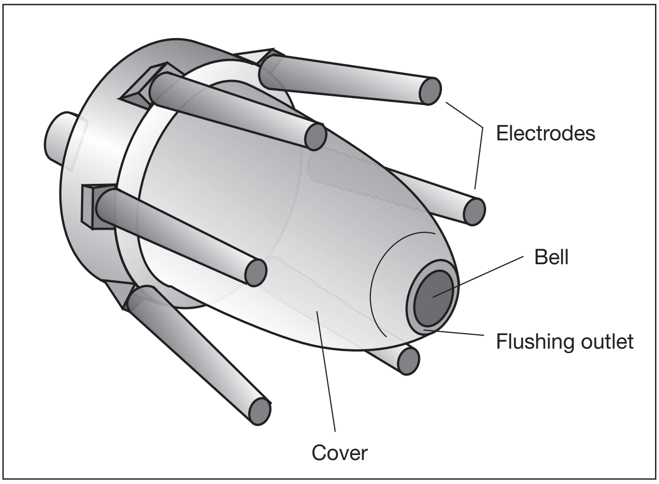


Fig. 4.2.67
High-rotation atomizer for external charging

The methods used to optimize the bell shapes included studying the flow conditions in the spray cone with laser cutting techniques [4.4.68]. Among the targets of the development efforts for high-rotation atomization is its use in effect coating. The different droplet spectra by comparison with pneumatic application should be noted, among other things. Pneumatic application results in a measurable increase in the proportion of effect material of the deposited coating film. The shaping air of bell atomization captures the large droplets of the spectrum less than the small ones because of the centrifugal forces acting and their greater inertia, with the result that the profile of the deposited droplet spectrum is shifted in the direction of the smaller and medium sized particles. This is the exact opposite of the situation with pneumatic application [4.4.69].

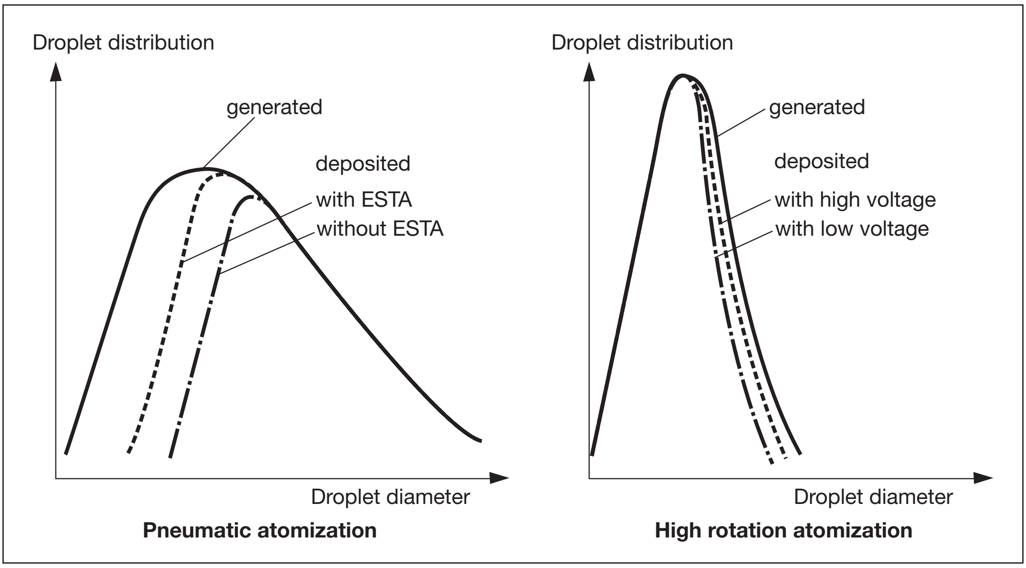


Fig. 4.2.68
Differences in the generated and deposited droplet size distributions for pneumatic and high-rotation atomization (ESTA = electrostatic application)

On the other hand, high-rotation atomization results in disproportion at ion of effect substances, particularly metal bronzes, in the droplets and thus to a nonhomogeneous distribution with poorer alignment at the same time in the deposited coating. This separation by means of centrifugal forces is also caused on the bell plate and by rotation of the resulting droplets [4.4.70].

In order to coat all areas of complex components (such as car bodies) with a uniform layer while achieving good flow at the same time, the spray heads in the automatic painting systems are configured such as to maintain consistent distances from the outlines of the object to be painted. The advantages of electrostatic assistance in general are the good throwing power and edge expansion of the spray jet. This means gentle transition zones and thus more uniform film thickness also on the back of the painted objects.

Thanks to ongoing refinements in the systems and atomizer bells, high-rotation atomization is today the most advanced, cost-effective and, from an environmental perspective too, attractive atomizing technology. The bells, which originally had diameters of

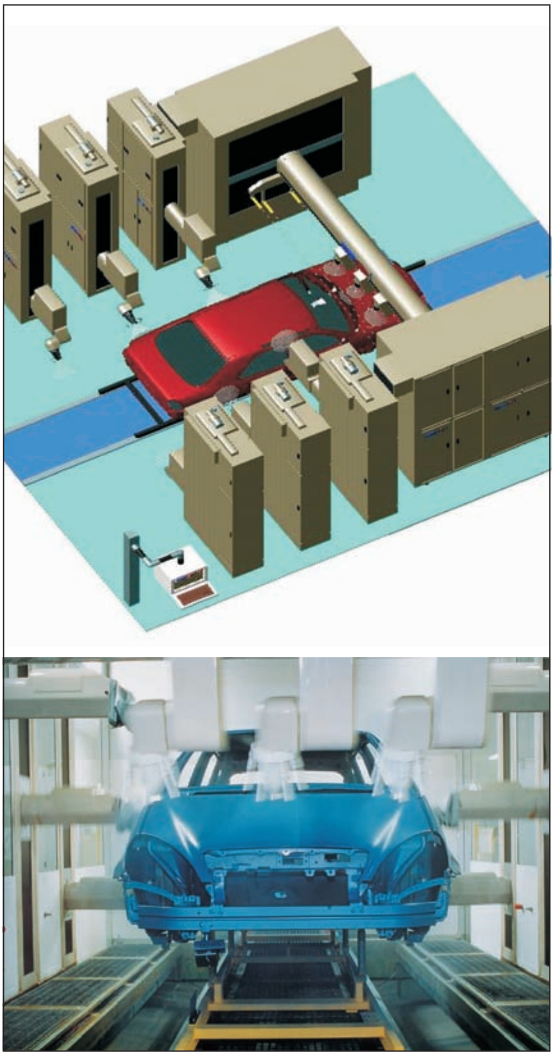


Fig. 4.2.69
Scheme and picture of a high-rotation bell application unit for coating cars

approx. 70 – 80 mm and speeds of 25,000 – 30,000 rpm have become ever smaller and faster over the years. Bell plates with a diameter of 50 – 55 mm and speeds of up to 60,000 rpm are now standard. Such bells are fitted with shafts with air-bearings for trouble-free operation. The smaller bells, which are at a shorter distance from the object, have the additional advantage of even better material yield. Because of their lower moment of inertia they can follow complex outlines and are therefore suitable for application with robots (see below) [4.4.71].

Ultrasonic atomization

If a comprehensive picture is to be given of the basic principles of the atomization of liquid coating materials, the interesting atomization techniques using ultrasound, though encountered only in other application areas, must not be forgotten. In capillary-wave atomizers thin liquid films are excited on ultrasonic oscillating plates to form waves. At a sufficiently high amplitude of the wave peaks, the tips start to neck and produce droplets. The size of the droplets is determined by the wavelength λ and thus by the frequency f of the exciting wave. The wavelength λ of the resulting wave formation of the film in turn depends on the surface tension σ and density ρ of the material to be atomized.

$$\lambda = 2 \cdot \left(\frac{\pi \cdot \sigma}{\rho \cdot f^2} \right)^{\frac{1}{3}}$$

Since the particle diameter d is approx. 1/4 of the wavelength, the following applies to the *Sauter* diameter d_{32}:

$$d_{32} = 0{,}5 \cdot \left(\frac{\pi \cdot \sigma}{\rho \cdot f^2} \right)^{\frac{1}{3}}$$

The unit itself consists of the upper stepped tube and a conical plate. This plate is excited to high-frequency oscillations through a piezo ceramic unit mounted on the underside, with the result that the liquid which is fed to the cone forms a thin film which is then converted into droplets. Compared with standard atomization techniques capillary-wave atomizers have the disadvantage of poor deposition of the generated droplets but also offer a number of advantages. The most important of these are unpressurized liquid feed, silent atomization and energy savings.

Another atomization method, which is of interest for higher-viscosity fluids and thus also for melts, is ultrasonic standing-wave atomization. This method uses the high-frequency energy produced by a generator for particle formation. Electrical energy is converted by piezo ceramics into mechanical oscillations of the same frequency by means of a converter.

The oscillations reach the sonotrode as the actual oscillating body via a booster. This emits the energy in the form of longitudinal ultrasonic waves with a correspondingly high intensity. If the sound waves hit a reflector or a second sonotrode, a standing wave is formed at certain distances with spatially fixed oscillation nodes. The oscillation nodes are at the same time pressure antinodes of the sound pressure of the standing wave.

The fluid to be atomized is introduced into the sound-pressure nodes through one or

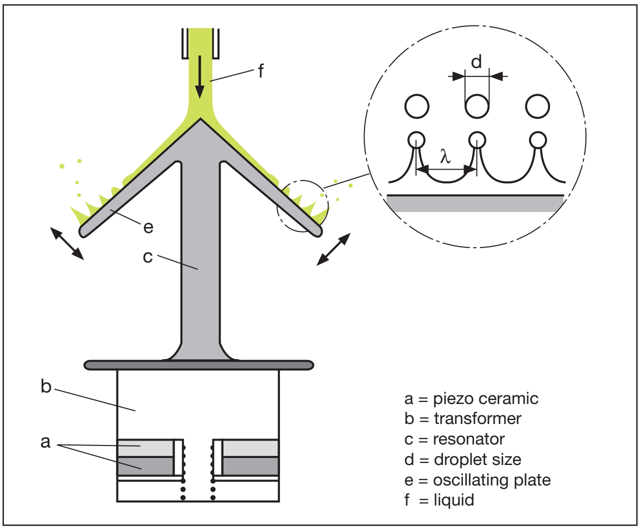


Fig 4.2.70
Atomizer unit of a capillary-wave atomizer

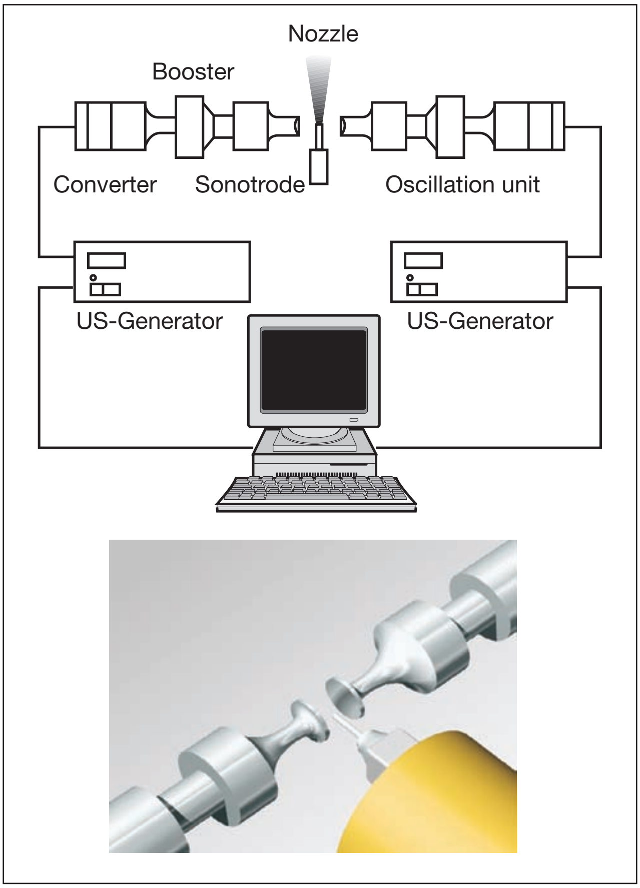


Fig. 4.2.71
Scheme and model of an ultrasonic standing wave atomizer

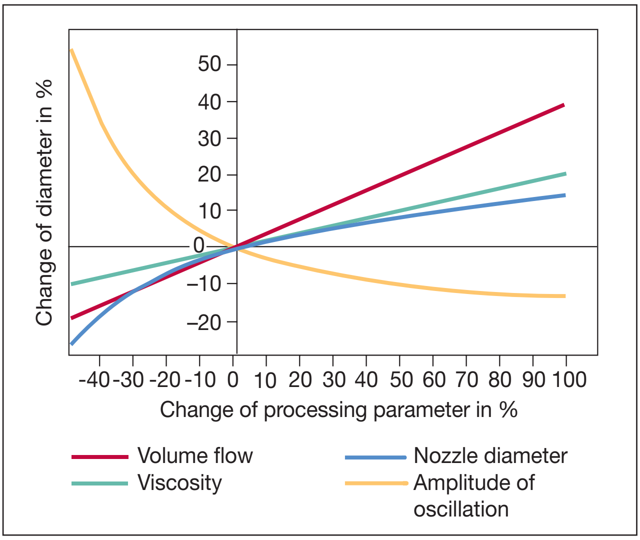


Fig. 4.2.72
Sensitivity diagram of an ultrasonic standing wave atomizer

more feed tubes. The high-frequency oscillation energy acting in the pressure nodes first causes localized deformation of the liquid jet which disintegrates into individual particles at the edge zones. The fineness of the generated droplets is determined to a significant extent by the mass flow rate and the positioning of the feed nozzle. On the material side, the surface tension and the viscosity are the most sensitive variables influencing droplet formation [4.4.72]. Figure 4.2.72 shows the percentage changes in the average particle diameters of an atomized polymer melt as a function of the different atomization parameters [4.4.73].

With regard to the atomization mechanism the existing experimental findings in conjunction with figures derived from the mathematical processing of such experiments show that it is not threads or lamellae but internally oscillating liquid platelets compressed in the standing-wave field which increase in diameter and turn into concentric rings which enlarge as they move outwards from the centre. Above a certain diameter these disintegrate further into largely uniform individual droplets [4.4.74, 4.4.75].

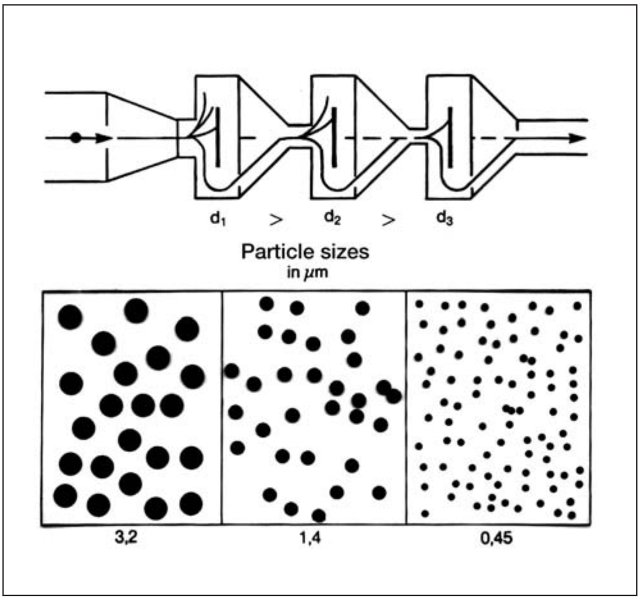


Fig. 4.2.73
Principle of spray droplet separation in a cascade impactor

Special methods for characterizing overspray

Because of the large influence of droplet size on the visual and functional properties (see chapter 2.3.3) of coatings it is very important to be able to measure and describe droplet sizes and distributions. Information on aerosols is important from an occupational health and safety perspective, too (see chapter 5).

This involves tests which have been specially developed for measuring paint droplets. A simple method of estimating droplet sizes when spraying consists of passing

foils through the spray jet and measuring the deformation of the captured droplets using image analysis. In another process the overspray is briefly directed to a nonmiscible liquid with the same density. The now nondeformed particles can be documented optically and again characterized using digital image analysis.
The cascade impactor, which is frequently used for health and safety tests, works on a completely different principle. This consists of a tube with several different constrictions and impact plates positioned after them. The aerosol droplets of varying size under analysis are introduced into the cascade impactor on an air current (see figure 4.2.73). Since the air speed increases with decreasing diameter of the constrictions, only the coarse droplets are deposited on the first plate, while the finer droplets are then deposited on the subsequent impact plates. Evaluation is again by means of measurements or digital image analysis.

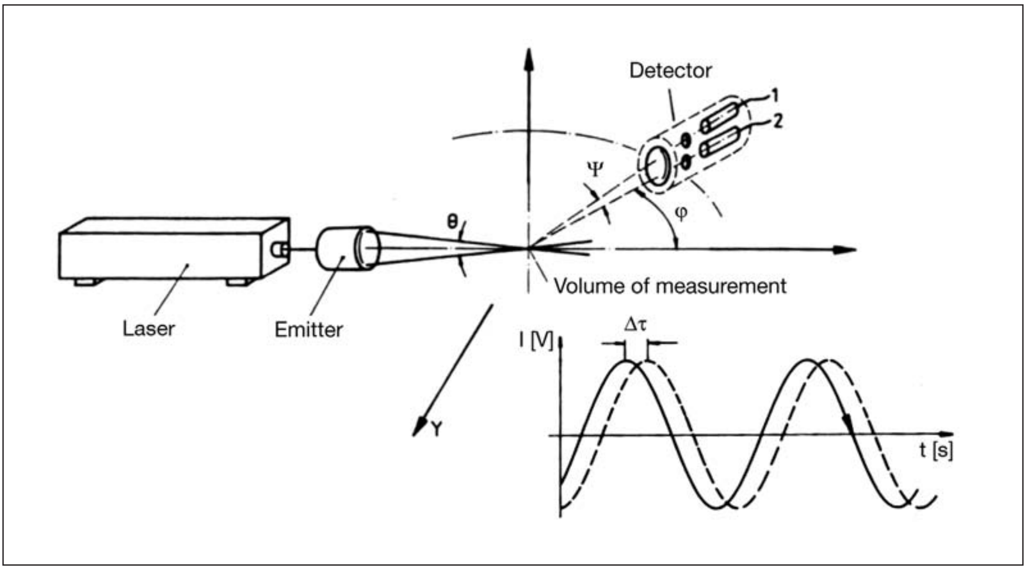


Fig. 4.2.74
Phase Doppler anemometer

The methods of light scatter and light refraction are also used for measuring the droplets in spray clouds (see chapter 2.3.3). Phase *Doppler* anemometry (PDA) is of great importance in characterizing a spray jet.
This measurement method is interesting because it provides information simultaneously on the average particle size, particle size distribution and particle speed. To this end a measurement volume is generated at the intersection of two laser beams in the spray cone of the paint. Interference occurs in the overlap area of the two jets as spray droplets pass through. Passing paint droplets scatter the light as a function of the speed and size of the particles [4.4.76]. In addition to the speed and size of spray particles, the local flow conditions between the spray head and the object to be painted are also of interest. In order to visualize the particle flows, the laser beams are expanded into planes by cylindrical lenses. The paths of the individual light points can be detected and calculated by recording them with a digital camera for processing electrical and optical signals (CCD camera).

4.2.1.4 *Paint Supply Systems*

If only small volumes of paint have to be manually applied to small surfaces or for repair work, material can be supplied by small containers for siphon-fed or gravity fed spraying integrated in the spray head (see above). Pressurized containers with a capacity of a few litres are frequently adequate where the quantities to be processed are not too large and for painting systems operating only temporarily. The material feed takes place by means of overpressure of 0.5 to 1.5 bar. If, on the other hand, continuous coating has to be carried out, separate supply systems in the form of circulation systems and paint-supply systems have to be used for material feed.

Circulation lines

Circulation lines usually have to be installed where material throughputs exceed 200 kg per day. To ensure greater security and economical operation of the system, the collection systems for spray heads are supplied with material by circulation systems. The characteristic feature of circulation systems is that the pipes coming out of the storage containers also return to them. In order to avoid the sedimentation of pigments in circulation systems, it is absolutely essential to exceed flow rates of 0.2 – 0.3 m/s in the pipes. The circulation volume should be significantly greater than the take-off volume.

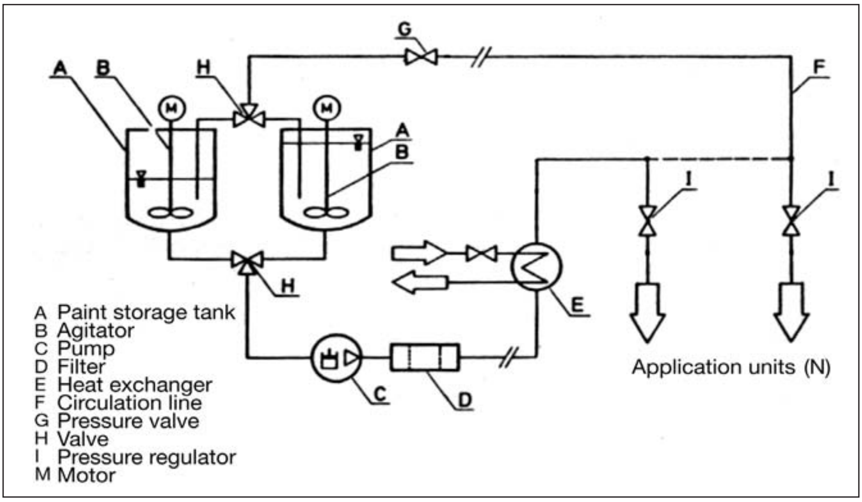


Fig. 4.2.75
Scheme and components of circulation systems for spray coating

This is the only way in which a relatively large number of spray booths can be supplied with a sufficient quantity of material without a reduced discharge rate.

The coating materials which are kept in a homogeneous state in the storage containers (A) with the aid of agitators (B) are brought to a material pressure of 10 – 20 bar by means of a paint circulation pump (C) and supplied to the individual paint take-off points (N) through the long pipes (F) which can be up to several hundred metres in length. After passing through a back pressure valve (G) the excess material, which is now depressurized again, returns to the storage containers (A) via a valve (H). Such systems enable paint consumers to make central adjustments in the material to take account of the processing conditions. Several processing units in one or more booths can be supplied at the same time. This ensures the best conditions for obtaining identical colors on an object, even if it has to be coated at several different units of the painting system.

Paint is drawn off in feed lines normally via material pressure regulators (I). They depressurize the material to a specified material pressure of 1 to 2 bar and guarantee a uniform discharge rate with constant viscosity, even where there are several take-off points in a circulation system upstream of the regulator. Sedimentation of pigments in the feed lines can be prevented, even when the gun is closed, by means of supplementary return lines from the material take-off point.

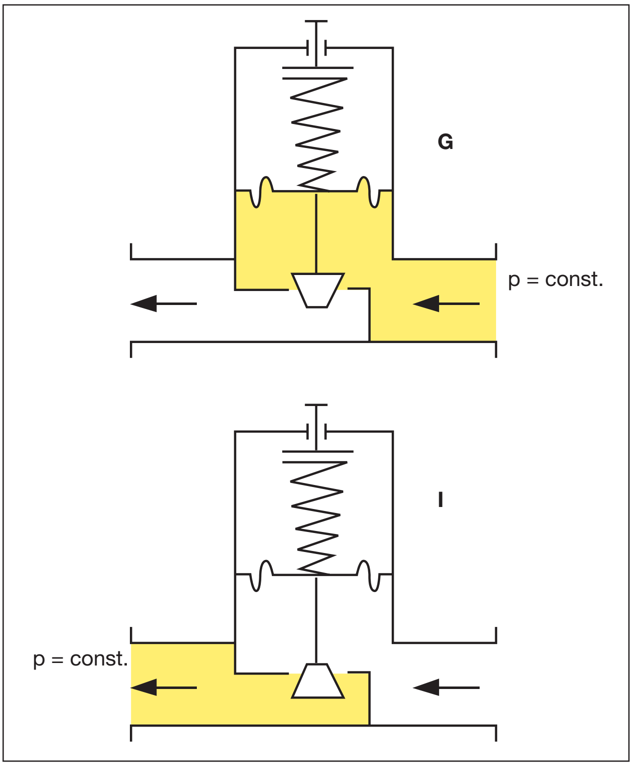
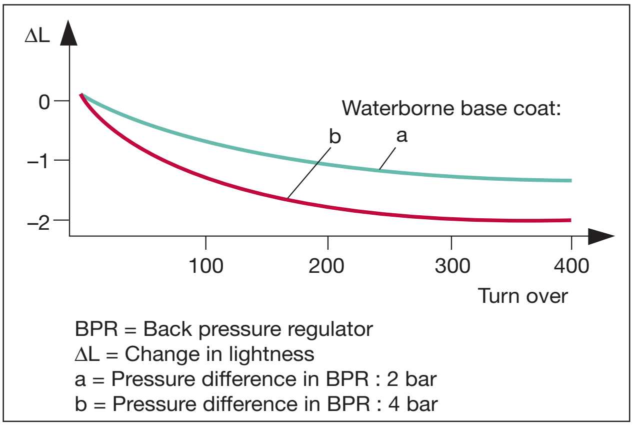


Fig. 4.2.76
Scheme of a pressure regulator (I) and back pressure valve (G)

In order to guarantee constant discharge rates and thus the same film thicknesses at constant material pressure, an additional thermostat (E in figure 4.2.75) is needed for the circulating material. In many cases it is better, and it is therefore becoming more and more common, to replace the material pressure regulators by metering pumps. Defects in the coating caused by dirt are largely avoided by the installation of dirt filters (D in figure 4.2.75).

The pumps necessary for generating pressure and thus for conveying the coating materials should impart as little shear stress as possible to the material. Gear pumps are therefore less suitable because of the high shear stress on the material, despite the uniform pressure build-up and uniform material conveying. A secondary dispersion of the pigments in solid colors and creasing of the thin platelets of the effect substances in metallic paints



BPR = Back pressure regulator
ΔL = Change in lightness
a = Pressure difference in BPR : 2 bar
b = Pressure difference in BPR : 4 bar

Fig. 4.2.77
Decline of lightness ΔL of metallic paints by shearing in circulation lines

can result in color and effect shifts. Pneumatic piston pumps have therefore proved successful for material transport in circulation systems. They switch off automatically on reaching the required pressure and switch back on automatically if the pressure falls below a specified setpoint. Pulsation during conveying can be significantly reduced by means of double piston pumps and the additional installation of pressure-equalizing containers.

Figure 4.2.77 shows the color shifts which occur as a result of the influence of the return check valve after an extended period and low material take-off [4.4.77].

A gradual reduction in the shear load in circulation systems is achieved if the coating material in the circuit is no longer depressurized when it is returned. This can be done by installing circulation containers which are permanently pressurized. Since the return check valve is not needed, shear forces are then only transmitted in the pumps. The necessary material feed to the circulation container is carried out discontinuously depending on the level from the paint supply container which is under normal pressure. Such systems have failed to gain acceptance yet because of the cost of the equipment.

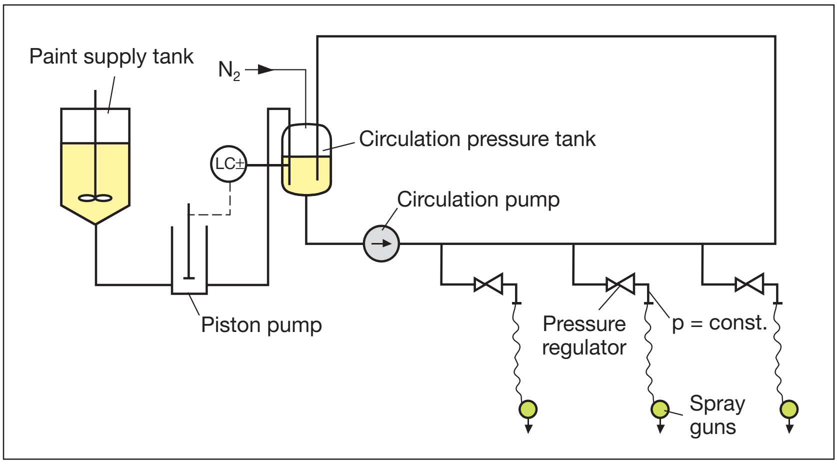


Fig. 4.2.78
Circulation line without shearing back pressure valves

The material from which the circulation system is made also has to take account of the coating material circulating within it. The standard materials are iron for solventborne paints and stainless steel or plastic for waterbased paints. Polyamide should not be used if polyurethane paints or waterbased paints are being processed as it is known to absorb up to 5% water from the air. This would result in moisture-curing of isocyanates taking place while they are still in the circulation system.

Principles of flow in pipes

Accurate knowledge of flow properties in pipes is essential in order to check liquid volumetric flow rates and to design liquid-supply systems.

The flow rate u in pipes is equal to the volumetric flow rate per unit cross section $\dot{V}/A$.

$$u = \frac{\dot{V}}{A} \quad \text{or} \quad \dot{V} = u \cdot A$$

The volumetric flow rate can be converted into a mass flow rate by replacing $\dot{V}$ by $\dot{m}/\rho$:

$$\text{because of} \quad \dot{V} = \frac{\dot{m}}{\rho} \qquad \text{follows} \quad \dot{m} = \rho \cdot A \cdot u$$

For incompressible liquids, therefore, the following applies when flow is stationary at all locations within the pipe, irrespective of the diameter

$$\dot{m}_1 = \dot{m}_2 = \dot{m}_i = k \quad \text{or} \quad \rho \cdot A_1 \cdot u_1 = \rho \cdot A_2 \cdot u_2 = \rho \cdot A_i \cdot u_i = k$$

$$A_i \cdot u_i = k$$

Incompressible liquids have different flow rates in pipes of different diameter and thus different kinetic energies. Disregarding gravity effects and internal friction initially yields the following energy balance for the individual flow sections.

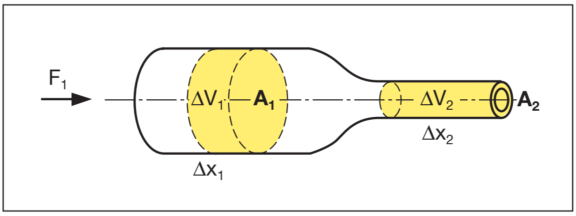


Fig. 4.2.79
Flow in pipes with different diameters

Because of the incompressibility the transported volume is the same in all sections of the pipe, irrespective of the pressure:

$$\Delta V_1 = \Delta V_2 = K \quad \text{or} \quad A_1 \Delta X_1 = A_2 \Delta X_2$$

The volumetric work performed in section 1 $\Delta W_1 = p_1 \Delta V_1$ as part of the total energy is not equal to the volumetric work ΔW_2 in section 2 because of the different flow rate.

$$\Delta W_1 = \Delta x_1 \cdot A_1 \cdot p_1 \quad \text{and} \quad \Delta W_2 = \Delta x_2 \cdot A_2 \cdot p_2$$

p_1 and p_2 represent the pressures acting in the sections.
Because of the higher speed u_2 in section 2 the kinetic energy is also greater than in section 1. Because of the law of conservation of energy the difference in kinetic energy $m/2\ u^2$ must be equal to the difference between ΔW_1 and ΔW_2, i.e.

$$\Delta W_1 - \Delta W_2 = \frac{m}{2} \cdot u_2^2 - \frac{m}{2} \cdot u_1^2$$

$$p_1 \cdot A_1 \cdot \Delta x_1 - p_2 \cdot A_2 \cdot \Delta x_2 = \frac{\rho \cdot A_2 \cdot \Delta x_2}{2} \cdot u_2^2 - \frac{\rho \cdot A_1 \cdot \Delta x_1}{2} \cdot u_1^2$$

$$\text{because of} \quad A_1 \cdot \Delta x_1 = A_2 \cdot \Delta x_2 \quad \text{follows}$$

$$p_1 - p_2 = \frac{\rho}{2} \cdot u_2^2 - \frac{\rho}{2} \cdot u_1^2 \quad \text{or}$$

$$p_i + \frac{\rho}{2} \cdot u_i^2 = P$$

Here P is the total pressure which is divided in the flow of ideal liquids, i.e. excluding internal friction and gravity, into the static pressure p and the dynamic pressure $\rho/2\ u^2$. Flow rates can be calculated using the relation derived by *Bernoulli*.

Any consideration of flow properties in pipes must also take account of energy losses through the exchange of momentum as internal friction. Since the liquids in the pipes adhere to the walls, i.e. show a flow rate of 0 m/s at the interface, there must be different flow rates when transporting liquids as a function of the distance from the wall. The individual zones cause mutual interference as a result of the exchange of momentum. According to *Newton* the following applies for parallel shifting in liquid layers, laminar flow (see chapter 2.3.2):

$$\tau = \eta \cdot D$$

If *Newton*'s equation is applied to flow in pipes, the flow profile u(r), i.e. the rate distribution about the pipe radius R at the distances r from the centre point, is given by:

$$u = \frac{\Delta p}{4 \cdot \eta \cdot l} \cdot (R^2 - r^2)$$

The result is a parabolic function for the flow rate profile for laminar flow.
This indicates that all liquid molecules move parallel to each other in the direction of flow with a speed vector.
The *Hagen-Poiseuille* equation applies to the volumetric flow rate with laminar flow (see also 2.3.2).

$$\dot{V} = \frac{\Delta p \cdot \pi \cdot R^4}{8 \cdot \eta \cdot l}$$

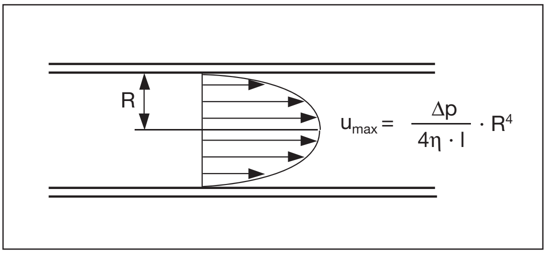


Fig. 4.2.80
Speed profile of laminar flows in pipes

When calculating the throughput in pipes as a function of the pressure differential for a constant pipe diameter and a specified pipe length, it is recommended that the *Hagen-Poiseuille* equation be transformed by logarithmizing to simplify demarcations from other flow states and to simplify classification.

$$\ln \dot{V} = \ln \Delta p + \ln\left(\frac{\pi \cdot R^4}{8 \cdot \eta \cdot l}\right) \qquad \text{laminar flow}$$

If ln $\dot{V}$ is plotted against ln Δp, the result is a linear relation with the slope 1 (see figure 4.2.81) and the y-intercept ln b with $b = \pi \cdot R^4/(8\eta l)$.
The experiment shows that the *Hagen-Poiseuille* equation is no longer valid where $\dot{V}$ rises because an increase in pressure after a transitional state which cannot be clearly described mathematically is exceeded. Although the discharge rate increases linearly again at higher pressures, it is considerably slower with the slope 1/2. Extrapolation of this line to the y-axis gives a new intercept ln b'.

$$\ln \dot{V} = \frac{1}{2} \cdot \ln \Delta p + \ln \sqrt{\frac{\pi^2 \cdot R^5}{2 \cdot \eta \cdot l \cdot \rho}} \qquad \text{turbulent flow}$$

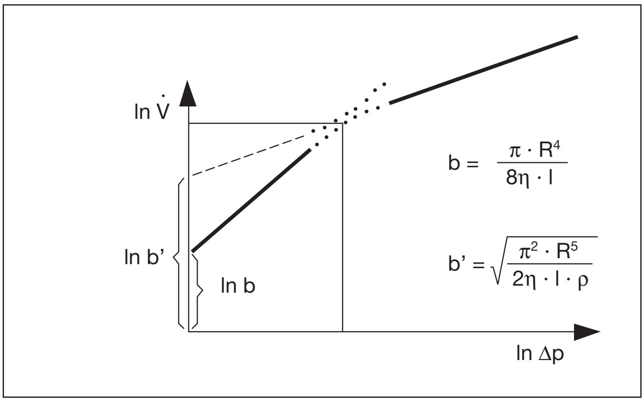


Fig. 4.2.81
Flow rate as a function of pressure

The reason for the significant change in flow behaviour is the transition from laminar to turbulent flow. The characteristic features of turbulent flow are that the parallel shifting of liquid films is overlapped by vortices and that no laminar flow elements remain if the flow rate is further increased. Since the average distance travelled by the moving molecules therefore increases, the rise in the discharge rate also becomes lower. Turbulence can be recognized in that the speed profile is no longer parabolic. The speed vectors are of almost the same magnitude across the entire pipe cross section before falling steeply in the vicinity of the wall.

The transition from laminar to turbulent flow is characterized by a critical flow rate u_{crit}. The transition point is also transferable to other technical equipment if all the variables associated with the flow state can be linked with each other in a dimensionless mathematical manner to form the *Reynolds* number. Thus the transition from laminar to turbulent flow can be predicted for flow in pipes by determining the critical *Reynolds* number. This is approx. 2000 for the flow of water.

The calculation of the *Reynolds* number is of interest from an economic perspective because the throughput with laminar flow considerably exceeds that with turbulent flow despite the same pressure differential. This is taken into account when designing circulation systems, with the result that the usual flow rates of 0.2 –0.3 m/s generate laminar flows in the pipes used without the sedimentation of paint constituents becoming an issue.

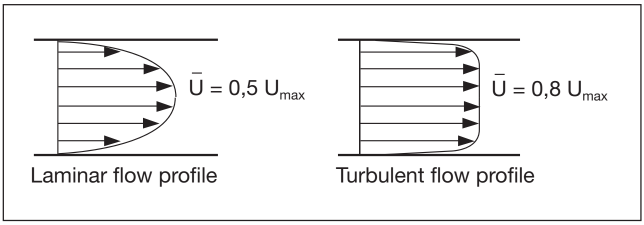


Fig. 4.2.82
Profile of laminar and turbulent flow in pipes

The energy losses of moving liquids, which are a function of viscosity and flow rate, i.e. internal friction, are indicated by a pressure drop along the pipe. This pressure drop can be quantified by reformulating the *Hagen-Poiseuille* equation. If the *Hagen-Poiseuille* equation is resolved to Δp:

$$\Delta p = \frac{8 \cdot l^2 \cdot \eta}{R^2 \cdot t}$$

and if the equation is expanded with $u \cdot \rho$, it follows that:

$$\Delta p = \frac{4 \cdot 8 \cdot l^2 \cdot \eta \cdot u \cdot \rho}{D^2 \cdot t \cdot u \cdot \rho} \quad \text{or} \quad \Delta p = \left(\frac{64}{Re}\right) \cdot \frac{\rho}{2} \cdot u^2 \cdot \frac{l}{D}$$

The last relation only applies to laminar flows. To transform this into a universal form, i.e. also applicable to turbulent flows, the term 64/Re must be replaced by a variable λ which is a function of Re. If this dependence is known, the pressure drop in pipes can be calculated for all flow conditions.

$$\Delta p = \lambda(\mathrm{Re}) \cdot \frac{\rho}{2} \cdot u^2 \cdot \frac{l}{D}$$

So if log λ is plotted against log Re, different linear functions are obtained for laminar and turbulent flows whose y-intercepts are K and K', respectively.

$$\lambda = \frac{K}{\mathrm{Re}} \qquad \lg \lambda = \lg K - \lg \mathrm{Re}$$

If K or K' is known, it is possible to calculate λ and thus the pressure drop or the throughputs for smooth pipes for all flow states, i.e. all *Reynolds* numbers.

An interesting feature is that the pressure drop is independent of the roughness of the pipe walls in the laminar flow range. The laminar interface "hides" the roughness. The turbulent range, on the other hand, is largely independent of Re, but is dependent on the roughness of the pipe walls.

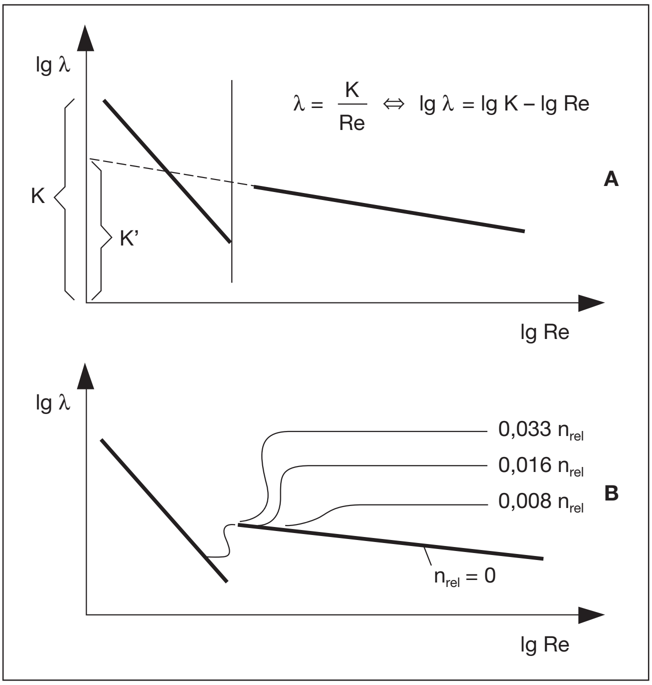


Fig. 4.2.83
Dependence of λ(Re) for smooth (A) and rough (B) pipe walls

The artificial movement of liquids also results in resistance when solid bodies are encountered because of the kinetic energy acting during flow. *Stoke*'s Law quantifies the force F_W transmissible to a fixed sphere of radius r by a liquid at a speed u in the laminar flow range.

$$F_W = 6 \cdot \pi \cdot \eta \cdot r \cdot u$$

In order to generalize *Stoke*s' Law for all flow states and also for nonspherical bodies, the dependence of the resistance on the flow state and the shape of the body against which flow occurs must also be included. To this end *Stoke*s' Law is expanded and transformed using the *Reynolds* number

$$F_W = \frac{6 \cdot \pi \cdot \eta \cdot r \cdot u^2 \cdot \rho \cdot d}{u \cdot \rho \cdot d} \qquad F_w = C_w(\mathrm{Re}) \cdot \frac{\rho}{2} \cdot u^2 \cdot A$$

Validity for all flow states and shapes of the body in question is achieved by replacing 24/Re by the Cw value which is also a function of the *Reynolds* number.

The movement of real liquids can only be guaranteed with a permanent pressure differential because of the energy consumption caused by internal friction. This is generated by means of pumps, thereby creating the appropriate conditions for the continuous transport of liquids in pipes.

Pumps
Paint manufacturers and processors use numerous pumps which, on closer analysis, can be divided into two types of design. The essential difference between the two groups lies in the constancy of the output. A distinction is therefore drawn beween positive-displacement pumps and other pumps. The first group includes those which move defined volumes, largely irrespective of the viscosity and pressure differential. Important representatives of this category are piston pumps, gear pumps, fan pumps and roots pumps. Important units which do not feature positive displacement are centrifugal pumps, airlift pumps and jet pumps.
Despite the disadvantage of the pulsating pressure build-up piston pumps have proved extremely successful for conveying rheologically complex paints in pipes because of the low shear load. Together with gear pumps, which are also of the positive-displacement type, and centrifugal pumps, whose output is a function of pressure, these are the most important units for conveying paint material.

Piston pumps consist of a cylinder closed by valves in which a piston is moved. By coordinated opening and closing of the cylinder chamber, the valves create the necessary conditions for transport of the liquid which is independent of the back-pressure. The principle consists therefore of the autonomous intake and filling of the chambers, closing and subsequent emptying. Piston pumps have an extremely good efficiency with slippage, i.e. the proportion of the volume not transported during a stroke, of 5 – 10%.
Because of the pump design the volume of liquid, which is determined by the piston stroke, cross section and number of strokes, is transported without difficulties in viscosity ranges from 10 mPa·s to 50 Pa·s and pressures up to 100 bar. Piston pumps play an extremely important role in moving coating materials in circulation systems, not least because of the smooth handling of pigmented coating materials. The disadvantages of valve wear when handling coating materials with abrasive pigments and extenders are accepted in just the same way as the pulsating pressure build-up. To cancel out pressure peaks, therefore, pressure-equalizing containers must be integrated in the system. The pressure pattern is smoothed by means of an air chamber separated by a rubber membrane which reduces pressure peaks and compensates for the periodic pressure drop in the pump by means of a phase shift.

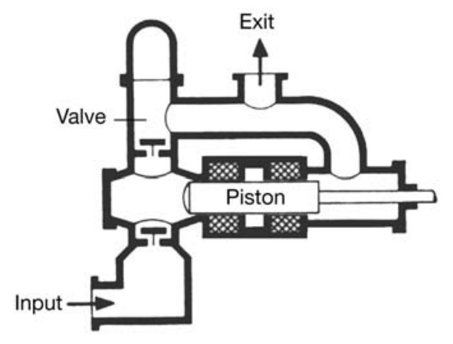


Fig. 4.2.84
Cross section of a piston pump

Gear pumps, which are also from the positive-displacement pump family, are rotary pumps and therefore work without valves. They convey liquids with viscosities up to 10 Pa·s in a nonpulsating manner with back-pressures of up to 20 bar.

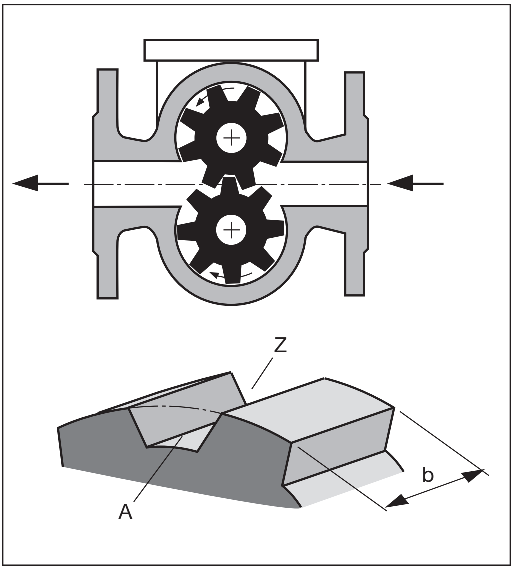


Fig. 4.2.85
Cross section of a gear pump

Two volumes b·A are transported in the free tooth spaces z in the upper and lower parts of the pump as a function of the speed n in the direction of flow. These volumes are greater than those in the central return-flow area. The return volume is substantially smaller than the transported $\dot{V}$ because of the meshing of the teeth in the central area. It depends on the pressure differential Δp and the viscosity η of the transported liquids because of the incomplete seal in the return-flow area. γ is a factor which has to be determined experimentally.

$$\dot{V} = 2 \cdot z \cdot A \cdot b \cdot n - \frac{\Delta p}{\eta} \cdot \gamma$$

Gear pumps are simple and reliable conveying devices, though they bring high shear forces to bear on the paint as it enters the pump. This causes excessive abrasion and creasing or breaking of the thin aluminium flakes in metal effect paints. Gear pumps are therefore not recommended for transporting every type of metallic paints in circulation systems. Like piston pumps, gear pumps as positive-displacement pumps should always have a bypass as a safety kit which is opened by an adjustable minimum pressure in the event of pipe blockages.

Of the non-positive-displacement pumps only the **centrifugal pump** is worth mentioning in the context of paint production and paint processing. It is a particularly simple and ”kind” conveying device, but is nowhere near as important in the paint and coatings industry as in other industrial sectors because of the frequently excessively high viscosities of the material to be conveyed. The transport of media with viscosities in excess of 200 mPa·s is extremely difficult to achieve.

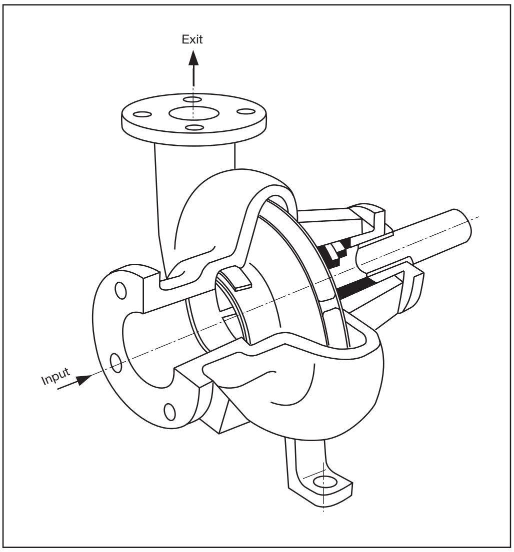


Fig. 4.2.86
Cross section of a centrifugal pump

The centrifugal pump works on the same principle as a propeller.

Moving vanes draw the material in axially and then discharge it radially. The material is therefore moved without pulsation, though not in defined volumes. This pump design has the further disadvantage of not being able to draw liquids in independently and of only being capable of overcoming certain heights.

On the other hand, the drawback of reducing output with increasing back-pressure also means self-regulation or restriction of the pressure build-up in the event of closed or blocked pipes. As a result of the permanent circulation of the viscous liquid the temperature rises, meaning that the pump shuts down automatically on reaching a setpoint temperature if fitted with a thermostatic switch.

Measuring, dispensing and homogenizing

For many applications, such as processing two-component paints, material flows have to be dispensed, the throughput measured and corrected, and the material homogenized. Only in this way can constant discharge rates or constant mixing proportions for the individual components and thus constant quality in the coating result be guaranteed. The numerous methods for determining throughputs are based on different measuring processes:

- Volumetric measurement methods
- Differential-pressure methods
- Pressure drop in pipes
- Force action on bodies against which material flows
- Magnetic induction methods
- Incubation methods
- Thermal methods
- Ultrasound
- Mass flow measurement with gyroscopic methods

Whereas the volumetric methods indicate the material flow directly as a measured variable, all the other methods first determine physical variables which are converted into volumetric or mass flow rates by mathematical linking with other variables.

The simplest methods of measuring material flows are the **volumetric measurement methods.** The equipment used in these includes positive-displacement meters, to which positive-displacement pumps also belong. These are suitable measuring instruments if the pressure necessary to induce flow is generated by other units. The number of strokes in a piston pump is a measurement of the throughput if the volume moved per stroke is known. Gear pumps can also be used as measuring instruments for the reproducible processing of industrial paints. With 1-component paints they serve to monitor the discharge rate and with 2-component systems to maintain constant mixing ratios. Oval-wheel flowmeters work on a similar principle.

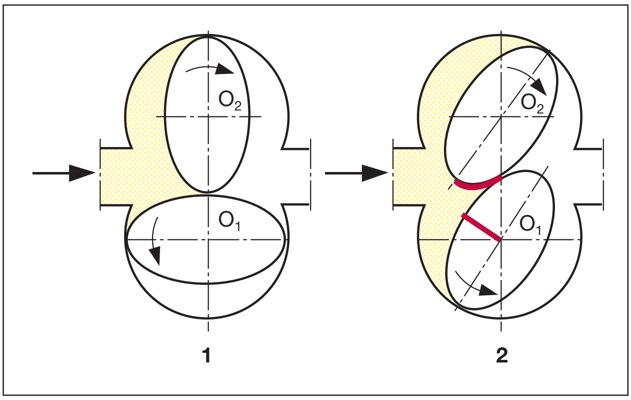


Fig. 4.2.87
Principle of an oval-wheel flow meter

Gear pump-type meters and oval-wheel flow meters have measurement errors of approx. 1%.

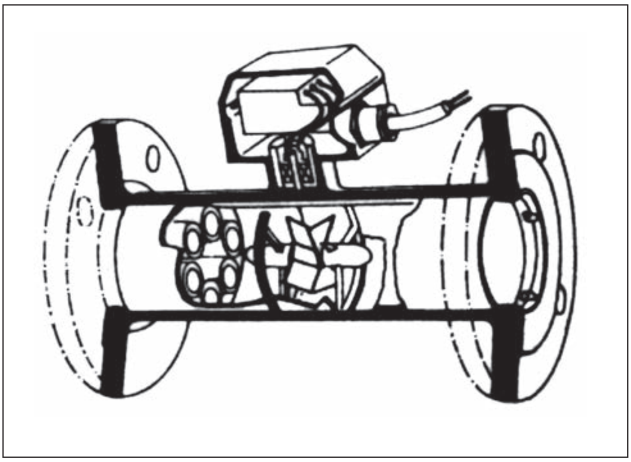


Fig. 4.2.88
Turbine meter with induction measurement

The turbine meter uses a different volumetric measurement principle. This type of measurement basically involves a centrifugal pump being used to determine the throughput rate. The speed resulting from the flow of the liquid can be measured either mechanically or as an induction voltage by the turbine moving in the magnetic alternating field. Corresponding calibration curves are recorded to determine the throughputs as a function of the pressure differential and viscosity of the liquid. This measurement principle is therefore in the category of indirect processes.

Differential-pressure methods are based on pressure measurements and make use of the influence of moving liquids on the distribution of the total pressure into the dynamic and static pressures. In accordance with the *Bernoulli* equation which is valid for ideal liquids the sum of the potential and kinetic energy is constant along the direction of flow, provided the internal friction is negligible because the measurement sensors are positioned close together. The different pipe cross sections of this measuring system cause changes in the dynamic pressure which are measured and used to calculate the volumetric flow rates (see above). A variant of this differential-pressure method involves measuring the pressure drop in pipes. In this method the pressure gauges are positioned at relatively large distances from each other with a constant pipe cross section. If $\lambda(Re)$ and the density of the liquid are known, the flow rate can be calculated by

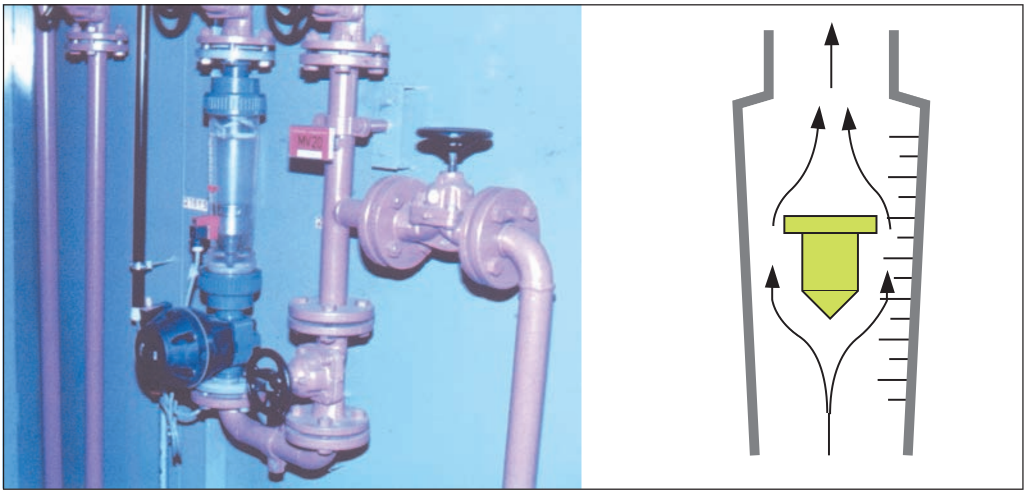


Fig. 4.2.89
Picture and scheme of volume flow meter by floats

measuring the pressure drop between the measurement sensors and, if the cross section is known, the volumetric flow rate (see above).

Throughput measurements from the force transmitted to bodies against the flow are based on the already mentioned resistance law after *Stoke*s (see above). The principle of throughput measurement with floats uses the counteraction of gravity and frictional drag. In a vertically configured measurement tube the liquid to be measured flows from bottom to top (see figure 4.2.89).

Volumetric flows become measurable if the equipment also sets different Cw values at different flow rates when a slightly conical measurement tube is fitted. However, prior calibration of the measuring system with the particular liquids to be measured must be carried out.

In the **magnetically inductive process** electrically conductive liquids are moved in a tube of diameter D in a magnetic field of magnetic flux B. This induces a voltage U which is proportional to the volumetric flow rate $\dot{V}$. This can be measured directly if insulated pipes are used.

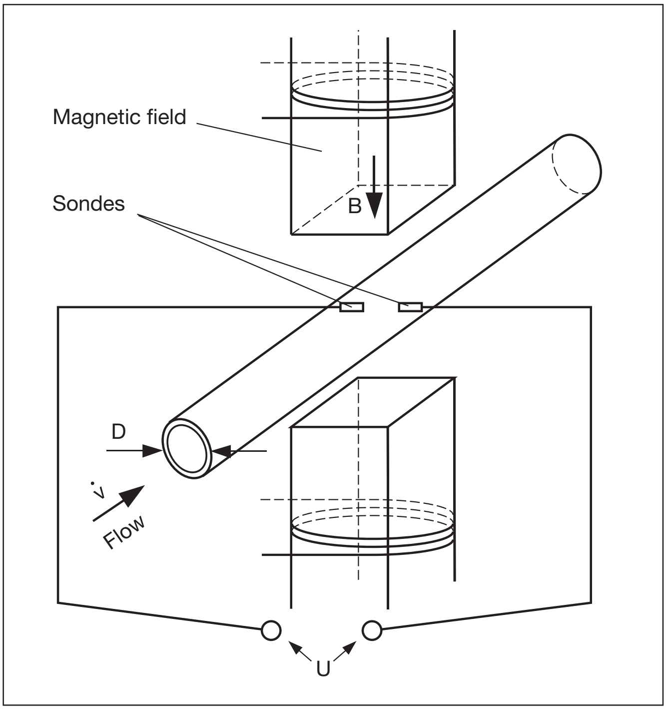


Fig. 4.2.90
Principle of magnetic inductive volume flow meter

$$\dot{V} = K \cdot \frac{D \cdot U}{B}$$

This measurement method is preferred with waterbased paints. Calibration for the various paints is necessary.

When measuring in accordance with the **incubation method**, heterogeneity of the flowing system is regularly but briefly induced at a particular location in the pipe. This can

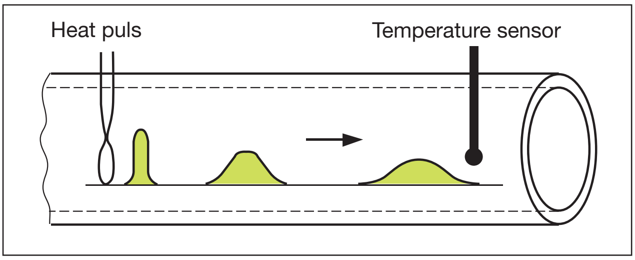


Fig. 4.2.91
Principle of the incubation method for volume flow meters by heat pulses

be done, for example, by means of a heat pulse or by incubating with a salt solution. The localized change in temperature or increase in electrical conductivity can then be monitored at another location. Throughputs can be calculated on the basis of the time delay between incubation and measuring the incubation variable.

The incubation methods are very accurate, but can only be used in the case of continuous flow. Interruptions mean that the pulses do not reach the measurement sensor, and calculation is therefore impossible. Throughput measurements with the incubation method cannot be used to determine discharge rates for manual spray application because of the frequent associated interruptions.

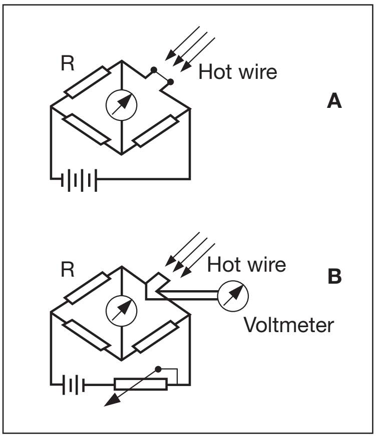


Fig. 4.2.92
Hot-wire anemometer with indicator type (A) and (B)

The measurement principle of the **hot-wire method** is based on the speed-dependent cooling of wires through which a current has flowed. The resistance of a wire heated by the flow of a current is determined in a measuring cell via a *Wheatstone* bridge. At a specified voltage U the galvanometer of the previously calibrated bridge shows a deflection (A) proportional to the throughput. The cause of this lies in the flow-dependent cooling of the measurement section heated previously by the electric current and the associated change in resistance.

Because this measurement method is highly sensitive, it is only suitable for low flow rates. If higher throughputs have to be measured, calibration can be achieved by raising the bridge voltage (B). The rise in the potential difference between the input and output of the measurement section represents then the value of the flow rate.

Measurement sensors which detect **temperature increases** in the volumetric flow to be measured $\dot{V}$ after the input of a defined amount of electrical energy have also proved successful. By contrast with

$$\dot{V} = \frac{\dot{q}}{\rho \cdot c \cdot \Delta T}$$

the pulse method heat energy $\dot{q}$ is fed continuously to the liquid via a hot wire. The temperature rise ΔT is then a function of the material type to be heated with the parameters density ρ and heat capacity c and of the volumetric flow $\dot{V}$.

The principle of the method involving **throughput measurement with ultrasound** is the dependence of the speed of sound on the speed of the flowing liquid. Depending on the flow rate, a sound emitted by a transmitter reaches a receiver faster or more slowly.

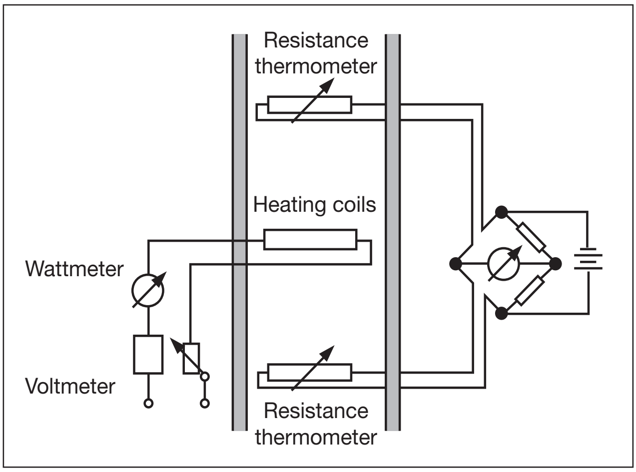


Fig. 4.2.93
Volume flow measurement by temperature rise caused by defined energy input

If the receiver and transmitter are positioned on opposite sides of the measuring circuit, the beam passes through the entire flow profile and determines the flow rate as a mean. Positioning the receiver and transmitter exactly perpendicular to the direction of flow does not provide any meaningful readings (see figure 4.2.94)

An increase in the accuracy of the throughput measurement method with ultrasound is achieved with the "sing-around" method. Measuring system 1 is working in the direction of flow, while 2 is against the direction of flow, with the transmitter and receiver positioned at a distance l from the tube. The transmitters only deliver pulses if the sound has not yet arrived at the receiver. When the sound reaches the receiver, the transmitter is switched off, before being switched back on again at the end of the sound information. Thus two different pulse sequences of durations t_1 and t_2 are received. The speed of sound c is increased in system 1 by the flow rate $\bar{u}$ as a function of the incident angle β and reduced in system 2. The flow rate is calculated by mathematical processing of the electronically measurement time differences.

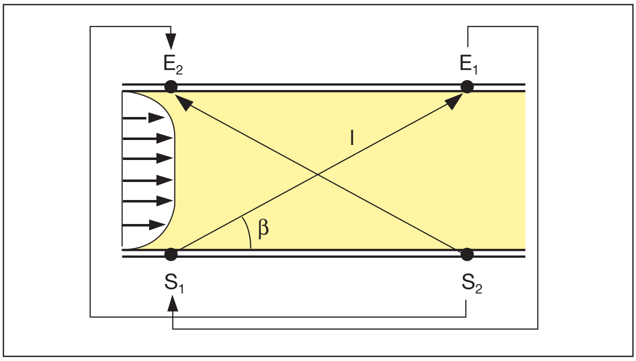


Fig. 4.2.94
Volume flow measurement via ultrasound

$$c + \bar{u} \cdot \cos\beta = \frac{l}{t_1} \quad \text{and} \quad c - \bar{u} \cdot \cos\beta = \frac{l}{t_2}$$

$$\bar{u} = \frac{1}{2 \cdot \cos\beta} \cdot \left(\frac{l}{t_2} - \frac{l}{t_1} \right)$$

The most accurate method for measuring mass flow rates involves a measuring instrument working on the **gyroscopic principle**. It consists of a U-tube, through which the liquid to be measured flows after it has been made to oscillate electronically. A speed-

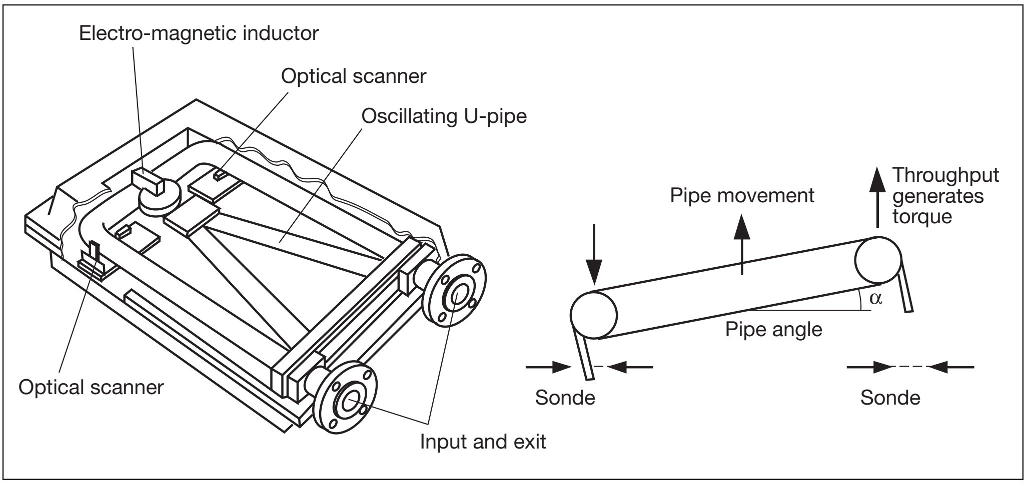


Fig. 4.2.95
Principle of mass flow measurement with gyroscopic method

dependent *Coriolis* force, which twists the U-tube with a radius of curvature r out of its horizontal position, then acts on the mass of particles moving within the tube. The torsional angle α which is measured at a specified oscillating frequency f, is proportional to the mass flow rate $\dot{m}$.

$$\dot{m} = k \cdot \frac{\alpha}{f \cdot r}$$

This method has numerous advantages over all the others. Its accuracy is excellent, with an error rate of ± 0.3%. The results are independent of the liquid's rheological properties and are unaffected by fluctuations in material pressure or different surface tension and density.

The gyroscopic method can also be used to measure pulsating flows and two-phase mixtures. The latter is important when dispensing dispersions [4.4.78].

The large number of measurement methods presented can be explained by the fact that no one method can be used for all requirements, e.g. for the transport of paints and for all flow rates. This is because the accuracy of the measurement methods is a function of the throughput.

For example, the differential-pressure method is only sufficiently accurate if large volumes are being transported, whereas the incubation method is only suitable for small volumetric flows.

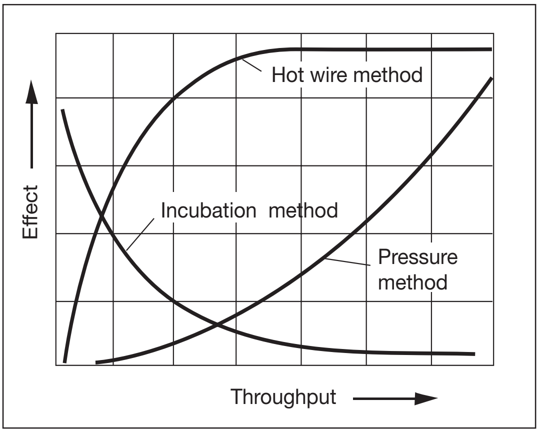


Fig. 4.2.96
Sensitivities of different volume flow measurement methods to the amount of volume flow

Homogenization in 2-component application systems

In the industrial processing of 2-component paints, consisting of the base

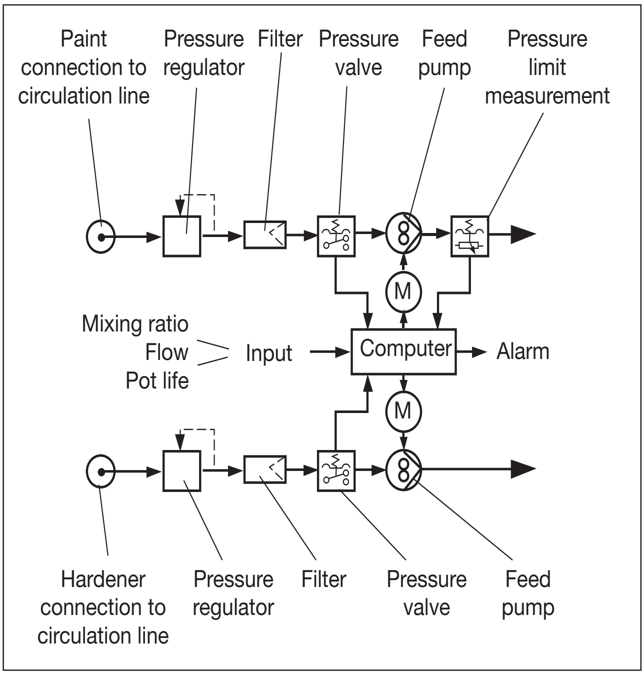


Fig. 4.2.97
Electronic control of 2-component spray systems

and hardener with a pot life of just a few minutes, it is important, apart from precise dispensing of the volumetric flows, to achieve perfect and rapid homogenizations of the two components in order to obtain a uniformly good coating quality. Small mixing volumes should make color changes economically viable. In addition, a circulation system, which has to be purged with dry nitrogen in the case of isocyanate-containing materials, has to be installed for transporting the hardener.

The dispensing systems used as standard in the past with two mechanically linked piston pumps have largely been replaced by computer-controlled gear pumps. This has eliminated the problems of pulsating pressure build-up and achieved greater flexibility in setting different mixing ratios.

Two process variants have proved successful with regard to electronically controlled dispensing systems.

In the first the base quantity is determined by paint pressure regulators, and the volumetric flow rate is measured continuously with a flow meter. This rate is transmitted to a computer which then actuates the stepper motor of a gearwheel meter for the hardener circuit. The second design does not use paint pressure regulators and dispenses the volumetric flows with computer-controlled gearwheel meters in order to achieve constant discharge rates, constant mixing ratios and greater flexibility when setting different mixing ratios. This method is the more important one.

When processing 2-component paints the homogenization of the volumetric flows is also important for the quality of the coating. This should be done as shortly before application as possible. Static mixers have proved successful for this and other reasons,

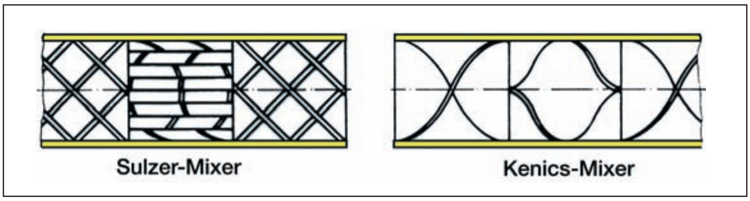


Fig. 4.2.98
Scheme and function of Sulzer mixer and Kenics mixer

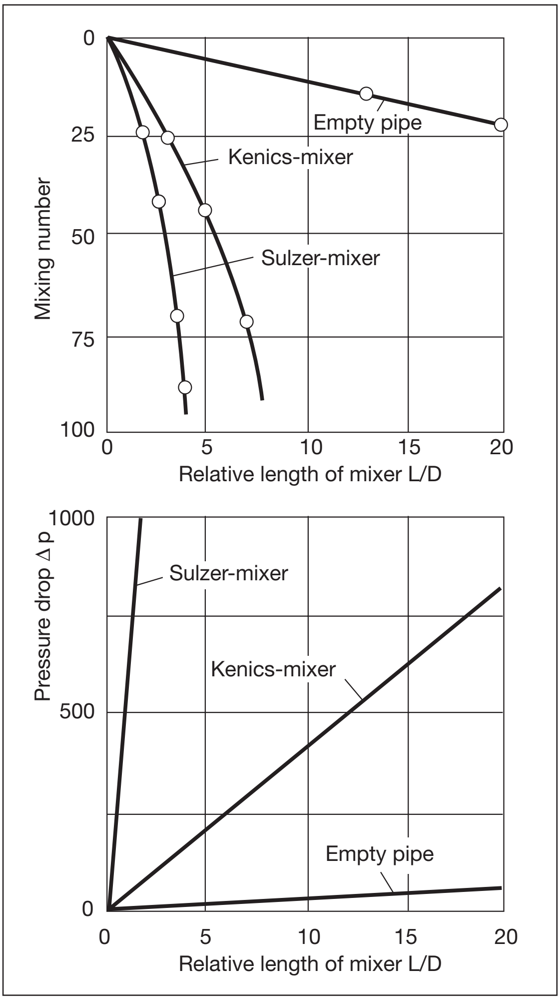


Fig. 4.2.99
Diagrams of mixing states and pressure drops of Kenics mixer and Sulzer mixer

with the *Kenics* mixer turning out to be the best compromise of all requirements for paint processing.

Static mixers are devices in which two product flows are homogenized using the flow energy [4.4.79].

According to this definition a simple empty pipe into which the two components are fed is, in principle, a static mixer. In such a pipe homogenization is only achieved with turbulent flow if the pipe section length is approx. 90 times its diameter. For that reason the empty pipe is fitted with baffles which considerably improve the ratio of length to cross section. In all cases the improvements are associated with an increase in the pressure drop. Of the many static mixers the *Kenics* mixer offers the best compromise between a low pressure drop and a high mixing quality. It consists of alternating left- and right-hand spirals with a transposition angle of 180° (see figure 4.2.100). The individual spirals are configured behind each other in an empty tube and twisted through 90°. In this way laminar flow effects are used to divide the volumetric flow into two halves.

The number of pitch increments as a function of the number of spirals n is given by 2^n. Where 24 spirals are in use, this means no fewer than 16,777,216 sub-layers. In order to achieve an optimum mixture it is important when selecting materials to ensure that the viscosity differentials in the volumetric flows to be homogenized are as small as possible. Static mixers, and *Kenics* mixers in particular, have become firmly established for the industrial processing of 2-component paints because of their good mixing quality, low stresses imparted to the product, continuous operation, low space requirement and low capital costs. Because of their low space requirement they can even be integrated in spray heads.

Waterbased 2-component polyurethane paints, which have become more and more popular in recent years, require a continuous extremely fine emulsification of the hardener components in the aqueous phase of the base dispersion. This means that there are even greater demands on the homogenization quality. To this end the organic solution containing the isocyanate groups is injected into the aqueous polyol phase in droplets of

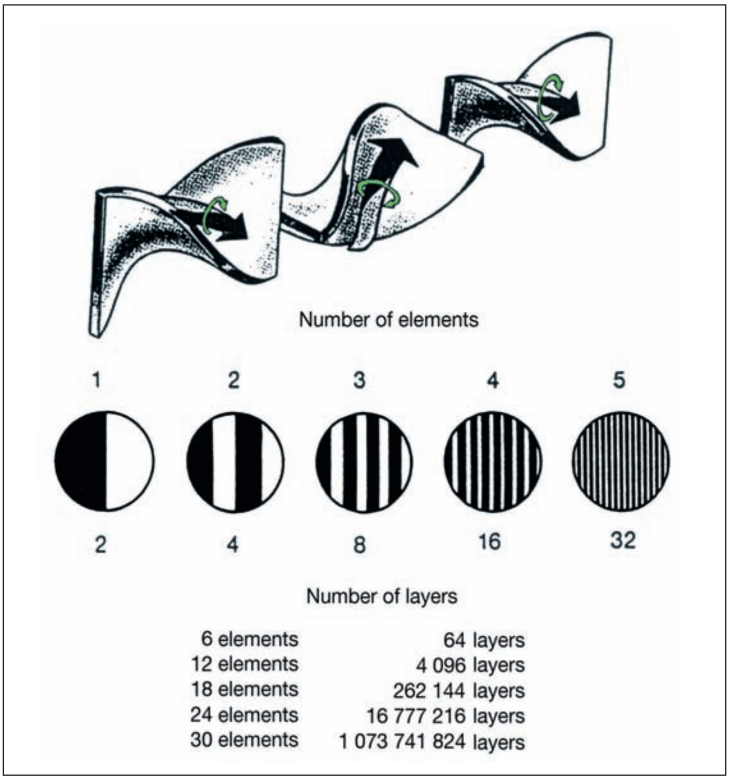


Fig. 4.2.100
Construction elements and mixing number of Kenics mixer

5 – 20 µm using an injector nozzle before it is broken down further into particle sizes of 0.5 µm in jet dispersers [4.4.80].

4.2.1.5 Booth Conditioning and Overspray Elimination

Overspray is a characteristic feature of indirect paint processing by atomization. This involves the emission of solvents to the environment and the already described overspray itself. Action must therefore be taken for occupational health and safety and environmental protection reasons to reclaim or dispose of the not inconsiderable quantities of solvents and overspray which does not hit the object to be painted. The resulting overspray therefore has unwanted side effects on the process itself. Straying overspray can contaminate already painted objects if it deposits on the fresh, still viscous coating. Film defects in the form of craters are often the consequence (see chapter 6.2).
It is therefore necessary to keep overspray and evaporating solvents under control. Bodyshops have small spray booths which handle these tasks by extracting and filtering solvents and overspray by routing air through water curtains behind the spray booth.
In industrial-scale processing the spray equipment is enclosed in larger booths. In these the evaporated solvents and the overspray are removed by supplying fresh air. This ensures air flow which is as laminar as possible from top to bottom in the booth. For vertical rates of air descent of 0.2 – 0.5 m/s, therefore, 0.2 – 0.5 m^3/s or 720 – 1800 m^3/h conditioned air must be supplied continuously per m^2 booth surface area. With booth

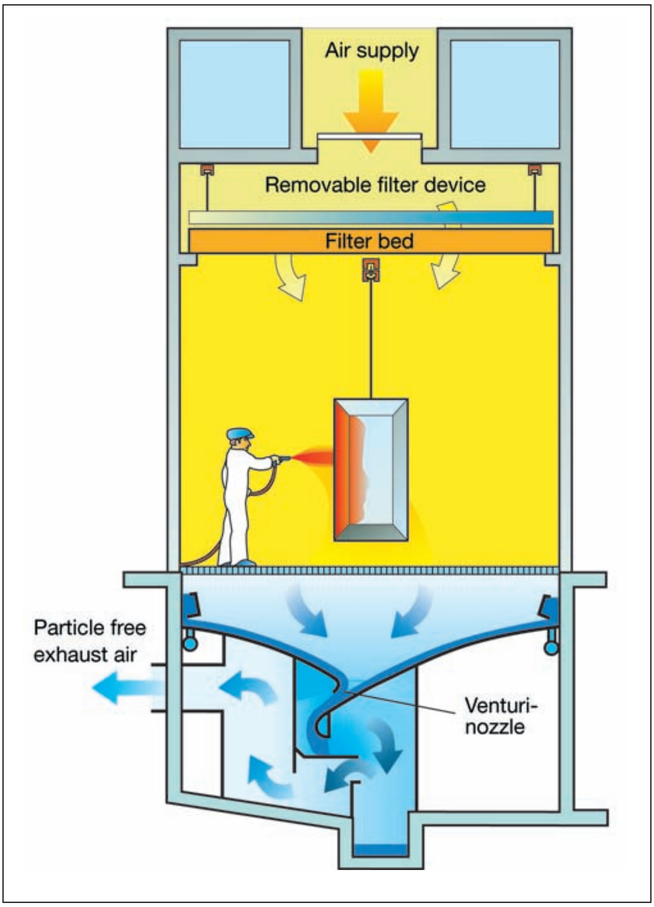


Fig. 4.2.101
Scheme of a spray booth

floor areas of 200 m^2 that means up to 400,000 m^3 cleaned and conditioned fresh air per hour. This enables paint defects to be avoided and the regulatory MAC values for the materials to be complied with.

The air supplied must first be cleaned, tempered and, when processing waterbased paints, also adjusted to the appropriate relative humidity. This is achieved by means of fans, humidifiers, heat exchangers and microfilter units upstream and downstream with pore sizes of 10 – 0.1 µm.

Although the amount of foreign matter in the air is low at 0.1 – 0.3 mg/m^3, this represents an extremely large number (1000 – 7000) of dirt particles in the outside air. For 300,000 m^3 fresh air per hour without cleaning this would mean approx. 100 g foreign dirt consisting of more than 1 billion particles being introduced into the booth. Since dirt particles with sizes of more than 10 µm can cause paint defects on freshly coated objects, it is important to pay special attention to the elimination of dirt.

Of the usual process-engineering methods of particle separation only deep-bed filtration can be used because of the extremely small size of the particles. Wet-cleaning methods cannot be used because they increase the air humidity excessively, and cyclones are not suitable because of their inadequate separating action. Filter bags are used with microfiltration in order to achieve the largest possible filter surface area in a small space. Large interchangeable microfilter mats are fitted in the booth ceiling for air distribution to ensure laminar air flow in the booth.

This fresh air absorbs solvents which evaporate during the painting process and transports these and the overspray to the overspray traps. If only a little paint is being processed or if a processing method is being used which only gives rise to a little overspray, such as the purely electrostatic process, filter mats can also successfully be used for extended periods for separating the overspray. When processing large volumes of paint and in the event of large amounts of overspray, impact plates can be fitted upstream of the dry filter mats to extend their service life. Because of the inertia of the droplets a large proportion is separated in advance as the air which is loaded with overspray is forced to change direction. The overspray is then disposed of by removing the paint from the paint-covered impact plates and replacing the used filter mats. Depending on the type of paint, the paint-contaminated filter mats must be disposed of as domestic or special waste.

Different technical conditions must be provided for ongoing painting in continuous systems. Assuming a material consumption of 7 kg paint per car and material spill of 20% during daily production of 1000 cars, the daily overspray is approx. 2 t. Because of the short service life of dry filter systems, large-scale industrial coating systems are fitted exclusively with wet scrubbers. These are located below the booth. Their task is to ensure the most intensive interaction possible between the overspray droplets and the flood sheet fluid and thus to transfer the overspray to the aqueous phase. The overspray is then separated from the flood sheet fluid again and disposed of as paint sludge.

In order to promote rapid and complete overspray absorption, the overspray is greatly accelerated by constrictions in the extraction devices before it is absorbed into the aqueous phase at a high relative speed. Diffusers operating in accord-

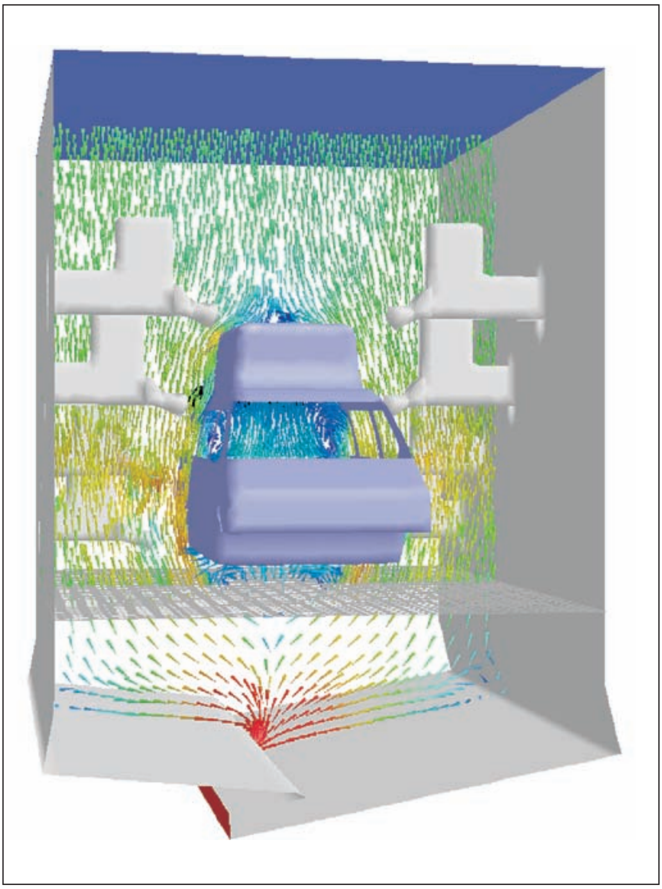


Fig. 4.2.102
Air flow in a spray booth

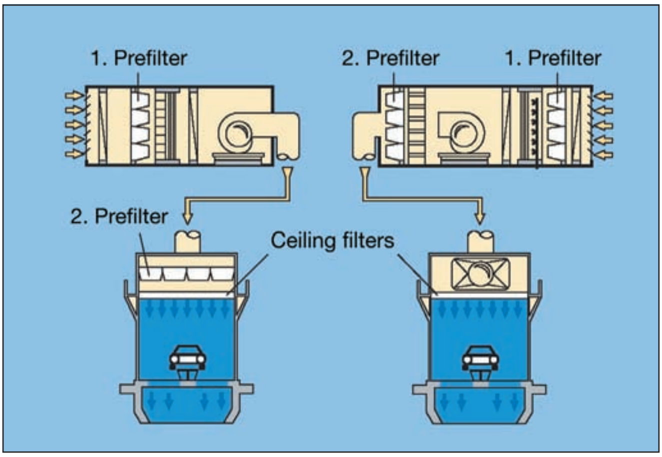


Fig. 4.2.103
Conditioning of air supply for a spray booth

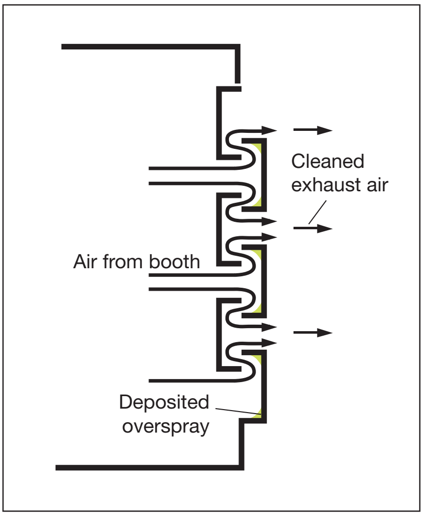


Fig. 4.2.104
Overspray deposition with impact plates

ance with the *Venturi* principle work particularly well. After acceleration of the overspray-charged waste air, the expansion of the aperture cross section of the *Venturi* nozzles causes pronounced eddies. The resulting vacuum draws the flood sheet fluid into the air current, leading to the capture of the overspray.

The degree of separation achieved by such systems at average droplet sizes of 25 – 30 µm is extremely good at 99.8 – 99.9%. As a rule the statutory regulations relating to aerosol residues in the spray booth waste air are met.

Tensides and special coagulating agents are added to the flood sheet fluid to ensure better absorption of the overspray and, in particular, better separation from the fluid which is recirculated.

Jet, cascade or vortex scrubbers are also encountered in practice. Jet scrubbing is the longest established system. In this the scrubbing liquid is atomized via a series of noz-

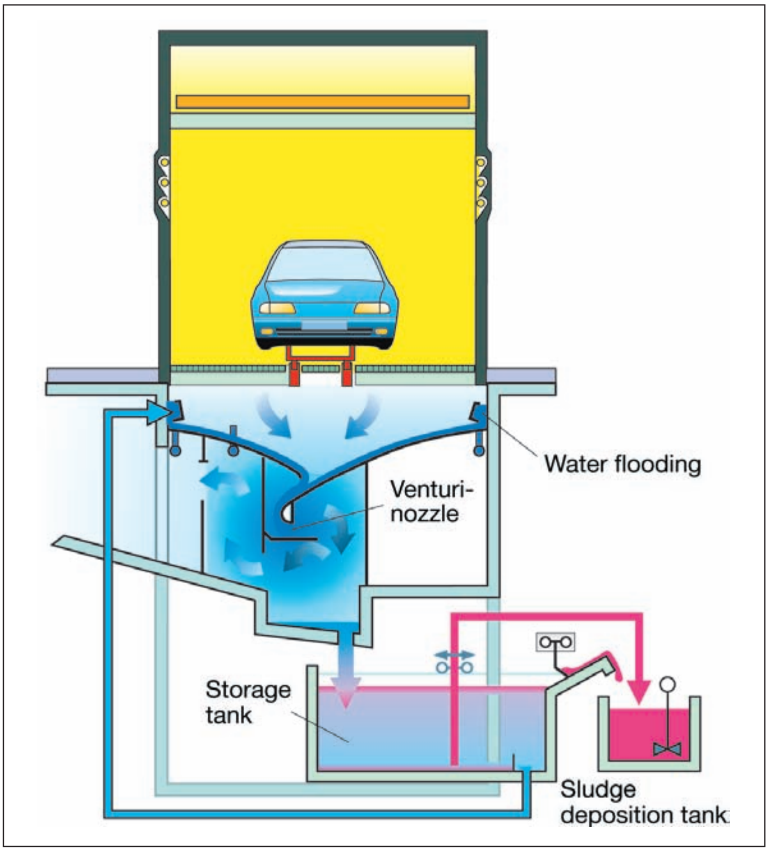


Fig. 4.2.105
Wet deposition of overspray using Venturi nozzles

zles in the waste air stream. With optimum settings, good efficiencies of up to 99.5% are achieved. Jet scrubbing is a relatively high-maintenance process because of the possible soiling of the nozzles.

Cascade and vortex scrubbers are better in this regard. In cascade scrubbers the flood sheet fluid runs from an overflow container in a closed film through a cascade, consisting of several semi-circular curved impact plates. They are configured such that the water entrained upwards with the air forms water curtains as it flows back down and absorbs the overspray.

In vortex scrubbers the waste air is sucked through a narrow gap between the liquid and a demarcation plate. As a result of the geometry of the gap and the rapidly moving waste air the flood sheet fluid is atomized in similar fashion to the scrubbing methods already described before capturing the paint droplets.

The energy input required to separate the overspray is provided in jet scrubbers by the artificially moved flood sheet fluid and in all other systems by the kinetic energy of the waste air stream.

All overspray treatment processes include a water treatment stage which ensures that the paint sludge is separated and that the water treated in this way can be recycled to the flood sheet fluid again.

The systems described are not suitable where only a small amount of overspray occurs. Under such circumstances, electric filters with their superior efficiency are particularly attractive. Their use is always recommended if complete removal of the overspray is required. This is the case, for example, where air is recirculated in spray booths (see chapter 5).

As already described in the section on the electrostatic atomization of paints, a field strength E of such a level is generated at a filament-shaped cathode that ionization of the air occurs and the overspray is therefore charged. The speed u_{st} at which the aerosols with the diameter D migrate to the inner wall of the anode, down which water flows, is given by

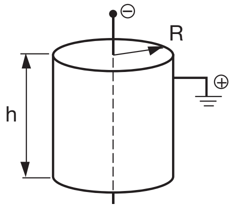
$$u_{st} = \frac{Q \cdot E}{3 \cdot \pi \cdot \eta \cdot D}$$

If account is also taken of the fact that the charged particles must cover the distance R, the air speed may not exceed u_{air} in the electric filter.

$$u_{air} = u_{st} \cdot \frac{h}{R}$$

It therefore follows that

$$u_{air} \leq \frac{h}{R} \cdot \frac{Q \cdot E}{3 \cdot \pi \cdot \eta \cdot D}$$



The charged overspray is separated at the pipes or planar walls connected as the anode and trickled with water and is then captured by the water.

Disposal of the paint sludge and booth air

While overspray-charged filter mats must be disposed of by landfilling or incineration, the paint overspray must be chemically and physically modified to remove it effectively

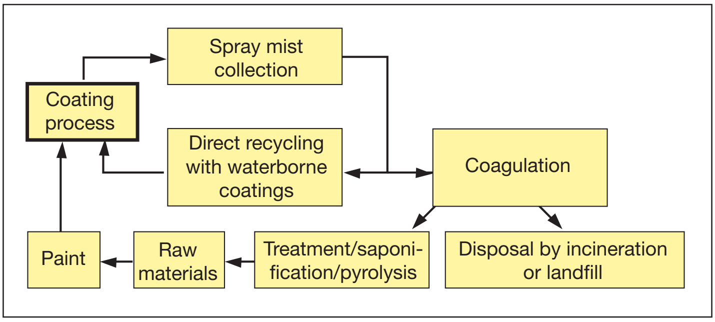


Fig. 4.2.106
Methods of overspray treatment

from the circulating flood sheet fluid. The aim of this is to prevent pipes and pumps from becoming clogged by rendering the overspray droplets nonadhesive and at the same time creating better conditions for separating the organic overspray from the aqueous phase. Wet separation is therefore accompanied by various methods of paint coagulation. The processes, which have been proven in practice, can be divided into chemical and physical methods.

Saponification of the organic components of the paint sludge with caustic soda is no longer a state-of-the-art method. A better method, because it is more universal and less aggressive, involves treatment with less basic metal hydroxides. In this relatively mild environment with pH 9 the paint droplets are destabilized and enclosed in colloidal aluminium or iron hydroxide. The destabilization of the pigment dispersion with the effect of forming relatively large agglomerates is a desired side effect. The use of wax dispersions also renders the paint sludge nonadhesive by means of adsorption. An effective adsorption method uses the physical interaction of alumina with the overspray droplets in the circulation water. Alumina initially forms the substrate for the paint droplets and then, in the second step, extracts the organic solvents still remaining in them, with the result that a nonadhesive coagulate remains. To ensure that the service life is as long as possible, foam inhibitors should be added with the actual coagulation agents and biocides to prevent bacterial attack.

In all cases steps must be taken to ensure that the coagulated paint sludge is removed by means of scrapers or decanters after sedimentation or after it floats to the surface as a result of CO_2 formation as in polyurethane paints and is processed for further use.

In some appropriately designed booths watersoluble paints are captured in the flood sheet fluid before being concentrated again by ultrafiltration or electrochemical coagulation and returned to the process (see chapter 5). This is only useful and cost-effective if few or, preferably, no color changes occur, e.g. when processing primer surfacer paints or primer material [4.4.81].

For various reasons the booth air generated by processing overspray is not recycled in most cases but instead is discharged to the atmosphere after waste-air treatment, usually in the form of activated carbon adsorption (see chapter 5). These reasons include, on the one hand, compliance with the MAC values for solvent concentrations in the booths, so that it is possible to enter the booths, if necessary, while painting is in progress, and, on the other hand, in the cost of processing the humid waste air arising from the waterbased paints which are generally used in the automotive industry.

4.2.1.6 *Automated Systems and Robots for Paint Processing*

Industrial-scale paint application by spray coating requires spray heads which cover the object under constant conditions in specified, coordinated paths at the same distance in order to apply uniform paint films. Classic paint processing using pneumatic or hydraulic atomization, mainly carried out manually in the past, is now being carried out increasingly by automated painting systems (reciprocators) and robots in industrial coating technology. Manual application is limited today only to areas of difficult access and occasional reworking during or on completion of coating work.

Since application using purely electrostatic spraying or high-rotation atomization cannot be carried out manually, it is even more understandable that industrial paint processing is moving towards automated processing technology. Savings on staff, increases in material and energy yields and a constant good quality are just some of the conspicuous advantages.

Since the use of automated systems means that the experience of the painter can no longer be called on to compensate for fluctuations in material, process and ambient parameters, all the processes which influence application, equipment and material variables must be regularly, ideally continuously, measured and maintained at a constant level. If such conditions are guaranteed, paint application can, in principle, be automated (see figure 1.1.7). Paint can then be applied by appropriate automated painting systems or robots, depending on the complexity of the product to be painted. Such machines, as described below, can be fitted with almost all types of spray heads.

The simplest form of automation involves the use of **reciprocators**. The workpiece is moved past the vertically moving spray head, with the result that the spray cone can coat the entire surface of the workpiece. It is necessary in this process to match the forward and lifting speeds of the automated system's arm to each other. If this is done, the result is a sawtooth spray pattern because of the regular lateral motion of the lifting arm in conjunction with the direction of movement of the object.

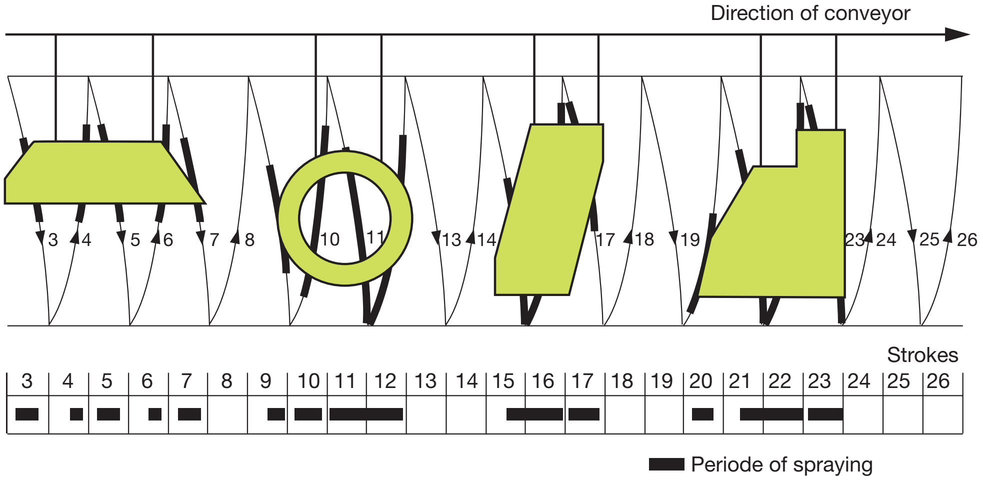


Fig. 4.2.107
Example of programming paint output at reciprocators for different parts

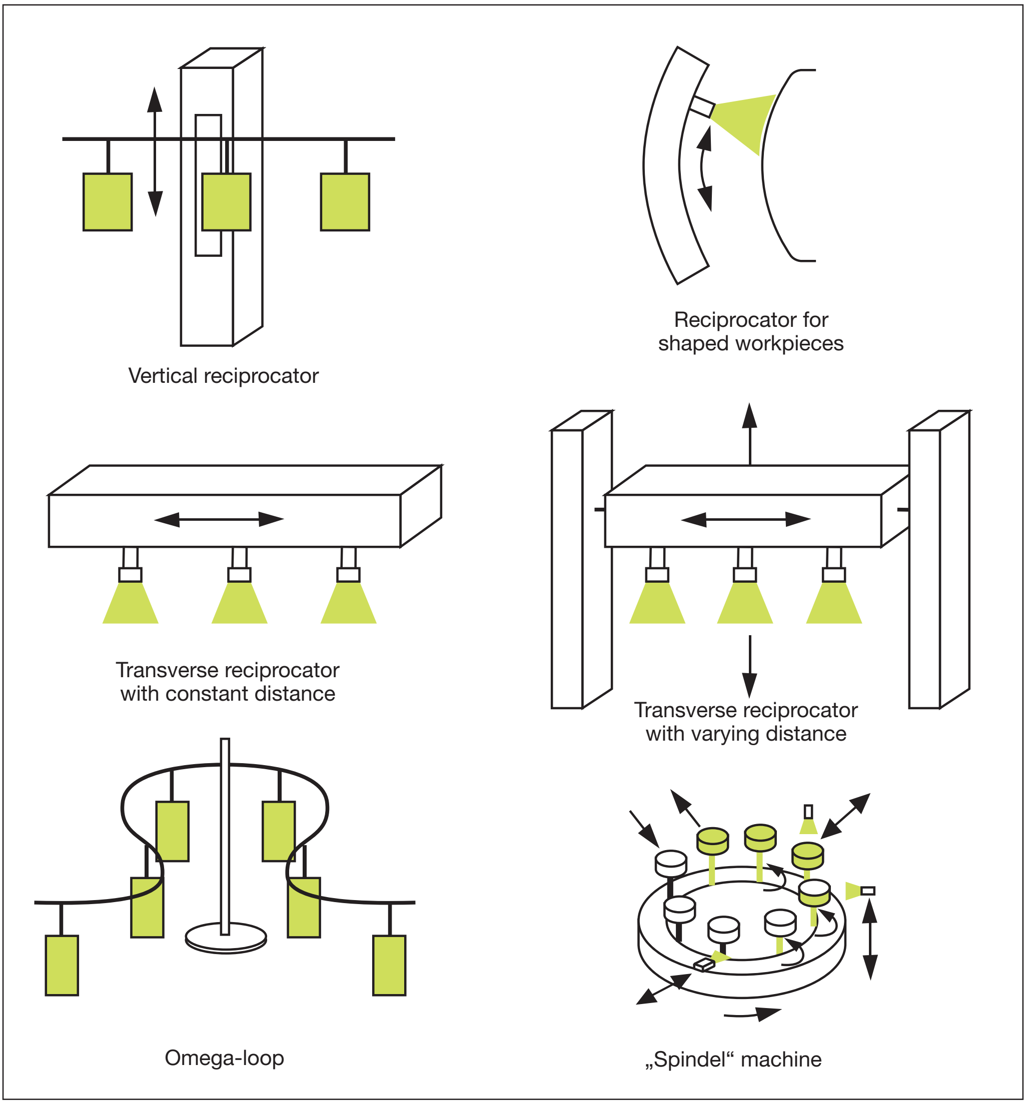


Fig. 4.2.108
Reciprocator types and other machines for spray application

The spray heads have to be switched on and off at specified, precisely determined intervals in accordance with the shape of the parts to be painted. In addition, the spray jet width must be coordinated with the feed rate to ensure a uniform film thickness at the overlaps of the paint paths (see figure 4.2.107).

Apart from described automated systems **transverse reciprocators** with an appropriate horizontal direction of movement are also used for coating horizontal surfaces. Transverse and rotary movements can also be carried out for special applications in addition to the horizontal movement. This makes it possible to cover the outline of the workpiece uniformly at a constant distance.

In the automotive industry side and roof machines with several degrees of freedom represent the state of the art for painting with high-rotation bells.

Fig. 4.2.109
Picture of roof and side reciprocators for automotive coating with externally charged bells

Manual application at the front and rear parts of car bodies can now be dispensed with entirely because of rotatable horizontal automated systems. However, this machine cannot be used to coat concealed items such as lips or flanges, door entries and cavities.

The solution to this problem is offered by **painting robots** which can simulate the movements of the human arm. They consist of a manipulator, an electrical actuator unit and an electronic control unit.

Fig. 4.2.110
Paint robots at work

The manipulator can emulate all the movements of a human sprayer by means of five or six continuously operating electric drives. The actuator unit contains all the drive systems and sensors for monitoring movements. The electronic controller contains the robot's memory in the form of a computer program which enables a movement, once specified, to be repeated identically as often as required.

Programming, the ”teach-in” process, can be carried out indirectly or directly. In the former case a separate manual controller is moved to store the electronic data, and the data determined in this way is transferred to a program for the robot movement. In the direct teach-in method, the robot arm is moved by the programmer. The path movements are stored and then copied identically by the robot [4.4.82].

Additional process parameters such as the quantity of paint and the atomizing air must be programmed separately. Extremely precise and coordinated timing is required for the required volumes of air and paint. Delays of the order of mere milliseconds can result in paint defects or reduced quality in the paint finish. The exact position of the part to be coated is another important prerequisit.

There were also problems in the past with the use of robots with regard to limiting the masses to be moved. Robots were unable to move heavy guns or high-rotation bells with a high moment of inertia with sufficient accuracy and degree of reproducibility. New generations of robots and smaller bells now offer better conditions for successful processing with high-rotation bells on robot arms [4.4.83].

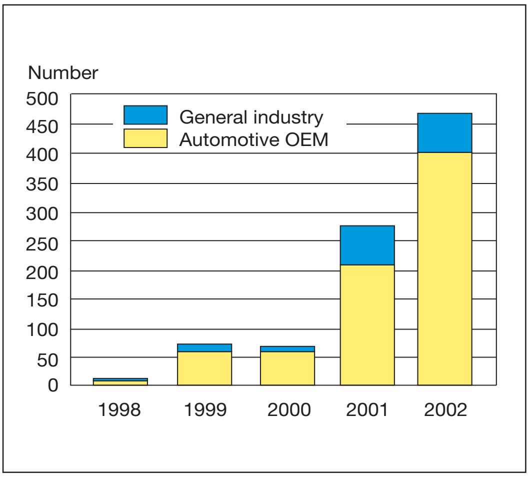


Fig. 4.2.111
Development of the amount of robots for industrial coating application of one selected manufacturer

A very high coating quality can be achieved with robots, provided they are properly programmed. However, constant material and ambient conditions have to be set to achieve this. The advantages that can be achieved with robots are significant. To constant film thicknesses, lower paint spill and lower material consumption can be added the opportunity to replace the painter completely. The availability of painting robots has now reached such high levels that the high capital costs are quickly offset by the advantages and savings. New painting lines for mass-produced coatings are now only built with robots.

4.2.1.7 Conveyors

Apart from application units, systems to eradicate overspray and supply systems for the coating materials, effectively operating painting lines also require conveyors. Their job is to convey the workpieces which are to be coated cost-effectively and reliably to the individual surface treatment units. Depending on the flexibility of the painting line and the type of parts to be painted, either straightforward circular conveyors or power-and-free conveyors are used as floor or overhead conveyors. Circular conveyors consist of a rail system, on which an endless chain fitted with hangers collects the workpieces, generally by means of a manual bracket, and then releases them again using the same method after they leave the final stage of the coating line. The chains in the rails run on idlers and are driven by infinitely adjustable motors. Depending on the particular system, conveying speeds of up to 15 m/min can be set.

It is a different situation with power-and-free conveyors. These consist of two conveyor rails located either underneath or next to each other. The power rail (forming a circular conveyor) which supplements the carrier rail (free line) enables objects to be

Fig. 4.2.112
Scheme and picture of a circular conveyor

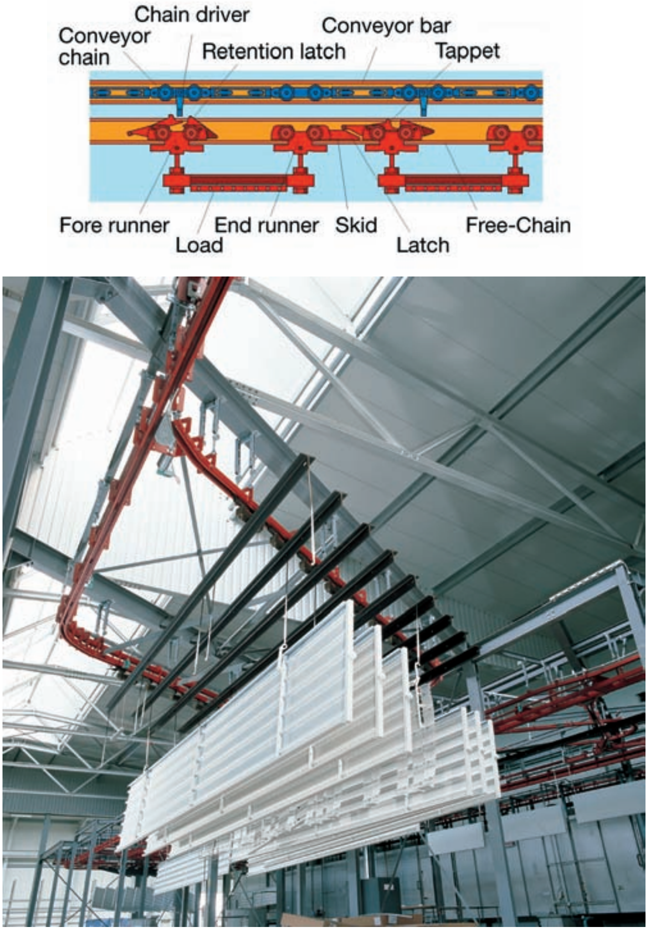


Fig. 4.2.113
Power-and-free conveyor

discharged from or added to the material flow by means of appropriate drivers without stopping the conveyors.

In this way buffer zones can be formed, and products returned for reworking can be diverted to another carrier rail. Furthermore, power-and-free conveyors make it possible to switch between continuous and batch operational modes [4.4.84]. A further advantage is that loading and unloading of the conveyors can take place after discharge while stationary or on a side path. In addition, the individual conveying processes can be automated using programmable logic controllers.

From the painter's point of view, conveyors are a potential hazard if the objects are conveyed in suspended form because of possible contamination of the still fresh coating. Paint defects in the form of craters or inhibited wetting can be caused by grease or oil particles falling from the lubrication of the conveyor rollers. Such faults can be avoided by using crater-free lubricants or installing guards.

As mentioned above, floor conveyors can also be used in addition to the usual overhead conveyors, depending on the specified task and the workpiece. These are either chains running in rail sections in the floor or induction loops which feed the generally large object to be painted on adapted carriages termed skids to the individual units. If only planar parts have to be conveyed, as in the woodworking and furniture industry, simple conveyors using rubber, synthetic or metal belts are adequate.

4.2.1.8 Paint Removal

A specific problem with spray application is the unwanted coating which is also applied to the conveyors, the booth walls and the grilles in the booth floor. Since the conveyors always enter a oven downstream of the application system together with the object to be painted, the paint deposits caused by straying overspray are also baked. This process is repeated regularly because the conveyors are circulating continuously. To ensure trouble-free operations, therefore, such paint must be removed from all parts of and equipment in the booths at regular intervals. Otherwise the paint film becomes so thick that operation of the conveyor system can be impaired or pieces of film flake off since they have become brittle as a result of repeated baking and are a source of contamination.
The cold removal of paint using solvents based on chlorinated hydrocarbons, which was frequently employed in the past, is only seldom encountered nowadays. It is a different story with hot paint removal using soda or caustic potash solution plus organic swelling agents. Because of the different chemical resistance coatings containing amino groups in particular such as cathodic electrocoats are treated in acid baths, with due observance of environmental legislation, while alkaline paint-removal agents are more suitable for baking enamels and 2-component polyurethane systems.
Furthermore, high-pressure paint-removal and pyrolysis (thermal paint removal) processes are also used. When removing paint by high pressure specially designed equipment is used which accelerates heated water at pressures of up to 1400 bar through fine nozzles such that mechanical separation of the coating is enabled.

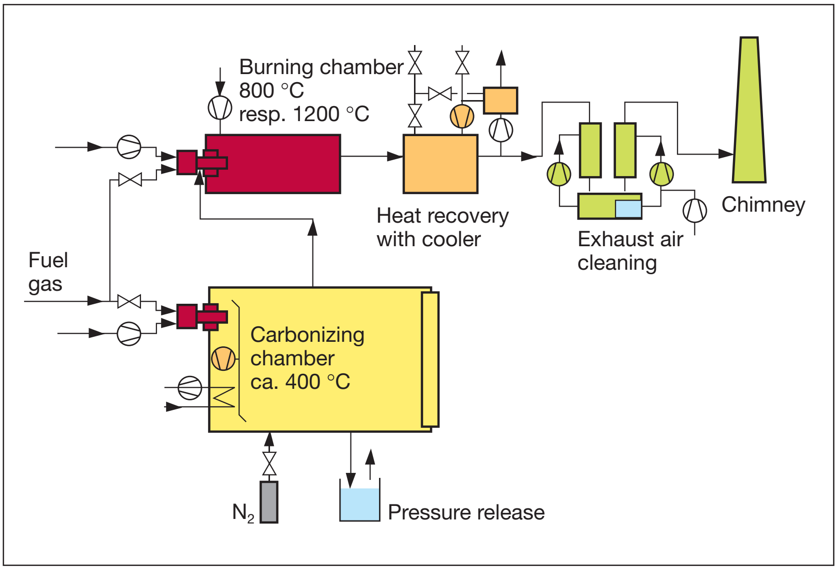


Fig. 4.2.114
Scheme of a thermal paint removal process with heat chamber

If the parts from which paint is to be removed are treated in advance with special primers, the subsequent paint-removal process is significantly easier. Primers with different coefficients of thermal expansion are sometimes used for this so that tension forms cracks once the coating cools down. If ultrasound is then also used, the coating largely falls off automatically. The cryo-clean process described earlier (see chapter 4.1.2) can also be used for the final paint removal.

Other primers contain water-soluble film forming agents or carbonate-containing extenders. The former dissolve easily in aqueous paint-removal processes, while the latter foam when heated and thus assist the paint-removal process.

As far as thermal paint removal is concerned, which is the most important process in industry, pyrolysis is initiated in chambers or fluidized-bed containers filled with aluminium oxide at temperatures of 400 – 500 °C. The resulting pyrolysis products are burnt in separate combustion chambers with heat-recovery systems and appropriately processed in compliance with environmental legislation by means of a subsequent exhaust air cleaning system. The recovered thermal energy is used for technical purposes. The advantages of the thermal paint-removal process are that it can be used for almost all paint systems and that it is at the same time inexpensive and environment-friendly.

4.2.2 Processing Powder Coatings

Unlike liquid coating materials, powder coatings are processed as solids before being melted in the baking oven to form films. Because of the lack of solvents the application of powder coatings causes almost no emissions. Furthermore, any overspray consisting of powder particles can be recovered and recycled to the process. From an environmental perspective, therefore, powder coatings are the most attractive alternative to many solventbased wet paints (see chapter 5.6.4).

Several methods are available for transferring the powder coating particles to the object. One way consists of using the fluidized-bed coating process to coat the objects which have been heated to above the melting temperature of the powder coating with fluidized powder as in the classic dip-coating process. In electrostatic powder coating the particles are electrically charged which causes them to fly along the field lines of a nonhomogeneous electrical field to the earthed object to be painted (electrostatic powder application). Furthermore, methods of processing the powder coating with the aid of a liquid medium have also proved successful. Aqueous dispersions in water (slurries) or in electrocoat paints (EPC) are two examples (see chapter 4.2.1 and 5.6).

Despite the major environmental advantages over other paint systems, powder coatings have not succeeded in gaining access to all areas of industrial coating. Excessively high baking temperatures mean that powder coating technology is unsuitable for thermally unstable substrates such as plastics and wood. However, the results of new research also give hope for a breakthrough in these sectors too, and so an additional increase in the already high growth rates can be anticipated in future [4.4.85, 4.4.86].

4.2.2.1 Retrospective

Powder coating technology has its origins in the German invention of the fluidized-bed coating method for processing thermoplastic powder coatings in 1952 [4.4.87]. The

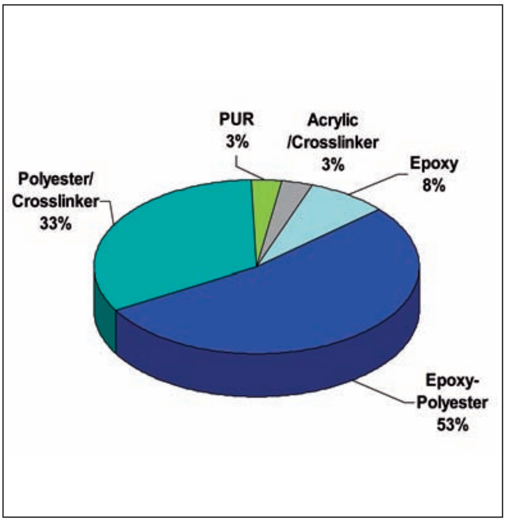


Fig. 4.2.115
Market share of resins for powder coatings in 2003

fluidized-bed coating method did not become an important process because of its excessive film thicknesses and the technology for the electrostatic processing of powder coatings developed a short time afterwards in the US. The launch of reactive powder coatings by Shell and further optimization in application and fluidization technology awakened renewed interest in Europe. As a result industrial applications increased, slowly at first but then steadily. It was not until 1969 that companies in the Far East began to look into the question of expensive polyacrylics under licence from various American paint companies. When US companies turned to epoxy resins and polyesters in the early 1970s, powder coating technology was already well established in Italy and Germany. Acid polyester, epoxy polyester and pure epoxy powder coatings were being successfully processed on an industrial scale. New resins and crosslinkers like acrylics and blocked isocyanates appeared recently. The technology seemed so mature at that stage that new applications for it were being sought even in the automotive industry. It was thought that classic powder coatings, slurries or EPC paints ought to make the so-called reverse process attractive, if used as primers (see chapter 4.2.1). These methods were in use for a short time but were discontinued again after just a few years.

Growth in the powder coatings market was only slight up till 1980. Up to that time application equipment were too expensive and film thicknesses were too high to be economically viable. Problems with color changes and high baking temperatures significantly limited the range of colors, effects and substrates. As environmental awareness grew, so too the application of powder coatings grew more than that of conventional paints. Today powder coatings have a worldwide market share of almost 10% with reference to solids content (see figure 5.6.8).

New fields of use and new powder coatings were discovered by intensifying and coordinating research activities for powder coating technology in Germany and in Europe as a whole [4.4.88] as well as in US. The coating of temperature-sensitive materials such as wood and wood-based substances became both technically and financially feasible thanks to new powder coatings in conjunction with radiation curing. Better powder-dispensing techniques, new knowledge on friction charging (tribocharging) and better booth designs have come from such knowledge. Powder coatings have therefore become more widely used. In the automotive industry they already enter the state of the art in terms of primer surfacers and clearcoats [4.4.89].

4.2.2.2 *Plant and Equipment Details*

Fluidizability is a fundamental prerequisite for handling powder coatings. This makes it possible to dispense powders using pneumatic pumps and to convey them in pipes. Fluidization is also, of course, an important condition for technical application processes.

Fluidization

Fluidization is used to mean the processing of the powder by using compressed air such that the resulting powder/air mixture is fluid, i.e. takes on liquid-like properties and passes into a conveyable state. Processing of the powder takes place in hoppers which are permeable to air but not to powder. However, special powder grades require horizontal vibration in the hoppers to ensure that fluidization can occur smoothly.

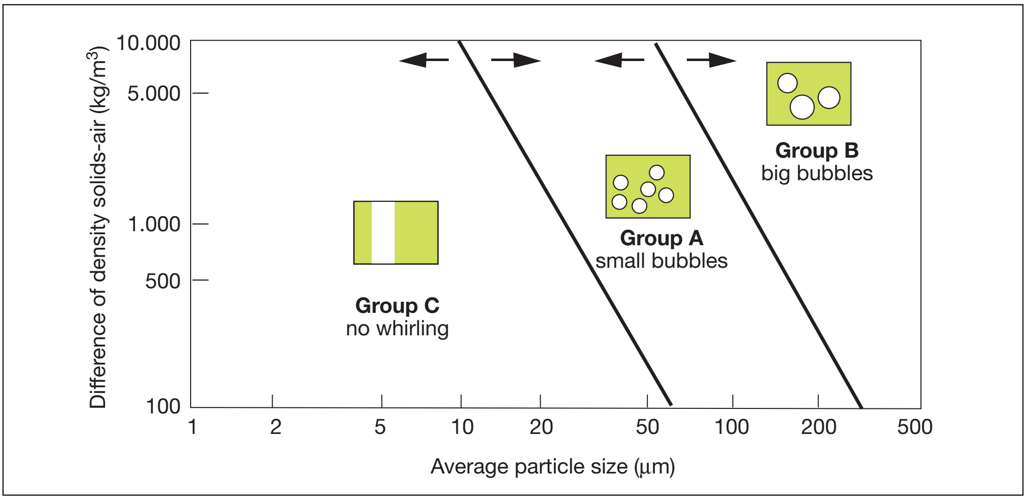


Fig. 4.2.116
Product characteristics of powder and their respective processing areas according to Geldart/Molerus

Powder coatings can be divided into three categories with reference to their fluidizability, as a function of their specific density and particle size as the essential physical properties. Group A is easily fluidizable, group C exhibits channelling and group B large blisters when air is introduced. The powders suitable for use in coating technology are mainly in the transition area between group A and C.

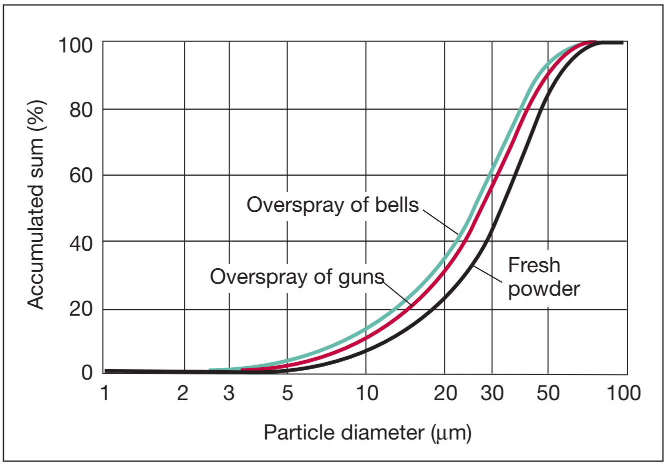


Fig. 4.2.117
Typical particle size distribution of industrial powder coating and related overspray

The usual particle sizes of powders which are suitable for application range between 20 and 45 µm. The particle size distribution is also of decisive importance for smooth handling and to ensure that the required range of film thicknesses can be achieved. The rule here is that the closer the distribution, the better the handling. The fractions with particle sizes of less than 10 µm are a negative factor in many cases. There is an excess of such fractions in overspray, and these shift the material's fluidizability towards the unfavourable channelling range during recycling. Furthermore, they have a marked tendency towards agglomeration

Powder transport and conveying

Powder coatings consist of solid particles and obey different laws from liquid paints in transit because of the necessity for fluidization. Different pipes and pumps from normal are therefore used for transporting the powder to the spray heads or returning the excess powder [4.4.90].

Because of the different requirements relating to precision when transporting powder coatings a distinction is drawn between precision conveying for the feed of the powder to the guns and mass conveying when transporting from container to container.

The entire powder-dispensing system for precision conveying consists of the storage container, a metering screw and the injector. The powder injectors are located in front of the spray gun and convey the powder coating at a constant feed rate from the storage container to the gun where it is then mixed in a defined manner with further volumes of air.

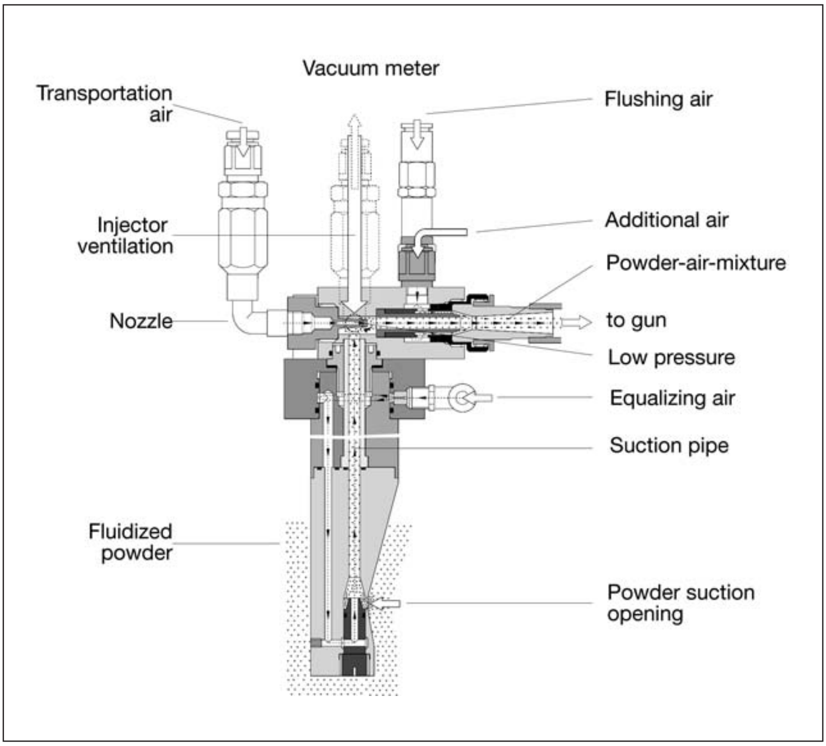


Fig. 4.2.118
Cross section of powder injector

Material is drawn up by means of a vacuum generated in a nozzle by accelerated conveying air. An appropriate quantity of powder coating is drawn up, depending on the air speed, and blown into the pipe to the gun. In order to guarantee a uniform powder discharge, the throughput must not pulsate when drawing up the powder. More or less supplementary air may be necessary to ensure uniform feed of the powder coating particles to the spray head, depending on the quantity conveyed. The length and diameter of the conveyor hoses, their positioning and the discharge height also have a significant impact on the powder transport.

Only 100 – 500 g/min have to be transported in precision conveying, but the system has to cope with up to 5 kg/min during mass conveying, so precise dispensing of the powder coating flow plays a subordinate role in mass conveying. Economical operation and gentle handling of the powder are more important. Screw conveyors, oscillating conveyors, but also high-performance injectors or powder pumps are used.

In a pulsating powder pump the powder drops out of a storage container into a pipe after the upper valve has been opened. After the valve closes and a second valve in the pipe opens the material is transported with a short pressure pulse lasting approx. 0.5 s. The valve is then closed once more so that the process can start all over again. Thanks to the pulse method used, the process requires little air so no additional filters or cyclones have to be installed at the end of the pipe.

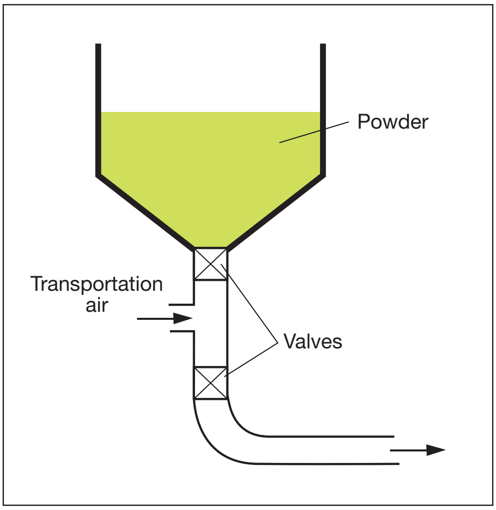


Fig. 4.2.119
Scheme of a pulsating powder pump

When being conveyed through hose lines, the powder can become electrostatically charged as a result of friction. The main factors influencing this are the materials from which the hose lines are made and their cross sections. Small cross sections require high flow rates when powder particles tend to cake onto the line because of frictional and impact effects. With large cross sections the air flow is often insufficient to maintain the powder in a fluid state for the full length of long hoses. This results in pulsating powder flows which naturally cause different film thicknesses.

Application of powder coatings

Despite the very high film thicknesses of the mainly thermoplastic coatings and despite introduction of other processing methods for particular applications, **fluidized-bed coating** has established a place as a niche application. It is a dip-coating method in which objects that have been carefully pretreated and heated in advance are dipped in a bath of fluidized powder coating. The air which flows into the bath from underneath via a screen fluidizes the powder. The fluidized powder coating comes into contact with the surface of the preheated parts onto which it is melted if the object temperature is high enough. A correspondingly thick film forms depending on the dwell time and, after being conveyed to the baking oven, this film can then melt and flow as a result of the

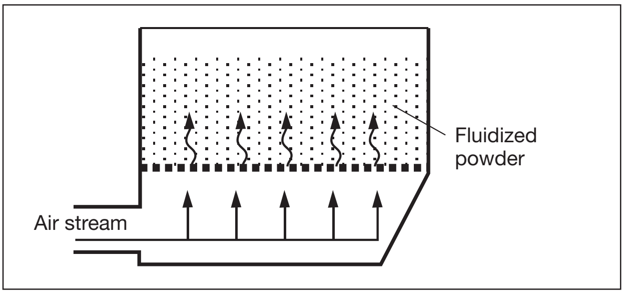


Fig. 4.2.120
Principle of fluidized-bed coating tank

further increase in temperature and can also become cross-linked when reactive powders are used.

Electrostatic coating with powder coatings is achieved by conveying electrically charged powder particles in the electrical field and subsequent deposition on the object to be painted by electrical forces.

The equipment required for this type of powder coating includes storage containers, supply systems, equipment for charging powder, spray systems and booths with units for extracting and recovering the overspray.

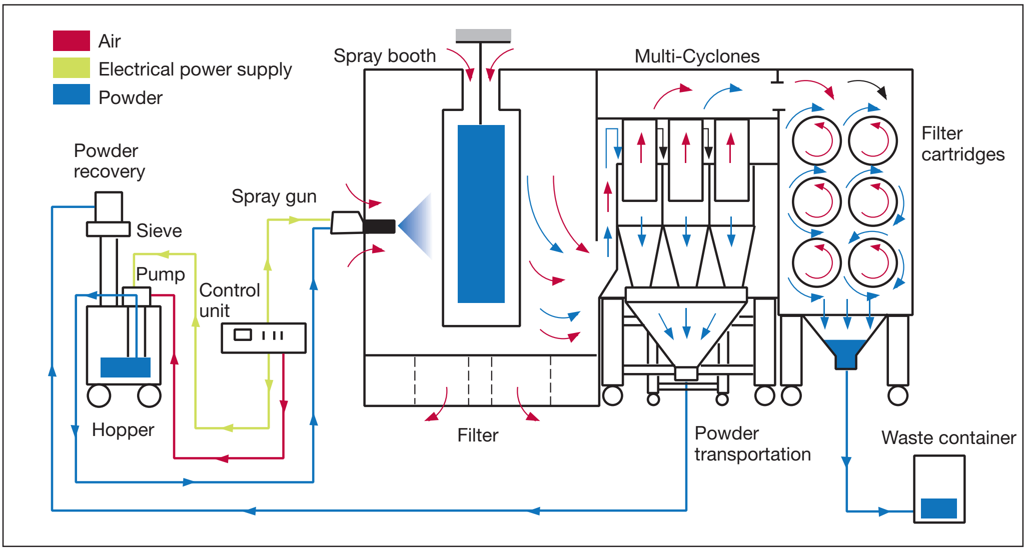


Fig. 4.2.121
Scheme of a powder coating unit with electrostatic application

Two mechanisms exist for electrically charging powder coatings [4.4.91]. The first involves generating air ions, which then attach themselves to the powder particles in an electrical field by means of corona discharge at peaked electrodes. The charged powder particles migrate along the field lines to the object to be painted which has the opposite charge.

For this commonly called "**corona charging**" most guns operate with external electrodes. The workpiece itself is the counter-electrode. The result is a high flow of electrons or ions to the workpiece which is to be coated. Since the powder particles are only charged when they leave the gun, there are only minor problems with soiling of the gun. With internal charging there is a charging electrode and also an earthing point installed within the gun. Consequently there are substantially fewer electrons available for the screening space charge. This results in better cavity coating (see figure 4.2.123). However, problems occur with soiling of the groun-ded electrode inside the gun. The size

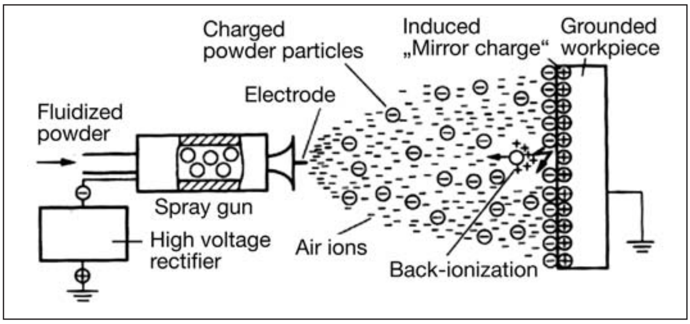


Fig. 4.2.122
Scheme of spray guns for powder application with external charging

and shape of the powder coating particles are also of particular importance for the charging process. In theory spherical powder coating particles offer the best conditions for a uniform charge. The bizarrely and irregularly shaped particles produced by today's grinding technology therefore result necessarily in non-uniform charges of the individual particles and thus to different deposition properties. The magnitude of the charge for corona charges is approximately in the range 4 – 12 µC/g.

The second method of electrical charging of the powder particles can occur as a result of friction on suitable materials and then require no electrical field. In this **tribocharge** generated by friction of the powder particles on a nonconductor with a different electronegativity electrons are exchanged between the two materials. Depending on the chemical nature of the paint resin and the plastic wall with which the particles come into contact, they are positively or negatively charged. The functionability of this electrokinetical method depends to a great extent on the nature of the film forming agent. With growing electron work function the tendency to attract electrons also in-

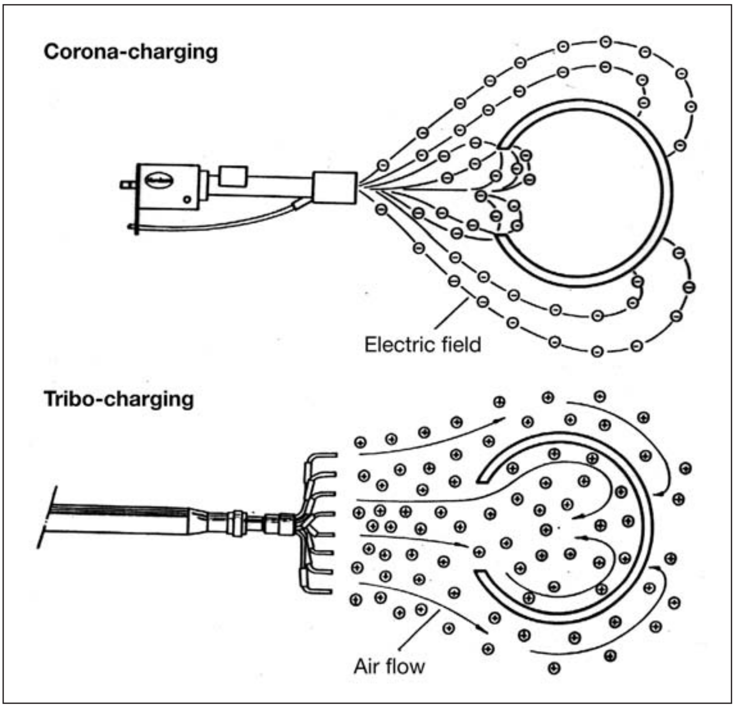


Fig. 4.2.123
Deposition of powder particles by corona charging and tribo-charging

creases (PMMA, PVC, PTFE). If, on the other hand, the ionization energy is low (PA, PPO), the material emits electrons more easily. The most important powder formulations are positively charged in tribo-application devices. In the spray heads with tribocharge the powder particles flow through a spiral insulation duct. As a result the powder coating particles are pressed against the walls by centrifugal forces and therefore pick up their charge in direct contact with the duct wall. If the thus charged particles are then brought into the vicinity of an earthed object by means of suitable spray heads, these form a discrete electrical field with the workpiece. If a charged particle is already in a cavity, it also forms a field there. By contrast with the processing of powder coatings with external fields, particle deposition is therefore also possible in cavities.

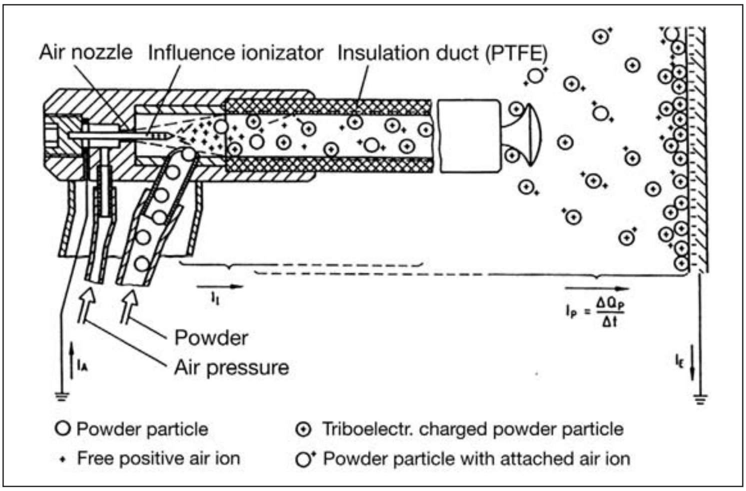


Fig. 4.2.124
Scheme of a gun for tribo-charging of powder coatings

There is only a small number of tribo-capable film forming agents, and this means that this will not become a widespread application. However, chargeability by friction can be improved by the use of additives such as aluminium oxide. In such formulations the dependence of the charge level on the relative humidity and the ambient temperature must be noted in the event of extreme conditions. The achievable powder particle charges by means of tribo-charging are approx. 2 – 10 µC/g.

There are a number of reasons for tribo-application only having achieved about 15% market penetration to date. On the one hand, not all powder resins are suitable for effective charging, furthermore there is the low performance as a result of the low material output. Finally, small particles are difficult to charge and process. As a result recyclability is limited. Because the particles are bigger than with electrostatic application good flow cannot be achieved for all uses.

Atomization of the powder coating is carried out in the usual spray guns by fanning the air current out with mouthpieces. These either contain jet impact plate systems with free swirl flow or are fan jet or finger nozzles. The use of bells rotating at 2,000 – 10,000 rpm is relatively new. They create a broad spray cloud and are therefore particularly suitable for large workpieces. The output quantity at up to 700 g/min is extremely high. Spinners in conjunction with an Ω-loop for the parts to be coated are a variant for the spray head design. The powder particles which are distributed horizontally to all sides form uniformly thick coats on the parts which are moved in a loop and also, if necessary, rotated about their own axis.

Unlike the guns, the atomization parameters of the spinners or rotating bells can be modified by means of the speed while in operation.

While the charged particles are on their **way to the object** electrical forces, gravity and air resistance act on them in the electrical field. The electrical forces must be greater than gravity so that the particles can largely follow the field lines to the object. These conditions are present with particle sizes of less than 100 µm. As a result of air friction the particles quickly become stationary. The migration rate is around 1 – 2 m/s.

Because of their lower overall charge smaller particles deviate from their path sooner than larger ones. They tend to be more readily collected by the recovery systems and do not reach the workpiece. As a result of this enrichment with the fine components, the recovered powder has a different composition from the sprayed material (see figure 4.2.117). To ensure a constant coating quality, therefore, a modified distribution profile of the particle sizes of the refill material is frequently set.

As a result of their high electrical resistance the powder particles which reach the workpiece during **deposition** only transmit a small part of their charge to the conductive, earthed object. The remainder of the charge remains on the particles until they enter the oven. This charge causes the formation by induction of opposite charges on the electrically conductive material surface after deposition on the object. As a result coulomb forces act in the form of image forces which hold the powder even on vertical surfaces (see figure 4.2.126).

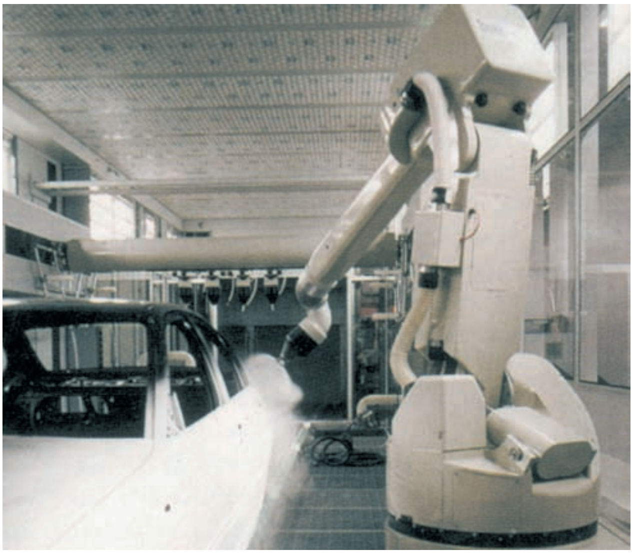


Fig. 4.2.125
Application example of powder coating atomization by rotational bells

When applying very thick powder coats, generally in excess of 150 µm, effects occur when a corona charge is used in the application which are attributable to the fact that a great excess of ionized air accumulates at the interface between the applied paint and the spray cloud. At a certain moment the breakdown potential is exceeded, discharging happens and creates bipolar particles which drift away from the substrate (“backionization“, s. figure 4.2.122). The quantity of air ions can be reduced by means of a supplementary electrode mounted on the atomizer. This collects the free charge carriers and thus instigates low-ion spraying. The action of this component, termed a counter corona or super corona, can be demonstrated by means of the current flowing from the substrate. It is smaller by a factor of 3 – 4. The powder charge itself is

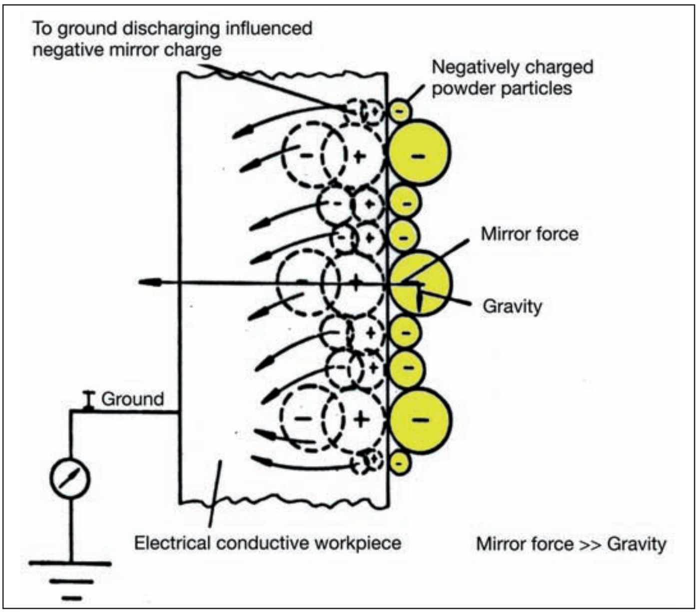


Fig. 4.2.126
Powder adhesion on conductive vertical substrates

unaffected, which can be seen in the same coating efficiencies of both processes. The surface quality is also considerably improved. Naturally, the re-ionization process just described does not occur with tribo-application.

Some applications can be found using the electromagnetic brush (EMB) technology. It provides a high speed application technique for thin films mainly on sheets [4.4.92]. EMB can be desribed as a roller coater for powder.

Recovery

Because the initial coating efficiency of powder coatings at 30 – 50% is low by comparison with liquid paints, reprocessing of the overspray, which therefore represents 50 – 70% of the paint used, is both economically and environmentally mandatory. There is no problem with this in terms of the properties of the powder material. Technically reliable recovery systems are available.

The overspray is routed out of the booths by gravity and the air flow which is directed vertically. Cyclones and plate, cartridge or bag filters are used for recovery. In **cyclones** the air flow which is charged with powder coating material is made to rotate by means of tangential feed. The rotation of the air can be enhanced by vanes. Centrifugal forces move the powder particles to the wall of the cyclone where they fall downwards because of gravity and are then gathered in a collecting container.

Application process	Current
Counter corona with 60 kV	7 – 8 µA
Corona with 60 kV	29 µA
Counter corona with 90 kV	11 µA
Corona with 90 kV	40 µA

Fig. 4.2.127
Effect of counter corona on current at the substrate with an polyester-epoxy-hybrid powder coating

The degree of powder separation depends on the particle size. Fine components are not completely recovered from the waste air stream by cyclones. Since the deposition efficiency reduces with increasing cyclone diameter, the air flow is divided in multicyclones into several individual flows. Horizontally configured multicyclones have also recently been incorporated directly in the booth wall (see figure 4.2.121).

Other methods of powder recovery are based on the use of plate filters. The plate material consists of sintered polyethylene with a porous polytetrafluorethylene coating which enables easy separation of the powder from the filter surface. The processes with filters

Fig. 4.2.128
Multicyclone for powder recovery

run discontinuously. The filters have to be cleaned once a certain amount of material has accumulated. With an admittedly high pressure drop separation levels of 99.99% can be achieved despite the high throughput. The very long service life compared with other filter media must, however, be seen against a relatively high price. Cheaper cartridge or bag filters not only have shorter service lives, they are also clearly less effective, with efficiencies of only 99.0 – 99.9%. Furthermore, they are more difficult to clean.

In order to ensure trouble-free operation of the painting line, agglomerates, foreign matter (dirt) and, if appropriate, the fine-grain component must be removed from the powder coating material recovered by cyclones or filters. If there is no foreign matter, simple vibrating screens are often sufficient, frequently used in conjunction with cyclones.

Turbo screens work on a different principle. The powder/air mixture is drawn through the screen by suction, and dirt and fibres remain on the screen surface from where they have to be removed manually. Turbo screens, vibrating screens and ultrasonic screens are suitable for operations involving color changes because of their good cleanability.

Centrifugal and tumble screens are suitable for continuous operation. In the former, the powder coating particles are routed to the cylindrical screen jacket by means of rotation. Dirt and screen oversize are continuously removed from the screen by a device and collected at the end. The operation of a tumble screen is similar. Several screens of different mesh size move such that the powder falls through the screens in a tumbling motion. The individual fractions collect at the edges of the individual screens in corresponding collecting channels.

Powder booths

Trouble-free powder coating processing which also complies with occupational health and

Fig. 4.2.129
Ultrasonic screen for powder regeneration

safety legislation requires the units for feed, application and powder recovery, and also a booth which is operated with underpressure. This primarily serves to prevent the escape of the powder into the environment and enables controlled air feed for recovery. Furthermore, this avoids the flammability limits for the powder/air mixture being exceeded. Supplementary conditions have to be met because of the risk of explosions and fire when processing powder coatings with high voltages (see chapter 5.2.4).

The booth walls are made of steel, stainless steel or plastic. Steel booths are inexpensive and easy to assemble and meet all safety regulations without difficulty. The disadvantages are the susceptibility to soiling and the cost of cleaning after every color change. The advantages in this regard are smooth, joint-free plastic walls. Because of the poor electrical conductivity these repel the powder. The use of plastics as the housing material makes compliance with the relevant safety regulations more difficult.

The same applies to pipes as for the booth material. Plastic pipes must also be earthed because of the danger of brush discharges.

Fig. 4.2.130
Picture of a powder application unit for industrial coating

Manually operated equipment is only rarely found in industrial powder-coating booths for technical and safety reasons. The guns are introduced into the booth through slits on powered arms and operated from outside. The powered arms also ensure uniform distribution of the powder over the workpiece. At the same time the number of guns necessary for a uniform film thickness is lower than in a static configuration. The speed of vertical movement of the powered arms should not exceed 0.5 m/s in order not to cause coating defects arising from turbulent air flow.

Color changes in powder-coating booths require significantly greater input than when processing wet paints. It is not only the booths and pipes which have to be designed such as to make cleaning easy; the power-supply centre and the filters or cyclones for powder recovery must also be appropriately designed.

Many of the cleaning stages can only be carried out manually. The booth walls are air-blasted in two stages for periods of 5 – 6 minutes and then wiped down with sponges. In addition, the guns and hoses must be cleaned, and the immersed pipes and injectors must be blasted through. The control devices for the application equipment are usually located outside the booths, and so they do not have to be cleaned in the event of a color change. As a result, it is possible to carry out a color change nowadays in less than 20 minutes.

With appropriate investment in several interchangeable booths color changes can be carried out without any production downtime [4.4.93].

4.2.2.3 Powder Coating Materials

Powder coatings consist of thermoplastic or reactive polymers which are solid at room temperature. Today thermoplastic powders are only used to a very small extent in the fluidized-bed coating method for thick coatings.

Most powders are reactive one-component systems which liquefy, flow and then crosslink as a result of treatment with heat. The most common film forming agents are epoxy resins, epoxy resin-modified polyesters, pure polyesters with hardeners containing epoxy groups or blocked isocyanates and acrylic resins with various crosslinking agents. Epoxy resins are used for the formulation of primer powders. Such powder coatings feature excellent anticorrosive protection and good mechanical/technical properties. They can be cured with dicyandiamide or polycarboxylic acids (see chapter 2.1.1). The marked tendency of pure epoxy resin powders towards yellowing and their low resistance to longterm outdoor exposure are disadvantageous. The group of epoxy-polyester powder, often also termed hybrid powder coatings, is a mixture of epoxy resin and acidic polyester resin. The mixing ratio can range from 1:1 to 1:9 in favour of the polyester. Hybrid powder coatings feature excellent mechanical/technical properties. The tendency towards yellowing and chalking is lower than with pure epoxy resin powders. The hybrid powders are inadequate for stringent longterm outdoor exposure specifications. In such cases polyester or polyurethane powders should be used. Polyester powder coatings consist of acid polyesters together with a low-molecular hardener (see chapter 2.1.1). Triglycidyl isocyanurate (TGIC), which was successfully used in the past, has been replaced by toxicologically safe alternatives because of the suspicion of mutagenic effects. Glycidic esters of isophthalic acid or β-hydroxyalkylamides of adipinic acid can be used as replacements for TGIC. If weather-resistant, mattable surfaces are required, polyurethane powders based on OH-functional polyesters and capped isocyanates are suitable systems. The hardeners which are capped with ε-amino-caprolactam release the capping agent in the baking oven and contaminate the waste air from the oven, so the exhaust air has to be treated. Uretdiones do not have the disadvantage of forming cleavage products and are therefore gaining increasing prominence.

Acrylic powders were unable to establish any major application fields in the past despite their excellent resistance to longterm outdoor exposure and good flow. It was only once the use of clearcoats for sealing metallic basecoats in the automotive sector became settled that acrylic powder coatings began to compete with the other powder types. The acrylic resins used in those formulations contain glycidylmethacrylate and react with carboxyl-functional crosslinkers.

Powder coatings are also processed in the automotive industry in the form of slurries which have the same chemical basis but are dispersed as microfine powders in water. Their curing temperature is rather low at 140 °C (see chapter 5.6.3).

The rheological properties of powder coatings can only be influenced to a limited extent because of the lack of solvents. The processing properties are therefore largely determined by the film forming agents. The molecular weight, molecular shape, polarity and reactivity determine the viscosity and shape the entire flow phase. The temperature control in the oven in conjunction with the viscosity profile of the powder coating is one of the most important process-engineering variables to ensure a smoothly levelled, sag-free coating. In the interests of good flow the viscosity should reach its minimum as

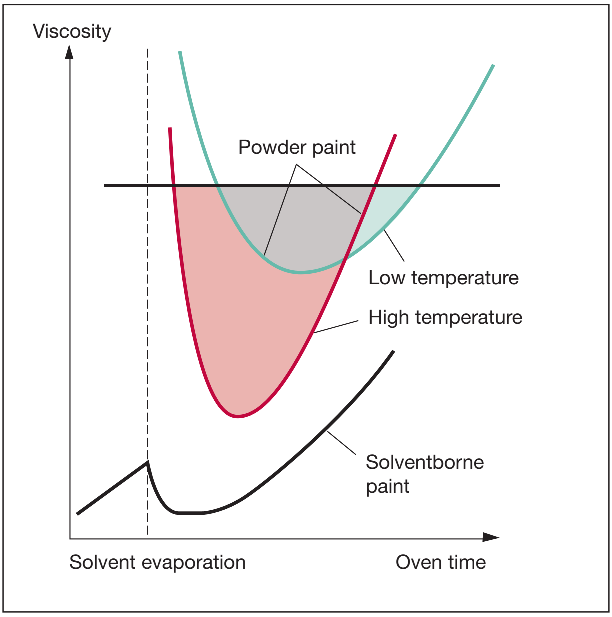


Fig. 4.2.131
Rheology profile of powder coatings depending on temperature rise in baking ovens compared to solventborne paints

quickly as possible as a result of the rise in temperature and remain at this level for a sufficient time. The minimum viscosity level and curve of the viscosity rise initiated by crosslinking are decisive factors in achieving good flow.

The practice of using the time which a powder melt spends below the target viscosity as a criterion for the flow properties has proved useful. The area marked in figure 4.2.131 is termed the fluidity integral and is a characteristic feature for the flow of powder coatings (see chapter 3.1.4).

Powder coatings include large volumes of air during application. This air has to escape during melting and before crosslinking. Benzoin and its derivatives are suitable as additives for this purpose. Aluminium oxides or pyrogenic silicic acids are used to set and maintain the flowability for trouble-free processing. Aluminium oxides also have an impact on the chargeability of the powder particles.

4.2.2.4 Powder-Specific Test Methods

Because of the specific properties of powder coatings many of the proven test methods for wet paints cannot be used. As solid powders, powder coatings obey different physical laws when being processed (see above). Properties such as gel time, flowability, fluidizability, bulk density and bulk volume are significant physical variables for storage, transport and processing. Since these properties, just like the flow of the already applied material, are also a function of the particle size or particle size distribution, this variable must also be called upon when describing the application properties of powder coatings (see chapter 2.3).

Gel time and Tg

When using powder coatings the specified storage and transport conditions should be observed. Temperatures above 30 °C cause agglomeration of the powder particles and preliminary chemical reactions. Low temperatures prevent this and therefore ensure stable flow properties over a period of 6 – 12 months, depending on the powder type.

Preliminary crosslinking can be tested by reference to the gelling time, the measurement method for which is described in ISO 8130-6. However, preliminary reactions which took place during manufacture or storage can also be quantified by thermal analysis methods such as DTA or DSC. Shifts in the glass transition temperature Tg and a reduction in the reaction enthalpy are regarded as indicators of inexpert treatment of the powder coatings during manufacture and storage.

Flowability

As in the viscosity measurement with liquid paints, a certain quantity of powder passes a defined aperture in a fluidization hopper. The discharge time is used as an indicator of the flowability. The volume required to fill the hopper is weighed in advance and converted into the bulk density as an additional indicator.

Fluidizability

Fluidizability is the most important quality-determining variable when evaluating processing properties, with particular reference to transport, dispensing and fluidized-bed coating. A certain amount of the powder coating in accordance with the load requirements is fluidized in a glass cylinder by an air current (determined by the air pressure) flowing through a porous base plate. The resulting depth of the fluidized powder, relative to the original depth h_0, is then a measure of its fluidizability. Since the results depend to a great degree on the equipment and conditions, precise and detailed agreements must be drawn up between customers and suppliers.

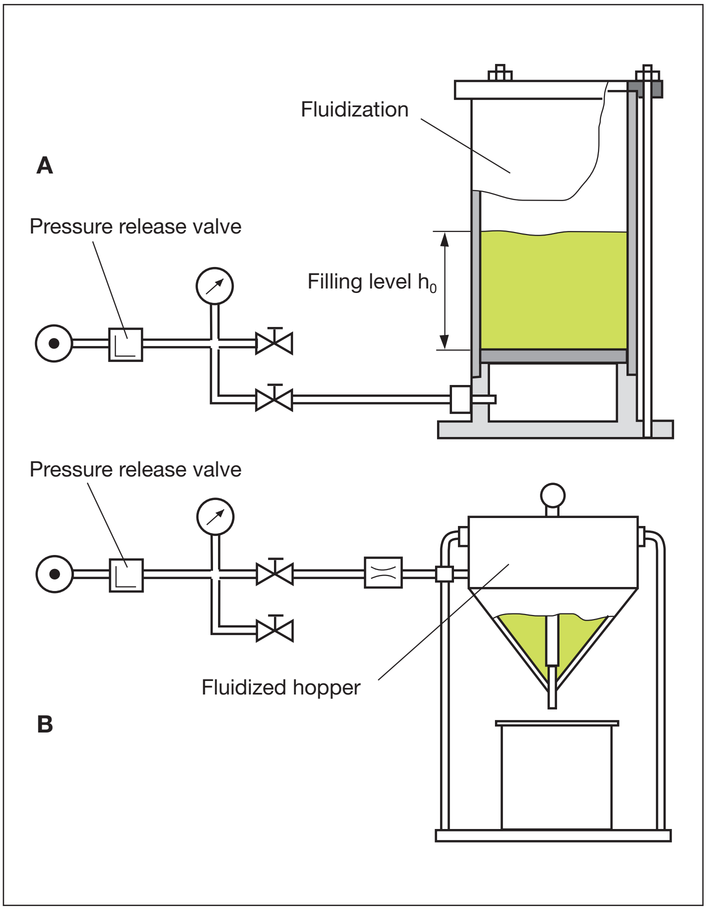


Fig. 4.2.132
Instruments for testing the workability of powder paints: fluidization (A) and flowability (B)

Good online characterisation of the fluidization state for process control is possible by measuring pressure fluctuations in the fluidized bed. The occurrence of gas bubbles creates pressure fluctuations at a piezoelectric pressure transducer which, when processed as a standard deviation, yields a characteristic value for the degree of fluidization. Different curves are produced for the different levels of fluidizability as a function of the gas speed of the air flow.

Chargeability

The time-dependent pick-up and release of electrical charges are specific properties for electrostatic powder processing. Chargeability with a high voltage connected and tribocharging have to be examined. Since the electrical resistance of the powder material is linked to its chargeability, this easily measured variable is used as an indicator. A resistance-measuring cell, a high-resistance ohmmeter and a plotter are required for measurement purposes. The resistance-measuring cell itself consists of an insulated inner cylinder with an electrode. The electrically insulated outer sleeve contains the second electrode. After pouring the powder into the electrode interspaces and connecting a voltage of 1000 volts the resistance is read or recorded at various times. The final value after 5 minutes is defined as the measured reading.

Powder coatings with a specific resistance of more than 10^{14} Ω·cm are regarded as very suitable for electrostatic processing. At low resistances the coatings are thinner, and the influence of the relative humidity results in low stability of the image forces. Powder coatings with specific resistances of less than 10^{12} Ω·cm are therefore unsuitable for electrostatic processing.

Tribo-chargeability is measured using similar apparatus to that employed for measuring flowability. The charge Q is determined as the product of the current I and time t. If currents of more than 1.5 µA are flowing, the powder coating is well capable of tribocharging. The transmissible, charge per unit mass Q/m is also used as a further characteristic value. To ensure good tribo-charging properties the charge transition per unit mass should always be in excess of 0.5 µC/g.

4.2.3 Summary

A number of methods have proved successful for processing coating materials. Depending on the size and nature of the objects to be painted, the coating speed and the desired quality of the coating dip, curtain, flood, roller or spray coating are suitable paint application methods.

Among dip-coating methods, electrocoating has gained acceptance worldwide for metallic objects because of its environmental and economic advantages. Whereas flood- and curtain-coating systems are encountered in only a few areas of coating technology, spray systems can be found in every sector. The advantages of this application method are its ability to coat intricate objects of complex shape and the rapid color changes possible. However, the optically attractive coatings with various effects must be weighed against the disadvantage of the high material spill. Spray systems use pneumatic, hydraulic, electrical or centrifugal forces caused by rotation to atomize the paint. Spray systems for industrial-scale paint processing require a broad range of peripheral systems to supply material, energy and air and the appropriate equipment for disposing of the overspray and scrubbing the waste air.

Roller coating has a particular attraction because of the opportunity to precoat planar coiled sheet metal which is only later formed into consumer goods. The concentration of surface processes in just a few large systems with high coating speeds and little environmental pollution means that coil coating is becoming ever more important.

Apart from the range of application processes for liquid paints there are also methods for processing coating materials in the form of solvent-free solid powders. The nonstick particles can be recovered without difficulty if they miss the object to be painted and can then be recycled into the process. To date powder coating technology is only successful for thermally stable painting substrates and from an environmental perspective it is the most attractive alternative to conventional coating technology with solvent-containing liquid coating materials. New research results on the rheological properties of powder coating melts and new plant-engineering knowledge mean that powder-coating technology is also of interest for thermally unstable materials such as wood and plastic. These potential new applications give hope for above-average growth rates. If the film thickness, which is still too high for good flow properties, can be reduced without any loss of optical attractiveness, the overall economic balance will also be positive compared with all other conventional coating technology alternatives.

4.3 Drying and Curing

The physical and chemical principles of film formation were introduced and explained in chapter 3.1. The film forming process is a mass-transfer process involving the emission of solvents in conjunction with chemical reactions in the case of crosslinking systems. Both processes are accelerated or initiated by heat input. In the case of curing liquid paints with organic solvents or water it is necessary to ensure that removal of the volatile components is as complete as possible and that the polyaddition or polycondensation reaction is accelerated by thermal initiation. The heat transfer necessary for this is achieved by heated air in the case of convection drying or by irradiation with electromagnetic waves in the IR range.

Paints which cure by means of polymerization reactions do not require any heat transfer. In such cases short-wave UV or electron-beam radiation is suitable for initiating the chemical crosslinking reaction. The paints formulated for this would emit the most volatile polymerizable reactants if heat treatment were used and result in completely different coatings.

If the coating is carried out in systems in which thermal energy is transmitted by means of IR radiation, heat conduction or convection heat for curing with physical drying at the same time, these are ovens. If heat or short-wave radiation without accompanying emission of solvents, as in the case of radiation curing, for example, is the only cause of film formation, these are curing systems.

In the case of thermal curing, heat and mass transfer are the sensitive variables which can influence the final coatings properties [4.4.94]; in the case of radiation curing it is the formation of start radicals by means of high-energy radiation which initiate the double bonds in the film forming agents or reactive thinners.

4.3.1 Film Formation by Heat Transfer

Heat transfer to organic substances such as paints results in the molecules of the paint components absorbing energy by means of oscillations, extensions or rotary motion. If the energy input is sufficient, they can cross the boundary between the solid, liquid and gaseous states. Chemical reactions continue to be accelerated by molecular excitation.

4.3.1.1 *Theory*

Since mass and heat transfer are intended to be economical and environmentally compatible, there are certain requirements relating to the design and operation of ovens. Particularly effective heat exchange is required which also takes account of the different specific heats and thermal conductivities of the individual materials and the design of the workpiece such that uniform heating of the painted object and thus uniform coating properties are possible.

A straightforward calculation of mass and heat transfers is only possible if certain restrictions are imposed. Because of the dynamic processes of heat and mass transfer in the ovens either only short periods are examined without any significant shifts in concentration and temperature or a calculable stationary state is created by permanently loading a continuous-flow oven. Overall balances of mass and heat transfer can be determined in this way without having to address the changing conditions with reference to the individual object.

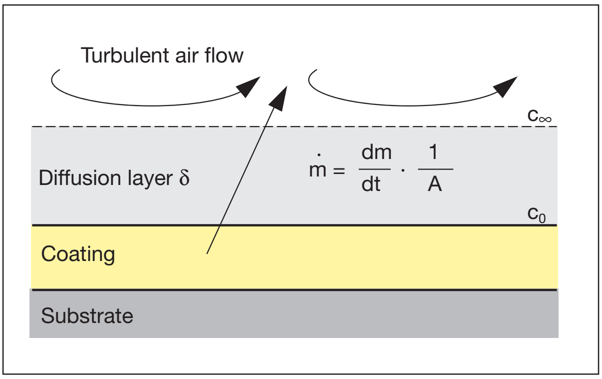


Fig. 4.3.1
Exchange of material transfer by diffusion

To calculate the **mass transfer** of solvents the rate of emission $\dot{m}$ is determined, over short periods, by means of the difference in concentration in the vapour immediately at the coating surface c_0 and the turbulent environment in the convective vapour c_∞. The mass flow $\dot{m}$ per unit area A is defined as:

$$\dot{m} = \frac{dm}{dt} \cdot \frac{1}{A}$$

This mass flow per unit area $\dot{m}$ is proportional to the difference $c_0 - c_\infty = \Delta c$. In this c_0 is particularly high if high temperatures increase the kinetic energy of the solvent molecules such that a large number of molecules overcome the enthalpy of evaporation. The proportionality factor between $\dot{m}$ and Δc is defined as the mass-transfer coefficient β.

$$\dot{m} = \beta \cdot \Delta c = \frac{D}{\delta} \cdot \Delta c$$

The comparison with *Fick*'s First Law explains the physical importance of the mass-transfer coefficient. It is the quotient of the diffusion coefficients of the solvent D and the thickness of the laminar diffusion layer δ. This variable, which determines the rate of mass transfer with convection drying, can be reduced to a thickness of just a few µm by means of artificial air movement in the vapour chamber. Large mass flows can therefore be set by means of large differences in concentration Δc and a thin laminar interface. This is practically the case with high air speeds and high temperatures at the same time. The former lowers the thickness of the laminar interface. The latter increases the

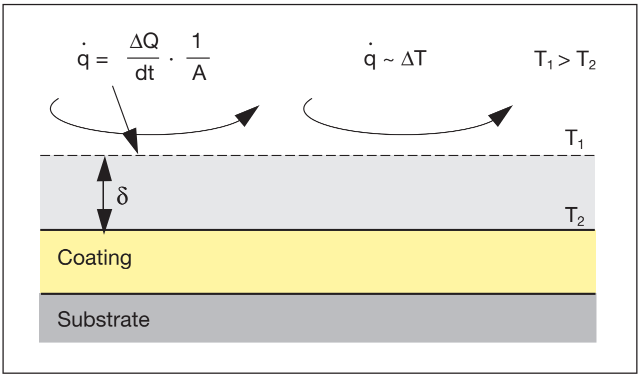


Fig. 4.3.2
Mechanism of heat transfer during drying in convection ovens

vapour pressure and thus the concentration of the solvents at the interface. For the reasons cited, nozzles and air showers are installed in technical ovens in order to meet the target air speeds of up to 15 m/s.

Although the temperature and speed of the air define the drying process, they are limited in terms of their settings by potential film defects such as dirt transfer, matting and pinholing (see chapter 6.2). Excessively rapid film hardening during drying and crosslinking makes it harder for solvents to move to the interface. Low film thicknesses in the coating are therefore beneficial in ensuring complete mass transfer (see chapter 3.1). Rapid heating also initiates or accelerates the rate of chemical reactions. Film forming processes are therefore enhanced not only physically by the input of thermal energy. Efforts should also be made to achieve rapid **heat transfer** in the oven.

The transfer of heat to paint films can be achieved in three different ways. The usual indirect method consists of heating gases, generally air. The heated air transfers only thermal energy to the colder object to be painted. The carrier gas cools down itself in the process and, to ensure ongoing heat exchange, has to be constantly reheated. Ovens which use artificially circulated air as the carrier gas are termed **convection ovens.** If a solid with a higher temperature is brought into direct contact with a colder solid such that heat can flow directly via thermal conduction into the colder object, this is referred to as heat transfer by **conduction**. Furthermore, it is possible to excite molecules in the coating material or in the substrate to oscillate by means of **infrared rays** as electromagnetic waves and to transfer thermal energy without contact or interaction with any heated material.

Because of the turbulent air circulation in the case of convection ovens the temperature gradient necessary for heat transfer is only found at the extremely thin laminar interface between the object and the surrounding gas space. Here, by contrast with the adjacent turbulent air flow, heat is transferred from molecule to molecule by molecular impact. The thickness of the laminar interface therefore also determines the rate of energy flow. The aim for heat transfer, as with mass transfer, must be to keep this layer particularly thin. The time-related heat flow per unit area $\dot{q} = dQ/dt/A$ is proportional to the temperature difference ΔT:

$$\dot{q} = \alpha \cdot \Delta T$$

where $\alpha = \lambda/\delta$. For its part the heat-transfer coefficient α contains the thermal conductivity λ of the air and again the film thickness δ which cannot be directly determined experimentally. As already mentioned, the thickness of this interface can be influenced by the speed of the carrier gas.

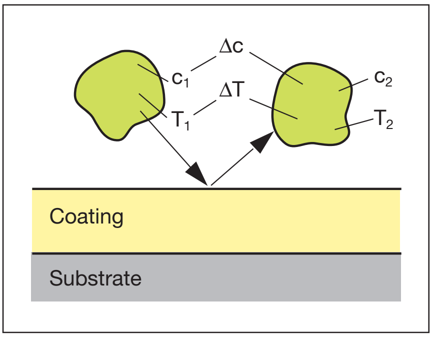


Fig. 4.3.3
Mass and heat transportation during drying by convection

When designing ovens, knowledge of the correlation between the mass-transfer coefficient β and the heat-transfer coefficient α is important. Looking at these transfers mechanistically, the following model can be assumed. When the turbulent air meets the coating numerous tiny vortices interact with the coating surface, transfer their heat energy and remove the solvents from the diffusion interface.

The concentration of the solvents in the oven air corresponds to the solvent mass included in the volumetric flow rate:

$$\Delta c = \frac{\dot{m}}{\dot{V}} \quad \text{or} \quad \dot{m} = \dot{V} \cdot \Delta c$$

Since $\dot{m} = \beta \cdot \Delta c$ also, it follows that β is identical to $\dot{V}$ in the present case. Since the heat transfer $\dot{q} = \alpha \cdot \Delta T$ can also be calculated from the volume of circulated air, it follows that:

$$\alpha \cdot \Delta T = \dot{V} \cdot \rho \cdot c_p \cdot \Delta T \quad \text{or} \quad \alpha = \dot{V} \cdot \rho \cdot c_p$$

$$\text{or} \quad \alpha = \beta \cdot \rho \cdot c_p \text{ , because } \dot{V} = \beta$$

Mass and heat transfers are thus directly proportional, as expected.

The thermal energy transferred to the surface of the object to be painted results in the surface being heated up and thus in a temperature gradient relative to the parts of the object which are not accessible for heat transfer. This causes the initiation of a heat flow in the object itself which is proportional to the temperature gradient ΔT in the object.

$$\dot{q} = \frac{\lambda}{\Delta x} \cdot \Delta T$$

where λ is the thermal conductivity of the solid to be heated.

If the thermal conductivity is high as in all metals, the thermal energy flows relatively rapidly from the transfer point to the colder parts of the painted object. The heat flow rate decreases with increasing distance Δx.

The situation is different with plastics. The considerably poorer thermal conductivity results in the outer areas heating up quickly. Continuation inwards is hindered by the low thermal conductivity. The risk of overbaking the outer part of the coating with simultaneous undercuring in the internal areas cannot be discounted.

Differences in the temperature profile of objects of complex shape occur not only as a result of differences in the heat transfer and thermal conductivities. Differences in the object temperatures are also bound to occur with rapid heat flow and uniform energy distribution if different-sized masses have to be heated up in the individual areas of components of complex shape. Rocker panels of cars have a greater mass than the thinner panels used for the roof.

Since the quantity of heat transferred in the oven by the air

$$\dot{q} = \dot{V}_{air} \cdot c_p \cdot (T_1 - T_2)$$

is equal in both cases, it follows for part A in figure 4.3.5

$$\dot{q} = m_A \cdot c \cdot \Delta T_A$$

and for part B

$$\dot{q} = m_B \cdot c \cdot \Delta T_B$$

As with the different masses m_A and m_B so the temperature difference ΔT_A is different from ΔT_B.

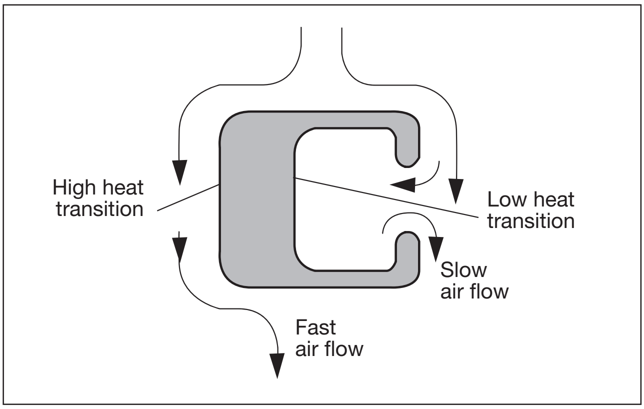


Fig. 4.3.4
Reasons for temperature differences of complicately shaped parts

Irrespective of the heat-transfer method, it is still not possible, despite great efforts, to set identical temperature profiles at all parts of the forming film for the entire time because of the sometimes complex design of the object to be painted and the associated different energy transfer. Despite this, no or only negligible differences in the coating quality to be achieved under those conditions are permitted. In other words, the time-related and local fluctuations in the process conditions may not exceed an agreed tolerance.

An important term in the context of the drying process is the processing window of the coating materials. This provides information on the processing tolerances within which the specifications can be met.

A large processing window for paints means that a constant quality can be achieved despite fluctuations in the oven conditions. The area of specification compliance in the temperature/time graph for drying can be cited as a measure of the processing window in the oven.

Since hardness and scratch-resistance are deficient in the case of underbaking, i.e. at too low a crosslinking level, and elasticity is impaired in the case of overbaking as a result of an excessively close mesh density in the highly crosslinked resin molecules, the limit curves for the admissible drying conditions can be determined experimentally by specifying the minimum acceptable hardness and elasticity. The tolerance band between over- and underbaked films decreases with decreasing drying time. Shortening the drying time by increasing the temperature is then no

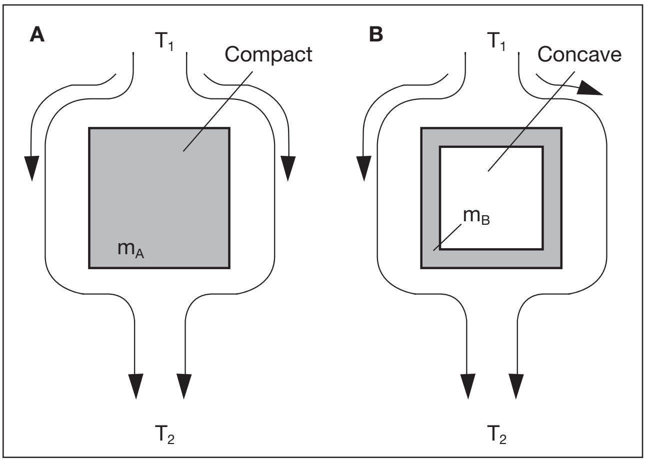


Fig. 4.3.5
Heating of same-shaped parts A and B of different masses

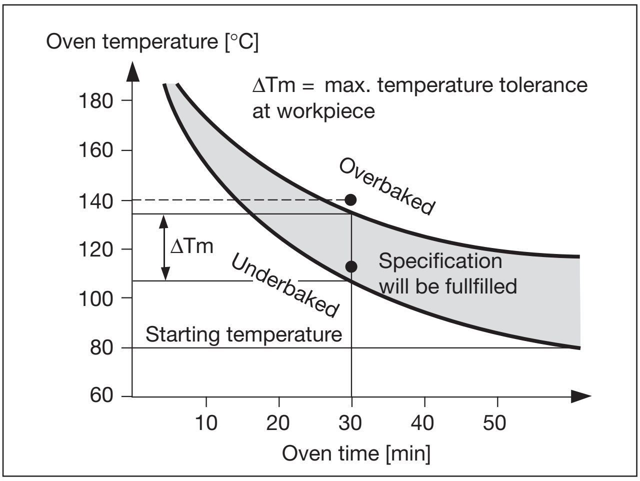


Fig. 4.3.6
Typical curve of operating window of baking enamels for convection ovens

longer possible since the temperature spread on the object to be painted exceeds the permitted temperature interval. The outcome is that the object exhibits areas of both under- and overbaking.

The temperature tolerances for the permitted range of drying conditions depend not only on the paint systems, but also on the different colors. The pigment type and, particularly, the pigment quantity have an impact on hardness, but also on adhesion and elasticity. Knowledge of the processing window enables predictions to be made relating to the reliable and economical processing of a new color before the paint is even used (see chapter 6.3).

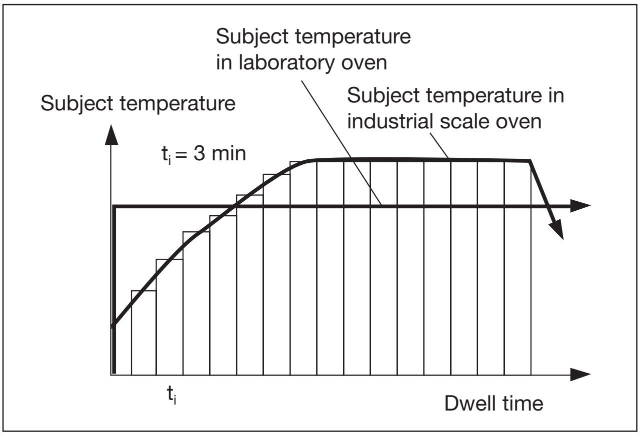


Fig. 4.3.7
Transfer of temperature profiles from industrial ovens to laboratory ovens

In the event of a necessary change in the baking conditions the time/temperature curve which is usually determined empirically for optimum crosslinking can be recalculated for other baking times or temperatures, if the activation energy ΔE_A is known. If, for example, the optimum baking temperature T_1 is known for a particular baking time t_1 which is determined by the throughput time in the oven, it is possible to calculate the baking temperature T_x which has to be set to achieve an identical degree of crosslinking or an identical coating quality if the baking time is shortened to t_x:

$$\ln\left(\frac{t_x}{t_1}\right) = \frac{\Delta E_A}{R} \cdot \left(\frac{1}{T_x} - \frac{1}{T_1}\right)$$

The above formula can also be used if the sometimes complex oven curves for production ovens have to be transferred to laboratory ovens. The oven curve is divided into several segments with the same throughput time to this end. Thus 10 segments each of 3 min are usual for total throughput times of 30 min.

The drying times t_0 in the laboratory oven corresponding to the individual time intervals of three minutes are calculated by

$$\ln\left(\frac{t_i}{t_0}\right) = \frac{\Delta E_A}{R} \cdot \left(\frac{1}{T_i} - \frac{1}{T_0}\right)$$

where T_i represents the relevant average temperature in the individual segments of the large-scale oven. The sum of all t_i then yields the total drying time in the laboratory oven for a specified constant baking temperature T_0.

The object temperature increases with increasing dwell time in the oven as a function of the rate of heat transfer and the rate of heat flow in the painted object. The thus permanently decreasing ΔT between the circulating air and the object to be heated results in retardation of the rate of heat transfer. In order to reach the required object temperatures nonetheless in an appropriate time, it is helpful to set circulating air temperatures in the initial section of the oven higher than the desired maximum temperature of the object, depending on the paint system. Such operating conditions can only be managed provided no faults occur in a continuous system. If the belt were to come to a stop, this would lead to overbaking of the coating.

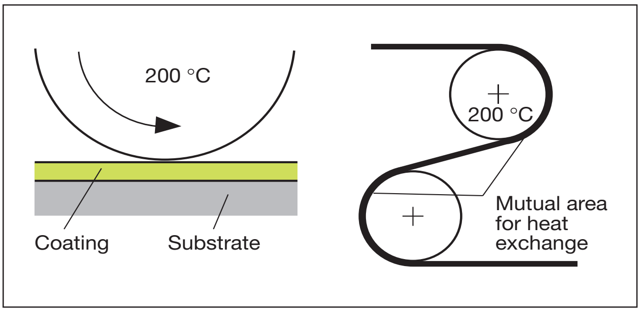


Fig. 4.3.8
Heat transfer by conduction

Another way of transferring thermal energy to the coating requires direct contact with heated solids, **conduction**. If heated rolls are brought into contact with a coating, energy transfers are possible which can result in solidification of the film. High temperature differences are necessary to ensure satisfactory heat transfer because there is only a small contact area between the rolls and a planar object. Contact drying has therefore only proved successful in practice with flexible paint substrates. Paper, cardboard or plastic foils are suitable substrates for a uniform heat transfer by means of conduction.

Contact drying by conduction offers an additional advantage when processing water-based paints on wood. Wood fibres which have swollen because of osmotic processes protrude after coating and would result in surface defects if they were not pressed back into the coating by the rolls. A sanding process can be saved in this way.

Instead of the copious method of indirect heat transport by means of heat transfer from gaseous or solid materials, the direct method using electromagnetic waves in the form of **IR radiation** of suitable wavelength can also be used. If the wavelength of natural radiators is such that the radiated energy quanta can excite molecular oscillations in a coating material, the transfer of thermal energy is also possible without carrier materials. The optimum wavelengths for heat transfer are 0.8 – 6.0 µm, i.e. in the long-wave range outside of visible light.

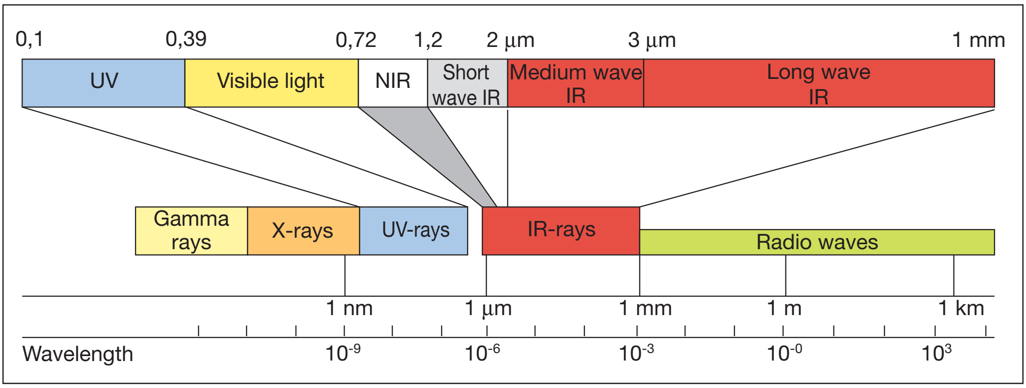


Fig. 4.3.9
Spectrum of wave length of electromagnetic waves

The principle of a transmitter of IR radiation is that a material such as tungsten is made to oscillate by appropriately high temperatures. In the process electrical charges are periodically transferred, with the result that the material emits electromagnetic waves. The wavelength of the radiation decreases with increasing temperature. The wavelength ranges suitable for energy absorption by paints are therefore set by the temperature of the radiator.

It should be noted that with fixed radiators no discrete wavelength is emitted because of the molecular interaction of the charge transfers. A wavelength spectrum is produced with radiation intensities which depend on the wavelength. The quantitative dependencies are summarized in *Planck*'s radiation law [4.4.95].

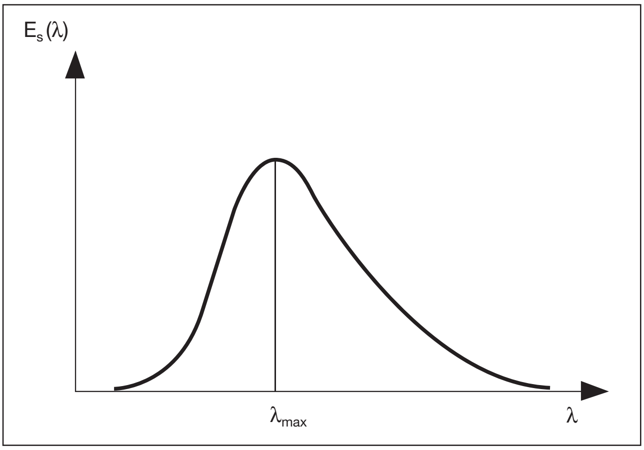


Fig. 4.3.10
Energy distribution of an IR radiation source according to Planck' law

$$E_s(\lambda) = \frac{c_1 \cdot \lambda^{-5}}{c^{\frac{c_2}{\lambda \cdot T - 1}}}$$

The total radiation output per unit area integrated via the wavelength can be calculated by the *Stefan-Boltzmann* law. *Stefan* and *Boltzmann* predicted theoretically and confirmed experimentally the great dependence of the output of a radiator on its temperature. The radiator output E_s per unit area is proportional to the fourth power of the absolute temperature T. The proportionality factor c_s for the theoretical ideal black body was calculated at 5.77 $W/m^2/K^4$.

$$E_s(\text{black}) = c_s \cdot \left(\frac{T}{100}\right)^4$$

Material	**ε**
Ideal black	1
Cu, polished	0,03
Al, polished	0,05
CO_2, gaseous	0,1
Flames	0,5
Cu, oxidized	0,6 – 0,9
Cast steel	0,65
Steel, oxidized	0,8
Water vapour	0,8
Clay brick	0,9
Porcelain	0,9
White coating	0,9

a

Surface temperature		**E_s**	**λ_{max}**
[°C]	**[K]**	**[kW/m²]**	**[nm]**
200	473	2,84	6125
400	673	11,63	4305
600	873	32,90	3318
800	1073	75,10	2700
1000	1273	148,80	2276
1200	1473	266,80	1967
1500	1773	560,00	1634
2000	2273	1513,00	1275
2200	2473	2120,00	1171
2500	2773	2250,00	1045

b

Fig. 4.3.11
Table of ε-values of different materials (a) and radiation energy in relation to temperature of radiation source (b)

No real materials reach the radiation number of the theoretical black body. The quotient of the real and theoretical black body c_{gr}/c_s determines the ability to emit infrared radiation. The quotient which is defined as the ε-value lies between > 0 and < 1.
The emitted energy is also defined by the ε-value and the temperature.

$$E_s(\text{real}) = \varepsilon \cdot c_s \cdot \left(\frac{T}{100}\right)^4$$

It has already been pointed out that raising the temperature does not only increase energy output. At the same time the maximum on the radiation curve shifts to shorter wavelengths in accordance with *Wien*'s displacement law.

$$\lambda_{max} \cdot T = 2897{,}8\ \text{K} \cdot \mu\text{m}$$

In order to describe energy transfers by infrared radiation quantitatively, it is necessary to know the properties of the medium and of the receiver in addition to knowing the properties of the radiator with the temperature T_1. It must be borne in mind that the receiver emits radiation itself in accordance with its temperature T_2. The radiator and receiver surface area A, the unit conductances c_1 and c_2 and the difference between the outward and return flows of the radiation energy

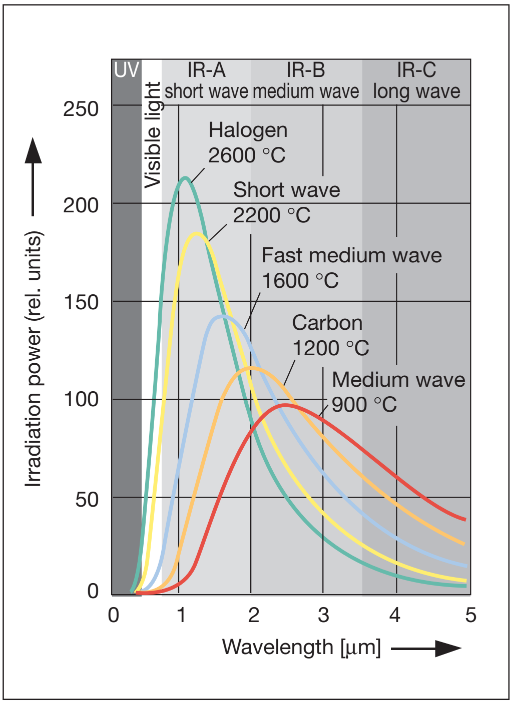


Fig. 4.3.12
Effect of radiation source temperature on radiation energy of IR rays according to Stefan-Boltzmann-law

E_{eff} are factors in calculating the thermal energy $\dot{q}$ which can be effectively transmitted. If $\dot{q} = E_{eff} \cdot A$, it follows that

$$E_{eff} = \frac{1}{\frac{1}{c_1} + \frac{1}{c_2} + \frac{1}{c_s}} \cdot \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right]$$

The interactions of the radiation with the receiver furthermore must be noted in order to understand radiation curing. A proportion E_R of the radiation E_{tot} striking the painted object is reflected, while the rest penetrates the coating. As it passes through the coating, a further portion E_A is absorbed in the coating and converted into heat. The rest E_D is allowed to pass through to the substrate where either it is absorbed or it leaves the painted object unused.

$$E_{tot} = E_R + E_A + E_D$$

The sizes of the individual portions depend to a great extent on the wavelength of the radiation. The ratio of absorbed to unusable portions is determined additionally by the

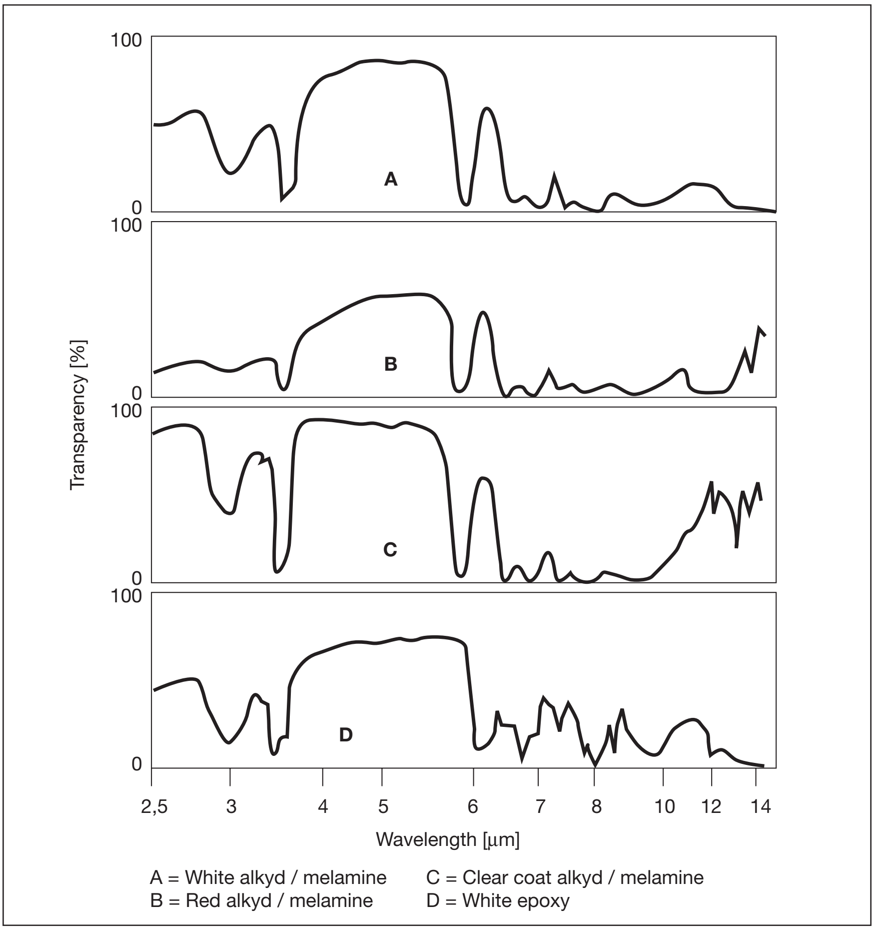


Fig. 4.3.13
Absorption spectra of coatings in the IR-area of electromagnetic waves

film thickness. If effective use is to be made of infrared energy for drying and curing coating materials, the specific absorption and reflection properties of paints must be known. Absorption and reflection spectra in the wavelength range of interest for practical operations lie between 0.8 and 6 µm.

Radiators with a maximum wavelength of more than 6 µm emit far too little energy at a radiator temperature of approx. 200 °C for infrared radiation to be used meaningfully for rapid drying. It is only from wavelengths of 5.5 onwards to 4 µm at about 400 °C that radiators with outputs of up to 20 kW/m^2 begin to become technically usable. These are termed dark radiators since they do not emit any visible radiation components below 700 °C. However, almost all coating materials absorb practically nothing in the range of 4 – 5.5 µm. With radiation-impermeable metallic substrates this energy component which is not used for conversion into heat for the coating is not lost. It is converted to heat in accordance with the properties of the substrate, i.e. it heats the substrate. This therefore offers the possibility of heating the coating from underneath, which is advantageous in many cases compared with convection drying in which the heat is transferred from above. The risk of film defects in the form of pinholing is consequently reduced. For this reason dark radiators have become an accepted means of drying thick paint films despite the low energy output.

If the radiator temperature is increased to figures of 600 – 1000 °C, maximum wavelengths of 3.5 – 2.5 µm can be calculated in accordance with *Wien*'s displacement law. The advantage of the substantially higher energy output is supplemented by the marked substance-specific absorptions of the CH, OH or NH groups in the film forming agent. Because of their higher temperature, the emissions from radiators of this medium-wave range are in the visible part of the spectrum. Thus these are bright radiators. The outputs per unit area extend to 50 kW/m^2.

Type of radiation source	**Surface temperature [°C]**	**Wavelength of maximum energy λ_{max} [nm]**	**Technically reachable specific power [kW/m^2]**
Short wave	2000 – 2300	1300 – 1100	20 – 100
Medium wave	800 – 1000	2700 – 2300	8 – 50
Long wave	300 – 500	5000 – 3800	< 20

Fig. 4.3.14
Classification of technical IR-sources

Radiator temperatures of 2000 – 2500 °C produce energy in the short-wave IR range with wavelengths of 1.6 – 1.2 µm. The significantly higher radiation energy output in excess of 100 kW/m^2 results in changed absorption and reflection properties in the coating materials. Depending on the type of quantity of color pigments and effect substances, coatings exhibit particularly marked differences in the reflection properties in the short-wave range. Whereas white paints pigmented with TiO_2 reach reflectances in extreme cases of over 80%, there is still almost complete absorption in black paints pigmented with carbon black, irrespective of the wavelength.

Because of the increasing reflection in light pigments short-wave radiators with a high energy output are not capable of effectively transforming the energy output into heat. It should be noted, furthermore, that absorption is color-specific and thus heating of the coating is also color-specific.

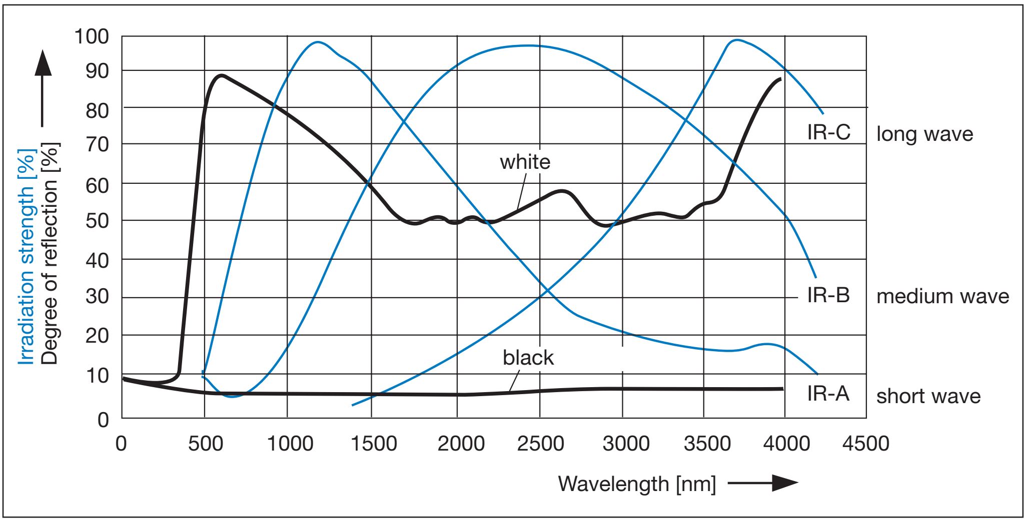


Fig. 4.3.15
Degree of reflection of white and black coatings in the area of short-wave, medium-wave and long-wave IR-radiation

Metallic coatings are heated more slowly than solid colors because of the strong reflection by the aluminium flakes. The object temperatures which occur with the same energy output but with various colors and different degrees of lightness differ correspondingly.

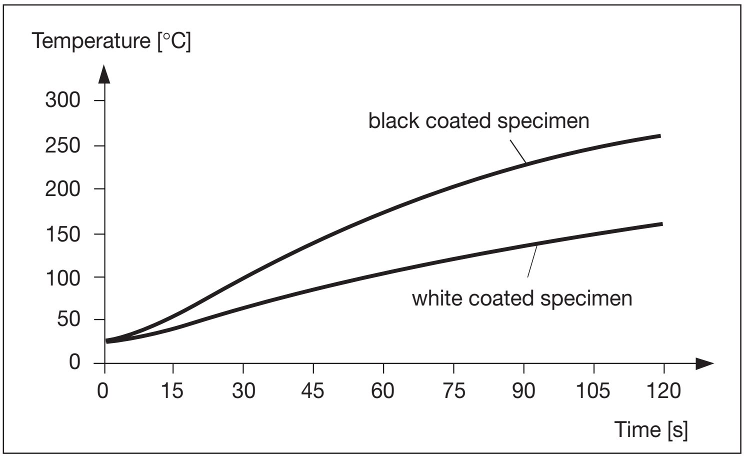


Fig. 4.3.16
Heating curve of white and black coatings at the same radiation energy of 10 kW/m^2

Consequently different energy intensities have to be offered to achieve uniform cross-linking of coatings, depending on the color. The energy-transfer process must be controlled by means of non-contact temperature measurement in order to give the entire color and effect range the same properties in use. The use of such control technology has enabled processes to be implemented giving access to even shorter-wave ranges with even higher radiator temperatures, despite sensitive color dependency and the increasing danger of overcuring.

With wavelengths of 0.8 to 1.2 µm, radiation in the short wave or near-infrared (NIR) range is of extremely short wavelength and thus particularly high in energy. The particular advantages of NIR stem from the high penetration depth of the electromagnetic waves as far as the substrate. Components reflected there can even leave the film again before they are returned to the coating by the radiator's reflectors. This results in an energy input which is homogenously distributed across the entire film as if by multiple reflection. Curing can take place in seconds because of the uniform energy distribution and the ultimately complete absorption [4.4.96]. Even powder coatings are melted and hardened within just a few seconds with NIR. The short energy-transfer times also permit the coating and curing of thermally unstable substrates such as wood or plastic with powder coatings, provided the substrate has correspondingly poor thermal conductivity [4.4.97].

No description of the energy transfer from the radiator to the receiver would be complete without mentioning the medium. Absorptions of the radiation by the ambient gas would cause the gas to heat up and thus impair the energy transfer. Carbon monoxide, carbon dioxide and water vapour are powerful absorbers of IR in the wavelength ranges of 2 – 5 µm and 12 –16 µm. Because of the low CO_2 concentration in the atmosphere this disadvantage has little impact. Dry air has little tendency to absorb and is thus a good medium.

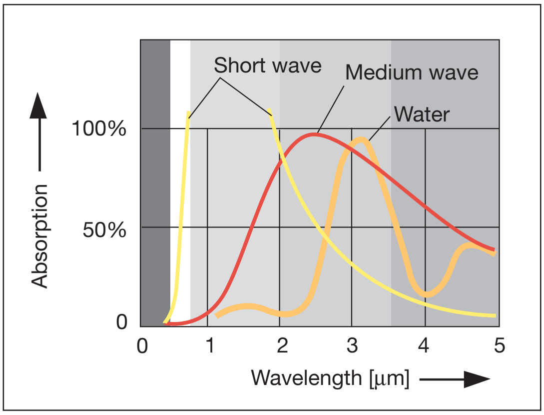


Fig. 4.3.17
Absorption spectrum of water vapour

The situation is different when processing or drying waterbased paints.

Medium-wave IR is greatly absorbed by water and would therefore be lost to the evaporating water if used for heating waterbased coatings. Only short-wave radiation and NIR penetrate the water vapour and thus heat the coating.

As already described, the energy output of natural radiators with wavelengths above 6 µm is too low and thus they are not used. Because of the very marked and, at the same time, color-specific and material-non-specific absorptions, long-wave radiators would be of interest if their energy output were higher. This can be achieved with laser beams. The CO_2 laser has turned out to be usable for coating purposes. At 10.6 µm its emissions are in the extremely

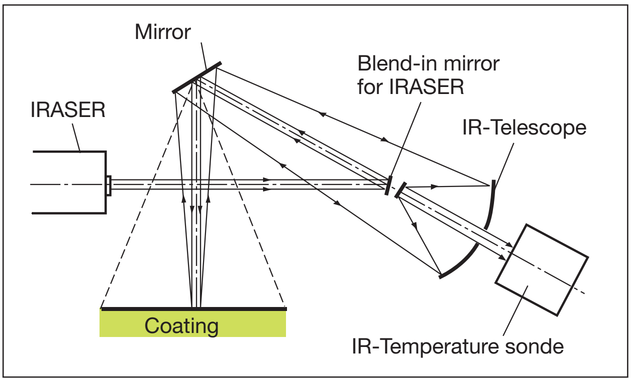


Fig. 4.3.18
Radiation curing by laser

long-wave radiation range where all coating materials guarantee high energy use. Because of the high energy densities of the IR laser (IRASER) the radiation must be scanned with an oscillating mirror. Noncontact measurement of the object temperature is necessary for rapid control of the intensity of the laser beam (see chapter 3.2.1).

Heating paint by means of the even longer-wave microwaves was successfully tested in the 1960s. Systems were installed specifically for the printing ink sector, first in the UK and Denmark, and later in Germany. The usual radiation frequency is 2.5 and 5.8 GHz. There is a functional correlation between the radiation to be absorbed to heat paint films and the dielectric constants or dielectric dissipation factor. The substrates also influence the outcome. Wooden substrates and aqueous dispersions have proved particularly suitable for microwave drying [4.4.98].

Other methods of heat transfer

Other electrical phenomena can also be used to generate heat for special applications. To paint wire, for example, an **electric current** passing through the freshly painted wires develops sufficient heat to cure the paint. The phenomenon of **induction** of eddy currents in metallic materials can also be used to heat metals and crosslink paints thermally [4.4.99].

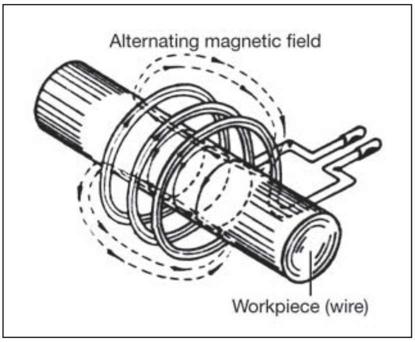


Fig. 4.3.19
Induction heater

If solid components have to be coated and cured solely by thermal methods, eddy-current heating at a correspondingly high frequency for the primary voltage offers the opportunity to heat up only the surface. Curing of adhesives with magnetic pigments such as γ-iron oxide is another method which merits a mention in this context. The thermal energy is generated by magnetic reversal effects when electromagnetic alternating fields are connected.

4.3.1.2 Oven Design

For the technical transfer of the thermal energy needed for accelerated film formation the objects to be painted must pass through a housing which is insulated against heat dissipation. Depending on their shape, size and quantity, the workpieces are conveyed either in batch or continuous mode. In the former case the painted object is conveyed into the oven which is fitted with doors where, after the doors have been closed, it is heated for an appropriate period to the object temperature required for the crosslinking of the coating. In continuous ovens the tunnels which are equipped with a conveyor are open at their entrance and exit. This enables the painted goods to pass through the oven line continuously.

Gas- or oil-fired boilers are used for heat generation and transfer in convection ovens. The thermal energy contained in the flue gas is transmitted to the oven air via heat exchangers.

If pure natural gas is used, it is also possible to dispense with the heat exchanger and use the fuel gases directly. In specific cases this can lead to film performance deficiencies like adhesion failures for next coating layer [4.4.100]. However, the advantage of the lower energy loss must be weighed against the risks of contamination of the still fresh coating surface by soot or SO_2 and film performance issues. In rare case the circulating air is also heated by means of superheated steam or electric heaters.

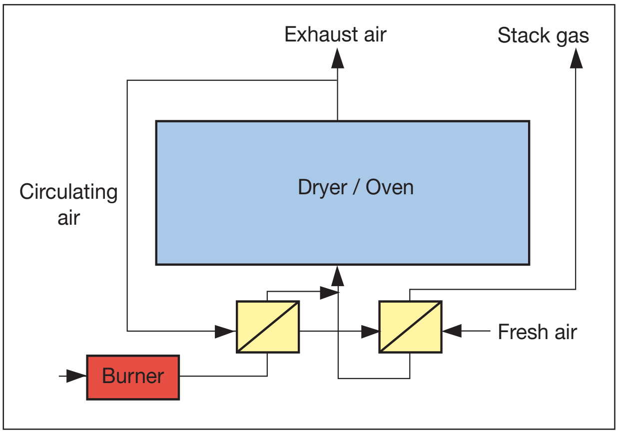


Fig. 4.3.20
Components of an indirect convection oven

The air circulation which is needed for rapid heat transfer to the painted object is provided by fans in conjunction with flow apertures, as a result of which air speeds of 2 – 5 m/s are attained. In individual cases the air speed in jet ovens can be considerably higher in order to achieve more rapid heat transfer.

The distance which the heat carrier, air, has to cover in the oven varies, depending on the oven design. Transverse or longitudinal ventilation can be applied to the chambers in the oven depending on the object and paint system and thus on the quantity of escaping solvents and cleavage products. Because of the falling ambient air temperature caused by heat transfer to the painted objects the circulating air should first flow over the solid parts which are therefore more difficult to heat, in the event of an uneven mass distribution.

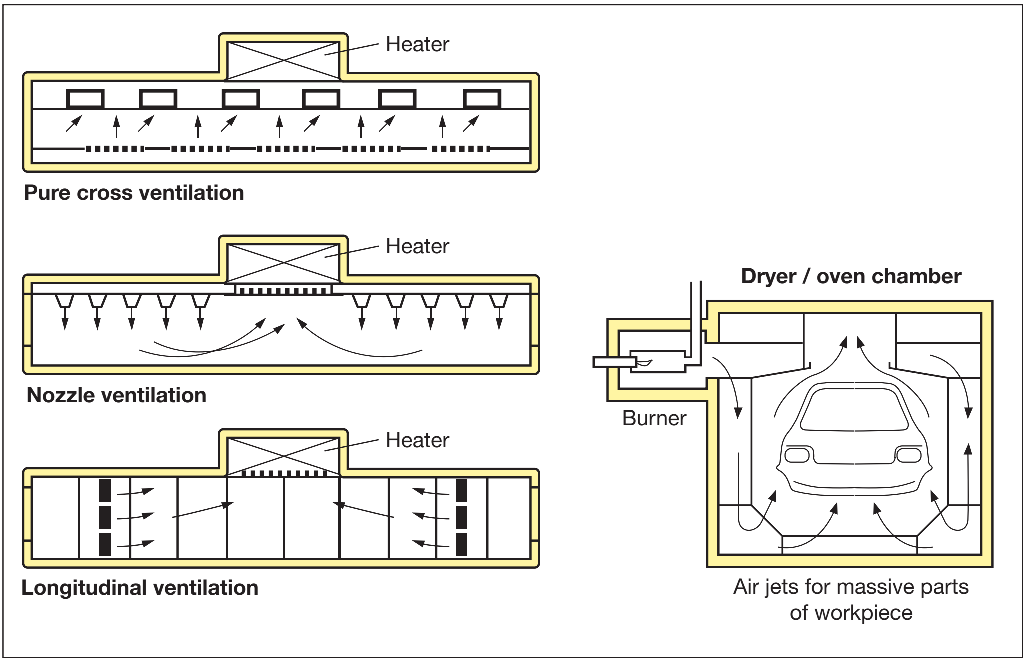


Fig. 4.3.21
Different air movements in ovens

For safety reasons the oven air has to be diluted with fresh air, depending on the proportion of solvents and on the quantity and type of cleavage products. Operating in pure recirculation mode would continuously increase the concentration of flammable components and consequently possibly exceed the lower explosion limit. In addition, there is an increasing risk of the formation of condensation. Because of the explosion hazard uniform statutory regulations relating to the circulating air concentration in ovens have been drawn up. In Germany this is in the form of orders BGV D25 and BGV D24 issued by the employers' liability insurance associations. BGV D25 specifies 0.8% vol/vol as the upper threshold for flammable organic components in the oven air. The necessary volumes of fresh air can be calculated if the volatile organic components released during film formation are known.

The feed of fresh air results of necessity in the same volume of solvent-containing, still hot exhaust air. This calls for secondary measures of heat recovery and reduction of the gaseous emissions from the exhaust air. Limit values for this are specified in Germany's Clean Air Guidelines or the VOC directive (see chapter 5.2). To reduce the process energy input the entrances and exits of continuous ovens are lowered or air locks are formed by transverse flows.

There is no point in equipping the entire oven with its own heating and air circulation system because of the constantly changing film states as the product passes through the oven, i.e. with reference to object temperature, degree of crosslinking and the emission of solvents and cleavage products. It is usual to divide the oven into 3 to 5 individual units, each with a separate energy supply. Separate control of the circulating air/fresh air ratio must also be possible in the individual sections.

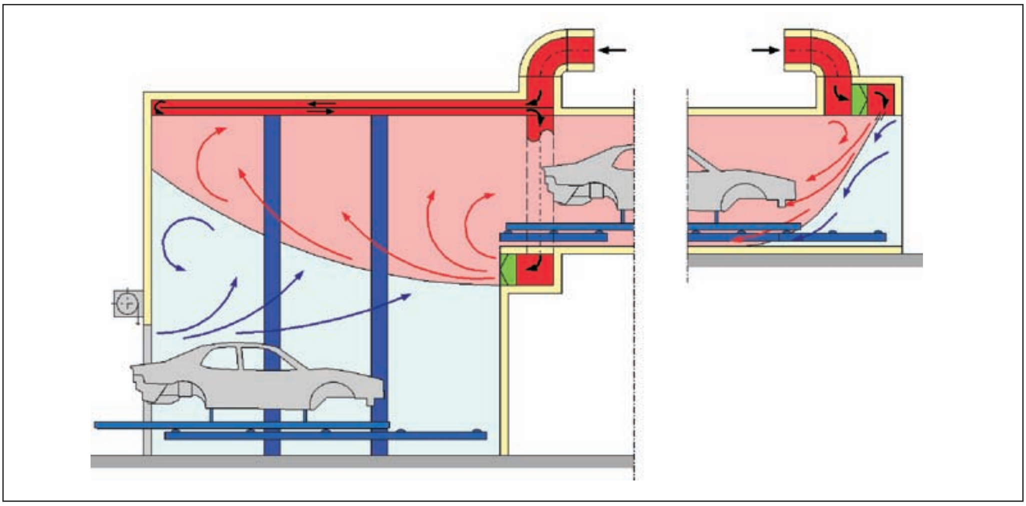


Fig. 4.3.22
Scheme of an A-oven with and without air locks

In the first zone, the heating zone, the object temperatures are still low and the solvent content correspondingly high. In the following holding zone the coating undergoes major changes in terms of flow and solidification during drying and curing. The main portion of cleavage products leaves the film in this area. Solvent emissions are completed in the subsequent holding zones. Hardly any cleavage products leave the coating

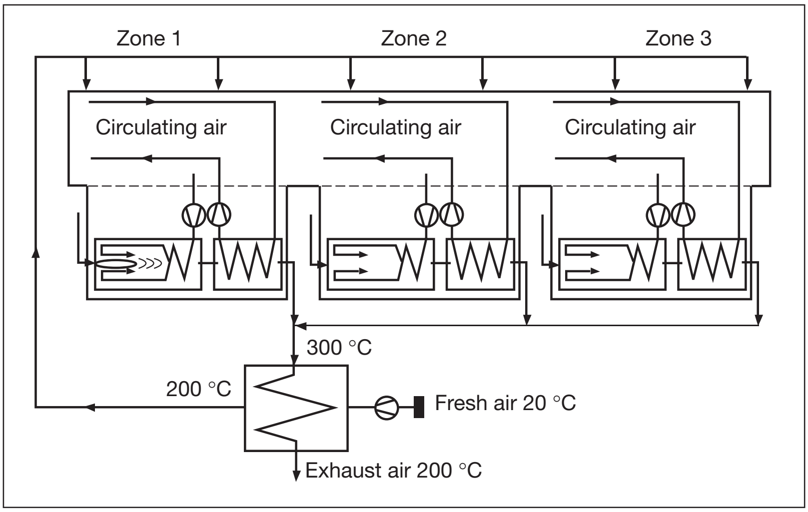


Fig. 4.3.23
Scheme of multistage oven

film any more. Despite the degree of crosslinking rising only slightly further, the qualitative changes in the coating in these areas are still substantial. The film properties only reach their target values in the last section of the oven.

In order to operate ovens economically the circulating air component should be kept as high as possible while complying with the threshold concentrations specified for safety reasons. This results in the concentrations of organic emissions in the oven air being of the order of several g/m^3 and thus well above the limit values specified in the Clean Air Guidelines and the VOC directive of most countries. The exhaust air from the oven must therefore be processed in secondary cleaning systems in order to meet the permissible limit values. Various methods are available, of which thermal incineration and material recovery by adsorption using activated carbon are the most common (see chapter 5.3). Since the thermal energy generated in the recombustion process can also sensibly be used to heat the ovens, thermal incineration systems are often an integral part of drying systems.

To accelerate the heating of painted objects infrared radiators are frequently installed in the first oven zone to supplement the heated circulating air. Dark or bright radiators are used, depending on the particular task (see above). Dark radiators consist of metal or ceramic pockets through which the heated air is routed. The walls of the radiator pockets are heated to approx. 300 °C. Because of the large masses of the radiator pockets these dark radiators have a very sluggish control response. They assist in the heating of solid components.

Short-wave bright radiators consist of chromium-nickel or tungsten coils melted into quartz glass. If a sufficiently high electrical voltage is connected, they reach temperatures of up to 3000 K.

Reflectors should be employed to make effective use of the radiation energy emitted by the radiator. The IR rays are focused and thus intensified in different ways, depending on the design. Materials with small ε-values (see above) should be used as the reflector material. Depending on the wavelength of the radiation gold or aluminium reflectors

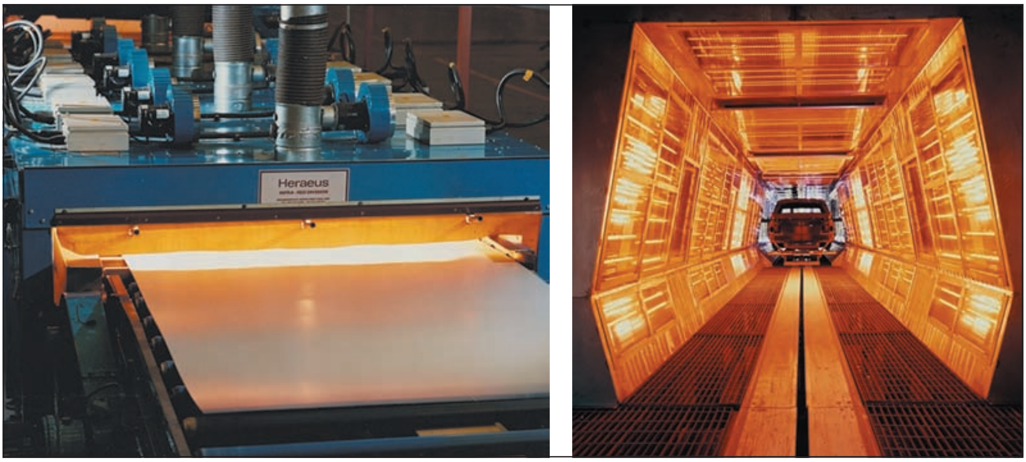


Fig. 4.3.24
IR-ovens

with ε-values of 0.02 – 0.04 have proved to be effective materials. Even despite the unusable visible components, reflector losses, absorption on the quartz sheath, and scattering, reflection and transmission losses, about 70% of the installed power of short-wave IR radiators is still available for heating the object.

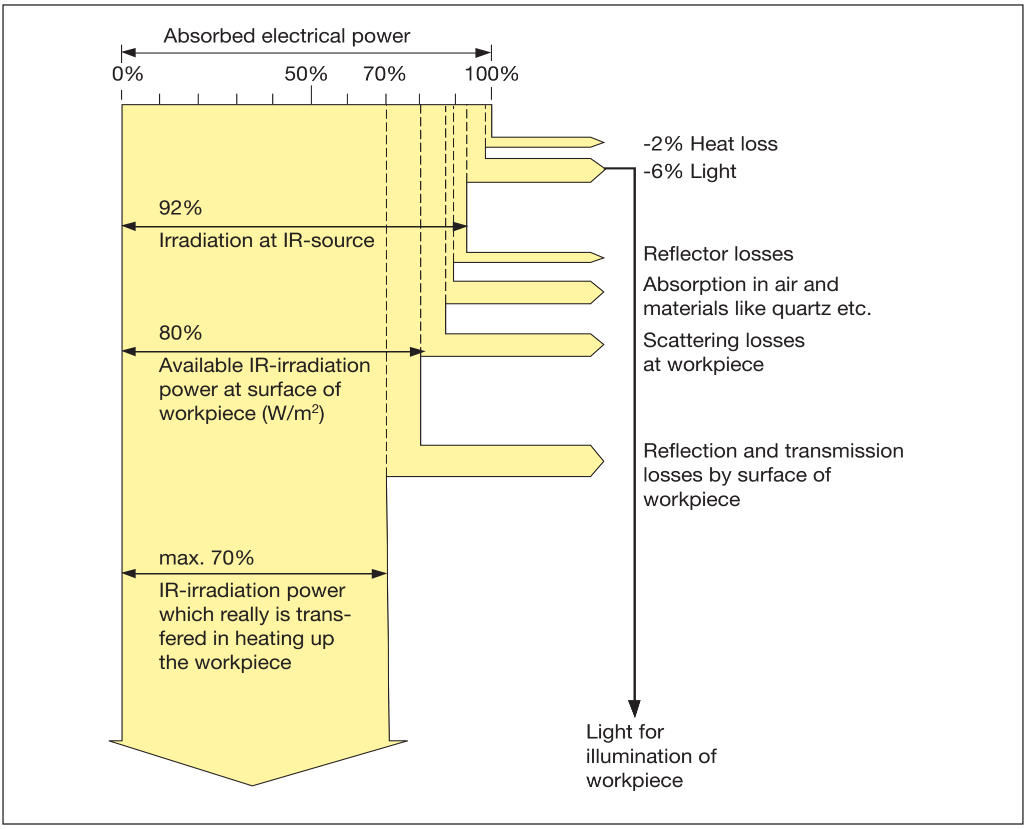


Fig. 4.3.25
Yield of short-wave IR-radiation

Energy balance of a convection oven

When seeking to determine what steps to take to save energy it is not enough simply to draw up overall balances. It is more important to have a breakdown of what the energy is specifically used for and where it is lost in the process.
The total energy $\dot{Q}_{tot}$ input in the drier is calculated from the volume of circulating air $\dot{V}_{circ}$ and the difference in temperature between the entrance and exit of the oven.

$$\dot{Q}_{tot} = \dot{V}_{circ} \cdot c_p \cdot \rho \cdot \Delta T$$

Unfortunately this amount is not used solely to heat the coating.
The sum of the individual energy portions $\dot{Q}_{tot}$ per unit time to be provided corresponds to the following individual items:

$$\dot{Q}_{tot} = \dot{Q}_{pa} + \dot{Q}_s + \dot{Q}_{tr} + \dot{Q}_{surf} + \dot{Q}_o + \dot{Q}_{em}$$

$\dot{Q}$ is given in kJ/h.
The following applies when calculating the exhaust air energy $\dot{Q}_{em}$

$$\dot{Q}_{em} = \dot{V}_{em} \cdot c_p \cdot \rho \cdot (T_{oven} - T_{environment})$$

The limit value for the concentration of the organic components of max. 0.8% vol/vol as specified in BGV D25 is the calculation basis for $\dot{V}_{em}$:

$$\frac{V_{so}}{V_{em}} < 0{,}008$$

If the volume of solvents emitted in the oven is known, the proportion of exhaust air energy can be calculated. In practice the exhaust air volume calculated in this way is increased by a factor of 3 – 6, depending on the paint system, to prevent the formation of condensation.
The energy requirement $\dot{Q}_s$ to heat the workpieces (substrate) is calculated from

$$\dot{Q}_s = m_s \cdot c_s \cdot (T_s - T_{env})$$

The energy requirement $\dot{Q}_{tr}$ to heat the conveyor (transportation) is calculated from

$$\dot{Q}_{tr} = m_{tr} \cdot c_{tr} \cdot (T_{tr} - T_{env})$$

where in most cases $c_{tr} = c_s$ and $T_{tr} = T_s$.
The energy losses caused by the oven design must also be determined. The volumes of air escaping from the openings $\dot{V}_o$ can only be estimated.

$$\dot{V}_o = \frac{2}{3} \cdot A \cdot u \cdot z$$

A = cross-section of oven entry
u = stream of leaving oven air (for orientation: $0{,}2\ m \cdot s^{-1}$)
z = opening factor of oven doors (z = 1, if always open)

In ovens with a raised entrance (see figure 4.3.22) and exit the air losses are negligible. When the oven losses $\dot{V}_o$ are known, the heat loss $\dot{Q}_o$ can be calculated as

$$\dot{Q}_O = \dot{V}_O \cdot \rho_{air} \cdot c_{p_{air}} \cdot (T_{circ} - T_{env})$$

In addition, there are energy losses because of heat exchange between the oven walls and the ambient air.

$$\dot{Q}_{surf} = K \cdot A \cdot (T_{circ} - T_{env})$$

K = coefficient of heat transition
A = outer surface of oven

The coefficient of heat transmission K is a function of, among other things, the oven insulation. A value of 0.5 kJ/m^{2}hK can be used in calculations.

The energy requirement $\dot{Q}_{pa}$ to heat the paint film and to evaporate the residual solvents is negligible in comparison with the other components. Although the heat of evaporation of water at approx. 2000 kJ/kg significantly exceeds that of organic solvents at 300 – 500 kJ/kg, it remains marginal as a proportion of the overall consumption at only 1 – 2%.

If the individual items are referred to concrete cases, it has been shown that the greatest energy inputs when coating industrial goods such as car bodies or refrigerators are caused by waste air losses and heating the objects to be painted.

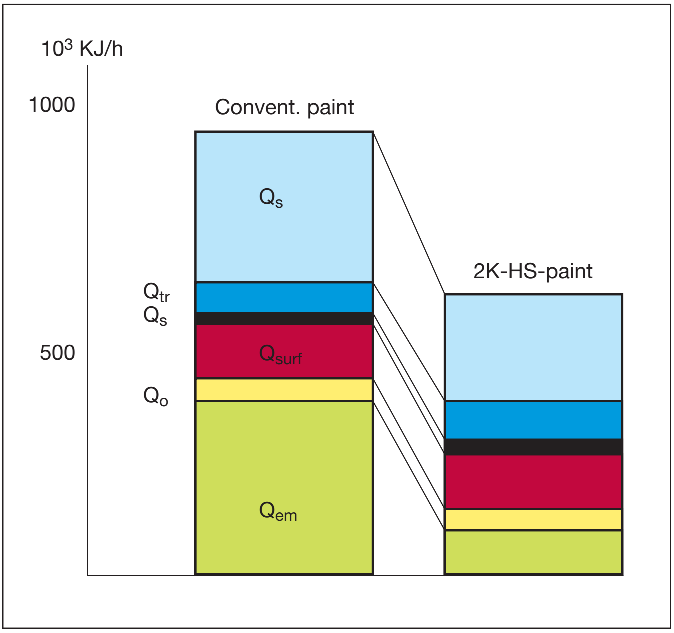


Fig. 4.3.26
Energy consumption of different paints in convection ovens

Such a balance also provides information on the ratios of input to lost heat energy and indications of where potential savings may be made. Since the exhaust air volume is determined by the solvents and cleavage products escaping in the oven, energy savings can be achieved by using high solid and polyaddition paints which do not form any cleavage products without reducing the baking temperatures as a result of using lower volumes of fresh air. It has been shown in practical operations that raising the solid content from 50% to 70% and replacing a solventbased baking enamel by a 2-component polyurethane system enables the exhaust air energy losses to be reduced to approx. 50% of the original value at the same baking temperature of 130 °C.

4.3.2 Curing by UV and Electron-Beam Radiation

The possibility of initiating rapid, energy-saving chemical crosslinking reactions without heating the paint and substrate and with only low emissions was the motivation for applying photochemical reactions to the specific requirements of coating technology in the 1950s and 1960s.

It was known that the high-energy short-wave components of solar radiation can trigger chemical reactions without heat action by means of photochemical radical formation. This type of reaction quickly found a technical application in polymer chemistry (see chapter 2.1.1). Unsaturated polyesters which until that point could only be cured thermally or by the catalytic cleavage of peroxides were now curable in seconds by the action of radiation without any heat input or any pot-life restrictions. ”Cold” UV curing was especially useful for planar and thermally unstable wooden materials in the furniture industry. Initially used only for the crosslinking of clearcoats and later also for thin nonopaque pigmented coatings, radiation curable paints also conquered the printing ink sector and the printed-circuit board industry. Acrylic-acid-modified resins specially developed for UV curing have partially superseded classic unsaturated polyester resins (UP), despite being more expensive, because of their higher reactivity (see chapter 2.1.1). To ensure a successful technical application, photoinitiators are absolutely essential for starting polymerization with UV-light. Most of them split homolytically into radicals as a result of the influence of UV rays in the wavelength range 350 – 370 nm.

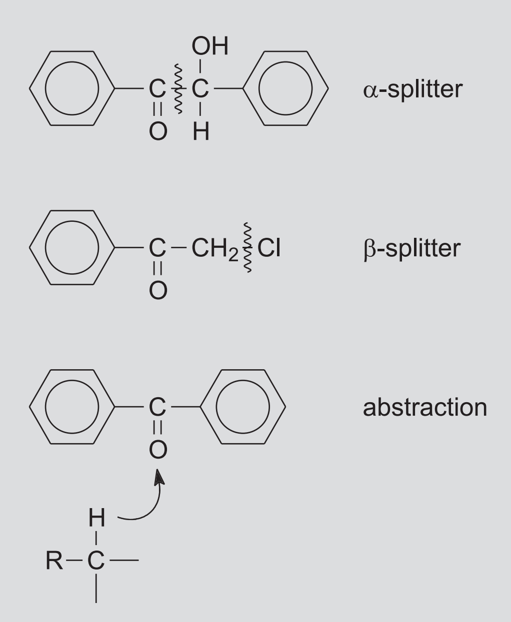


Fig. 4.3.27
Generation of radicals by different photoinitiators

The replacement of UV rays by accelerated electrons (electron beams) opened up new routes for even faster curing of coating materials, again in the form of cold curing, without the inhibition which occurs with UV-absorbing paint components. Despite the qualitative, environmental and energetic advantages large-scale systems for electron-beam (EB) curing are relatively rare. High capital costs, the formation of X-rays and qualitative problems when coating metals have delayed the wider acceptance of EB curing to date. However, the few industrial-scale systems are operating successfully in coating wood in the form of doors, wood cement panels and parquet flooring or for curing printing inks.

The reasons for the sluggish success of the EB curing system lie in the refinement of the technically simpler UV technology. New photoinitiators enabled the wavelength of the molecule-splitting radiation to be shifted to the short-wave visible range. It is then possible, using modified radiators, to adapt maximum emissions to the absorption proper-

ties of the new photoinitiators, with the result that optically opaque paints pigmented with titanium dioxide can now be cured by means of electromagnetic radiation.
It should be noted in conclusion that cationic polymerizations can also be initiated by UV radiation, in addition to radical polymerization. Strong *Lewis* acids released by UV rays start ring-opening polymerizations, as familiar, for example, from the curing of epoxy resins with boron fluoride (see chapter 2.1.1). There are advantages of UV-initiated cationic compared with radical polymerization in terms of complete curing from only short action by UV rays and by the formation of OH groups, leading to better adhesion on metallic substrates.

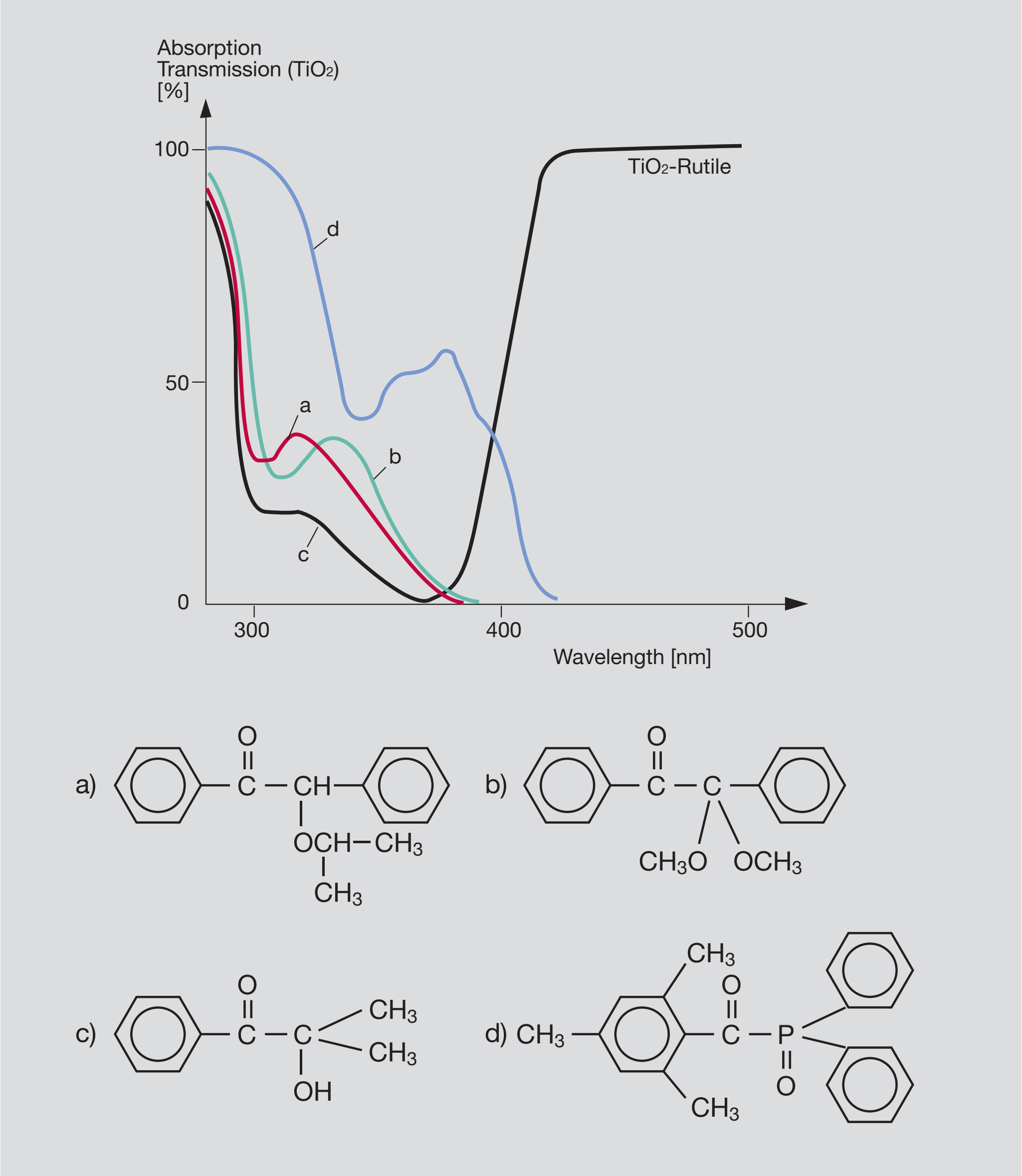


Fig. 4.3.28
Absorption spectra of photoinitiators and transmission data of TiO_2

Chemical principle of UV curing

The double bonds which are necessary for the radical growth reaction can be found in both the resins and the reactive solvents, known as reactive diluents. The role of the latter is to liquefy the paint and thus make it processible. By contrast with the classic solvents they do not leave the solidifying film, but become linked to the film forming agents through copolymerization (see chapter 2.1.4).

To start a polymerization reaction UV rays must act on the coating material to be cured. Although direct excitation of the double bond of the carbon in the film forming agent chains is possible in principle by means of short-wave UV rays with a wavelength of 280 nm, this method is not usual in technical applications because of the design costs of appropriate radiation sources. Simpler methods are possible using long-wave and technically less complex mercury-vapour lamps. They can be employed when appropriate additives are being used to help form radicals with the relatively long-wave radiation components of 365 nm. These photoinitiators or sensitizers are substances which absorb the UV rays in this wavelength range, resulting in carbon bonds being opened such that two radicals are produced in each case (see chapter 2.1.4).

The energy absorption of the photoinitiators is impaired when light-protection agents are used and pigments are present unless their absorption properties are matched to each other [4.4.101]. It is therefore important to use UV absorbers and pigments which do not absorb in the photoinitiator’s absorption range. Zinc sulphide is a suitable white pigment for radiation curable paints because of its favourable absorption properties. If it is desired or necessary to use other pigments, for example titanium dioxide, the above matching with the classical photoinitiators is not in place.

It was only possible to solve this problem by developing new process materials. In conjunction with UV rays in the wavelength range above 370 nm the acylphosphine oxide group (see chapter 2.1.4) is capable of initiating the curing of coating materials pigmented with titanium dioxide which do not absorb in this range (see figure 4.3.29).

The process of UV curing is accompanied by undesirable secondary reactions with the ambient air. The chain-terminating effect of the biradical oxygen during crosslinking results in oxygen inhibition. This can be combated by chemical (see chapter 2.1.1) or plant-engineering methods. Curing speed can be monitored by FT-IR [4.4.102].

Equipment for UV curing

Appropriately designed radiators have to be used to produce a radical concentration which is sufficient for crosslinking. Mercury-vapour lamps emit the necessary energy quanta for splitting the photoinitiators in the range 320 – 380 nm in several bands [4.4.103].

At 1 W/cm length of the rod-shaped radiator, these low-pressure mercury-vapour lamps have a low output in the UV range by comparison with high-pressure radiators which are considerably more powerful at up to 50 W/cm. The correspondingly slower curing when low-pressure radiators are used gives paraffin in appropriate coating materials sufficient time to float into the interface. This diffusion barrier for oxygen prevents inhibition. The slow curing reduces the danger of ”freezing” internal strains. Furthermore, the loss of volatile reactive thinners is lower because of the low operating temperature. Low-pressure lamps are primarily used for preliminary gelling before the subsequent main crosslinking is carried out with high-pressure radiators.

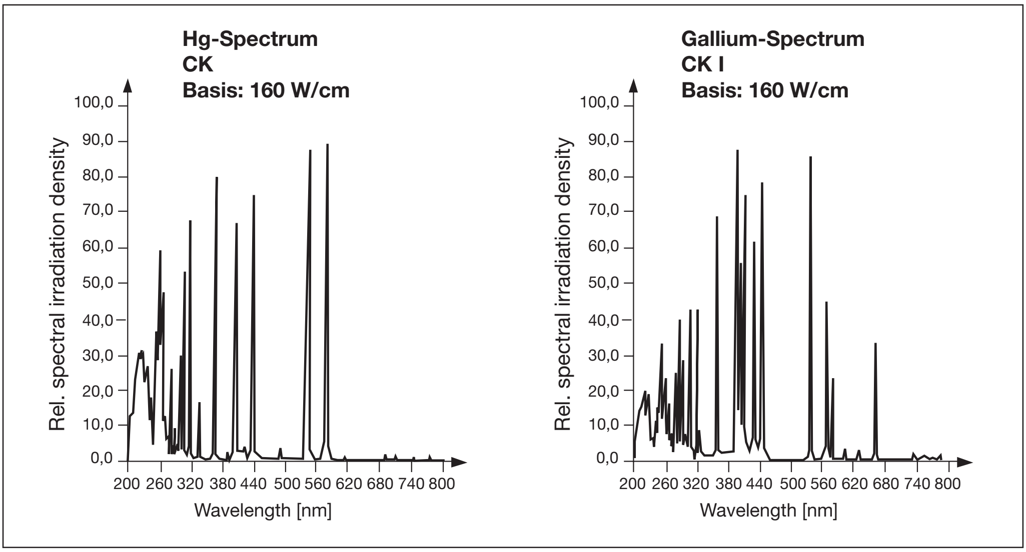


Fig. 4.3.29
Emission spectra of standard and gallium dotted Hg-vapour UV-lamps

The spectrum of mercury-vapour lamps particularly in the range above 400 nm can be expanded to include new emission bands by doping them with gallium, indium or iron. Such lamps are particularly used for curing pigmented paints.

As with IR drying, reflectors should be used to make the maximum possible use of the radiation energy of the UV lamps for paint curing. Although the reflectance of aluminium reflectors is sufficiently high at over 90%, they have failed to gain acceptance with high-pressure radiators. The cause of this is the high reflection of the IR components contained in the mercury-vapour lamps' spectrum which heat the resulting coating excessively and thus result in unwanted emissions of the reactive thinner. Reflectors made of highly temperature-resistant special glass are more suitable because they are permeable to visible and infrared radiation but not to UV rays. As with IR radiators mirror designs exist for UV radiators too which scatter or focus the light.

To ensure a sufficiently high and at the same time constant energy input the radiators are controlled either in several increments or infinitely variably, and their energy output is monitored. If minimum values are not met, an acoustic or optical signal is triggered. Modern systems enable the UV levels to be measured continuously and, in the event of fluctuating conveying speeds, to readjust the setpoint values via closed-loop control circuits. Because of the infrared rays emitted by the UV lamps, the radiators must be intensively cooled to permit longterm constant operation.

The ozone generated by UV light makes it necessary to house UV radiators in ducts and to supply fresh air to ensure that the MAC value of 0.1 ppm is not exceeded.

If the inhibition of crosslinking near the surface of the coating caused by oxygen is to be prevented by engineering measures, the systems must be purged with nitrogen as an inert gas. This stops the formation of ozone at the same time.

Since uniform crosslinking is only possible with a constant energy input, the use of UV-curing systems has been limited to date in practice to the coating of planar components. The numerous advantages of rapid and intensive crosslinking and the associated high hardness and scratch-resistance of UV-cured coatings mean that this technology is also of interest for highly stressed surfaces such as those of cars. Because of the three-dimensional form of the surfaces to be coated and cured the fixed radiators in normal continuous systems have to be replaced by movable radiator arms [4.4.104]. Program-controlled robot arms follow the outlines of the surfaces at a constant distance and thus ensure consistent quality. The improved scratch-resistance and environmental benefits makes the use of this technology in automotive coating probable [4.4.105].

Electron-beam curing

In the early 1970s attempts were made to progress from UV curing and use other forms of radiation curing. It was known that accelerated electrons in the form of β-rays can trigger photochemical reactions. The effect is based on the fact that molecules are directly excited or ionized by the β-rays before decaying into radicals or radical ions. The use of such a technology renders photoinitiators superfluous. The accelerated electrons cause extremely rapid crosslinking of film forming agents or reactive diluents which cure with polymerization. The reactions are complete in fractions of a second, permit high coating speeds and offer the ideal conditions for economical coating. A further advantage of electron-beam curing lies in the ability of the accelerated electrons to penetrate deep into pigmented films and to ensure perfect curing of all the pigmented coats.

As with UV coating, it is recommended with electron-beam curing, too, that the influence of atmospheric oxygen be counteracted by purging with inert gas.

All the film forming agents which have been described as suitable for UV curing can be used in the same way for electron-beam curing. The only difference from UV curing is the radical formation mechanism. Accelerated electrons can release bonding electrons from the film forming agents, depending on the kinetic energy, which gives rise to ionized molecules and radicals or radical ions.

$$AB \longrightarrow AB^{\oplus} + e^{\ominus}$$

$$AB^{\oplus} \longrightarrow A\cdot + B^{\oplus}$$

If the energy of the exciting electrons is too low to release electrons, excitation of the resin molecules (AB*) may be possible. Radical formation can take place by means of subsequent homolytic decomposition.

$$AB \longrightarrow AB^{*} \longrightarrow A\cdot + B\cdot$$

Electrons with even lower kinetic energy are captured and transformed as anions into radicals and radical ions. Most interactions between the electrons and the film forming agents result ultimately in the formation of radicals and thus in the start of a radical polymerization.

The energy of the accelerated primary electrons is so high that they can penetrate films which are several hundred micrometres thick. They generate slower secondary electrons which usher in rapid and complete curing in accordance with the mechanism described above [4.4.106].

Application engineering

The free electrons necessary for curing are released by electron accelerators, also known as electron guns. The devices, which are similar to a *Braun* or cathode-ray tube, contain a hot cathode, an anode with a punctiform opening, and a focussing device for the electrons which are released and accelerated by the high voltage connected.

The force F from the product of the elementary charge e and the electrical field strength E which acts on the electrons causes an acceleration which imparts the kinetic energy $m/2 \cdot u^2$ to the electron. This corresponds to the work $F \cdot s$ and consequently:

$$\frac{m}{2} \cdot u^2 = F \cdot s = Q \cdot E \cdot s = Q \cdot U$$

or $$u = \sqrt{\frac{2 \cdot Q \cdot U}{m}}$$

Q = elementary charge
m = mass of electron

The electron of mass m and charge e, whose speed u is a function solely of the connected high voltage U, passes through a 10 – 15 µm thin titanium window and thus reaches the atmosphere. The window, which absorbs 15% of the energy and converts it to heat, has to be cooled to relieve the stress on it. Because of its high intensity the electron beam has to be permanently scanned in two dimensions.

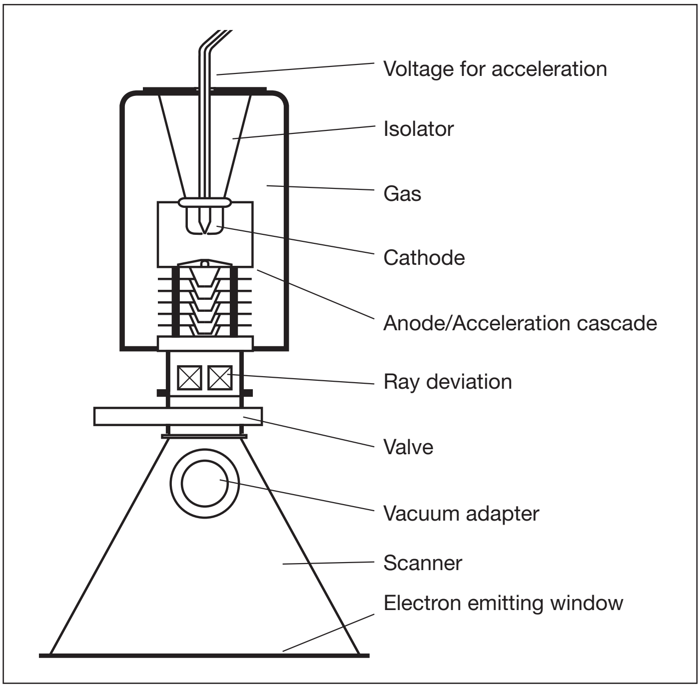


Fig. 4.3.30
Elements of an electron accelerator

The kinetic energy of the electrons achieved by the electron gun can be given in electron-volts (eV). 1 eV is the kinetic energy which an electron receives when it passes through a potential difference of 1 volt. 1 eV thus corresponds to $6.25 \cdot 10^{-18}$ Ws. It was usual in the past to give the radiation dose as the energy in rad relative to the irradiated quantity. Since 1 rad at $6.25 \cdot 10^{13}$ eV/g is a very small unit, the radiation dose was converted to Megarad: 1 Megarad = $6.15 \cdot 10^{19}$ eV/g = 10 Ws/g = 10 Joule/g or recently 10 kgy (kilogrey).With current paint systems 50 J/g or 50 kgy are usual to ensure adequate curing of the coating. Another important characteristic is the dose rate per unit time which is given in kgy/min.

150 – 300 kV are applied in general to accelerate the electrons, or up to 500 kV in rare cases. The highly accelerated electrons exiting the titanium window interact with the air and are significantly braked as a result. Electron beams therefore have a limited range. Furthermore, the electrons are scattered by interaction with the paint and consequently form new secondary electrons. Only these are slow enough to be able to target molecules for ionization and to form radicals. The retardation of the primary electrons also results in short-wave X-ray bremsstrahlung. Electron beam systems are therefore subject to radiological protection legislation in most countries and must be screened to prevent the emission of X-rays by a 12 mm thick lead lining or 50 cm thick concrete walls.

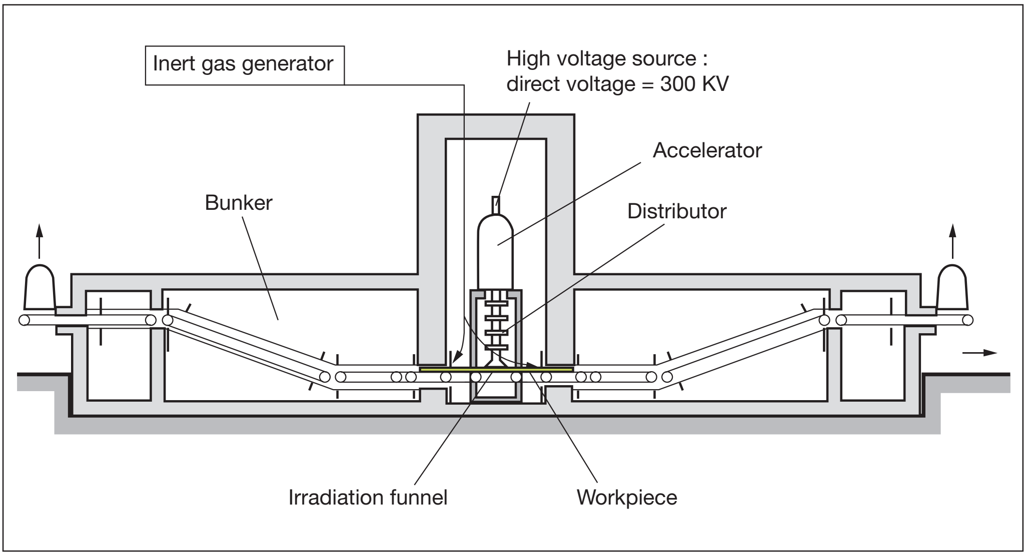


Fig. 4.3.31
Scheme of electron beam curing equipment

Amongst commercially available electron guns a distinction is drawn between devices with punctiform electron sources whose beam has to be deflected, i.e. scanned, to ensure its trouble-free use, linear accelerators and guns with plate cathodes. Linear accelerators have a rod-shaped hot cathode which extends over the entire width of the coating to be cured. The linear accelerators in turn are divided into guns with and without grille scattering. In the former case the tungsten cathode is surrounded by a grille as a counter-electrode. As a result an electron cloud forms. A second grille transforms the electrons into an electron cloud aimed at the object so that it contains its final energy before it exits the titanium window. A curtain of accelerated electrons generated in this way is wide enough and therefore requires no additional scanning.

Electron guns without grille scattering produce direct acceleration of the electrons emitted by the tungsten wire.

Apart from linear accelerators, plate-type guns have also proved successful. Several linear cathodes release electrons which are accelerated in two dimensions through a grille-type counter-electrode in the direction of the discharge window. Although the uniform distribution of the radiation intensity does not match that of linear accelerators, its cathode has a better service life.

Curing coatings by means of electron beams is an extremely attractive proposition with regard to energy consumption. A simple energy calculation clearly illustrates the positive energy balance by comparison with convection drying. With a throughput time of 30 minutes and a baking temperature of 150 °C the consumption of a convection drier with a temperature difference of 130 °C, a specific heat for the paint of 2 J/g, and an energy ratio for the paint to be heated of 1% of the drier's total energy consumption is: 130 x 2 x 100 = 26,000 J/g (see chapter 4.3.1).

Electron-beam curing, on the other hand, assuming a 100% efficiency, is significantly cheaper at only 50 J/g coating material**,** i.e. its energy consumption is 500 times lower than with convection drying. Even when taking the real efficiency into account, the necessary energy requirement is approx. 10% of drying by heat transfer.

4.3.3 Summary

Drying and curing systems are mainly used in industrial painting processes for film-formation purposes. They accelerate the physical drying process by emitting organic solvents or water and activate the crosslinking reactions by the transfer of thermal or radiation energy. Heat transfer takes place by convection with a carrier gas, by conduction or indirectly by IR and microwave radiation.

The ”cold” curing method with UV and electron beams is an interesting alternative to conventional methods from an environmental and economic perspective [4.4.107]. The increased interest in radiation curing by UV has been triggered by the new options provided by computer simulation and the use of robots which are making it possible to coat and cure even objects with complex three-dimensional shapes.

The geometry and materials of the substrates to be coated determine the choice of methods.

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5 Safety, Environmental Protection and Health

Responsible care for the environment in the handling of raw materials and products, from their manufacture and utilization to their final recycling or disposal, is today a generally accepted principle. By way of example, we can note that many software companies have now started to tackle the task of gathering and processing the abundance of data related to this problem (see chapter 5.5).

For some time now, the development and manufacture of paints and coatings have been governed by different guidelines on ”Responsible Care” and ”Sustainable Development” issued first by the chemical industry associations and quickly followed by the paint and coatings industry around the world. The underlying principle of these guidelines is that the industry is responsible for and takes into consideration all risks with their products and should only place as much strain on the environment as it can withstand through natural regeneration. In terms of the development of paints and coatings, both ”responsible care” and ”sustainable development” demand a comprehensive risk assessment from the points of view of the protection of health, environmental compatibility and other risks inherent to the handling of paints and coatings or the coated and cured object. This demand has increasingly had repercussions on the composition of the products, the choice of application processes and the recycling of all substances involved after their use.

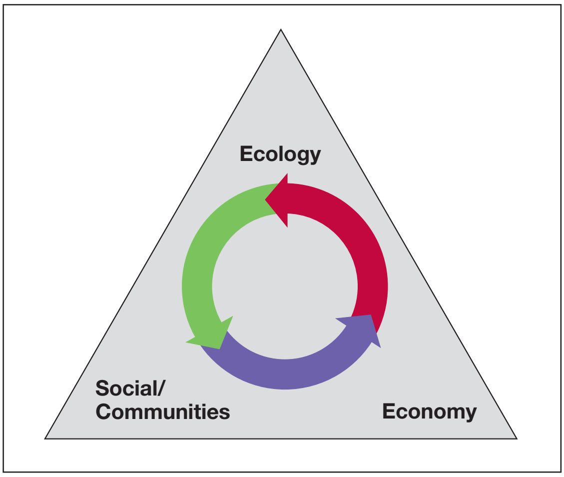

Fig. 5.1
The three dimensions of a sustainable and future related development

In other words, we in the present undertake to leave future generations a world that is fit for life.

This form of voluntary undertaking by the paint and coatings industry is not sufficient for lawmakers in European nations and the USA, with the result that a full range of legislative provisions have been drawn up to regulate paint and coating systems.

5.1 Legislative Framework

The production and handling of paints and coatings has been in the sights of lawmakers all over the world for several decades. In USA the Environmental Protection Agency (EPA), formed by the Congress in 1970, consolidated environmental regulations under one agency. EPA emphasized air quality through the Clean Air Act (CAA) which has the goal

- to protect the public's health
- to oversee the activities of the states
- to identify those pollutants that might cause or contribute to air pollution
- to have the EPA set regulations by establishing National ambient Air Quality Standards (NAAQS) for each pollutant
- anticipate pollutants which might endanger the public health or welfare

This was simply controlled by measuring the volatile organic compounds (VOC) being used for manufacturing processes, when they enter the respective plant. This was the key factor for the rather specific development of high solids, i.e. low solvent products in North America.

Additional important laws of interest to the paint and coatings industry include the Occupational Safety and Health Act (OSHA,1970), the Toxic Substances Control Act (TSCA,1976), the Resource Conservation and Recovery Act (RCRA, 1976), the Comprehensive Environmental Response Compensation and Liability Act (CERCLA, 1980), Superfund Amendments and Reauthorization Act (SARA, 1986), and the Clean Water Act (CWA,1977) with their respective several amendments until today. Most are based on the National Environmental Policy Act (NEPA) from 1969.

In Europe, Germany, together with the Scandinavian countries, stands out as a particularly regulation intensive country before European laws have been established, which was controlling the industrial processes by emission or immision measurements and forcing the industry to invest in abatement technologies. In the past, this discrepancy has led to widely divergent situations inside the European countries in their handling of paints and coatings as well as between Europe and North America.

In the framework of the European unification and the harmonization of national laws, the first task was to safeguard the free trade of products, plants, appliances and waste materials. Consequently, the first areas of European regulation were the law on hazardous substances, the law on hazardous goods, the law on protection at machines and the law on waste management. Since the seventies, environment related laws have moved into the foreground, and they now play a major role, with sometimes highly controversial debate. These laws include the VOC Directive (see chapter 2.3.2) and in particular the in 2007 established directive of introducing and using chemical substances, so called “REACh” (Registration, Evaluation and Authorisation of Chemicals).

The legal basis for the manufacture, storage, transportation and application of paints and coatings is still the specific local legislation of the individual nations. This legislation, through updating, is now increasingly influenced by Europe wide framework directives. These directives establish the minimum requirements for the laws, provisions and regulations that must be introduced in the individual member states.

The basic legal foundations described below refer to German law, which in many cases is similar to that of the other member states of the European Community.

The laws and their associated regulations for implementation applicable to all industries that handle paints and coatings can be classified into three main risk areas:

1. Handling of paints and coatings
2. Environmental pollution by emissions into the air, wastewater and landfill sites
3. Health risks

This classification is based on the types of danger that can be caused by coating materials:

Physical features	*Explosive* *Oxidizing* *Highly inflammable* *More inflammable* *Inflammable*
Health features	*Very toxic* *Toxic* *Harmful to health* *Caustic* *Irritating* *Cancerogenic* *Mutagenic* *Reproduction toxic* *Sensitizing*
Environmental features	*Harmful to environment*

The associated laws, provisions and technical regulations often overlap in complex interrelationships, so that the handling of paints and coatings is covered by legal requirements from a variety of sources. Together with Europeanization, which intervenes at different levels of German legislation, this complexity is one reason why considerable expertise is now necessary in the production and application of paints and coatings in order to satisfy all the legal requirements (see above). Assistance is provided by the relevant industry associations, such as, in Germany, the Verband der deutschen Lackindustrie (VdL – Association of the German Paint and Coatings Industry), a part of the Verband der chemischen Industrie (VCI), with head office in Frankfurt. Additionally, many software companies have been set up to offer an update service on the legal requirements, often on a world-wide basis, together with the associated consequences for labelling, the formulation of safety data sheets, storage provisions, transport provisions and other questions affecting the operations of the paint and coatings industry.

In Germany, the basis for the handling of coating materials is the ”Chemikalienrecht” (Chemicals Act). Important subsidiary laws include the ”Gefahrstoffverordnung” (GefStV – Ordinance on Hazardous Substances), the ”Bundesimmissionsschutzgesetz” (BimSchG – Federal Immission Control Act), the ”Wasserhaushaltsgesetz” (WHG – Water Resources Act) and the ”Kreislaufwirtschafts- und Abfallgesetz” (KrW-/AbfG – Waste Management Act). Many other ordinances and administrative provisions are derived from these laws.

One important and long established instrument that provides the cornerstone for the safe handling of paints and coatings is the Material Safety Data Sheet (MSDS). The legal obligation to provide the MSDS in the individual European countries was established by EU Directive 88/379/EEC, later replaced by 1999/45/EC (new directive on chemical preparations). Under this Directive, the manufacturer of paints and coatings is obliged to present the MSDS at the latest on first delivery of the product and must update the MSDS, with the obligation to provide proof thereof, in the event of any modification of the product. The format specified in EU Safety Directive 91/155/EEC has been further developed by the CEPE, the European umbrella organization for national associations of the paint and coatings industry, in collaboration with the VdL, and has now been introduced in TRGS 220 (”Technische Regeln zur Gefahrstoffverordnung” – Technical Regulations Relating to the Ordinance on Hazardous Substances). This format covers all relevant information on product composition, potential dangers of a technical nature and dangers to health, and it explains the necessary protective measures and the remedial action to be taken in the event of accidents and incorrect handling of paints and coatings. These aspects have been structured on a European level in 16 points, as shown in Figure 5.1.1.

1	Identification of material, composition and company
2	Description of composites
3	Potential Dangers
4	First Aid
5	Fire Fighting Recommendations
6	Measures at unintentional releases
7	Handling and Storage
8	Exposure limits and personal protection
9	Physical and chemical properties
10	Stability and Reactivity
11	Informations to Toxicity
12	Informations to Ecology
13	Recommendation for Disposal
14	Informations to Transportation
15	Instructions
16	Additional Informations

Fig. 5.1.1
The 16 mandatory topics of the EU-Material Safety Data Sheet Directive 91/155/EWG

Moreover, the identification of the products on packaging has been supplemented to enable rapid evaluation of the potential dangers, on the basis of visible and easily understood symbols.

These are different in Europe and USA as seen in figure 5.1.2. The United Nations (UN) is under way to harmonize the labelling of chemicals on a worldwide basis. The form of the American MSDS is recommended by OSHA which belongs to the US Department of Labor. It must comply with the OSHA Hazard Communication Standard 29 CFR 1910.1200 which identifies both contents of the MSDS and of health and safety label requirements. In the United States, the Departement of Transportation is responsible for Hazardous Materials Transportation regulations under 49 CFR.

In Europe substance-related data for the preparations of coating materials is often added electronically on the basis of standard wording in R (= risk) phrases and S (= safety) phrases. The R phrases describe the potential risks, whilst the S phrases give corre-

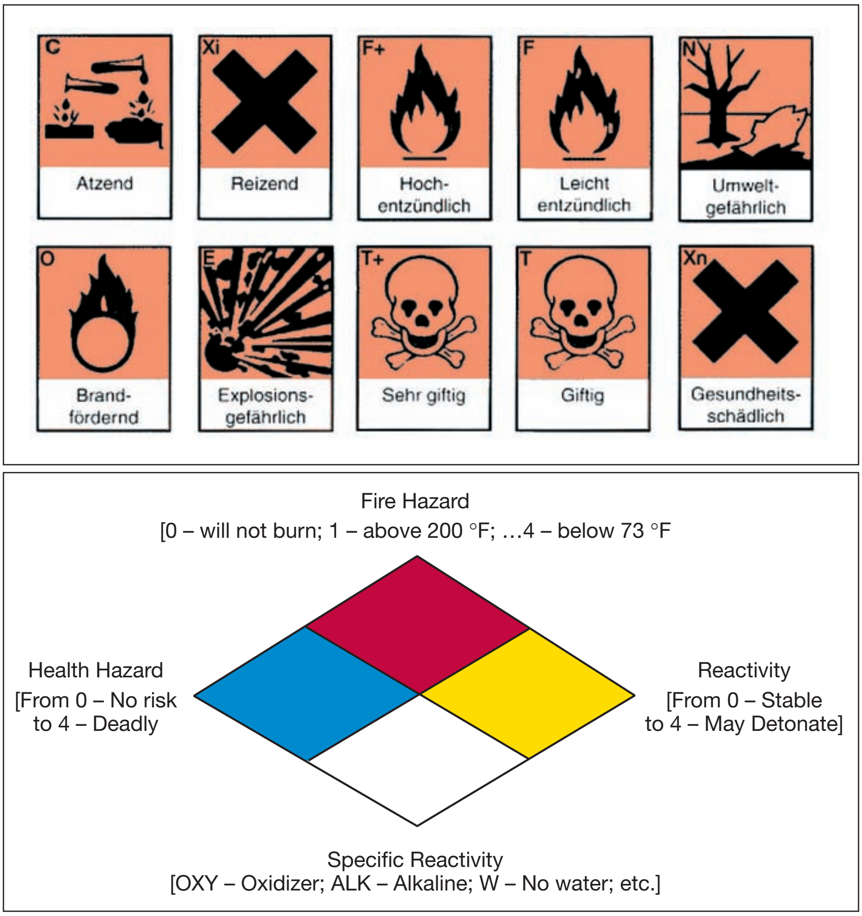

Fig.5.1.2
The most important symbols of danger of substances according to GefStV (Germany) (above) and TSCA (USA) (below)

sponding safety instructions. These phrases are then included in the Material Safety Data Sheet and product labelling.

In Germany, assistance and state-of-the-art updates on safety questions are provided by, among others, the ”Berufsgenossenschaften” (Accident Prevention and Insurance Associations), which conduct safety inspections with the relevant companies in the event of accidents, inform the sectors concerned and issue corresponding workplace regulations.

This process applies to the state of the paints and coatings before and during application. Due to their polymeric character, applied and hardened coats are generally uncritical in industrial use, although their disposal must always be more closely evaluated and is increasingly becoming the focus of legislation within the framework of life cycle analyses. One striking example in Germany is the ”Altautoverordnung” (Used Car Ordinance), which lays down a 2-phase timetable for achieving a recycling rate > 95 % of the mass of all cars by the year 2015.

Legislation in Europe is not only changing fast as a result of Europeanization, but also, given the dynamization clauses frequently employed in the laws of individual countries, it is following the technical state of the art and the latest findings in the fields of safety, environmental protection and health.

For new products to be introduced into the coatings market in USA raw materials including polymeric resins of the coatings must be registered with the EPA under TSCA. The EPA regulates the application and determines the necessary toxicity investigations to be completed and risk assessment evaluated prior to the determination of whether the EPA will allow commercial use of the chemical. Chemicals are normally registered by a CAS (Chemical Abstract Service)-Number for better worldwide communication. Specific application of raw materials and coatings are necessary for the food and drug industry. The US ”Food and Drug Administration”(FDA) has worldwide acceptance for their registration system.

Under the Canadian Environmental Protection Act (CEPA), proclaimed in 1988, registration procedures for new chemicals for commercial application and use in Canada was established. These are similar to the USA. However, Canada uses a tiered approach to both risk assessment and registration.

In Europe the ”Stoffrichtlinie” also only applies for new low molecular weight raw materials for the coatings industry. A new approach has been made recently by a so called ”White Paper” by the European administration to introduce an application and risk assessment system for all chemicals including paints and coatings.

In Asia the legal situations are very specific to the respective countries. They reach from almost no requirements to medium level requirements compared to Europe and USA.

From today’s point of view, one problem with further legal developments is the sector-by-sector approach, i.e. provisions are updated solely with a view to air, water or soil, so that there is practically no overall co-ordinated optimization. Also, European environmental legislation does not necessarily mean harmonization, because the member states can impose additional requirements when enacting the Directives.

In the chapters that follow, important features of the current legislative position in Germany and Europe are explained on the basis of the main focuses of the legal texts covering the specific fields of technical safety in the handling of paints and coatings (Chapter 5.2), environmental protection for air and water (Chapter 5.3) and the protection of human health (Chapter 5.4). The state of the art necessary to meet the legal specifications in Germany for the manufacture, storage, transport and application of paints and coatings can only be achieved by careful study of the laws in collaboration with the authorities.

5.2 Safety

Both the application and production lines for paints and coatings are exposed to dangers of explosion and fire due to the solvent content of solventborne and, in some cases, waterborne paints and coatings, and also due to potential particulate emissions from powder coatings. The provisions on workplace safety are therefore oriented towards the prevention of potential dangers and the elimination of known dangers. One particular hazard in this respect is electrostatic paint application.

Moreover, additional laws and provisions regulate the handling of paints and coatings as a function of the potential dangers of the substances within the process chain between production and application, i.e. during storage and transport. In some cases, these regulations also include emission related health protection, which shall be discussed separately later in this chapter (see chapter 5.4).

For all stages in the production and application of coating materials, legislation requires a complete set of operating instructions, which must be made known to all employees concerned and must serve as the guiding basis for their working procedures.

In the annual statistics issued by the Accident Prevention and Insurance Associations in Germany, the chemicals industry, which includes the paint and coatings industry, tops the list as the ”safest” industry segment.

5.2.1 Manufacturing

The legal provisions and standards for protection against dangerous working substances during the planning and operation of a production site for liquid paints and coatings include the ”Regeln der Berufsgenossenschaft” (BG-Regeln – Accident Prevention and Insurance Association Regulations), formerly termed ”Unfallverhütungsvorschriften” (UVV – Accident Prevention Regulations) and the ”BG-Richtlinien” (BG Directives), formerly termed ”Sicherheitsregeln” (ZH - Safety Regulations). These provisions are continuously updated by the Accident Prevention and Insurance Associations on the basis of analyses of actual accidents.

From the point of view of safety, one of the key legal texts governing the use of inflammable paints and coatings containing solvents is the ”Explosionsschutzrichtlinie” (EX-RL – Explosion Protection Directive), which provides comprehensive information for the evaluation of explosion risks as a function of the substances to be observed and their flash points (see figure 2.1.150) and provisions for safety measures, including struc-

Zone 0:

Rooms/areas where an explosive atmosphere is present in permanence or for long periods.

Zone 1:

Rooms/areas where it must be assumed that an explosive atmosphere can occur occasionally during normal operation.

Zone 2:

Rooms/areas where it can be assumed that an explosive atmosphere does not occur during normal operation. If it does occur, it does so only for a short period.

Zone 20:

Rooms/areas where an explosive atmosphere is present in permanence or for long periods or frequently in the form of a dust cloud in the air.

Zone 21:

Rooms/areas where an explosive atmosphere can occur occasionally during normal operation in the form of a dust cloud in the air. Deposits or layers of combustible dust are usually present.

Zone 22:

Rooms/areas where it can be assumed that an explosive atmosphere does not occur during normal operation in the form of a dust cloud in the air. If such an atmosphere does occur, it does so only for a short period or while accumulations or layers of combustible dust are present.

tural and technical precautions for the prevention of explosions or deflagrations. One essential section of this Directive is the description of precautions for preventing explosive air mixtures. This section classifies sites into different zones according to their degree of danger. It also describes precautions and safety measures for repair work.

In general, the law stipulates that electrical appliances in explosion hazard rooms must conform to the Explosion Protection Directives (EX-RL/ZH1/10). For example, switches designed to meet this provision prevent any sparks induced by the switching operation from entering into contact with explosive vapour/air mixtures.

The assessment of the required scope of further protective measures is based on the risk assessment of the relevant production areas:

For the application of inflammable paints and coatings (see chapter 5.2.2), separate rooms must be provided and must be isolated by fireproof means from other rooms and buildings. The same applies to the store, generally situated next to the application line, for supplying coating materials to the application installations. All these rooms must be marked with the notice: ”Fire, open light and smoking prohibited”. Floors and walls must be noncombustible and must be easy to clean. The doors have to open outwards, must be closed during normal operation and must shut automatically in the event of a fire. Rescue routes must be designed and marked to ensure that the paint room can be evacuated by the shortest possible route. A minimum number of ABC fire extinguishers is stipulated: 2 for a floor area up to 50m^2 and a further 2 for every additional 200 m^2, each containing 12 kg of extinguishing powder. In addition, extinguishing covers and showers for extinguishing burning clothing must be installed in a visible position in the rooms.

The application installations and the workstations handling paints and coatings, e.g. measuring stations, transfer filling installations etc. must be fitted with air extraction systems that prevent the formation of explosive solvent/air mixtures. After switching off the relevant equipment, the extraction systems must remain in operation until the formation of explosive or ignitable air/solvent mixtures is reliably eliminated. In the event of failure of the extraction systems, the application equipment and its downstream plant components must be automatically switched off.

All conductive equipment and building parts, e.g. walls, ceilings, floors, conveyers, dispersion machines and containers must be earthed to prevent the generation of a static charge that can be discharged by sparking, in particular during transferral, dispersion and mixing.

Particular attention must be paid to the floors. They must be electrostatically conductive with a maximum permissible leakage resistance of 1 MW. In this respect, it must be borne in mind that accumulations or deposits of paint and coating residue can increase the earth leakage resistance. Consequently, the floor must be regularly cleaned.

5.2.2 Storage

The storage site for supplying the application equipment and every storage site used during the manufacture and application of paints and coatings are subject to the ”Verordnung über brennbare Flüssigkeiten” (VbF – Ordinance on Combustible Liquids) and the associated ”Technische Regeln für brennbare Flüssigkeiten” (TRbF – Technical Regulations for Combustible Liquids). These provisions apply to products classi-

Class	Characteristics
A	Liquids with flash points not above 100 °C and not performing like group B concerning water solubility:
A1	Liquids with flash points < 21 °C
A2	Liquids with flash points of 21 – 55 °C
A3	Liquids with flash points of 55 – 100 °C
B	Liquids with flash points < 21 °C which are soluble in water at 15 °C in all ratios or which combustible components are soluble in water at 15 °C in all ratios
B2	Liquids with flash points of > 21 °C and < 55 °C which are soluble in water at 15 °C in all ratios or which combustible components are soluble in water at 15 °C in all ratios
Remarks: Combustible liquids of group A2 and A3 have to be treated equal to those of group A1 when heated above their respective flash points.	

Fig. 5.2.1
Classification of combustible liquids according to "Betriebs-Sicherheits-Verordnung" (Operating Safety ordinance)

fied in specific hazard classes. As from the end of 2002, the Vbf shall be replaced by the "Betriebs-Sicherheits-Verordnung" (Betr.Sich.V. – Operating Safety Ordinance).
The technical and physical criteria of these provisions include flash points and water solubility. The flash point is the lowest temperature at which a solvent or a preparation such as paint under specified conditions releases such large quantities of vapour into the air that an inflammable mixture is generated. This characteristic value is measured in technically standardised apparatus (see chapter 2.3.2). The substances are classified into different "classes of endangering" according to the position of their flash point and water solubility (see figure 5.2.3).
Under TRbF 20, storage sites are classified into storage not subject to compulsory visual notice and permission and storage subject to compulsory visual notice and permission, depending on the quantities stored and the location. Here, limit values are laid down as a function of the class of danger, the type of container and the type and size of the rooms.
The storage of combustible liquids and paints in passageways, thoroughfares, stairwells and generally accessible corridors, on the roofs of residential buildings, hospitals, office blocks and similar buildings and their penthouses, in guest rooms and canteens and also in workrooms is prohibited. Moreover, no emptied containers may be stored in these places if they were previously used to store liquids of classes of danger A1, A2 or B. This requirement must be strictly observed, because even small quantities of combustible liquids constitute an explosion hazard.
This ordinance is not applicable to workplaces where combustible liquids are stored for only short periods and in small quantities to ensure uninterrupted continuation of work in progress.

5.2.3 Transportation

At European level, the transportation of dangerous goods is governed by the European Agreement on the International Carriage of Dangerous Goods on Road, the ADR (= Accord europeen relatif au transport international des marchandise dangereures par

route). The latest amended version of this agreement entered into force on 1.7.2001 and must be adopted in the laws of the individual member states by the end of 2002.
The corresponding laws in Germany are the Gefahrgutverordnung Straße/Schiene (GGVSE – Ordinance for the Transportation of Dangerous Goods by Road/Rail) and Gefahrgutverordnung See (GGVSee – Ordinance for the Transportation of Dangerous Goods by Sea).
The principal elements of these laws are a classification of dangerous goods specifically for transport, the corresponding markings and provisions specifying the capacity and size of containers and transportation system.
All inflammable paints and coatings are governed by these regulations. The regulations also apply to waterbased paints due to the risk of groundwater contamination.
To improve safe handling all companies dealing with loading, unloading and transportation of dangerous goods have to meet the EU Directive 96/35/EC, which requires to have a qualified Dangerous Goods Safety Advisor (DGSA) [5.8.1].

5.2.4 Application

The laws and provisions governing technical safety in the handling of paints and coatings in paintshops are described in chapters 5.2.1 and 5.2.2. One special case is electrostatic spray application, because here solventborne or waterborne paints and powder coatings are applied at high voltages of up to 100 kV. The associated moments of danger are firstly in the ignition of solventborne and waterborne paints having high solvent contents (< 55 % water) and of their solvent/air mixtures and secondly in the possibility of incorrect operation of the devices by the application personnel. The risk of ignition also exists with powder/air mixtures and must therefore also be taken into account during powder coating.

Protection of persons
The safest and simplest protection against contact with voltage-conducting systemcomponents consists in enclosing these components in closed booths. The necessary access points in the form of doors or gates must be integrated in safety circuits, so that when they are opened the voltage is automatically switched off. Additionally, the system components must be earthed, and in general an alarm must be triggered before contact can occur.
Electrostatically assisted hand-held devices must be designed with an electric circuit that ensures that any contact with live parts has no effect on the relevant persons and a short circuit is prevented if the gap between the gun and the object being coated is too small. Paints and coatings with flash points <21 °C must not be applied by handheld devices, and voltage sources and their connections must not be installed in the booth.
Conductive, usually waterbased paints and coatings require insulation of the feed tank, because there is a danger of short circuits across the dispensing lines. These dispensing lines must also be insulated.
Triboelectric spray devices for powder coatings do not need high voltage electrodes. They generate the necessary voltage by friction of the powder at the spray units (see chapter 4.2.2). The currents generated during application are in the µA range and are uncritical. However, a high charge may occur in the event of incomplete grounding of

all live parts. The same also applies to the application personnel, who must therefore wear conductive footwear and operate on conductive floors.

Explosion and fire protection

There is a danger of explosion in electrostatic coating lines if the following combination of conditions occurs:

1. an explosive air mixture is present,
2. an ignition source with a higher energy content than the minimum ignition energy of the explosive air mixture is present and
3. a spark discharge is generated from the ignition source.

The aim of the safety standards and therefore of all coating plants and application personnel is to eliminate at least one of these conditions with as high a probability of success as possible. Here, the prevention of explosive air mixtures takes top priority. This task is relatively simple with a suitable air intake and its monitoring in the paint booths. For example, when the air supply falls below a specified value, the high voltage can be automatically switched off.

For powder coatings, this precaution is also significant but it cannot be safely employed in practice due to the accumulation of powder particles and the swirling of these particles in the air line. Ignitable mixtures occur at levels greater than 20 g powder/m^3 air.

However, for both liquid and powder coatings, these measures are ineffective in the spray jet itself. For this reason, precautions must be taken at the ignition sources.

Firstly, all ignition sources other than the application devices themselves must be absolutely prohibited. Moreover, the spray guns as ignition source must have an energy limiting system and a mechanism to prevent spark discharge. Proof of the technical safety of the various types of spray system is provided by tests conducted by State test bodies such as the Technische Überwachungsvereinen (TÜV – Technical Control Boards) or the Physikalisch-Technische-Bundesanstalt (PTB – Federal Physical and Technical Institute) in Braunschweig. Air/gas mixtures with known ignition energies are used for these tests. Guns for the triboelectric charging of powder coatings are officially approved if their charge currents do not exceed a maximum of 15 µA.

An grounded state by appropriate earthing must be ensured in less than 2 seconds after the high voltage is switched off, so that the system components can be touched without danger.

The following requirements apply to the earthing:

- Grip components of hand-held guns must be at least 20 cm^2 from an electrically conductive and earthed contact surface.
- All conductive parts, such as booths, operating devices and other objects must be fully earthed.
- Application personnel must wear electrically conductive footwear.
- The leakage resistance between the personnel’s footwear, the floor and earth must not exceed 1M W.
- Booths for applying liquid coatings must be made of electrically conductive material and must be earthed.
- The resistance at points of contact between each workpiece and the earthed pole of the high voltage source must not exceed 1 MW during the coating process.

This last requirement can only be met by careful and frequent cleaning of all suspended devices. Also, in this context, an inspection of the suspended devices for properly grounded state used in the coating process is highly advisable.

5.3 Environmental Protection

5.3.1 Exhaust Air

The agreement reached by the international community on 12.11.2001 in Marrakech under the auspices of the UN laid down concrete measures for the implementation of the previous year's Kyoto Protocol. The aims of this climate protection agreement is to reduce the emission of greenhouse gases, including carbon dioxide, by an average of 5.2 % by 2012, as was agreed in a subsequent undertaking [5.8.2]. The Federal Republic of Germany has set itself the target of a 21% reduction. Further reaching targets are contained in the 5th and 6th European Union Environment Programme and the United Nations Environment Programme. These targets form part of a package that also includes improvement in the quality of life and a reduction in the ozone concentration at near ground level. It is precisely here, in the lower atmosphere, that ozone is generated by hydrocarbon emissions, e.g. from cleaning systems, paint shops and automobile emissions in combination with oxygen and UV radiation.

Segments	**1988**	**1998**	**2010[1]**
Traffic	1461	462	250
Others[2]	585	243	245
Use of solvents[3]	1197	1000	500
Total	**3241**	**1705**	**995**

1. Target
2. Industry, Households, FCKW, etc.
3. thereof 165 kt for Coatings in 2010

Fig. 5.3.1
Contributions of organic compounds to the emission in Germany in 1000t

The share of the paint and coatings industry is roughly a third of the ”solvent use” segment of figure 5.3.1. The need for action to attain the targets set for Germany is much greater for the application of paints and coatings than for their production, which today takes place almost exclusively in closed systems. For this reason, the main focus of the descriptions that follow will be on paint and coating application.

The ”Technische Anleitung zur Reinhaltung der Luft” (Clean Air Guidelines), or ”TA Luft” for short, is applicable to plants requiring approval as defined in the ”Bundesimmissionsschutzgesetz” (BImSchG – Federal Immission Control Act) and serves as the generally recognised technical standard for the competent authorities. Solvent emissions from the production and application of paints and coatings in industrial plants is regulated by the 31st ”Bundesimmissionsschutzverordnung” (BImSchV – Federal Ordinance on Immission Control), which is the adopting ordinance for incorporating the European VOC Directive of 1999 into German law.

Paragraphs 1 and 22 of BImSchG lay down the qualitative targets for industrial plants:

> §1: ”The aim of this Act is to protect humans and also animals, plants and other things from harmful environmental impacts and also, in the case of industrial plants subject to permission, from dangers, significant disadvantages and significant pollution ... and to prevent the generation of harmful environmental impacts.”
>
> §22: Industrial plants not subject to permission must be installed and operated in such manner that
> 1. harmful environmental impacts that are avoidable according to the state of the art are prevented,
> 2. environmental impacts that are unavoidable according to the state of the art are limited to a minimum and
> 3. the waste materials generated by the operation of the industrial plants can be removed in accordance with regulations

Coating lines and paintshops are subject to permission if they use more than 25 kg of organic solvents per hour and/or if their annual consumption of organic solvents is greater than or equal to 15 t.
Specific emission limits are laid down for different industries. The 31st BImSchV permits solutions based on low emission paints and coatings in the form of reduction plans as well as solutions based on the aftertreatment of emissions. Overall, approximately 500 paintshops and coating lines are subject to permission under the BImSchG. These plants include automobile industry paintshops, package coating lines, coil coating lines and other coating lines for mass goods.
For all industrial plants, the 31st BImSchV lays down separate pollution limits for the emitted air depending on the pollutant class of the polluting components.

Industrial segment	**Permission Threshold**	**Emission limits VOC/m^2 coated area; mg/m^3 emitted air Europe**		
		New Plants	**Old Plants**	**Germany**
Automotive OEM	> 15 t Solvents/a	45 g VOC/m^2 (1)	60 g VOC/m^2	35 g VOC/m^2
Heavy Truck OEM	> 15 t Solvents/a	70 g VOC/m^2 (1)	90 g VOC/m^2	70 g VOC/m^2
Metal and Plastic	> 15 t Solvents/a	Oven: 50 mg/m^3 (2) Applic.: 75 mg/m^3	(3)	50 mg/m^3
Wood and Furniture	> 25 t Solvents/a	Oven: 50 mg/m^3 (2) Applic.: 75 mg/m^3	(3)	50 mg/m^3
Airplanes	> 15 t Solvents/a	Oven: 50 mg/m^3 (2) Applic.: 75 mg/m^3	(3)	50 mg/m^3
Paint Manufacturing	> 100 t Solvents/a	150 mg/m^3 (2)	(3)	50 mg/m^3

(1) Square meter of coated area
(2) Cubic meter of emitted air
(3) Limits for new plants as valid for old plants in 2007

Fig. 5.3.2
Pollution limits according to the 31st BimSchV for paint use and paint manufacturing

The legislative provisions are based on the principle of dynamization. For example, the limits should be considered simply as minimum requirements that must be attained within specified deadlines in the case of older plants. By contrast, new plants are assessed according to the current state of the art, which in environment laws is considered to mean the development and testing of advanced processes.

The ”TA Luft” of 1986, as a technical regulation for the attainment of emission limits, has been reformulated for this purpose, and the new version is in force since October 2002. However, ”TALuft” still only regulates particulate or dust emissions from the production and application of paints and coatings.

Product related emission aspects

The achievable progress in emission reduction through the development of new paints and coatings can be illustrated by the example of the coating process in the automotive industry.

These low solvent or solventfree paints and coatings have also found applications in industry as a whole. The adoption of the European VOC Directive in the form of the 31st ”Bundesimmissionsschutzverordnung” (Federal Ordinance on Immission Control) not only includes large industrial plants but also to a significant extent medium sized and small paintshops or other production sites that apply solvents. In most cases, the threshold solvent consumption triggering the obligation to obtain permission from the relevant authorities is reduced by a third to 5 t/a, but this value is further considerably reduced to 0.5 t/a for many small automotive refinish bodyshops. For Germany, the figure is 0 t/a. In the case of automotive paintshops the threshold is 15 t/a for large-scale mass production.

One important instrument of this ordinance, mainly for the smaller and medium sized paintshops, is the Solvent Management Plan (SMP). This plan calculates a solvent balance between the purchase and consumption of solvents in all relevant products, taking into account the assumed diffuse solvent losses in the application department.

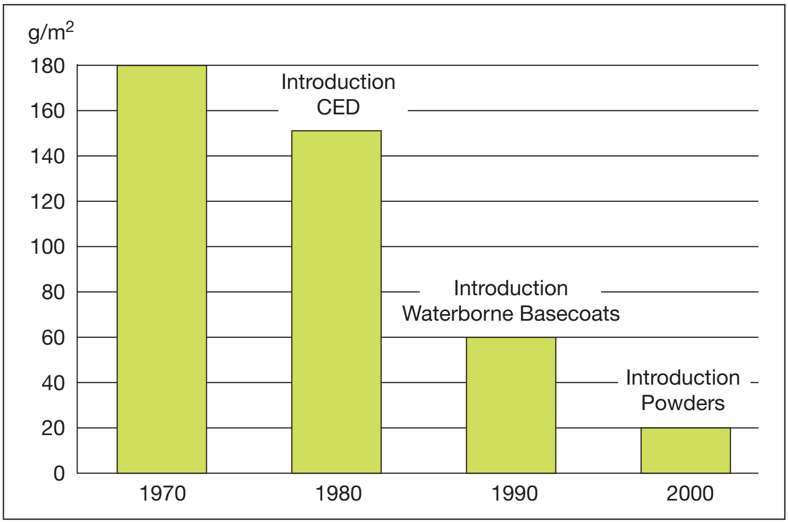

Fig. 5.3.3
Reduction of emission for automotive OEM coatings related to the coated area in m²

Irrespective of this management plan, obligations are laid down for the reduction and monitoring of emission sources. Here, paintshops are given the option of either adhering to the specified limits in mgC/m^3 (see figure 5.3.2) or presenting a reduction plan based on the solvent content per solids content. These reduction targets must be based on the current industrial standard and must be demonstrably attained in accordance with target deadlines to be agreed within the specifications laid down by law. Depending on the field of application, these specifications are between 150 l and 320 l of solvent emission per 400 to 200 kg of paint solids consumed.
A key feature of paints and coatings for drawing up an SMP is the ”VOC level” (VOC = Volatile Organic Compounds). This value applies to paints and coatings ready for application and specifies the content considered to be volatile and therefore a potential source of emissions. The VOC level is calculated by the following formula (see chapter 2.3.2):

$$\text{VOC (g/l)} = \frac{[\text{Mass of volatile contents (g)}] - [\text{Mass of water (g)}]}{[\text{Volume of coating material (l)}] - [\text{Volume of water (l)}]}$$

The distinction between volatile and nonvolatile (solid) is defined as follows for an organic compound:

> An organic compound is volatile if at 293.15 K it has a vapour pressure of 0.01 KPa or more, or if it has equivalent volatility under the relevant operating conditions. The creosote content that exceeds this vapour pressure at 293.15 K is considered a volatile organic compound.

Environment

A further criterion for determining the emission limit is the toxicological assessment of the extent to which organic substances are carcinogenic, mutagenic or toxic for reproduction. These substances are known as ”cmr substances” and have much lower emission limits than other organic substances (see figures 5.3.2 and 5.3.4).

Type of Emission	**Area**	**Limit Values of Emission**	**required by**
Dust/Particles	Application	20 mg org. C	TA Luft
	Spray Application	3 mg org. C	TA Luft
	Paint Manufacturing	10 mg org. C	TA Luft
Organic Substances		50 mg org. C	BImSchV
	R45, R46, R49, R60, R61	1 mg org. C	BImSchV
cmr-Substances$^{(1)}$	R40 (1)	20 mg/org. C	BImSchV
(1) R-Phrases: see chapter 5.1			

Fig. 5.3.4
Threshold of volatile cmr substances and other compounds per m^3 emitted air from paint shops according to 31st BimSchV in Germany

One characteristic that is not directly related to harmfulness is the smell of the emitted substances. Chapter 5.2.8 of ”TA Luft” lays down in general that any bothering by smell to the residents near an industrial plant must be prevented. The appropriate technical measures for the plant are listed. The emission-limiting requirements can be quantified on the basis of olfactometrically measurable values in accordance with VDI Directive

3881.1 - 4 (VDI = Verband Deutscher Ingenieure, the Association of German Engineers). For this purpose, the odor thresholds of solvents and other substances are determined by trained test persons. Here, it should be noted that substances such as hydrogen sulphide can already be smelled before they reach a harmful concentration. On the other hand, there are also substances that are odorless or that can act on the organism in harmful concentrations before they have a perceptible smell. Within the framework of industrial plants subject to permission, the ”Geruchsimmissionsrichtlinie” (Odor Emission Directive) must be observed.

Process engineering possibilities for emission reduction
Current legislation in Europe and other regions of the world such as North America also permits a process engineering solution for emission reduction in order to achieve the specified limits. In this case, the focus is on the pollution values of the exhaust air, which must be metrologically monitored on site.

In paintshops and coating lines, solvents can be emitted at three points, namely paint supply/paint storage, paint application and curing/oven.

Depending on the coating process, coating type and emission point, the air contamination levels can vary considerably. However, we can assume that for throughputs with much more than the legal threshold of 5 t/yr of solvents, the exhaust air must be cleaned if the requirements are not met by the use of low emission coating materials. Different processes have been found successful for high and low contaminant levels in the exhaust air.

For the relatively high contaminant level of the exhaust air from the baking oven compared to the spray booth, the preferred method is thermal afterburning, whilst for lower pollution levels at the paint supply and application stages the adsorption method has proved most successful. Large users of coatings such as the automotive industry combine the exhaust air flows, thereby meeting the emission limits by means of a central afterburning system for all emission sources.

Thermal afterburning is based on the complete combustion of the organic substances to form water, CO_2 and nitrogen oxides. The latter are generated partly by the nitrogen contents of the coatings, e.g. PUR coatings, and partly by the oxidation of atmospheric nitrogen at temperatures of 700 – 900 °C.

The temperatures necessary for complete thermal afterburning are attained by supplying additional fuels to the combustion chamber. In addition to the temperature, other important factors for achieving a high efficiency are the dwell time of the exhaust air and thorough mixing of the added fuel with the exhaust air.

The longer the dwell time in the combustion chamber, the better the

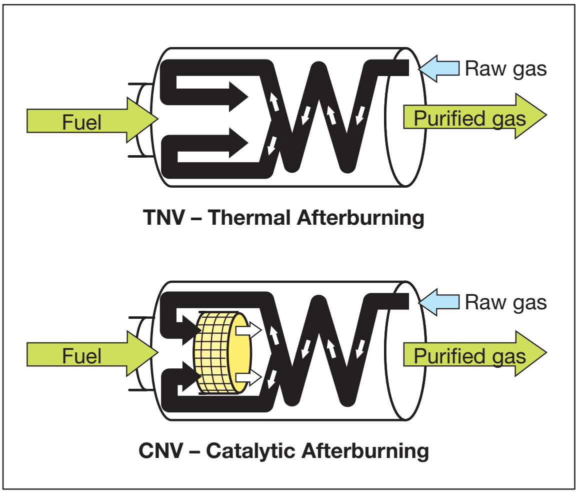

Fig. 5.3.5
Schemes of thermal afterburning equipment

cleaning effect of the system. A combustion temperature limit < 1000 °C is necessary, because above 1000 °C the formation of nitrogen oxides increases considerably and can exceed the permissible limits. On the other hand, a temperature as high as possible is favourable for reducing the carbon monoxide content. Modern systems can be set to the optimal conditions for the relevant coating materials and achieve highly efficient exhaust air cleaning.

As already mentioned, in all methods of thermal treatment of the exhaust air, problems are caused by the generation of secondary emissions. For example, if exhaust air with a low solvent content has to be aftercleaned to a level of less than 20 mg C/m^3, depending on the untreated gas content, up to 2 – 3 tonnes of carbon monoxide, up to 2 – 3 tonnes of nitrogen oxides and up to 1700 tonnes of carbon dioxide can be emitted per tonne of emitted VOC. Since carbon monoxide and nitrogen oxides play a part in the photochemical process that generates ozone in the lower atmosphere, this aftertreatment can be counter productive.

The thermal energy is generally utilised for the production process, for preheating the exhaust air flow or for other heating requirements. These ”integrated afterburning systems” operate economically with high exhaust air pollution levels.

In addition to thermal afterburning, the process of catalytic afterburning is used in individual cases. Like thermal afterburning, the catalytic method results in oxidation of the organic substances to water and CO_2. In this method, the activation energy of oxidation is reduced to 350 – 500 °C by suitable catalysts. Despite the energy advantages compared to thermal afterburning, in particular when integrated operation is impossible, this method has not found general favour because the catalysts that operate economically become contaminated by the substances contained in the coating lines and are consequently rendered inactive [5.8.3].

The adsorption methods are more significant, especially when the exhaust air flows are contaminated by low levels of organic substances. In this process, the organic substances from the vapour phase are deposited on a solid surface termed the ”adsorbent” and are thereby removed from the air flow. The bond with the adsorbent is primarily of physical nature and can therefore be reversed under certain conditions. One adsorbent with very high surface activity is activated carbon, which has also been found effective in plants for the paint and coatings industry. For problemfree operation, the exhaust air must be free of particulate matter. Activated carbon was previously used in solid bed systems that operated discontinuously with a through-flow of exhaust gas. Now, it is channelled continuously via perforated filters to a fluidized bed, so that the adsorbent can remove the solvents evenly from the exhaust gas. With a specific surface area of more than 1000 m^2/g, the highly porous activated carbon is channelled to a desorption system after charging with solvents from the exhaust air, in order to be freed of solvent either by overheated steam at 150 °C or by low-oxygen air (< 10 %) at 600 °C. The solvents are transformed to the liquid phase by cooling to room temperature.

The disadvantages of this process are the problems of solvent treatment by hot steam. If water-miscible substances are contained in the solvent mixture, they will not be in the organic but the aqueous phase. The water must therefore be treated. Depending on the type of solvent, desorption with inert gas or low oxygen air under conditions of thermal treatment at 600 °C will lead to more or less significant chemical changes of the solvent

on the catalytically active surface of the activated carbon. Regular partial replacement of the adsorbent is therefore necessary. The fact that that the adsorption rate of the solvents depends on their volatility and polarity should not be overlooked. Consequently, low polarity solvents with a low boiling point are more difficult to separate than the other components of the solvent mixture in the exhaust air.
The regeneration process is very energy-intensive.

Emission from coating films
For furniture or furniture surfaces and recently also the interior of automobiles, the evaporation of odor intensive or even physiologically harmful components of the coating, wood substrate or plastics is relevant [5.8.4]. For example, according to the "Gefahrstoffverordnung" (Hazardous Substances Ordinance), furniture emissions in closed rooms must not exceed specified limits. For formaldehyde, the maximum permitted value is 0.1 ppm (ml/m^3). Also, solvents remaining in the cured coating can constitute a health hazard or add to the pollution level in closed rooms. If necessary, control tests must be conducted under defined conditions (DIN 52 368 or DIN 55 666) in the normal environment or in a special test chamber.

5.3.2 Wastewater

The Wasserhaushaltsgesetz (WHG – Water Resources Act), in conjunction with the corresponding Water Acts of the individual German counties, specifies in detail the rules for the handling of groundwater and surface water. This Act applies to all industrial plants that either wish to or have to discharge contaminated process water into watercourses. The current new version of the WHG has adopted the principle of prevention, i.e. the prevention of wastewater, and the dynamization clauses of the Federal Immission Control Act. The federal structure of the "Wasserrecht" (Law relating to Water) requires the adoption of these new provisions in the water laws of the individual counties, in order to ensure their implementation throughout the Federal Republic.
The counties have passed ordinances on indirect discharging sources specifically for their own needs, laying down that substances dangerous to water must be discharged into main collectors. Direct discharge means that process wastewater is discharged directly into surface waters, e.g. streams or rivers.
Today, the general consensus of legislation is that the discharge of toxic metals and

Substances	Appendix 40 of German Waste Water Ordinance	Requirements of Communities
Aluminum	3 mg/l	
Iron	3 mg/l	
Lead	0,5 mg/l	1 – 2 mg/l
Phosphor	2 mg/l	
Hydrocarbons	10 mg/l	10 – 20 mg/l
Total Chemical Oxygen Demand (COD)	300 mg/l	ca. 600 mg/l

Fig. 5.3.6
Threshold values for environmentally dangerous substances according to the German Wastewater Ordinance at OEM's

chlorohydrocarbons is prohibited. Approvals for these plants can only be granted if wastewater treatment conforming to the state of the art is provided.

The ”Abwasserverordnung” (Wastewater Ordinance) describes the industry specific requirements regarding the pollution limits of different substances for direct and indirect discharging sources. Further reaching requirements, e.g. fees based on the pollution level (see below), may be imposed by local government statutes.

In order to meet the specific limits for contamination of wastewater, the lawmakers require systematic measures to increase the efficiency of process waters within the processes. These measures include the reduction of dredging losses from process baths, recycling of rinsing bath contents, minimization of rinsing bath discharges by means of closed circuit recirculation, longer operating times for process baths, such as floor washers in spray booths and other measures conforming to the state of the art.

In paint shops, the biggest sources of wastewater requiring treatment are the spray booth flood sheet fluid systems. Other important sources are wastewater from the electrocoating process in the form of diluted acetic acid or similar acids. However, these acids are nonhazardous, and their discharge conditions can be controlled simply by COD values to adapt to the capacities of the wastewater treatment plants. Other forms of wastewater can be discharged from the other units necessary for operation, e.g. in the form of cooling water etc.. These discharges have nothing to do with coating materials.

The legal requirement for recycling the waste at high quality product levels has led to a significant transformation in the treatment of wastewater from paint booths. For example, the water from the flood sheet fluid systems in spray booths for waterbased paints is in some cases not coagulated but poststabilized, so that ultrafiltration can then be implemented without problem, i.e. with longer operating times for the recovery of coating components. The circulating volume should be kept as low as possible to ensure the efficiency of ultrafiltration. In this way, the quantity of wastewater from the application of waterbased paints and coatings is drastically reduced.

If the recovery of solventborne paints and coatings or their components (see chapter 5.3.3) is required, the coagulating agents must be adapted to this process. Essentially, no aggressive coagulating agents may be used. The coagulants must achieve rapid phase separation and should form a coagulate with a low water content [5.8.5].

The generated wastewater is treated by known processing stages to ensure compliance with the limits for heavy metals and other substances. These stages are stripping, detoxification, flocculation, sedimentation and neutralization. The chemicals required are specific to each coating [5.8.6].

In the automotive industry, the normal procedure is to channel all wastewater from the paintshops to a single collector for appropriate treatment. Here, the chemical oxygen demand (COD) can be so high that pretreatment of the water/solvent mixture may be necessary in the paintshop before the collecting stage. For this purpose, known treatment processes are available, depending on the composition, quantity and location of the wastewater. These processes include biological decomposition similar to the process used in sewage plants, activated carbon adsorption or adsorption on molecular filters, reverse osmosis and chemical oxidation [5.8.7].

The coating materials, like their raw materials, are classified into three water endangering classes: slightly dangerous to water (WGK 1), dangerous to water (WGK 2) and very dangerous to water (WGK 3). The relevant class is specified in the Material Safety Data Sheet. Under the ”Verwaltungsvorschrift Wassergefährdende Stoffe” (Administrative Provision on Water-endangering Substances), the classification criterion is the toxicity of the substances to aquatic organisms, starting with algae and rising to miniature life forms such as waterfleas and culminating with fish. The most critical value obtained from all the tests is adopted. However, a good capacity for biological decomposition can lead to a more favourable classification, whereas poor decomposition capacity can increase the water endangering class. These last substances, termed ”persistent organic pollutants” (POPs) are currently the focus of considerable attention. Risk levels (A – D) are defined from the combination of the discharge quantity and the water endangering class (WGK) and lead to different basic requirements imposed on the relevant plants [5.8.8].

5.3.3 Recycling and Disposal

In Germany, this environmentally important theme is regulated by the ”Kreislaufwirtschafts- und Abfallgesetz” (KrW-/AbfG –Waste Management Act). This act requires firstly the avoidance of waste, then its reutilization by direct or indirect recycling and finally, if unavoidable, its conditioning for disposal.

For purely economic reasons, considerable importance is already attached to high utilization or efficiency during both the production and application of paints and coatings. As a result, today’s established coating processes such as coil coating, electrocoating and powder coating attain material efficiency levels of more than 98 %. In the case of electrocoating and powder coating, special processing measures are necessary, such as ultrafiltration or powder recovery (see chapters 4.2.1 and 4.2.2).

Waste cannot be totally prevented, in particular during spray application for the production of colored coatings. The overspray occurring during these processes cannot be directly recirculated to the coating process. Firstly, frequent color changes make recovery uneconomical, and secondly the significantly modified material properties of the dried coatings, frequently irreversible as in the case of 2-component systems, do not permit direct recovery.

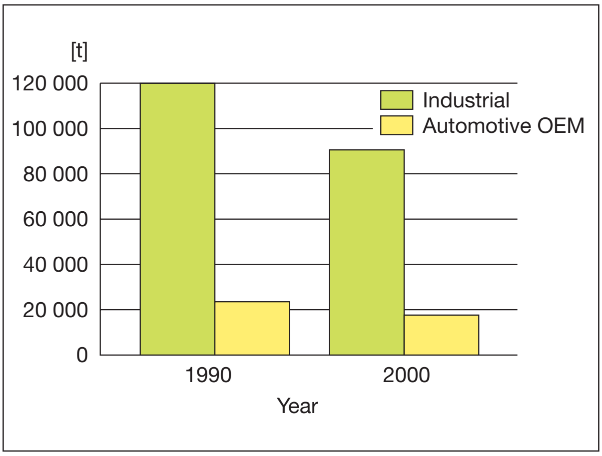

Fig. 5.3.7
Amount of waste by coatings in Germany

The paint sludge levels generated by different treatment methods in the industrial segment in Germany amounted to approximately 90,000 t in the year 2000. This figure represents 4% of the overall quantity of 2.1 million tonnes of applied coatings. As a proportion of industrially applied coating materials, the figure therefore represents slightly more than 10 %. In this case, despite its high share of spray coatings, the automotive industry is much more efficient (see figure 5.3.7) [5.8.9].

Much effort is constantly devoted to the prevention of waste in coating processes. In particular in the last few years, considerable progress has been made in the improvement of application conditions and faultfree coating processes.
Efforts to achieve the direct recycling of coating wastes in coating processes have been redirected as described to the optimization of processes. The reasons are that the various projects, e.g. for the treatment of waterborne primers or the separation of coating wastes into solvent, pigment and film forming agent fractions cannot be transposed into everyday industrial operation. Generally, this impossibility has not been due to technical feasibility but to cost estimates and the legislative position that gives priority to prevention rather than recycling. The recycling of the waste materials that are nevertheless generated takes place at a low level of material utilization. For example, waste materials are channelled to steel furnaces as carbon donors, are used as fuel or are converted to synthetic gas (see figure 5.3.8) [5.8.10].

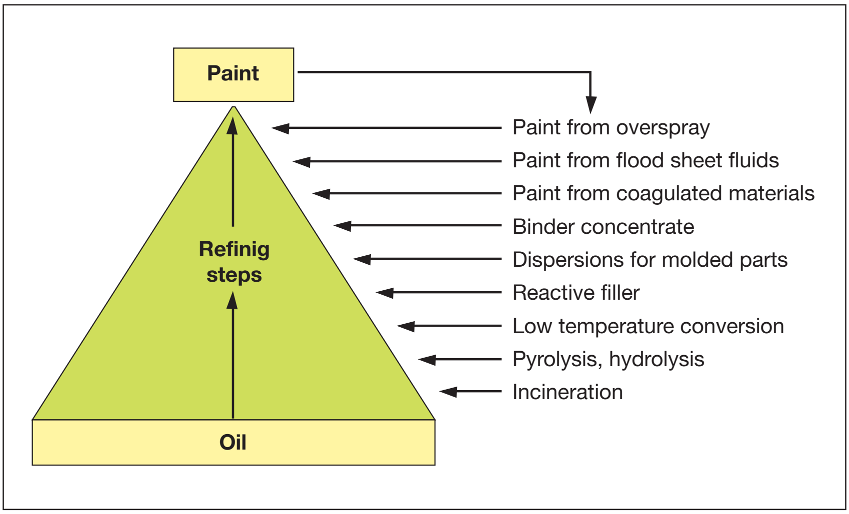

Fig. 5.3.8
Potential recycling pathes of organic materials

In the field of powder coating, the situation is much more favourable. Since the efficiency of the first application is only about 50 – 60 % and the associated loss of coating solids is very high, and in addition powder as a solid is easy to handle, direct recycling of the overspray is now standard practice. Otherwise, powder coating would lose its competitiveness against liquid coatings (see chapters 4.2.2 and 5.7).
Recycling is also an important theme in the packaging of paints and coatings. If there is a sufficiently good separation between the packaging and the filled product, i.e. the coating material, disposable packaging is channelled to the relevant material recycling system. In other words, cans are routed to steel extraction, whilst wood, cardboard and bags are generally incinerated. In the industrial field, returnable containers that can be reused after cleaning are the standard.
The dumping of waste from surface treatment in landfills is prohibited for most substances, because they have a loss on ignition > 3 % or can release soluble substances into leachate.

5.4 Health

The development, manufacture and application of coating materials in Germany are governed by the Chemikaliengesetz (Chemicals Act) together with the Gefahrstoffverordnung (Hazardous Substances Ordinance), the Technische Regeln für Gefahrstoffe (TRGS – Technical Regulations relating to Hazardous Substances) and the Unfallverhütungsvorschriften (UVV – Accident Prevention Regulations). Most paints and coatings are deemed to be hazardous substances as defined by law. Moreover, the principles of ”Responsible Care” applicable to the chemicals industry are also morally binding on the paint and coatings industry. This obligation is expressed in the ”Leitlinien zur Sicherheit, Gesundheits- und Umweltschutz” (Guidelines on Safety and the Protection of Health and the Environment) issued by the Verband der deutschen Lackindustrie (VdL – Association of the German Paint and Coatings Industry).

The European Directives initially passed as framework laws are increasingly intervening directly in the laws of the individual member states. For example, in one of the most recent ordinances of the ”Gefahrstoffrecht” (Law on Hazardous Substances), references to the EU Directives have been introduced, so that EU law will also be directly applicable in Germany after the normal periods allowed for the adoption of EU legislation into national law.

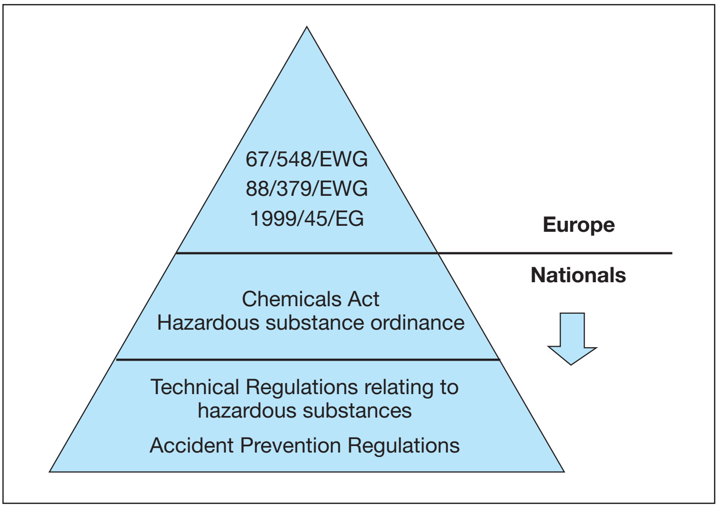

Fig. 5.4.1
Structure of the European Directives on hazardous substances

The recently revised ”Gefahrstoffverordnung” (Hazardous Substances Ordinance) has now also added the Materials Directive, the Preparations Directive and the Safety Data Sheet Directive as compendium.

The most recent noteworthy amendment at European level, i.e. Directive 1999/45/EG, has specified the classification of preparations as dangerous to the environment and the identification of sensitizing substances.

For the individual raw materials such as the solvents of coating materials (see chapter 2.1.2), acute toxicity values have been determined. These values, on the basis of Directive OECD 401, are determined orally (LD), dermally (LD) and on inhalation (LC), depending on the nature of the substance. Generally, the specified values are the doses found to be lethal to 50 % of the test animals, usually rats and mice, within 14 days. The substances are then classified by the Senate Committee into very toxic, toxic and harmful to health.

The aims of legislation and the principles of ”Responsible Care” are firstly to ensure safe handling and the prevention of health risks of all kinds and secondly to provide rapid and precise emergency information for public authorities, doctors and of course customers. Here, the basis is the Material Safety Data Sheet mentioned above (see chapter 5.1). The MSDS describes the risks in standardized ”R phrases” and the preventive measures in ”S phrases” and also recommends the remedial action to be taken in the event of accidents involving the relevant product. These recommendations essentially apply to acute accidents and their risks (see chapter 5.1).

	LD_{50}, oral	LD_{50}, dermal	LC_{50}, inhalative
very toxic	<25 mg/kg	<50 mg/kg	<0,5 mg/l x 4h
toxic	25–200 mg/kg	50–400 mg/kg	0,5–2,0 mg/l x 4 h
harmful to health	200–2000 mg/kg	400–2000 mg/kg	2,0–20 mg/l x 4 h

Fig. 5.4.2
Classification of substances according to Hazardous Substances Ordinance in mg/Kg body weight and mg/l concentration in air

When handling paints and coatings in development, production and application, contamination of the skin and eyes and exposure and inhalation are particular potential dangers. Contamination can in most cases be prevented by personal safety equipment such as overalls, safety shoes, protective gloves, protective goggles, breathing masks and if necessary complete protective safety suits. This equipment must meet the requirements of the relevant industry associations.

In the case of regular handling of products classified as dangerous to health, regular preventive medical inspections by doctors qualified in industrial medicine are also specified.

Depending on analyses or risk assessments of the relevant substances, the exposure of employees is limited under the ”Gefahrstoffverordnung” by the MAC levels (maximum allowable concentration at workplace) to a level considered uncritical to health. The MAC level of a substance is its concentration in the air, in the form of gas, vapour or suspended particles, which according to present knowledge does not adversely affect health with an exposure of 8 hours per day and 40 working hours per week. This level must be regularly monitored by measurements at the workplace conforming to specified methods. For substances that do not have a MAC level, the values of the ”Technical Directive on Hazardous Substances Concentration” (TRK) are applied. If the MAC and TRK levels are exceeded, suitable protective measures must be specified, such as breathing masks or extraction systems (see chapter 2.3.2).

To complete the risk assessment, the characteristic values in the working environment, in the form of the described MAC and TRK levels, are supplemented by limits on the quantity of substances or derived products in the human organism. On the basis of preventive inspections under industrial law, ”BAT” levels (”Biologische Arbeitsplatztoleranz” – biological tolerance at the workplace) for specific substances are laid down as limit concentrations in the urine or blood. If these values are exceeded, additional safety measures must be taken.

The legislation shows that a strategy for the prevention of risk containing formulations is being pursued. Special emphasis has been given lately to biological active components such as preservatives in coatings by the Biocidal Products Directive of the EU [5.8.11]. Another important example is "REACh", which specifies for market introduction and use that the danger of substances must be assessed during their entire life span (see chapter 5.1). In principle, the laws have the aim of reducing to a minimum the danger to the health of the population caused by products or processes.

5.5 Ecobalances

Up to about 1960, the main focus for the development of paints and coatings was on achieving technical progress in the functionality of the coatings and coating processes (see chapter 1.2). Later, considerations relating to environmental protection gained in importance. The pendulum temporarily swung disproportionately towards the ecological side. Legal interventions were responsible for this swing, with the main emphasis on emissions into the air and water. Since the early nineties, the economic and ecological objectives have come together for the benefit of technical and social progress as well as the environment.

For this purpose, evaluation models have been developed on the basis of the concepts of ”sustainability”, ”life cycle analysis” (LCA) and ecoefficiency [5.8.12, 5.8.13]. The essential and new element here is that now, for a manufacturing process, the raw material consumption, energy and environmental pollution are measured and evaluated all the way from the production stage, through product utilization to disposal. The same

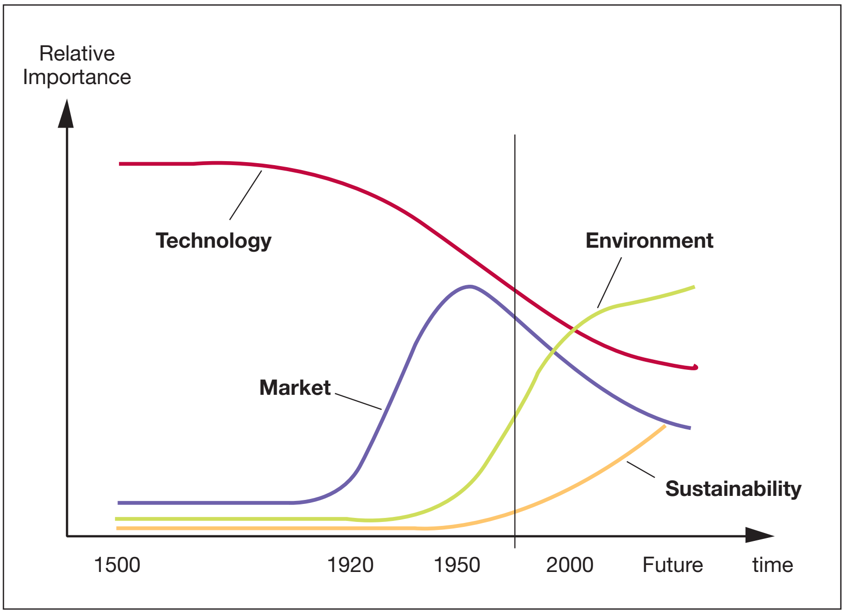

Fig. 5.5.1
Relative development of technology, economy, environmental protection and sustainability in the coatings industry according to Prof.Bancken

principle applies to ”life cycle engineering” (LCE), in which the main focus is on manufacturing processes. [5.8.14]. The concept of ”sustainability” extends the assessment of a commercial activity to include the aspect of social responsibility (see above).
Legislative strategies at European level are giving considerable backing to this approach. For example, the directive passed by the EU in October 2000 for the disposal of scrap cars demands recycling rates of 85 % for the year 2006. This figure applies to all materials used in the car and not just steel as the most significant material by weight. By 2015, the recycling rate must be increased to 95 %. In this context, there is frequent debate on the question of the stage at which to recycle the materials (see Figure 5.3.8). For example, thermoplastics can be recycled to the same production stage with a few qualitative reductions, whereas thermosetting plastics and their associated coatings must instead be transformed at the downstream stage at the level of the raw materials, e.g. as synthetic gas.
The coating process often represents the largest emission source for environmental pollution in many manufacturing processes for products such as trains, aircrafts and boats. Coating also involves considerable energy and investment costs, varying greatly in scale as a function of the type of coating and application process. It is clear that only a comprehensive assessment of all these factors can permit a meaningful comparison of the production process in terms of resource conservation and environmental pollution. These two aspects have emerged as the most important criteria for assessing suitably comparable processes.
Environmental pollution in turn is composed of the elements of emissions into the air, water and soil, toxicological hazards to humans and animals and recyclability.
At present, an absolute assessment of all components of a ”life cycle analysis” is still highly complex and costly, because the data structure is to a large extent just now in the process of development. Comparability is also limited by the fact that the system limits have not yet been standardized and are defined differently.
A simple but effective way out of this dilemma is provided for example by the ecoefficiency analysis [5.8.13]. The heart of this analysis is a product’s practical utility

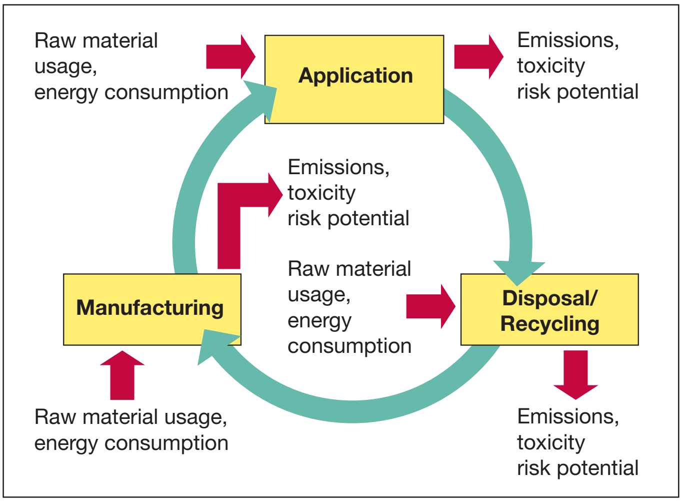

Fig. 5.5.2
Value added cycle

to the customer. In general, customers can choose between several products or processes to satisfy their requirements. The ecoefficiency analysis compares the economic and ecological advantages and disadvantages of these different problem solutions. In other words, products are not compared to one another as such, but instead they are compared in their applications such as the coating of a square metre of the front of a piece of furniture. Problem solutions are judged to be ecoefficient if they provide distinct customer benefits at lower cost and with less environmental pollution than other solutions. Lower cost, in this case, is synonymous with more sparing on resources. Here, the analysis is based on all stages of the value added circuit (see figure 5.5.2). The costs and environmental pollution of all processing stages, i.e. production, application and disposal or recycling, are measured. The processing stages before or after production are also included in the calculation.

The result of the analysis is summarised in an ecoefficiency portfolio.

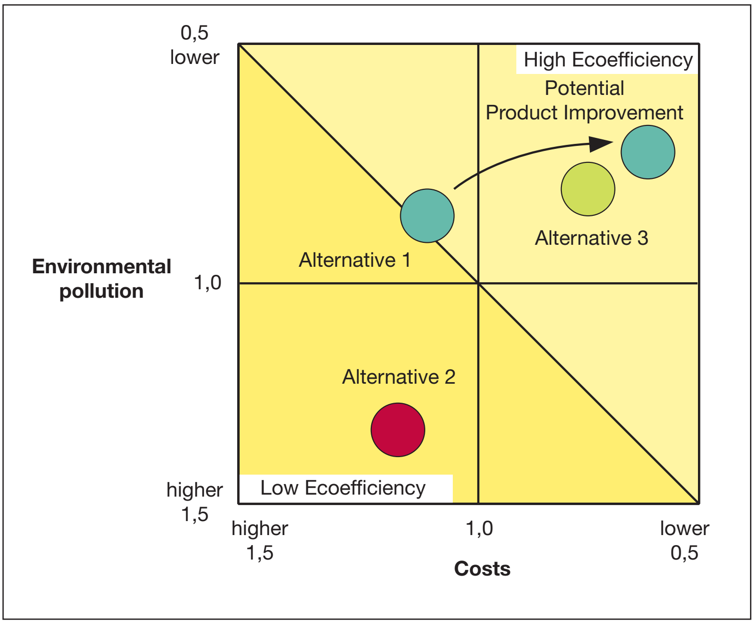

Fig. 5.5.3
Ecoefficiency portfolio

Costs and environmental pollution form the two axes. The scales are arranged so that the best solution is positioned on the right or at the top. The relative positions of all the products tested are then added. The products or processes positioned in the right hand upper field are ecoefficient. Anticipated future product improvements can also be determined and entered in the portfolio for visualization.

The environmental impact important to this assessment is described on the basis of five categories, which together constitute the ”ecological fingerprint”:

- Consumption of raw materials
- Consumption of energy
- Emissions into the air, water and soil (waste)
- Toxicity potential of the used and released raw materials
- Potential misuse and risk

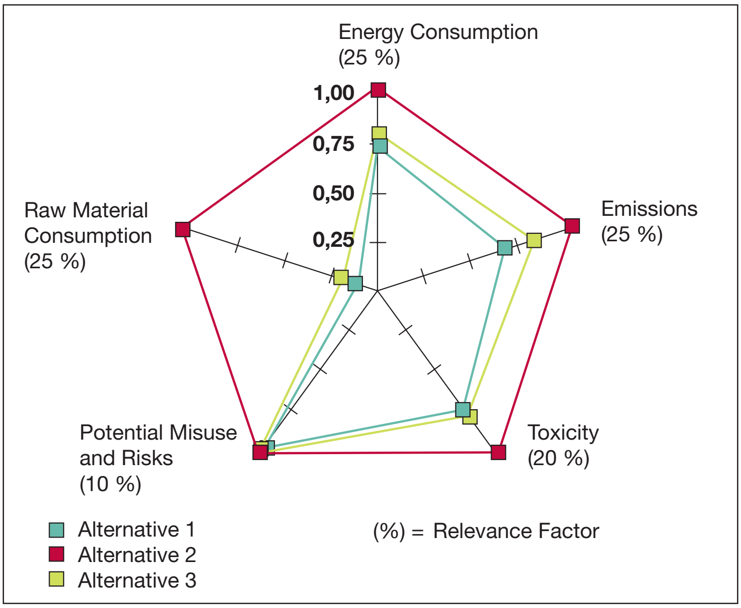

Fig. 5.5.4
Ecological fingerprint

Each of these five categories conceals a mass of detailed individual criteria which are grouped together to determine the overall environmental impact of a product or process in an ecological fingerprint. The significance and scope of the properties at the various stages in the life cycle is taken into account by ”relevance factors”. These factors specify the extent to which individual criteria are represented in the overall environmental impact, for example how the potential for ozone destruction is weighted against the greenhouse potential. In the case of consumption of raw materials, the availability, natural occurrence and associated different sustainability ranges are taken into account. The weighting can also take into account the importance that society attaches to the different forms of environmental impact.

The other axis of the portfolio is used to plot the economic data. Here, the material and energy flow of the compared processes and their resulting products are considered, including all relevant secondary flows. One important factor here is the definition of observation limits. Almost all clearly definable systems can be comparatively assessed by this method.

The costs and work involved in an analysis of this kind are considerable. However, experience to-date shows that processes found to be ecoefficient by this method, together with their resulting products, have prevailed on the market.

For this reason, the results of the ecoefficiency analysis enter into the development of product range strategies. Together with additional information from company divisions such as marketing, research, development and application, strategic orientations can be defined. This analysis contributes to founding the debates between industry and social forces on a factual and clear basis.

5.6 Environment Compatible Paints and Coatings

Over the last decades, the term ”environment friendly”, i.e. environmental compatible, has been established for certain types of paint and coating. In this context it should be noted that ”environment friendly” can be defined according to different aspects and emphases. The most popular method of evaluating paints and coatings primarily emphasises emissions into air, water and soil and secondly the toxicological components. The main spotlight is therefore on emissions, because the coating process generally requires a transfer agent, the solvent, to enable the paint or coating to be applied to the surface of the substrate. The reference point for evaluating environmental compatibility is conventional solventborne paint, which has a solids content of between 10 and 50 % and uses organic solvents as transfer agents.

In this light, the following paints and coatings are generally classified as ”environment friendly” by popular usage:

1. Paints and coatings with a high solids content, termed ”high solids”
2. Waterborne spray paints
3. Electrocoatings
4. Powder coatings
5. Certain radiation curable paints.

On taking a closer look at these paints and coatings, other factors can be identified as influencing their environmental compatibility in terms of the conservation of resources.

Coatings	Solvent Emission	Transfer Efficiency	Energy Consumption	Manufacturing/Transportation	Toxikology	Raw Material Consumption
High Solids	+	o	+	+	−	o
Waterborne	++	+	−	−	+	o
Electrodeposition	++	++	−	−	+	+
Powder	+++	++	+	+	++	—
Radiation Curing	++	o	+++	o	−	o

Fig. 5.6.1
Qualitative judgement of coatings in respect to their environmental compatibility compared to conventional solventborne systems (0 = comparable, + = better, - = worse)

It is not possible to give relative rankings, because environment compatible coating systems cannot be universally used to meet all paint and coating requirements.

Indisputably, second to powder coatings, electrocoatings and special radiation cured coatings stand out as particularly environment compatible. The latter have only limited application possibilities, because complex shaped parts cannot be uniformly cured by this technology. Moreover, not all formulations are solventfree. The low molecular, reactive compounds must also be subject to careful toxicological assessment and selection.

A more precise comparative assessment of coating systems, taking into account the necessary processes, can be provided for concrete applications by the ecoefficiency analysis described above (see chapter 5.5.).

In the case of conversion to environment compatible coating systems, plant adaptations and extra investment in the coating lines are almost invariably required. The most important aspects will be examined below.

5.6.1 High Solids

The technical definition of high solid paints is not unanimous and differs considerably between Europe and North America. In Europe, paints with a solids content > 50 % are generally classified as high solids, whereas in North America the solids content has to be > 55 %.

Two formulation principles are used for these paints, which are mainly developed in North America:

1. Low molar mass and high crosslink density of the film forming agents
2. Choice of solvents with high dissolving capacity

	Data/Unit	Physically Drying	Low Solids	High Solids
Molecular mass	Mw	> 100.000	10.000	4.000
Functionality	Mol/g	0	300	600
As delivered	NV* [%]	25 %	55 %	75 %
	Viscosity [mPas] (20 °C)	2.000	2.000	1.500
* at 2 h/130 °C				

Fig. 5.6.2
Technical data of resins for different coating systems

The viscosity of high solid paints on delivery is at the same level as conventional solventborne paints. In other words, virtually no investment in the application plant is necessary for converting to high solids. This is the decisive reason for the widespread use of this technology in North America.

The second principle mentioned above for the formulation of high solid paints has led to the increased use of ketones as solvents in North America. These solvents are more unusual in Europe and are considered undesirable due to their relatively intensive smell. The focus for further developments aimed at increasing the environmental compatibility is on the toxicology of the solvents and raw materials. An increase in the solids content by the formulation principles mentioned above is generally no longer possible in most paint systems. The threshold of 3.0lbs/gal (370 g/l) of solvents for liquid paints can only still be fallen short by waterbased or radiation curable coatings.

5.6.2 Waterborne Paints

The term waterbased paints and coatings includes coating materials that are mainly formulated on the basis of dispersions. Here, the distinction is drawn between primary and secondary dispersions. The former are produced with the aid of emulsion polymerization and are fine particle dispersions of high molecular binding agents, which can be airdried like decorative paints or crosslinked like the waterborne primers or waterborne basecoats in automobile painting. Secondary dispersions consist of film forming agents

Type of Dispersion	Particle Size [nm]	Solid Content [%]	VOC [g/l]	M_w
Secondary	100 – 400	20 – 40	50 – 250	<10.000
Primary	1 – 200	25 – 45	0 – 100	>100.000

Fig. 5.6.3
Typical data of waterborne dispersions

of medium molecular weight. They are either selfreticulating or have to be crosslinked with the aid of a reagent. They are manufactured in two production stages, firstly resin synthesis in conventional solvents and secondly dispersing in water. In many cases, the solvents are then removed by distillation at slightly increased temperature and reduced pressures. This process is termed ”stripping” in technical jargon and reduces the VOC levels considerably.

The stabilization of both dispersion types can be steric or electrostatic, and the latter can be anionic or cationic (see chapter 2.1.1). A typical example of the latter product class is the electrocoat, which was first introduced back in 1965 (see chapter 4.2.2). Today’s systems are characterized by very low solvent contents, leadfree composition and almost entirely closed circuit processes that now generate virtually no wastewater or waste materials.

	pH	NV	% Solvent/NV(1)	Pb	Biocide
AED 1970	8,5	10	55	yes	yes
CED 2002	6,0	18	8	no	no
(1) as delivered					

Fig. 5.6.4
Typical bath parameters of today’s (CED) and former (AED) electrodeposition coatings

Only few coating systems are based on film forming agents completely dissolved in water. Compared to organic solvents, water has a relatively low boiling point of 100 °C at 1013 hPa, but it has a very high evaporation energy of 2.26 J/g at 100 °C, a high evaporation value of 80 compared to diethyl ether, a high density of 1.00 g/ml at 4 °C, a high surface tension of 72.2 mN/m at 20 °C and a very low specific electrical resistance of 10 kWcm. These properties have an influence on the formulation of paints for spray application and on the appropriate choice of raw materials (see chapter 2.1.1). Also, in the case of a conversion from solventborne to waterborne coatings, expenses and conversion costs are caused due to the following physical and chemical properties of these coatings:

a. Corrosiveness
b. Evaporation characteristics of water
c. Electrical resistance

The first aspect requires a change from plain steel to stainless steel for the walls, pumps and other devices that enter into contact with the waterbased coating. If coating formulations are low in chlorine, one of the simpler stainless steel types such as 4.4301 is sufficient.

To monitor the quality of the coating materials used, the pH value, or the determination of acid and base levels, is specifically used for waterbased products (see chapter 2.3). The specific conductivity is also an indicator of constant quality.

In the case of solventborne coatings, the control of the important rheological behaviour during application and film formation is mainly determined by the evaporation characteristics of the solvent. In this respect, these coating materials often exhibit Newtonian characteristics in their shear/viscosity function. This relationship is different for waterbased coatings, because the evaporation rate of water is much slower (see figure 5.6.5) [5.8.15]. Moreover, the viscosity curve as a function of the solid content is characterized by a ”water mountain”. This viscosity peak occurs at a solids content at which a water-in-oil dispersion turns into an oil-in-water dispersion. Since the addition of water in technically high quality coatings does not generally achieve any improvement in application characteristics, and the solid content plays a decisive role in the economy of the paint systems, waterbased paints are generally delivered ready for application. For this purpose, by means of the formulation and composition, the coating materials are given either pseudoplastic or thixotropic properties (see chapter 2.3.3). A carefully adjusted rheological characteristic is decisive for storability and spray application. However, each type of application demands a specifically adjusted profile.

Consequently, the quality control of the technical application properties must be more carefully defined and can generally no longer be based on measurement in the DIN-ISO cup (see chapter 2.3).

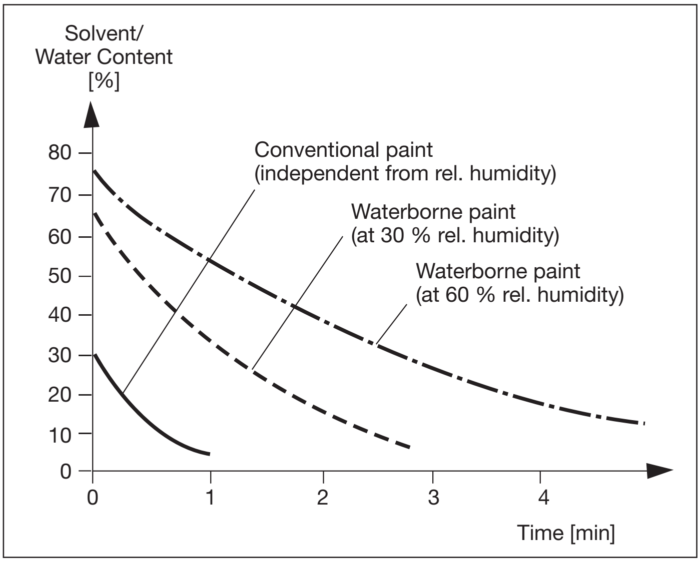

Fig. 5.6.5
Typical evaporation behavior of water in relation to relative humidity and in comparison to conventional coatings

Centrifugal pumps and similar pumps can only achieve sufficient precision in dispensing the material if the viscosity obeys the principles of Newtonian fluids. Consequently, for waterbased paints, in many cases pumps with volumetric delivery or forced delivery are used in order to dispense constant quantities even under non-Newtonian conditions. Geared pumps are among the types of pump used.

In the case of multilayer coating systems in industrial mass production, the high evaporation energy and necessary evaporation time must be taken into account in the design of ”flash-off zones” between the individual application stages. These zones can often be

shortened by means of IR radiation. The temperature profile in the baking oven should be specifically designed for waterbased coating materials, because rapid heating can lead to pinholing effects in the film (see chapter 6.2).
The high electrical conductivity and frequent color changes and consequent product changes have major effects on the supply of coating materials to electrostatic spraying apparatus. Insulation between the application device and the coating supply line is also necessary, together with careful grounding of the supply system (see chapter 4.2.1).
At levels of < 5% on organic solvents the danger of bacteria growth at the respective waterborne paints have to be considered (see chapter 2.1.4).

5.6.3 Slurry

One particular variant of waterbased spray paints is ”powder slurry”.

As Deliverd	
NV (1 h/130 °C)	35 – 38 %
Solvents	< 2 %
VOC	< 21 g/l
Particle size	3 µm
pH	6 – 7
Viscosity (1000 s^{-1}/23 °C)	200 – 250 mPas
Spec. density (23 °C)	1,05 g/ml
Appearance	milky

Fig. 5.6.6
Product data of a powder slurry clear coat

Powder slurry is a solventfree dispersion of powder coatings in water; it combines the advantages of powder technology with those of a dispensing and application system for liquids. In addition, this technology enables ultrafine powder particles with a diameter of about 3 µm to be maintained stable. This fine grain structure is necessary in order to be able to apply films only 35–45 µm thick. These film thicknesses are sufficient to obtain the necessary surface and utility properties and the required weathering resistance in automobile construction.
The use of slurries requires only minor adaptations to pumps and spraying apparatus and to temperature control in the drying oven compared to waterbased coatings.
This coating system is used for clearcoats in automobile construction [5.8.16, 5.8.17].
Further developments in this technological segment are directed towards a slurry that is no longer based on powder but on special dispersions, enabling the crosslinking of clearcoats with PUR structures.

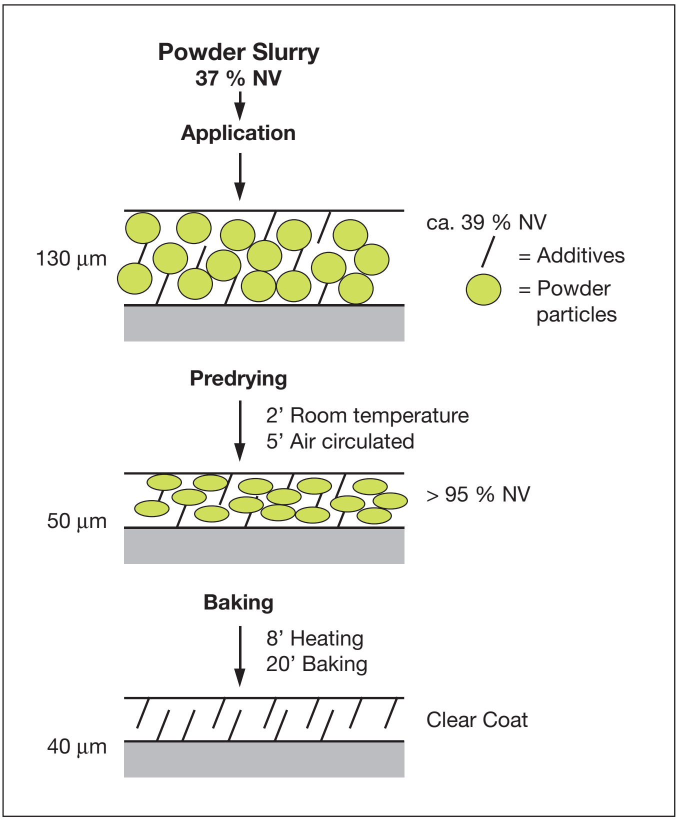

Fig. 5.6.7
From the slurry to the clear film

5.6.4 Powder Coatings

Powder coating (see chapter 2.2.4 und 4.2.2) is still a very young coating method and was first used in the mid sixties of the last century. In 2005, the worldwide demand for powder was 1.1 Mio. t.

In 2004, the estimated European applications for industrial powder coatings were in the following segments:

Architecture:	19 %
Heating/Radiators:	18 %
Metal furniture:	15 %
Care accessories:	9 %
White goods:	9 %
Machines:	7 %
Other:	19 %

In addition to the classic applications in the fields of domestic appliances and architecture, powder coatings are increasingly being used for add-ons and small parts in the automotive sector, such as wheels, axle and chassis components and also, over the last few years, automobile production paintwork. Consequently, today, the share of powder coatings in primers and clearcoats in automotive coating lines is estimated at approximately 8 %, with a clear predominance in the USA (see chapter 7.1).

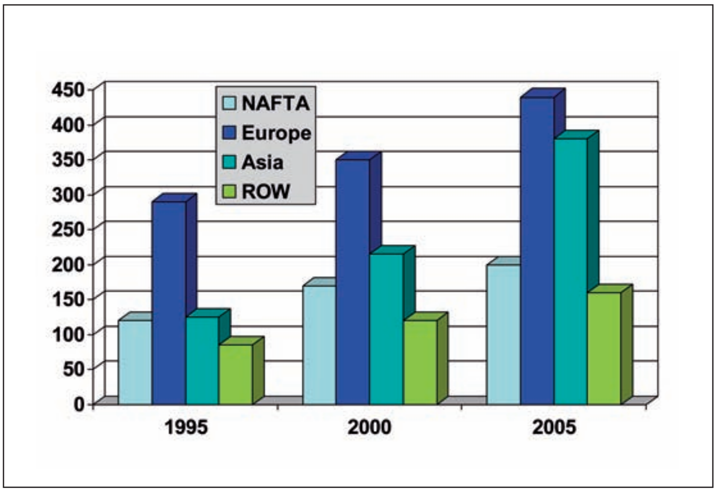

Fig. 5.6.8
Worldwide growth of the powder coatings market

Although, as a rough estimate, powder coatings cover approximately 1.5 times the substrate area per delivered kilogram compared to liquid coatings, their commercial use is constantly increasing. This fact can be explained by the following key characteristics of powder coatings:

1. No solvents are used
2. Legislation treats powder coatings essentially as nonhazardous material for storage, transportation and waste
3. High material application efficiency > 98 % due to recycling
4. Economical application of high film build where required
5. Competitive investment and operating costs.

When handling powder coatings, it is necessary to take into account other material properties than the properties familiar from liquid coatings. Based on the technical aspects of powder coating systems, the application process can be broken down into a sum of subprocesses that are defined by product and process parameters.

Key elements for successful handling of powder technology are the fluidizability of the powder, the dispensing system, the application equipment and material recovery (see chapter 4.2.2) [5.8.18]. The recovery and simple recycling of the overspray, combined with the absence of solvents, are the essential factors in the ecological attractiveness of powder coating technology.

The disadvantages are firstly the high film thicknesses of approx. 70 – 100 µm required for good flow, secondly the still awkward and time consuming procedure for color

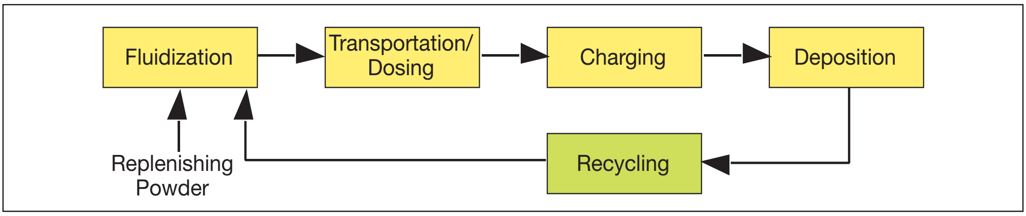

Fig. 5.6.9
Process chain of the powder application

changes and thirdly the high baking temperatures (see chapter 4.2.2). Developments aimed at radiation curable powder coatings (see chapter 5.6.5) using UV and near infrared (NIR) radiation indicate an increase in applications. The heat generated in the powder film by NIR radiation (see chapter 4.3.1) means that the melting and crosslinking process is completed in a few seconds [5.8.19].

In an overall assessment based on the life cycle analysis or ecoefficiency analysis (see chapter 5.5), the clearcoat film thicknesses of > 60 µm required to obtain attractive surfaces are very unfavourable. The reason for maintaining high film thicknesses is the need for average particle sizes of approximately 30 – 40 µm in the powder coatings in order to ensure safe handling. Reductions in film thickness for the purpose of obtaining more attractive surfaces would require finer powder particles, which still raise problems of stabilization and handling [5.8.20]. Numerous projects such as standing wave atomization (see chapter 4.2.2), powder production with supercritical CO_2 and powder slurry (see above) have been initiated to tackle this problem [5.8.21, 5.8.22].

5.6.5 Radiation Curable Paints and Coatings

Radiation curable paints and coatings (see chapter 4.3.2) have gained their environment compatible credentials mainly from two aspects (see figure 5.6.1). Firstly, they permit low emission formulations and secondly they make sparing use of resources, because the coatings curable by UV radiation or electron beam require very little energy for film formation and crosslinking. The matching of UV absorbers important for clearcoats with photoinitiators has helped to expand the possible range of uses [5.8.23]. The application technology for UV coatings does not differ to the systems for conventional solventborne coatings.

Radiation curable coatings have won themselves a market with above average growth. In 2004 worldwide about 174,000 t contributes by 0.6 % to the total coatings market (see figure 5.6.10). Main application area in the industrial coatings sector is the wood and furniture industry mainly with flooring coatings followed by the packaging and printing industry [5.8.24]. However, significant applications can already be seen in the automotive supplier industry in the production of headlamp systems [5.8.25].

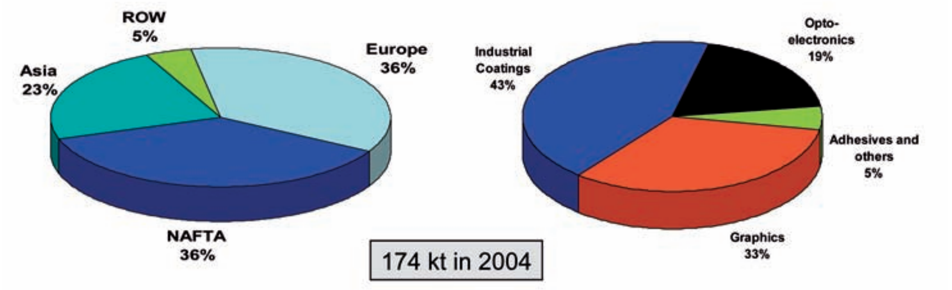

Fig. 5.6.10
Worldwide market for radiation cured surface coatings and their main application areas

Applications in the electronic field also include the coating and printing of CDs and DVDs [5.8.26].

Pure or modified acrylic resins are the most significant film forming agents used, with a share of 73 %. Cationic hardening is insignificant, with a share of 1 % by volume [5.8.27].

Radiation curable coatings consist of very low molecular film forming agents with a high proportion of polymerisable C-C double bonds, which are diluted in the liquid state with reactive monomers or solvents or are combined as aqueous dispersions with photoinitiators (see chap. 2.1.4) and other components to produce a coating formulation appropriate to the relevant application. The photoinitiators are activated by UV radiation and trigger a radical polymerization process. This phenomenon occurs in fractions of a second with normal energy inputs of approx. 1 J/cm^2 in the UVA radiation range. Pigmented systems with sufficient transparency require roughly double the energy input (see chapter 4.3.2). Depending on the formulation of the UV coating, predrying to release the solvent or water at approx. 70 – 90 °C is beneficial in order to produce smooth and defectfree surfaces [5.8.28].

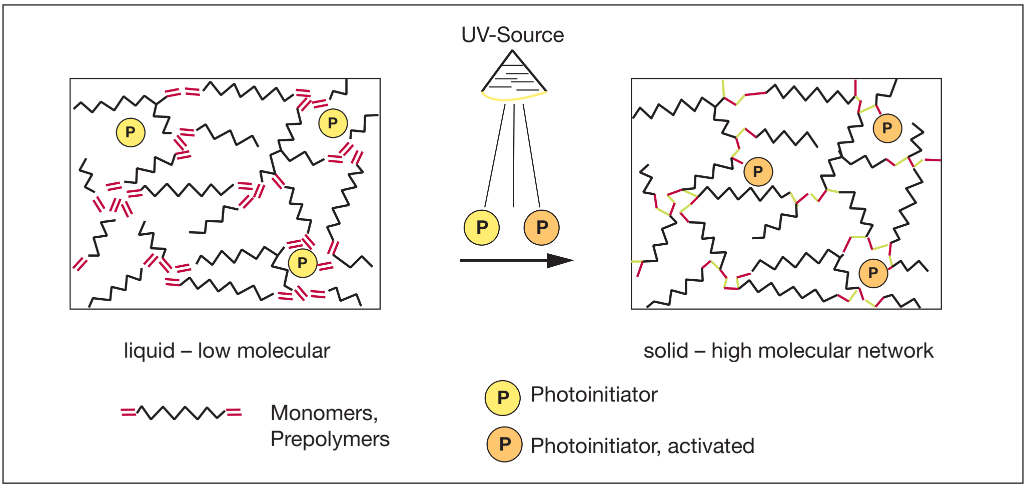

Fig. 5.6.11
Principle of UV-curing

The most important classes of film forming agents are unsaturated polyesters and specially designed and modified acrylic resins (see chapter 2.1.1). The first generation of UV wood coatings was limited to a coating line speed of 5 – 10 m/min due to the use of unsaturated polyester resins and styrene as reactive diluents. Monomer-free acrylic resins, which have a higher reactivity, permit coating lines up to 4 times faster. Even higher production and coating speeds are attained in foil production, e.g. for the furniture industry in a reel-to-reel production process similar to the coil coating process. Full hardening at a line speed of 140 m/min can only be guaranteed by UV coatings [5.8.29].

In all cases, the coating lines are much shorter than is the case with thermal curing. The energy consumption of UV curing amounts to only about 10 % of that of a thermal curing process, partly because the generation of UV radiation requires less energy and partly because the energy is only needed to crosslink the coating (see chapter 4.3.3). The substrate will not be heated.

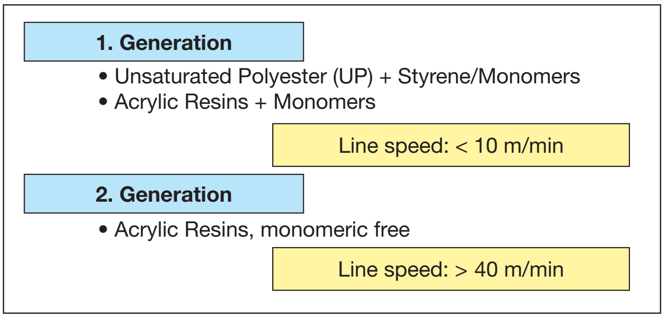

Fig. 5.6.12
Generations of UV-coatings for wood

Although attractive in this respect, radiation curing plays only a secondary role on the overall paint and coatings market, with a share of less than 1 %. There are several reasons for this. Firstly, the curing of complex shaped parts is problematic, and secondly not all pigmented coatings can be cured by UV radiation, because they do not have the necessary UV transparency. Furthermore, adhesion to metals is still not good enough, so that UV coatings do not attain the level of conventional primers. These coatings do not have enough of the polar functional groups required for anchoring on the metal surface, i.e. essentially OH, NH, CO and CONH groups etc.. Nevertheless, due to the very high crosslink density resulting from C-C double bonds, UV coatings provide very hard and scratch resistant surfaces, in particular as clearcoats.

In addition to classic applications such as furniture components, e.g. MDF boards and foils, UV products are used to coat and harden compact discs, glass fibres, lenses and reflectors for automobile headlamps as already mentioned and printing products. All these products are characterised by simple geometry.

Paint and coatings manufacturers are currently developing ”hybrid paints” that are crosslinked by both radiation curing and thermal curing. In these systems, the advantages of the high hardness and scratch resistance on the outside of the formed parts is obtained, whilst the inside is given the necessary film properties by thermal curing, generally at 80 °C, with the conventional crosslinking reactions. The high crosslink density of UV cured hybrid systems is also utilised for coating plastic SMC parts, in order to prevent the recurrent outgassing from SMC products [5.8.30].

The disadvantages of the low penetration depth of UV light in pigmented coatings are overcome by curing pigmented coatings with electron beams in the electron beam curing process (see chapter 4.3.2).

Recently, UV powder technology has gained a certain position in the USA and Italy for coating MDF boards for the furniture industry The combination of powder coatings with UV curing is understandably very attractive due to its ecological advantages, despite the fact that the direct coating of wood with powder is still beset with problems of adhesion [5.8.31].

5.6.6 Other Coating Systems

Coatings using supercritical CO_2 as solvent additive were on the market for a while [5.8.32]. CO_2 can be brought to the critical phase at temperatures above31 °C and pressures above 7.8MPa in. In this case the specific density is 0.464 g/ml.

The physical parameters are close to those of conventional spray conditions in industrial applications, with the result that coating systems were developed with high viscosity and low solvent content and were then brought to the necessary spray viscosity using supercritical CO_2 with the aid of a mixing system. 30 – 60 % solvent reduction can be attained by this method. The cost of equipment and a too fast drying of the applied film led in most cases to unsatisfactory coating results, so that this technology is now only used in niche applications.

In principle, the coil coating process can also be classified as environment compatible. Here, the paint composition plays a secondary role, but the application process has an efficiency of more than 95% due to the high solid content of the coatings and the low material loss during the rolling process. Solvent emission can be almost entirely transferred to the baking oven at low cost due to the rolling process and the short distance between application and baking oven, with the result that emissions are almost entirely eliminated by means of thermal treatment of the oven air (see chapter 7.4).

5.7 Economy of Coating Processes

As described when discussing the ecoefficiency analysis (see chapter 5.5), a company wishing to install a coating line has first to calculate the economy of the coating process before it can take the final decision on an investment. The economic aspects include the investment costs, their amortization, the running costs for operating the coating line and the costs of the coating materials.

The running costs in turn consist of a multitude of cost blocks that are very specific to the relevant application process and the coating system used. These cost blocks include the disposal or utilization of overspray, the costs of the air supply, the energy required for application and baking or crosslinking, the cleaning of the suspended apparatus and of the coating line and all personnel costs required to operate the coating line (see figure 7.1.3).

To ascertain the comparability of the coating cost factor, i.e. the costs of the coating materials, the standard unit ”costs/m^2 of coated surface area” has become generally recognized. This factor must be carefully calculated but is not always easy to determine for every coating process.

Type of Coating	**Film thickness** (µm)	**Specific Density of Solid** (g/cm^3)	**NV therefore** (kg/m^2)	**Transf. efficiency**	**Price**[1] (Euro/kg)	**NV of replanished Paint** (%)	**Costs for Coating** (Euro/ $100m^2$)
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Powder	80	1,60	12,8	98 %	3,00	100	39,2
Liquid	30	1,50	4,5	80 %	3,80	50	42,8
CED	22	1,45	3,2	95 %	4,00	42	32,1
[1] As delivered							

Fig 5.7.1
Calculation data for the economy of three different coating systems in Euro/100 m^2 (NV = Non Volatile)

In addition to the price per kg of delivered coating material, other factors enter into consideration, such as the content of nonvolatile components in the coating, the transfer efficiency of application, the film thickness and the specific density of the film.

This comparative calculation can be illustrated by the example of coating 100 m^2 of metal workpieces by three different methods – electrocoating, liquid spray coating and powder coating.

With reference to the headings in figure 5.7.1, the following formulae serve as basis for calculating the economy (7) of the coating method:

$$\frac{(1) \cdot (2)}{10} = (3)$$

$$\frac{(3) \cdot 100}{(4)} \cdot \frac{(5) \cdot 100}{(6)} = (7) = \text{coating costs/100 m}^2$$

Support for decisions in favour of particular coating lines can be provided on the basis of this simple mathematical statement. However, it must always be remembered that (7) only compares the coating costs. It does not take into account ecological aspects, capital costs or running costs (see chapter 5.5). Moreover, clear agreements must be reached between supplier and customer on the determination of the solid content, in order to keep material losses in the drying and curing process constant between the application and the lab.

A widely used parameter for comparing coating costs is the theoretical **yield E** of a coating material in m^2/kg. The yield is defined as the quotient of the paintable surface area A and the necessary mass of coating material m_{Pa} required to coat this area:

$$E \equiv \frac{A}{m_{pa}} = \frac{NV}{\rho_T \cdot S_D \cdot 100}$$

m_{Pa} is calculated in kg from the film thickness S_D, the density of the dry film ρ_T (see chapter 3.2.1) and the nonvolatile content of the coating material NV, using the following formula:

$$m_{Pa} = \frac{\rho_T \cdot S_D \cdot A \cdot 100}{NV}$$

Consequently, coatings are judged to have a particularly high yield when a high non-volatile concentration (NV) is combined with a low dry film density and a low covering film thickness, i.e. a high hiding power (see chapter 2.3.3). Here, it is assumed that the protective effect and function of the coating does not depend on its mass but essentially on its volume or film thickness. This is not always the case.

The mathematical relationship for calculating the yield can also be used to estimate the solvent emission quantities L. If we replace m_{Pa} by $m_{So} + m_{dr}$, i.e. respectively the solvent content and the proportion of dry film residue, and then insert this sum in the yield formula, we obtain:

$$\frac{A}{m_{So} + m_{dr}} = \frac{NV}{\rho_T \cdot S_D \cdot 100}$$

If we replace m_{dr} by ρ_T x S_D x A and resolve the equation, we obtain m_{So} = solvent emission L:

$$L = \rho_T \cdot S_D \cdot A \cdot \left(\frac{100}{NV} - 1 \right)$$

Therefore, if the film thicknesses to be applied S_D, the nonvolatile concentration of the coating material NV and the dry film density ρ_T are known, the solvent emission can be estimated for coating a given area A. The result is only an estimate, in that this formula is only valid to a degree for manual coating processes such as application by brush and roller, because it does in no way take into account the transfer efficiency and application conditions in industrial processes and plants [5.8.33].

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6 Principles of Quality Management

6.1 Evolution of Quality Concepts over Time

Industrial coatings are produced in large quantities and at high speeds, generally with a high quality level. In this respect, only small quantities of paint are usually sufficient to improve the decorative and functional features of the coated products. Consequently, particular attention must be paid to ensuring a constant quality level that satisfies all relevant requirements.

One significant aspect that distinguishes the paint and coatings industry from many other sectors is that it works with semi-finished products that are produced by the paint and coatings manufacturer with all due care for quality but that are then processed and applied in a different location by the user (see chapter 1). As a result, quality control by the manufacturer has to take place under different conditions to those applied by the customer. In addition, due to the highly technical nature of the production processes, the raw materials used in paints and coatings are in some cases still subject to variations, so that the manufacture of paints and coatings is not always a question of producing identical mixtures but of finding compositions that have identical application characteristics and maintain identical coating properties to previous batches. Whilst measurements of key physical properties such as density, viscosity, surface tension and solids content are certainly important factors in testing and inspection, they are not always sufficient to guarantee quality. This fact is one of the reasons why simulation of the practical stresses caused by bending, scribing, chipping or scratching and the visual assessment of test coatings are often adopted as additional criteria for evaluating quality (see chapter 3.3).

Given this situation, it is evident that close contact and exchange of ideas and experience between the supplier and application site are essential in order to ensure that the coating material is provided with the best possible basis for optimal quality before it takes form in the finished coating.

When we also consider that many paint shops procure their materials from different suppliers whilst insisting that the different products must be interchangeable in the application systems, it is also clear that general agreements on the performance of tests and inspections are not enough. Consequently, a worldwide body of standards lays the foundations for agreements on the preparation of test samples and the performance and evaluation of tests (see chapter 8).

In the first stage of this process, the originally purely inhouse ”working standards” were supplemented – but unfortunately not fully replaced – by national, neutral test specifications. Then, as a result of the globalization, agreements that went beyond national borders became necessary, so that today test methods are being under way to become harmonized at worldwide level. ASTM and ISO standards are increasingly being established and are gradually replacing works standards and national regulations. One example of the efforts to harmonize test methods on a regional level can be seen in ”VDA-Blätter 621”, a document issued by the German Association of the Automotive

Industry (VDA) to provide a snapshot of the test methods currently practised in the automotive industry [6.6.1].

Whereas standards simply contain methods for determining quality, a required minimum quality cannot be defined and met without agreements on the quality level itself. The technical delivery conditions or specifications of paint and coatings supply therefore not only specify the test methods for quantifying quality but also the limits and the permissible factors of uncertainty for the measured values (see chapter 2.3.1).

Nevertheless, forecasts on the quality of the end product are beset with imponderables. One of the peculiarities of the industrial coatings sector is the fact that whilst considerable investment and work is required by the coating manufacturer to transform the coating materials into a coating that will suit the conditions of the user, after delivery to the customer the coating is not always applied under identical conditions.

This state of affairs has led paint and coatings manufacturers and the application departments of their customers to come closer together and to consider the creation of quality as a common goal. Quality concepts developed over the last few years go far beyond mere product testing of the material and final coating. They have been considerably extended, to include services such as safety, adherence to lead times, clear quality agreements and openness in the exchange of information. However, in order to guarantee quality, the need is not only for reliable production systems, modern test equipment and controllable services but also for the appropriate mental approach of all employees in the company.

Quality management systems (QMS) must therefore induce a quality consciousness in the minds of all employees as a basis for the introduction of defect prevention concepts, so that faults are no longer only detected after production and corrected after the event. Total Quality Management (TQM) is one such concept [6.6.2]. To ensure that quality management systems or concepts are practicable and above all measurable in their effectiveness, the principles and practical steps towards TQM have been laid down in standards.

For example, the DIN ISO 9000 ff. and EN 29 000 ff. series of standards describe in detail the procedures for preventing defects (nonconforming products) and for ensuring reliable and punctual production and delivery.

The emphasis of testing and inspection is moving away from the exclusive focus on materials testing towards process monitoring, with the simultaneous introduction of control loops. The target of achieving zero defects in the production of coatings has still not been attained. Even in large paint shops such as those of the automotive industry, as pioneers for quality and quality consciousness, paint defects have still not been totally eliminated. However, intensive collaboration between the paint and coatings industry and its customers to control all process stages, including the quality strategy, has led to clear progress in both the quality level and reproducibility of coatings.

The much-improved capability of analysis of material and coating defects over the last few decades has contributed significantly to this progress. The next section will therefore provide a selection and identification of the most common coating defects.

6.2 Defects in Coating Processes and Applied Coatings

In the overall chain of production, sale and application of paints and coatings, a whole series of parameters, starting with the pretreatment process and extending to the paint properties and finally the application and curing conditions, have to be observed in order to achieve a coating result that satisfies the specifications. Nonconformances in one or more parameters can lead to a defective coating (see Figure 1.1.8).

These defects can include e.g. a marked orange peel surface texture or runs and sags on vertical surfaces, inadequate stone chip protection, a color deviating from the approved sample or localized or systematic surface defects of any kind. Expert application on specified substrates with carefully tested and approved coating materials almost invariably leads to defectfree coatings for the relevant purpose. On this basis, many nonconformances are remedied by careful analysis of the application parameters and inspection of the coating batches. Since the coating product and application process are highly interdependent, it is necessary to decide whether optimization of the application system or of the coating composition is the most economical, rapid and reliable starting point for solving particular problems.

One typical example can be seen in the problem of runs. If the most important film properties provide sufficient room for manoeuvre in the reduction of film thickness, optimization of the application process is the simplest and most economical remedy. If not, greater reliability in sagging resistance must be provided by modifying the formulation of the paint.

The focus for optimizing the reliability of coating processes has for many years been on localized or systematic surface defects in industrial coatings. These defects seldom lead to any diminishment of utility or ”adequacy”, but they considerably detract from the consumer’s subjective appreciation of the product’s value. By experience, on attempting to classify the causes of these defects, the underlying causes have often been found to be external disturbance factors in the substrates and their pretreatment, as well as in the coating material and coating process.

Substrate and pretreatment play an important role for wetting and adhesion. Nonconformances and processes deviating from standard can lead to cosmetic defects in the form of wetting problems and even, in the case of inadequate adhesion, to serious deficiencies in anticorrosion protection. In particular for materials such as wood and plastics, the type of pretreatment and its practical implementation must be reliably controlled by suitable process engineering.

Modern environment compatible paint and coating systems require greater care than solvent-borne systems permitting more robust formulation, because as aqueous or powder products they are to a certain extent in the metastable state and are highly liable under certain conditions to change suddenly to a more favourable thermodynamic state. This phenomenon can be reflected in agglomeration, phase separation and the formation of micelles in individual coating components. The application of such nonhomogeneous coatings leads to a variety of surface defects, such as roughness or craters and can also have an adverse effect on film properties.

In addition to these defect sources inherent in the coating itself, a whole range of external factors also affects the result of the coating process. The most important problem in this respect is known to many painters: it is dust, which is deposited e.g. during the slow drying of airdried paint surfaces and has the effect of contamination by dirt. Even in industrial coating processes, this factor is often the main problem (see chapter 7.1.6). Not only dust but also auxiliary substances in the paint shops and the object to be coated can lead to visible defects in the paint systems. In particular, the widely distributed oils, silicone based sealing compounds or perfluoro compounds should be mentioned. These materials are characterized by very low surface tension values of < 20 mN/m. Due to their incompatibility, they cause surface defects in almost all coatings, in particular waterbased and high solids coatings. In addition, the speed of the coating processes can lead to problems, e.g. due to insufficient evaporation of solvents, including water, in multiple layer paint systems. The correct calibration of spraying equipment is also necessary in order to achieve defectfree and smooth films (see Figure 1.1.7). The human eye is capable of discerning regular surface textures down to a depth of 0.5 µm.

Regardless which cause is concerned, if the quality requirements for these highly technical coating lines are very strict, any visible defects can lead to enormous repair costs.

If measurable defects occur in the coating process, rapid remedial action is therefore necessary. The need here is to use the right analysis methods and utilize the experience of application engineers in order to adopt a clearly targeted procedure for locating the cause of the defect and taking appropriate remedial action.

In this context, four action parameters can be distinguished:

1. Careful analysis of the surface defect
2. Immediate recording of the defect statistics with details of time and location
3. Checking of all application parameters
4. Analysis of the quality data of the coating materials

Depending on the severity of the incident, it may be appropriate to take all four approaches simultaneously. The interplay of the human factor, material properties and application parameters does not always lead to clear and rapid identification of the cause of a surface defect simply from its nature. The ability of all concerned to apply the methods of criminalistics, especially for multilayer paint systems, is needed, because localization of the defect is a decisive step towards detecting the cause.

In the chapters that follow, the possibilities of surface analysis and the form of known defects will be described in terms of corresponding errors in application or faults in the coating product itself.

6.2.1 Identifying Defects and their Causes

As already described, defects and failures in the coating of consumer goods can be subdivided into three classes, firstly visible defects due to localized surface defects, secondly visible defects due to larger-area surface defects and thirdly defects that affect the adequacy or function of the coating.

These defect classes can occur both individually and together in the many different coating processes [6.6.3].

Visible, localized defects in the surface are generally classified by their appearance. People thus speak of runs, craters, solvent boils, blisters, pinholing, dirt and similar terms, which in many cases give no clear indication of the cause. For example, without closer inspection under a microscope, an apparent crater may in fact be a large solvent boil. Moreover, this terminology is not clearly defined, making communication even between experts difficult. By contrast contamination of the coated surface by external dirt can generally be identified by microscopic analysis of the defect.

This kind of surface defect can occur sporadically or regularly in industrial coating processes. If it occurs sporadically, the cost of repair is lower, but the time taken to locate the cause and remedy the problem is greater than for frequently occurring defects. Here, in particular for automotive coatings, can coatings and the coil coating process, rapid action is a prime requirement.

The first step in remedying defects should always be the logging and visual classification of the surface defect at the production line, as a basis for cause analysis. This process includes a description of the defect, to the extent that it can be detected with the naked eye, and localization of the object and a record of the time sequence. If the visual assessment remains unclear, a magnifying glass or portable microscope should be used on the production line, in order to permit more extensive description of the defects and possible identification of the causes. If this analysis is insufficient for clear classification of the defect, the damaged area must be prepared for further investigation.

Here, depending on the substrate, three different processes are used:

1. More detailed visual analysis of the damage point using a scalpel for preparation and a stereomicroscope. In this process, the defect is cut into a wedge shape by the scalpel with two oblique cuts under the stereomicroscope, so that the defect is visible in the cross section of the paint system. By this method, in multiple layer coating systems, there is a high probability of classifying the source of the defect to the relevant layers. Once the technique is mastered, this method can be applied to all substrates.
2. Microtomy is used as a thin-section method, in which the coat is sliced off in stages of approx. 1 µm film thickness. These specimen slices can be examined under microscopes of every type in both reflected and transmitted light. In transmitted light, different contrast methods can be used to accentuate the effects. This method can only be used reliably with plastic substrates.
3. In the paint and coatings industry, the most common method used is the cross section preparation technique. Here, the defective point to be examined is cut out of the object and embedded in light curable or other curable plastics. This casting is then cut to the damage point, and a microscopic top view photograph of the defect point is taken.

After defect analysis by one of these methods, combined with visual inspection, engineers are generally able to classify the defect into dust contamination, craters, boils or pinholes, blisters and other defects.

This classification gives pointers, but it is not sufficient to identify the cause or source of the defect.

Another degree of difficulty then occurs when examining multiple layer paint systems, because for successful fault remedy it is essential to know in which layer the cause is located.

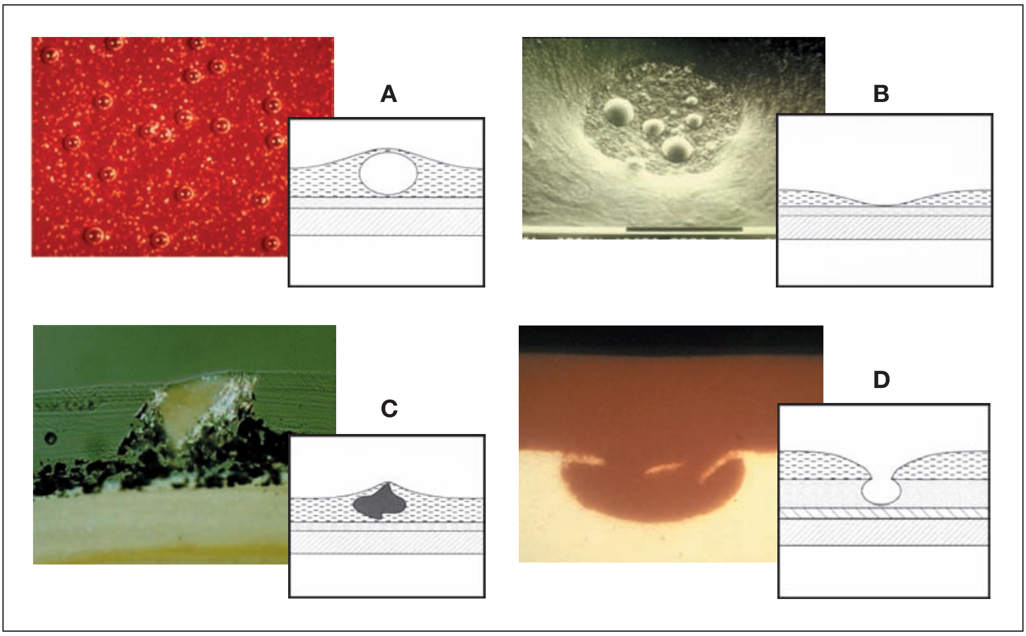


Fig. 6.2.1
Typical defects of coating surfaces : blisters (A), craters (B), dirt (C) and boils or pinholes (D)

Microscopy is usually highly successful for identifying defects caused by dirt or dust. If visual, microscope assisted analysis fails to localize and remedy the defect, analytical methods that are able to provide the clearest possible indications of the type of substance at fault are used. One effective method is *Fourier* transform infrared spectroscopy (FTIR), which with sufficient concentration delivers the structural characteristics of the contaminating substance on micropressings or with the aid of the IR microscope [6.6.4]. Energy-dispersive X-ray microanalysis (EDX) can also reveal structural elements in the defect area. The electron beam of the scanning electron microscope (SEM) triggers X-ray quanta in the target sample in inverse proportion to the atomic number of the relevant element [6.6.5]. This method provides element specific but not structure specific information and has its strength in the detection of inorganic components.

If coating defects are caused by boundary layer phenomena involving surface active substances, their concentrations in the coating surface are usually so small that detection with IR spectroscopy or EDX is not possible. Other more sensitive processes such as electron spectroscopy for chemical analysis (ESCA), secondary ion mass spectrometry (SIMS) and the laser microprobe mass analyzer method (LAMMA) are based on the method of bombarding the surface of the defect zone with a high energy beam or with mass particles, in order to obtain spectroscopic or mass spectrometric information from the reaction of the molecules. However, these processes are not sensitive enough to detect and measure impurities that are active at contamination concentrations in the ppm and ppb range [6.6.6]. When detecting contaminant substances in the surface, a low information depth or interaction of the bombarded surface signifies a high detection sensitivity, as illustrated in Figure 6.2.2. Local resolution and the size of the bombarded area also play an important role.

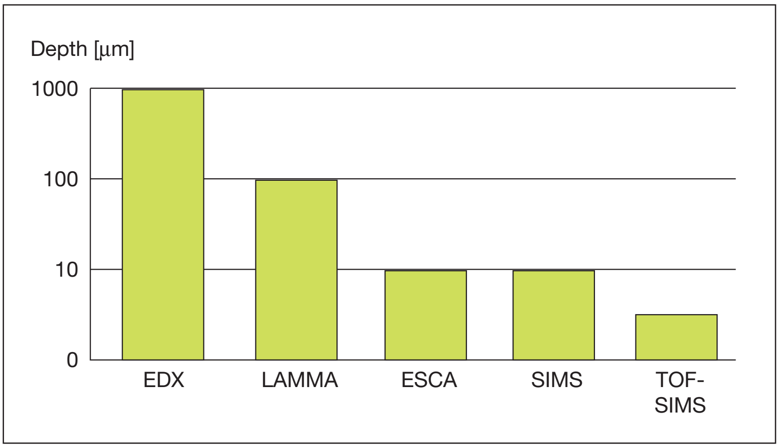


Fig. 6.2.2
Depth of informations at different analytical methods of surfaces

The devices developed by *Benninghofen* [6.6.7] on the basis of time-of-flight secondary ion mass spectroscopy (TOF-SIMS) satisfy the requirements of high sensitivity for the analysis of chemical substances on the surface of coatings. They enable low impact ionization by bombarding with argon or metal ions in order to generate secondary ions from the coating. This method is today well-established and has in many cases enabled engineers to identify the contaminating substances in defect zones.

Visible, wide area surface defects that can be rapidly and clearly analyzed by the trained eye include orange peel texture, haze, mottling, insufficient light-to-dark flop in metallic coatings and runs on vertical surfaces.

The cause locating procedure is exactly the same as for localized defects. In most cases, chemical analysis is not a viable option due to the macroscopic texture. The most frequently adopted approach to remedy these defects is to modify the application method and/or coating formulation.

The third class of defects, namely **adverse effect on film properties** only occurs during the later life cycle of the coated product and is therefore usually not detectable during the coating process. Here, the most common defects are delamination from the substrate or between coating films, chalking or excessively rapid loss of gloss, blistering, discoloration and premature corrosion.

Defects in adequacy of film properties must be prevented by means of a quality management system (see chapter 6.3).

As explained at the start of this chapter, although the phenomenological description of a defect does provide indications of possible causes, it does not always yield unambiguous results. In every doubtful case, the substrate, pretreatment, coating process and coating material must be checked for possible deviations from the standard. The types of defect and causes described in the sections that follow are classified according to their probability of occurrence in these fields.

To repair surface defects, the described classification based on visual inspection is generally sufficient to determine the necessary process, possibly in combination with light sanding (see chapter 7.1.6).

6.2.2 The Most Frequent Causes of Surface Defects

Substrate and pretreatment

Without exception, every substrate to be coated will require a specific form of pretreatment in order to ensure a lasting coating that conforms to specification (see chapter 4.1). Pretreatment that is not specific to the substrate and not up to standard can lead to considerable deviations from the desired surface quality. The simplest form of pretreatment for coating is to clean the surface of dirt or other deposits or alterations of the surface. More sophisticated pretreatment methods consist of cleaning with subsequent chemical modification of the surface, followed in turn by a further cleaning stage. For the most important classes of material, there are therefore specific focuses for potential causes of defects in the subsequent coating process.

Wood, as a natural raw material, is inhomogeneous and anisotropic. It therefore has irregular surface textures and pores, due e.g. to irregularities in growth (see chapter 4.1.1). Moreover, various constituent substances such as resins and water have to be taken into account, depending on the type of wood and region. The most common pretreatment stages therefore include the removal of substances incompatible with the coatings, e.g. by means of soap solutions, ammonia and in some cases solvents, sanding in several stages with papers having grain sizes to > 400 and the sealing and filling of pores and cracks. A multilayer coating system consisting of insulating basecoat, stain and several clear-coats helps to correct the substrate-derived defects of outgassing and moisture content for each layer.

Medium density fibreboard (MDF), which is widely used in the furniture industry, (see chapter 4.1.1) is also coated in several layers, comprising insulating primer, sometimes many primer surfacer, basecoat and clearcoat. In this process, any bleeding of glue from the boards must be avoided. When using waterborne coatings, projecting wood fibres can be a problem. If necessary, to counter this problem, the wood surface is wetted with up to 50 g/m^2 water and then smoothed after drying [6.6.8].

Unlike wood, **metals** are isotropic materials. However, this is not wholly true of the surface, especially if sheet metal panels have been passed through drawing and other forming processes. Also, spot welds in the production of formed parts can cause local problem points for pretreatment and coating. The auxiliary substances necessary for the manufacture of a metal part, e.g. anticorrosion greases for the storage and transport of coils or other sheetings and the drawing greases used for the forming process are not always compatible with the coating materials. If they are not fully removed before the coating process, they have an adverse effect on the formation of the initial inorganic conversion layer. Unwanted surface effects can then occur in the electrocoatings in the form of wetting defects and bleeding (see below). On the other hand, if the anticorrosion oil is not evenly spread over the surface, fallout or more severe rusting can occur, and although this surface rust can be removed by pretreatment such as sanding it will lead to unevenness in the coating. Welding globules and dirt on and in the part are other sources of defects. Non-conforming areas of roughness on the panel surface often lead to deviations in surface quality of the entire paint system.

Plastic components do not have a homogeneous surface and often have flow traces due to the production process in thermoplastic injection moulding machines. Mould release media and the bleeding of softeners and additives can lead to clearly visible textures due to different degrees of wetting during the priming process. One cause is known as ”bondline read out” [6.6.9]. The thermal characteristics and inner tensions of the plastic must be taken into account when formulating the coating materials. During the application process, the low conductivity of plastics is responsible for the high dirt inclusion. Wiping and cleaning the surfaces by manual processes should therefore be avoided if possible. In many foamed materials, the release of foaming gas during the coating process is a source of defects. If necessary, this problem can be remedied by ”tempering”, i.e. brief warming of the plastic part until close to the deformation limit in order to reduce its internal tension.

Glass-fibre reinforced plastics such as sheet moulding compounds (SMCs), which are manufactured on the basis of unsaturated polyesters with the use of monomer components such as styrene and are then moulded, have two major potential sources of defects for the coating. Firstly, the orientation of the glass-fibre segments can result in them standing out from the substrate, and secondly, during the coating process, cavities coated in a thin film can result in ”voids” or, on drying, to pores and holes in the coating.

Special plastics must be carefully conditioned in order to achieve homogeneous wetting by the coating material (see chapter 4.1.3).

Defects caused by the process or coating product

In **electrocoating**, the described defects such as craters, pinholing and dust contamination can occur exactly as in the other application methods and with the same causes.

One significant and specific source of defects for electrocoatings is the automobile ”body in white”. Depending on the type of product to be coated, welding pearls, metal particles and sweating of adhesives are the most frequent causes of defects in the electrocoating. The remedy here is cleanness and optimization of the cleaning processes in the body assembling shop or directly before electrocoating.

Moreover, it should be remembered that contamination of the tank by the overall production process must be avoided. The environment compatible electrocoat paints with low solvent contents can be contaminated by hydrophobic silicones or even in the ppb range by fluorinated hydrocarbons, to such an extent that craters can occur in the

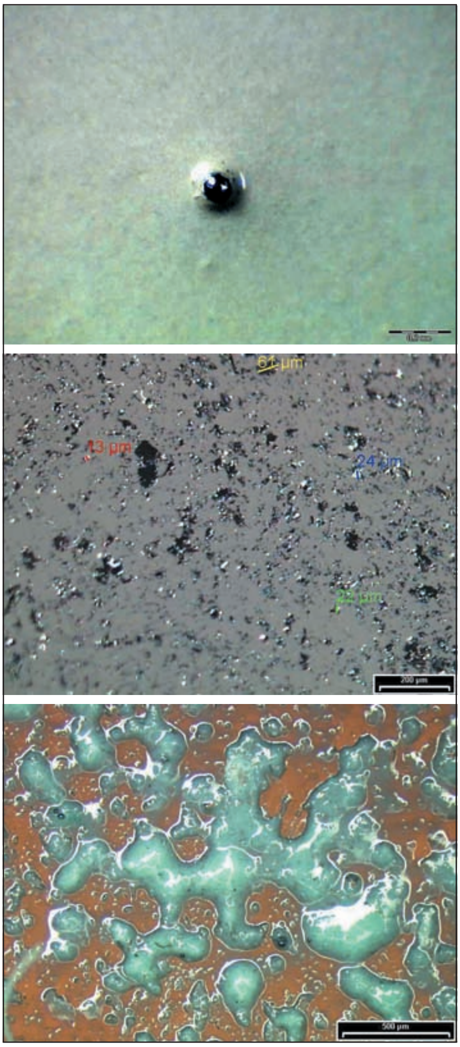


Fig. 6.2.3
Welding pearls, metal particles and body adhesives as contaminants in electrodeposition coatings

coating itself or even in the subsequent layer due to wetting defects. In addition, there are various very specific defects that can have their causes in the process, the bath stage or the paint quality. The most important of these problems is the rupture voltage effect, which is visible in defects ranging from small spots or pinholes to centimetre-large defects in the form of quasi-fused, coagulated and locally limited areas of the coating that can already be detected in the wet film before the curing oven. The causes can be excessively high voltage, bath temperature and bath conductivity during the process. Here, the appropriate remedial action can be to reduce the voltage or bath temperature and to discard a part of the ultrafiltrate and replace it by fully deionized water. As a rule of thumb, the application voltage must be at least 10% lower than the rupture voltage measurable in the lab. Another defect that can occur in continuous coating lines is the appearance of immersion marks in the form of beads and pinholes on the immersed part. The causes here can be foam on the bath surface or excessive current density in the immersion zone. Problems in the wetting of the substrate by the electrocoat paint can also lead to similar effects. In the rinsing process, water marks occur if rinsing is of poor quality and possibly occurs too late in the emersion zone, or in general if the quantity of ultrafiltrate generated for the entire rinsing zone is too low. Pinholes in electrocoatings are not necessarily traceable to the water or solvent content in the deposited film but more often to the bath composition, in particular a too low binder-to-pigment ratio or too low bath temperature. Last but not least, larger surface defects combined with the need for a significant change in application parameters in order to maintain the same film thickness and throwing power indicate bacterial contamination. This problem can be bacteriologically analyzed and combated with bactericides (see chapter 2.1.4).

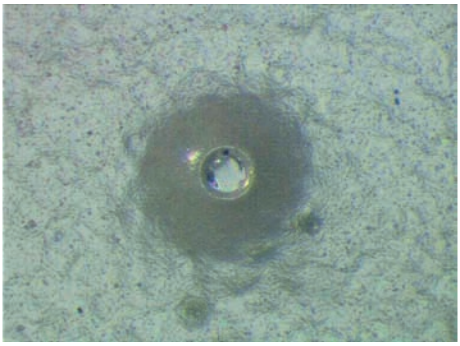


Fig. 6.2.4
Pinholes in an electrodeposition coating caused by local electrical effects

Depending on their function, **spray paints** have specific defect categories. For example, primers must be totally free of surface defects in order to perform their function as base for a topcoat with high smoothness and gloss in automobile production. Defect causes here can be classified into several subject areas. For example, residues of sanding dust from sanding operations can occur in cathodic electrocoatings, whilst residues of seam sealing compounds can also occur, especially if they are manually applied and if PVC is used as material. Spray mist incompatibilities at several stages in the application of the primer and finally dust contamination are other notable sources of defects.

Fig. 6.2.5
Overlooked rests of a PVC sealer on a body surface

The spraying equipment can lead to defective coatings both in primer and topcoat application. These defects can be excessively thin films due to incorrect dispensing quantities, over-rough films due to excessive propellant air and ”eggshells” due to deposits of coating material that accumulate on the spray heads and are then sporadically ejected onto the coated part.

The need for exact calibration of all parameters for a defect-free coating is therefore greatest in the case of topcoats, because they are responsible for the visible surface of the coated object. Regardless of the type of topcoat, dust contamination are the most frequent cause of defects (see below and chapter 7.1).

In the case of basecoat and clearcoat systems, e.g. for metallic paints, specific defects can be an imperfect metallic effect, spray mist incompatibility and pinholing or solvent boils.

The metallic effect, especially for very light shades of color, can be locally disturbed by black points. The cause of this defect is often locally incorrect orientation of the aluminum flakes due to the inclusion of impurities in the basecoat or underlying layers.

The appearance of large zones of incorrectly oriented metallic paints is termed ”mottling”. The immediate cause lies in differences in the evaporation and drying characteristics of the basecoat over significant areas. The ultimate cause must be sought both in the formulation of the relevant paint and in the application conditions. In addition to visual inspection, mottling can be detected by statistically assisted measuring processes (see chapter 6.3). Another large-area defect is known as the ”salt and pepper” effect. This defect is caused by the formation of *Bernard*’s cells during the basecoat evaporation time (see chapter 3.2.1).

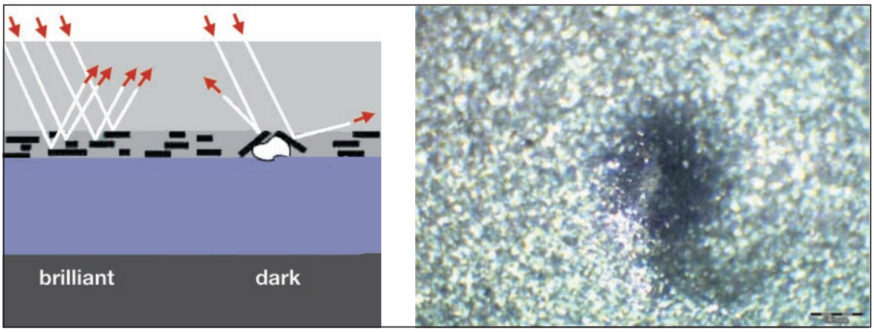


Fig. 6.2.6
Scheme and picture of a dark spot in a base coat

Spray mist incompatibility is evidenced by areas of very bad flow. This phenomenon is caused by the fact that previously coated areas, e.g. the door sills of a car body, are too dry on reaching the next application stage, so that the fresh spray droplets are no longer accepted by this film and can fully deliquesce. Possible remedies are an optimization of the spray zones and a ”longer” setting of the coating material.

Pinholing, solvent boils or craters are phenomena that can be very small in diameter and are not easy to distinguish from one another. The term ”pinholing” is generally used when this defect is caused by blistering from underlying layers during wet-in-wet application of multiple layers.

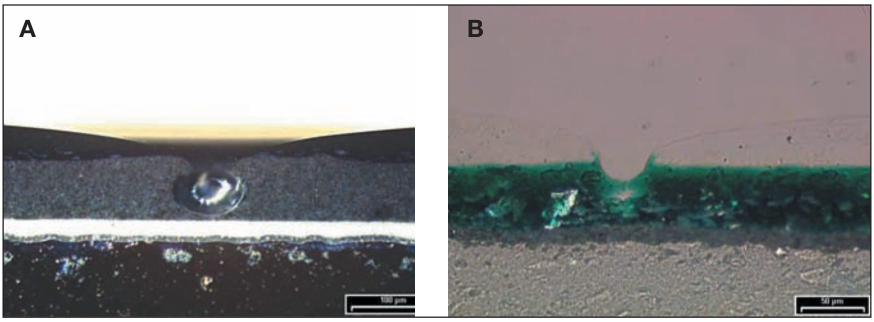


Fig. 6.2.7
Pinholes by boiling of primer surfacer (A) and basecoat (B)

The most frequent processing causes are firstly insufficient intermediate drying of the basecoat layer before application of the clearcoat and secondly air or solvent inclusions in the various layers.

Another major problem is inadequate matching of the formulations of the basecoat and clearcoat. In this case, incipient dissolving of the basecoat by the solvents and other components of the clearcoat can result in impressions of color and effect that deviate from the specified standard.

All layers of a topcoat including fillers must have optimally calibrated wetting characteristics. Nevertheless, even very small-scale contamination by a surface-active substance with low surface tension can lead to localized concentrations on a surface. In the next processing stage, these concentrations can lead to wetting defects, which are visible in the form of craters (see chapter 2.1.4).

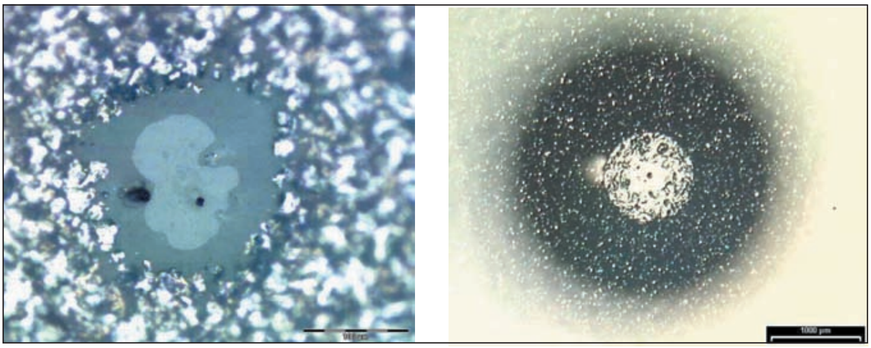


Fig. 6.2.8
Craters in an automotive top coat system down to electrodeposition coating caused by surface active contaminants

Surface defects of **powder coatings** are generally very specific due to the consistency of the coating material and to the application process. Consequently, in order to ensure a reliable coating process, very precise settings are necessary for electrostatic charging when applying with corona spray systems and for powder dispensing and powder recovery.

The most common problems with powder coatings and their causes include excessively thin powder films or insufficient coverage of the substrate.

Several causes can be responsible for this type of coating result. Firstly, the voltage at one of the electrodes of the spray unit may be too low. Here, the requisite action is to check the high-voltage source, the electrodes and the cables. In all cases, it is advisable to clean accumulated powder off the electrodes. Furthermore, the object to be coated may be poorly earthed. Here, the earthing of the suspension apparatus and conveyer belt must be checked. The contacts must be free of powder deposits. If powder throughput is too high, sufficient electrostatic charging will not be possible. In this case, reducing the powder flow rate will lead to more efficient coating. If the humidity in the spray booth is too high, the charge of the powder particles will be rapidly broken down. Correct humidity should therefore be set. In the case of a very low-efficiency first application, the recycled powder may lead to a shift towards smaller particle sizes. This factor should be checked by measurement; if necessary, the ratio of new powder to recycled powder must be increased. Excessive air in the powder feed line can lead to a lower collection of powder on the coating. In this case, either the air flow must be decreased or the distance to the substrate must be increased.

Another very frequent defect is excessive orange peel. The back-spray effects of powder application very often result in poor surface quality (see chapter 4.2.2). The causes can be excessive voltage, insufficient distance between the spray unit and the object, poor earthing or generally too thick films. To remedy these defects, the voltage must be reduced, the gap increased and earthing must be checked and improved, or else the powder flow rate must be reduced. In individual cases, the number of spray units can also be reduced.

Irregular and intermittent powder dispensing naturally also leads to irregular surfaces. The cause here can be low pressure in the dispensing or transporting air, so that the air pressure and the airlines must be checked for buckling etc.. Blockages in the application devices, lines or suction tubes may also be sources of defects. Regular cleaning is the recommended preventive measure.

Powder fluidization in the dispensing tank may be insufficient. In this case, the swirling air must be adjusted, and if necessary the tank must be cleaned and the powder in the tank must be changed.

Finally, powder agglomerates can spoil the surface with clearly visible defects. These ”eggshells” are soft agglomerates, generally of fine powder particles, which can form either in the powder lines or in the application device. Their generation can be traced to thermal or electrostatic causes. The following factors influence the formation of agglomerates:

- High proportion of regenerated powder in the mixing tank
- Insufficiently frequent cleaning of the lines
- Excessive humidity of the compressed air.

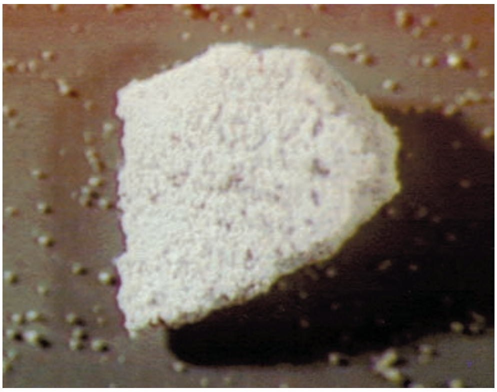


Fig. 6.2.9
Agglomerated particle ”Eggshell” of powder coatings

As with the other coating types, localized surface defects have two main causes. Firstly, external contamination may have occurred during the application process, and secondly the powder coating itself may have or generate contaminating substances. Contamination must be kept to a minimum by filtration during production and application. However, if a filter bag or strainer is torn loose, the released dirt particles or powder agglomerates will lead to defects in the coated film (see above). Powder agglomerates can also be formed in the lines and tanks. In this case, the dispensing system should be regularly blown clean as an important preventive measure. Excessive humidity of the compressed air can lead to powder agglomerates, as can an excess of recycled powder due to its smaller particle size. Finally, it should be noted that powder coatings only provide the criteria for optimal quality if the coated objects have been suitably pretreated. Whereas traces of grease or anticorrosion oils pose no problems for solvent-borne paints with their grease-dissolving solvents, the solvent-free powder coatings require absolutely clean and easily wetted substrates.

The high throughputs of coating materials in the **coil coating** process have a specific potential for defects. For example, there is a risk of rapid fouling by deposits in the baking oven in the absence of periodic cleaning in conformity with the oven design. Poor maintenance then results in major surface defects in the form of dirt particles on the surface. Craters, pinholes, blisters, fish-eyes and boils are the most common visible indicators of localized defects on the coil coating sheet. This problem occurs in particular with high-gloss coatings for the ”white goods” sector. Here, the demands for surface quality are correspondingly high. Insufficient degassing of the coatings, a steep oven curve and foam in the coatings can very easily lead to pinholing and blistering. A three-roller application process is required, especially in order to reduce defects caused by foam in the coating. In the event of wear of the transfer roller, coating defects in the form of score marks or striping will occur. In this case, the roller will have to be reground.

In general, the decisive factors for surface quality are the coating line and the parameters of the delivered coating product. Remedial action at the end user site is only necessary in the rarest of cases.

Even though today contamination by dirt or dust has been largely mastered by high automation and intensive work in the field of automotive coatings, dirt is still the most important source of defects and costs. The **dirt particles** that cause coating defects are not solely borne in coating lines by the fresh air supplied from outside. Other dirt-bearing contaminants include particles that may be borne into the booth by the application operator, the compressed spraying air necessary to atomize the coating or, in the case of powder coatings, the additional air required for dispensing, the ambient air or the object to be coated [6.6.10]. Whilst dirt admission via the spraying air can be largely controlled with appropriate investment in air filters and oil separators, contamination by the object to be coated and the handling system is in many cases still an unsolved problem. The outer skin of complex-shaped objects such as car bodies can be satisfactorily cleaned by cleaning systems with emu feathers (see chapter 7.1). However, dirt particles in the cavities are of course not removed by this method. In the case of air-assisted paint atomising, it is impossible to rule out the possibility that a portion of the dirt is released inside cavities and subsequently causes coating defects.

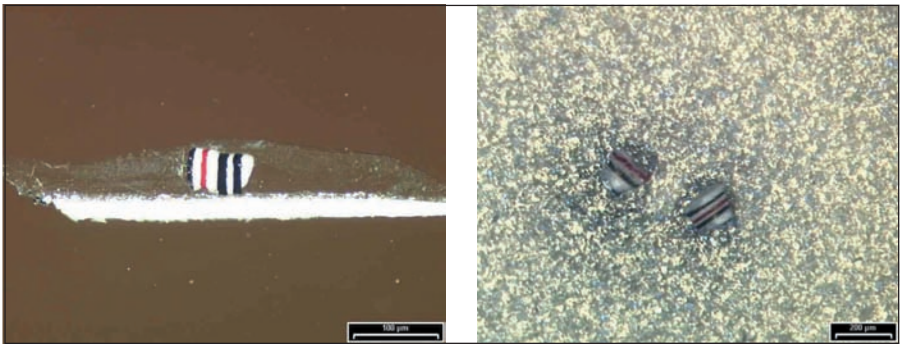


Fig. 6.2.10
Cross section and top view of dirt by repeatedly coated conveyor elements or distance holders

There has therefore been no lack of attempts to eliminate these sources of defects by additional pre-cleaning or by binding the cavity dirt borne by the body in white.

Type of Material	Product	Number of free fibres/m^2
Cotton	Cleaning rag	> 2.000.000
	T-Shirt	1.000.000
	Blue Jeans	800.000
	Floor cloth	500.000
Synthetics	All purpose cloth	43.000
	New overall	25.000
	Cloth for PVC cleaning	25.000
	Synthetic cloth with hot cutted edges	0

Fig. 6.2.11
Type and amount of fibres of clothing

In the case of manually operated application systems, the biggest problem is the contamination introduced by personnel on their clothing or during cleaning operations, in the form of fibres on coated surfaces. Here, the materials used for clothing and for cleaning the plant or object can be ranked according to the number of free fibres per m^2 of material.

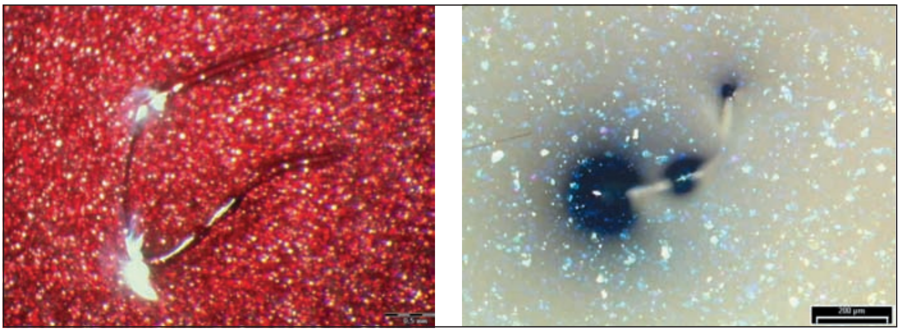


Fig. 6.2.12
Examples of fibres in a top coat

Size [mm]	Necessary Repair Work
< 0,1	nothing
0,1 – 0,3	grinding and polishing
0,3 – 0,6	spotrepair
> 0,6	spotrepair or new coating

Fig. 6.2.13
Sizes of defects by dirt and their related repair

The often visible surface defects generated by fibres can be very easily identified under the microscope.

Only fabrics having less than 100,000 free fibres per m^2, i.e. practically only synthetic materials, are recommended for equipment and clothing of coating line employees.

The work involved in repairing defects caused by particles, i.e. dirt or fibres, depends on the quality target defined for the coating, but can be roughly classified [6.6.11].

In all causes, repairs involve costs that can significantly contribute to the overall coating costs.

6.2.3 Summary

Coating defects can have very different causes. Since they are due to the type of application, the process or human factors, it is plausible that close collaboration between the supplier, plant manufacturer and customer is necessary in order to prevent defects. Today, suitable analysis methods are available to enable clearly targeted explanation of defects that are not always identifiable under the microscope.

6.3 Material Control

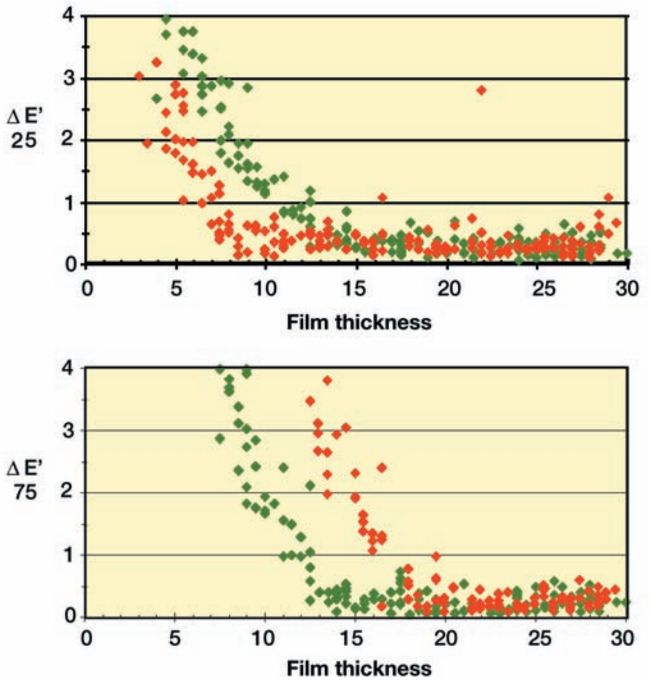
As indicated at the start of this chapter, the sources of quality assurance lie in the monitoring of the product, in order to reject it if does not conform to the tolerances agreed with the customer, then to seek the causes and if necessary to take remedial action. The first step was therefore to identify quality characteristics that could then serve as criteria for the ease of application, attractiveness and service life of the finished coating [6.6.12].

Subsequently, additional aspects of health and safety at work and environmental compatibility were integrated in the monitoring system. The inspection strategy therefore extended firstly to the properties of the materials during application and use, whilst also taking into account the product characteristics during storage and transport. There can be no question that the analytical determination of the composition of complex coating formulae is extremely useful, but it is just as indisputable that in the event of deviations this analysis cannot be adopted as a criterion for exclusion. Determination of the solid content, density, viscosity and surface tension are without doubt important indicators of identical quality of different batches, but variations, within certain limits, do not necessarily indicate quality failings. The quality criteria are therefore not only numerically definable physical and chemical characteristics but also the application properties, which often have to be determined by simulation of the application conditions and practical stresses.

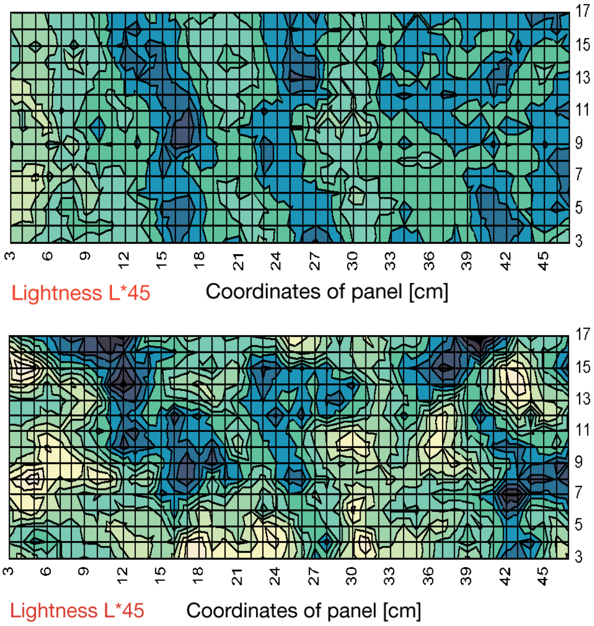
For example, whilst modern oscillation rheometers can provide detailed information on molecular interactions, it is sufficient in some cases simply to measure the run-out time from a DIN ISO cup to establish that two batches of the same product have identical performance.

It is an accepted fact that complete characterization of the properties of coating materials and coatings by measuring their physical characteristics is not yet possible in the majority of cases. Stresses that simulate the practical performance of a coating are still highly important test methods, and include cupping or bending on a conical or cylindrical mandrel, the cross cut test or the *Buchholz* indentation test (see chapter 3.2).

Nevertheless, it is certain that measurements of viscoelastic characteristics by means of a oscillation rheometer or thermomechanical analysis can provide important data for quality assessment [6.6.13]. Further measuring methods are aimed at exploiting the advantages of non-damaging and even in some cases contact-free sensing of characteristic data



(A) Green: light colored primer surfacer; red: dark colored primer surfacer



(B) Above: strong mottling; below: no mottling

Fig. 6.3.1
Statistical evaluation of coated specimen for determing the hiding power (A) as a filmthickness/ _E-diagram and mottling (B) as an area diagram

in order to determine the adequacy of coatings (see chapter 3.3). Measurement of adhesion capability by ultrasonic reflection or thermal conduction, film thickness measurements by heat waves or sound emission analysis are just some examples. Changes in viscoelastic parameters such as the elasticity modulus by means of artificial ageing make it possible to predict cracking tendencies long before the occurrence of the actual defect (see chapters 2.3 and 3.3).

All the tests mentioned so far relate to quality assessments of coating films under standardized conditions in a test lab or at the application center of a coatings manufacturer. A test programme designed to determine the application properties of these coatings has to be even larger and more varied. Due to the large number of different application systems used by paint shops and the undisputed fact that lab conditions are never identical to actual operating conditions, the coatings customer is often forced to retest new products or even individual batches under operating conditions, despite exhaustive prior testing by the coatings manufacturer.

Notable progress in the characterization and optimization of the application properties of coating materials has been achieved by means of statistical measurements on metal test panels coated with clearly defined film thickness profiles in a multilayer coating system consisting of basecoat and clearcoat [6.6.14]. These panels were measured at approximately 500 to 1000 points on each panel. The measured properties are the film thickness, gloss, color values and surface texture indicators (see chapter 3.2). Depending on the priorities, statistical analysis provides quantitatively describable evaluations of the application properties of the individual layers, e.g. in the case of a car body, the throwing power, color precision, gloss and surface requirements (see Figure 6.3.1). This method can be recommended for use in the development and quality testing of the relevant coating materials.

Depending on customer requirements, the costs of the described conventional quality assurance procedures can amount to up to 10,000 euros per batch.

6.4 Defect Prevention by Process Control and Control Loops

The coating result obtained under practice-oriented conditions must be assessable and modifiable. For this purpose, additional plant-specific analyses of weak points and deficiencies must be conducted. Only in this way can the quality-sensitive points of the process be detected. These analyses include data acquisition, failure reports and of course the corresponding activities for analysing and evaluating the mass of data, with the aim of developing defect prevention strategies. These strategies concern the personnel performing the test as well as the production equipment. In this context, qualified personnel and constant process conditions are the most essential preconditions for ensuring constant quality [6.6.15].

For rapid information in collecting data from the individual stations of the coating line and for evaluating the checklists, the aid of electronic data processing is indispensable. The most important application and coating line parameters here are viscosity, flow rate and the spray air pressure, to name but three of the variables that affect quality [6.6.16].

Modern quality assurance goes beyond the logging and description of defects. Process optimizations by means of control loops are the next step on the road to guaranteeing constant quality. Taking the example of spray coating, it has been demonstrated in practice that the monitoring and utilization of process data makes possible the creation of process controls that eventually lead to process automation. In this context **open-loop control** is a process by which one or more input values, such as viscosity, surface tension and temperature or the pressure of the spray air and material, influence the target variables of flow, gloss and film thickness on the basis of known physical laws. Open-loop process control therefore has the function of adjusting processes and – if required – maintaining them constant according to a predefined program. In this case, the result is not monitored by the controller.

By contrast **closed-loop control** is a process by which the controlled variable is continuously monitored and compared to a setpoint value and then adjusted accordingly [6.6.17]. The entire sequence is therefore a closed control loop, in which all disturbance variables are regularly detected and corrected. Each type of open-loop and closed-loop control therefore begins with metrological evaluation of the variables affecting the process. Due to the complexity of interdependent relations (see Figure 1.1.7), the input variables are initially compared against the output data obtained by experiment, so that calculation methods can then, where applicable, be found for the desired controller, e.g. with the aid of neural networks for interconnections.

One example of successful process control with effective closed-loop control circuits is bath control for electrocoating baths [6.6.18]. In order to maintain constant coating quality, numerous bath parameters must be regularly measured and adjusted during operation of the electrocoating baths [6.6.19]. Electrocoating baths undergo constant changes due to the discharge of paint material when coating the objects and also due to variations in ambient conditions (see chapter 4.2.1). The consumption of material causes the solids content of the bath to decrease, with the result that the pigment-to-binder ratio may also be changed in some cases. The introduction of pretreatment chemicals and compensation by refill material can also modify the degree of neutralization and therefore also the pH-value. Changes in the bath condition must if necessary be offset during compensation by ultrafiltration and the removal of liquid anolyte. At present this process is mainly manual, but in some plants the parameters relevant for control are digitally detected and used in automated open-loop process control. Since the solids content and pigment content cannot be directly measured, it is necessary to have recourse to other, indirect methods. Measurements of density and sound velocity have proved to be usable. They can be precisely, rapidly and digitally detected and have a direct functional relationship to the desired variables of solids-content and film forming agent concentration. Current consumption in electrocoatings is another basic variable that is used for e.g. open-loop compensation control (see chapter 7.1).

It can be assumed that experience of closed-loop process control for spray coating and the corresponding closed-loop electrocoating control will be utilized on a broader basis in future [6.6.20].

6.5 Quality Management

The traditional view of quality as the sum of properties (quality criteria) of a product compared to the properties of other products for the same purpose has evolved towards the more comprehensive definition of quality as the regular satisfaction of the requirements and expectations of customers, with the aim of complete and sustained customer satisfaction. In this context, the product properties must also be extended to include environment-related parameters. There is a clear trend from product quality to service quality.

Largely as a result of the globalization of their activities, companies are faced with more intense and geographically more widespread competition. Product quality as the assessment criterion for company capability has now been supplemented by services such as customer service, on-time-delivery and rapid response to problems at the customer’s premises and to changing customer requirements. Flexibility and an expanded vision of quality are the key foundations for meeting these criteria.

Observation of the company’s own products in use on the market and regular market analyses anticipate customer requirements and can also beneficially steer these requirements towards a more ecologically sound or more economical alternative (see chapter 5.5). These activities also form part of the foundations of a total view of quality and therefore serve as basis for a quality management system. Quality management has the aim of recognizing and appropriately controlling all quality-related measures during the life cycle of the product. This process includes observations and findings during product planning, production and utilization on the market. The quality criteria in this case are not only the product properties but increasingly services, adherence to lead times and competence in collaboration. They also have an essential influence on the corporate image of the company.

These criteria include measures to prevent defects. Experience has shown that the source of the vast majority of quality defects can be sought and found in the initial planning stage. These defects stem from latent weaknesses that only become detectable during production or utilization on the market.

It should not be overlooked that defect prevention involves costs. The efficiency of defect prevention can only be calculated when the incurred costs of defects can be set against the prevention costs.

As already mentioned, the modern interpretation of the term ”quality” focuses not only on the actual product but also on satisfying the demands and expectations of the customer. DIN ISO 8402 (1992) therefore defines quality as the totality of properties and characteristics of a product or service that are relevant to its suitability to satisfy predefined or assumed requirements. These characteristics include the product’s adequacy, durability and design but also the services and ecological aspects relating to waste disposal and resource conservation. This concept also takes into account the demand of producers to earn merited profits in order to ensure their continued existence for lasting cooperation in the interests of the customer.

The term quality therefore equally includes the interests of both manufacturers and customers. The definition of quality goes beyond product observation to the assessment of all the services provided by the company. Quality is therefore the regular compliance with the customers' requirements and expectations, to the customer's complete and enduring satisfaction.

This vision requires the participation of all departments of a company. Quality management is therefore a principle that encompasses the entire company and is in the final analysis the decision-making basis for all employees. In other words, quality management is a customer-oriented strategy of corporate management and must be rooted in all units of the company.

This concept of quality-oriented companies is known as "Total Quality Management" (TQM) and is explained in detail in the aforementioned DIN ISO 8402. In this standard, quality in the extended sense is the decisive variable to which all employees are committed, with the addition of a dynamic observation of quality implementation. The latter concept includes constantly sustained efforts to improve the product, technical processes and services, always with the aim of providing even better compliance with the customer's expectations.

The instruments of quality management include quality inspection and quality assurance (QA) in combination with the comprehensive vision of quality management (QM) itself. Quality assurance, by means of process monitoring and acceptance tests, is oriented towards the causes of nonconformance in the process, in order to eliminate them by means of control loops if they cannot be quantitatively remedied.

Numerous standards propose quality management systems and provide instructions for their implementation in the company. In addition, they define criteria for assessing the degree of implementation. Different quality management standards (QMS) of different companies can therefore be compared and audited.

One of the most accepted quality management standards, covering all sectors of the economy, is described in the DIN ISO 9000 ff. series of standards developed by the TC 176 committee of the International Organization of Standardization (ISO).

Whereas DIN ISO 9000 is essentially an instruction manual for other standards, DIN ISO 9001 deals with the installation of quality assurance systems and provides detailed system criteria that must be demonstrated. The standard also covers the company segments of development, design, production and customer service, concentrates on production and gives additional instructions on testing and inspection. DIN ISO 9001 also addresses in detail the tasks of management and personnel training. Other notable chapters include testing and inspection, statistical evaluation of test results, documentation, monitoring of test and inspection equipment contract agreements and customer satisfaction. DIN ISO 9004 provides instructions on the effectiveness and efficiency of the QM system during and after its introduction.

When introducing a quality assurance system, the company must start with the definition of responsibilities at the highest hierarchical level (creation of a quality assurance manual) and implement the basic principles of structural and procedural organization, taking into account the company-wide context. Only then are orders directed to the various divisions of the company with the aim of implementing quality directives. Finally, at the third level, the tasks and activities at the workstations are formulated and laid down as binding work instructions. These instructions must cover for example details on procedures in the individual departments and precise instructions on the handling of products, samples and the performance of tests and inspections.

includes	Distribution		Description
Companies Business units	**internal:** Corporate and business unit leader **external:** According to companie's rule	QM-Manual	Basics like missions and strategies, budgets, organisational aspects of structure and processes, responsibilities, competencies, hints to directives and standard of operations, includes organizational know how.
Departments	**only internal:** Respective departments	Directives	Detailled parts of the quality system; includes organizational know how, tasks and responsibilities
Topics Projects/ Execution	**only internal:** Working place	Standard of operation (SOP)	Detailled directives i.e. for quality assurance, testing etc; includes all technical know how

Fig. 6.5.1
Construction and description of quality assurance systems

The result is the creation of a self-contained quality assurance system, starting with market research for product development and extending to inspection of raw materials, the selection of production methods and final inspection. These provisions are supplemented by regulations governing sales and logistics activities, in combination with the methods of customer service and customer processing.

Compared to the previous version, it should be noted that DIN ISO 9000 has now been combined with the even older ISO 8402 to form the new ISO 9000:2000. The earlier series DIN ISO 9001 to DIN ISO 9003 has been unified into a single standard. DIN ISO 9004 remains in principle unchanged.

At the end of 2002, the validity of the predecessor standards from 1994 expires. Thereafter, ISO9001:2000 will be binding as the model for a process-oriented QM system with the aim of constant improvement of customer satisfaction [6.6.21].

Over the last few years, the principles laid down in DIN ISO 9000 ff. have been adopted and implemented in QA systems by numerous companies. Proof of conformity to DIN ISO 9000 ff. must be provided in the form of certification by independent bodies. Acceptance of this new idea of quality assurance is gaining ground worldwide. In the year 2000 more than 32,000 companies were certified under DIN ISO 9000 ff. in Europe, and worldwide the figure was more than 400,000.

Building on the DIN ISO standards, the automotive industry in particular has produced its own specific regulations. For example, the major American automobile manufacturers have agreed on QS9000 and now demand the relevant certifications from their suppliers [6.6.22]. In Europe, the French automobile manufacturers under the banner EAQF developed a set of regulations in the early 90s. German manufacturers introduced a QM system slightly later, within the framework of the German Association of the Automotive Industry (VDA), under the designation VDA 6.1. Starting in the year 2003 the worldwide automotive industry increasingly agrees on ISO/TS 16949:2002 based on ISO 9001:2000 as a binding standard for their complete supply chains replacing the regional standards described before.

However, corporate aims are not confined to quality assurance alone. Pollution of the environment by technical processes and the need for improvements in resource

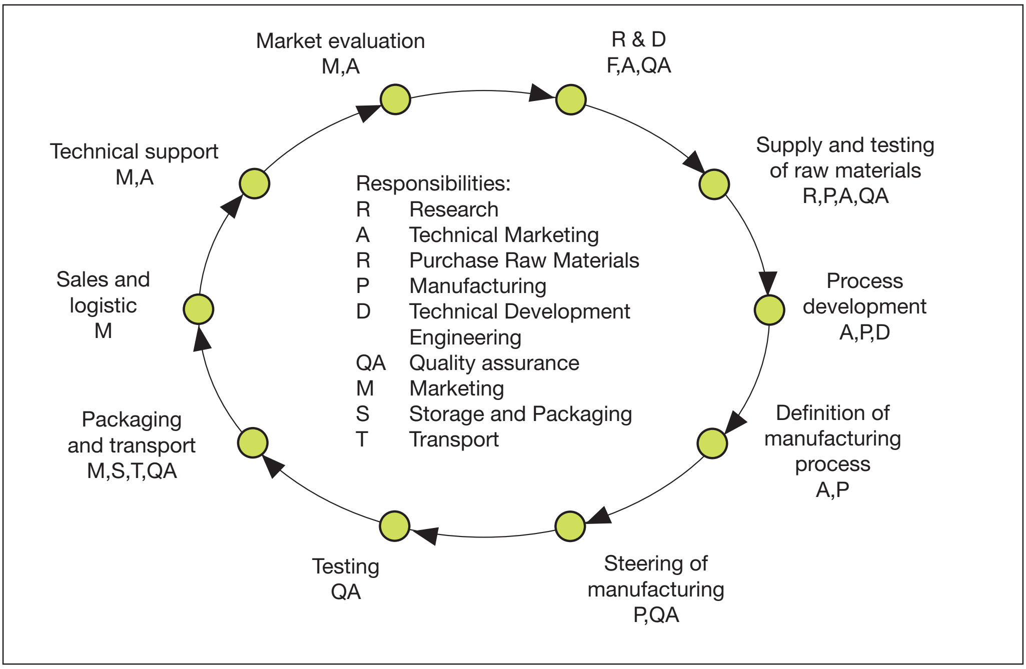


Fig. 6.5.2
Quality circle according to "Verband der chemischen Industrie" (VCI – Germany)

conservation are forcing industry to reduce emissions, waste and energy consumption. Beyond the existing laws, or more correctly in order to implement the existing laws and to dynamize the implementation of ecological principles, environment management systems (EMS) were initially developed in parallel with the QM systems and are now being integrated into QM. Whereas QM systems are now standard for modern companies, the implementation of EM systems is only in its early days.
The first approaches can be found in the EU Eco Audit Regulation of 1993. The basic concepts have since been revised and were integrated in April 2001 into EU Regulation 761/2000. This regulation provides guidelines for the voluntary establishment of an environment management system with a subsequent company audit. In the same way as the quality management systems, the EU Eco Audit Regulation aims to achieve

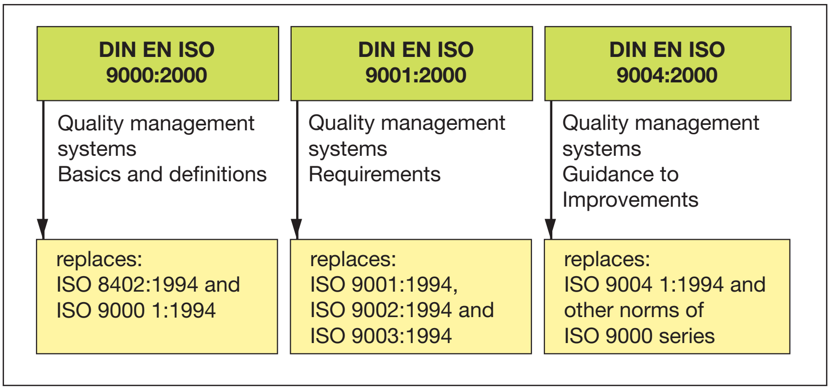


Fig. 6.5.3
System of norms in DIN ISO 9000

Norm	Title
DIN EN ISO 14001 1996-10	Environment management systems – specifications with guidance for use
DIN ISO 14004 1998-01	Environment management system – general description of principles, systems and instruments for implementation
DIN EN ISO 14010 1996-10	Guidances for eco audits general principles
DIN EN ISO 14011 1996-11	Guidances for eco audits –audit processes, audit of environment management system
DIN EN ISO 14012 1996-12	Guidances for eco audits – criteria of qualification of auditors

Fig. 6.5.4
List of eco quality norms

continuous, objectively assessed improvement of the company. One important criterion is the duty to provide information to the public on achieved performance and the active participation of all employees in the implementation of the set targets. A similar goal, but uniform worldwide and therefore providing the basis for worldwide comparative assessment of companies, is pursued by DIN EN ISO 14000 ff. published by ISO Technical Committee 207 in 1996. This standard consists of a total of 20 individual standards. The most important of these standards are partial provisions on the way to a worldwide harmonized environmental audit. The key standards here are DIN EN ISO 14001, DIN EN ISO 14004, DIN EN ISO 14010, DIN EN ISO 14011 and DIN EN ISO 14012.

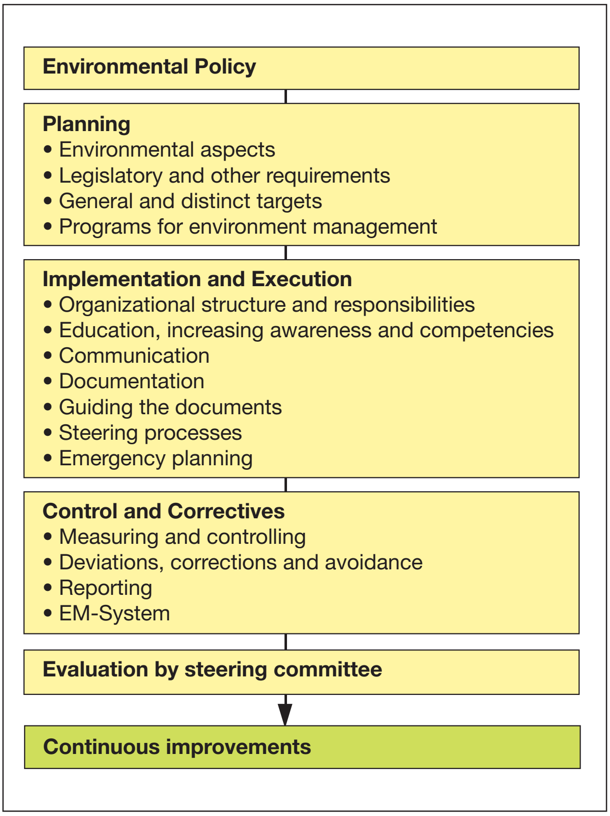


Fig. 6.5.5
Basic elements of an environment management system according to DIN ISO 14001

The basic philosophy of these standards is to provide companies with assistance and incentives to achieve sustained improvements in their environmental quality under their own responsibility. Unlike the EU Eco Audit Regulation, public information on individual activities is not prescribed. Details on the establishment of a UM system are shown in Figure 6.5.5.

Whereas QM systems have been able to establish themselves worldwide, the introduction of EMS is only starting. In the year 2000, only 3,700 companies could be certified under the EU Eco Audit Regulation, and only about 23,000 companies world-wide under DIN EN ISO 14001 ff..

Companies are therefore confronted with the task of integrating two different aims in their management. Qualityconscious and at the same time environmentally sound action are two distinct goals, but the methods for introducing the instruments and principles required to attain them are similar. One thing is clear: the introduction of environmental activities is now prescribed by legal documents. It is therefore a reasonable precaution, when drawing up the QM manual, to formulate environment-related concepts at the same time and to integrate them into the manual. Corporate strategies should harmonize QM and EM systems and also integrate workplace health and safety requirements into company guidelines.

QM and EM systems can therefore be integrated simultaneously or consecutively or else introduced separately. The procedure that each company finds most expedient will have to be decided in each individual case according to the particular situation of the company. Whatever the case, the automotive industry today demands that its suppliers have an EM system certified to DIN ISO 14001, so that many paint and coatings companies have by now established the relevant systems.

Among the multitude of instruments and programs available for business management control covering all aspects of corporate policy, the Balanced Score Card (BSC) has gained importance in the paint and coatings industry as well. The BSC takes into account financing and corporate goals as well as human resources, processes and customers, thus giving all instruments used, including the quality management system, the same strategic orientation. It is a concrete means of transforming the goals resulting from the company's vision and strategy into actual measures; a communication instrument suitable to define the strategy and a tool allowing the quantitative tracking of the measures. This is achieved by determining key factors that are specific to the company concerned and which are also referred to as "key performance indicators" (KPIs) [6.6.23].

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7 Coating Industries

The structuring of the world market according to aspects such as types of paint or coating technology is not homogeneous. The regional associations define the segments in different ways. According to an approximate system the market may be divided up into decorative paints for buildings, automotive production paints and automotive refinish paints, general industrial coatings and printing inks (see chapter 1.3). The largest segment is accounted for by decorative paints for buildings, followed by general industrial coatings. Together with automotive production paints and automotive refinish paints this segment is also referred to as "industrial coatings". In North America this segment and refinish coatings is commonly named industrial coatings and subdivided into Original Equipment Manufactures (OEM) and Refinish. Technologically it is the farthest developed. It includes industrial coating processes for mass-produced goods such as electrocoating, coil coating, spray coating with liquid or powder paints as well as radiation curing (see chapter 4.2 and 4.3). The most important industries by market share can be seen in figure 7.1.

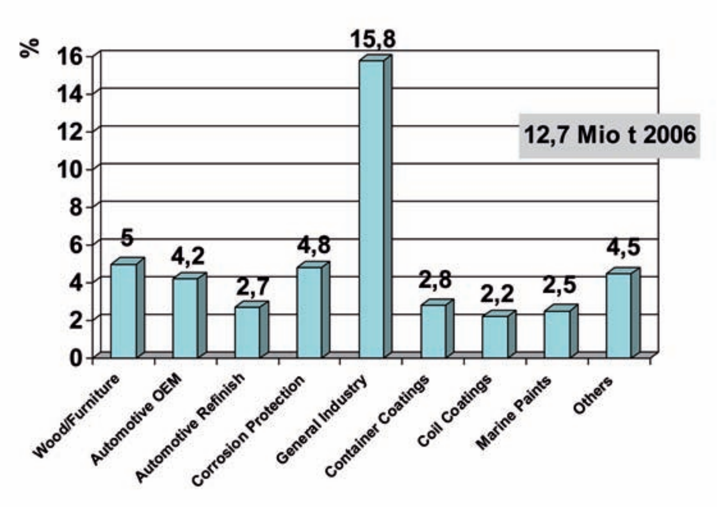

Fig. 7.1
Important branches for industrial coatings of the worldwide coatings market (source: VdL)

The manufacturers of commodities increasingly use different materials for the products to be manufactured. For example, in the automotive industry the production of vehicle bodies is always subdivided into components which then can be manufactured from the materials ideal for the various requirements. A significant step forward was the manufacture of plastic bumpers in order to exploit elastic material properties in the case of collisions at low velocities. In addition, the reduction in weight is a constant issue which has, in the meantime, led to the use of aluminium and magnesium and (in the year

2000) driven the proportion of weight accounted for by plastics down to 18% (see figure 4.1.20). Agricultural and construction plant contains more and more nonload-bearing parts (linings and covers) made of plastic. All materials have to look the same on the product; this can be achieved with specially developed paints and coating processes.

The furniture industry is opting more and more for prefabricated and coated materials. Special mention should be made of the improvement of surfaces using foils, which are usually sealed with UV clearcoats.

Apart from the technological trends in the various industries there was a considerable shift in responsibilities for the item being coated during the 1990s. Owing to its high level of application know-how the coatings industry has, supported by appropriate contracts with its customers based on cost per m^2 or cost per coating unit, assumed more and more responsibility for the results obtained in coating the product. The pioneer in this area is the automotive industry, which restricts itself to planning, investing in and operating the coating lines. Technical implementation, quality monitoring and logistics of the lines are increasingly in the hands of paint companies.

7.1 Automotive OEM Coating

In scarcely any other sector of surface coating have the former manual and lengthy coating processes evolved into such high-tech, high speed industrial application processes as in the automotive industry. Whereas the coating of vehicles used to take days or even weeks, nowadays vehicle bodies pass through an entire coating line with all the cleaning stages, pretreatment, electrocoating and the usual two to four stages for applying the topcoat in approx. 6 to 10 hours.

This was necessary as well in order to cope with the continuous increase in the number of vehicles being manufactured. Global annual production of motor vehicles including heavy trucks reached 65 million units in the year 2006. German manufacturers incl. DaimlerChrysler achieved a market share of 21% based on the worldwide production of German vehicle manufacturers. 5.5 million units were produced in Germany. The quantity of paint required for this was approx. 140,000 t. The worldwide paint market for automotive coatings totals approx. 0.9 million t. Development and introduction of new technologies are initiated not only by tasks brought about by economic necessity. Driving forces behind the development of paints and processes for coating vehicles include reduction in environmental pollution as well as qualitative improvement, e.g. in protection against corrosion and in durability, not to mention appear-

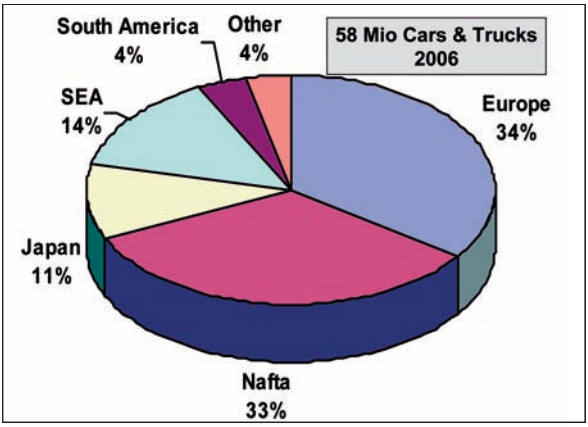

Fig. 7.1.1
Regional share of manufacturing cars (excl. heavy trucks) of about 58 Mio units in 2006

ance. Special requirements are made with regard to resistance to chemical influences due to aggressive atmospheric substances and salt loads as well as physical properties such as adhesion and elasticity, and a high level of hardness. This now is valid for the global market of the car manufacturers [7.12.1].

One should bear in mind to what extreme stresses the vehicles are exposed throughout their service life. High temperatures, e.g. up to 70 °C, for dark colors in Florida and other regions as well as extremely low temperatures of down to –50 °C in the polar regions, constant temperature fluctuations of 10 – 20 °C a day, stone chip stresses on crushed-rock roads and unmade roads, high loads of salt in coastal regions and due to road salt in winter months, high ultraviolet radiation, the action of acid and alkaline exhaust fumes as well as physical stress in vehicle washing installations are factors which only constitute some of the many different burdens and actions which tend to damage coatings (see chapter 3.3.2).

It is easy to understand that such a catalogue of requirements cannot be met with a single coat of paint. For this reason well-coordinated paints are used which, when applied in several layers, handle various tasks within the requirements profile for the vehicles.

Apart from the technical requirements made of a coating line there are organizational aspects such as process sequences and the paint supplier's responsibility for coating results which have become much more important [7.12.2]. This can be illustrated by taking a look at a cost analysis for the coating process. Of all the different types of cost such as capital investment, energy, staff, maintenance and paint, the latter only account for about 20% of the total cost block on average. If the cost of repairing defects or nonconforming surfaces is included in the overall analysis, crucial factors contributing to success and helping to ensure optimum coating results are on time deliveries of suitable quality paints to a well-designed coating line, and application conditions. These considerations prompted the automotive industry, together with the paint and coatings industry, to develop and increasingly implement exclusive supplier concepts and system supplier concepts.

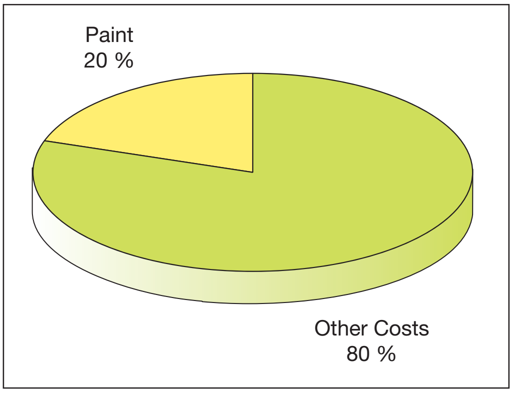

Fig. 7.1.2
Paint material cost as part of the total coatings cost

The various substrates such as steel, galvanized steel and aluminium, as used nowadays in the manufacture of vehicle bodies, are first of all cleaned and then, in pretreatment, are provided with an inorganic conversion layer made of metal phosphates with a film thickness of about 1 – 2 µm. This step increases protection against corrosion and by enlarging the surface area it substantially improves the adhesion of the organic coating (see chapter 4.1). That is followed by the primer, usually by means of cathodic electrocoating for passive protection against corrosion. The average film thicknesses reach 20 – 22 µm on the outer surface and about 5 – 18 µm inside and in cavities. The primer surfacer that follows is designed to cover any unevenness in the substrate and thus create such smooth surfaces that they can serve as a base for a bright topcoat without

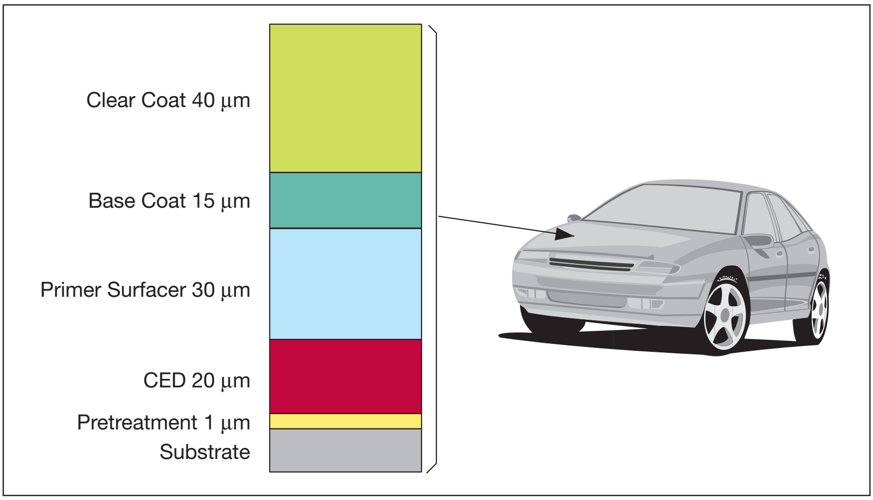

Fig. 7.1.3
Scheme of the multilayer coating of cars

the need for sanding. At the same time the primer surfacer fulfils the function of protection against stone chipping and has to provide anti-corrosive properties if, although it is rare, the electrocoat primer has been sanded through to the metal. The colored topcoat is usually applied in two steps "wet on wet" with a basecoat and clearcoat. "Wet on wet" means that the two coatings are applied in rapid succession without baking the basecoat so that they can be baked and crosslinked together. This topcoat system must then provide the correct color and a high appearance after interaction with the substrate and the other coating layers (see chapter 3.2.4).

In relation to the surface area of a standard vehicle body amounting to 70 m^2, which is covered by the electrocoat, and about 22 m^2 of external surface, which is covered by the topcoats, the average quantity of paint consumed is approx. 15 – 20 kg per body.

Application of cavity sealant, seam sealant and sound insulation is usually the responsibility of coaters. Seam sealant is applied after the electrocoat and it exploits the curing of primer surfacers for its solidification whilst cavity sealant is applied after the coating process. These process steps are necessary to ensure excellent protection against corrosion and acoustic comfort but they are unpopular with coaters on account of soiling (see chapter 6.2.7).

The starting point for the quality of coating in all requirements for protection against corrosion and the attractiveness of the surface is the conceptual design of the vehicle body. Coatability depends just as much on the shape and design of a vehicle as on the chemical and physical properties of the materials to be coated. Protection against corrosion and performance thus start on the design engineer's drawing board and in selection of the materials to be used. One must bear in mind that on the surfaces the various materials do not constitute homogeneous substances (see chapter 4.1).

The steel panels from various pre-refinement stages used for the automotive industry, e.g. pure steel, electrolytically galvanized (EG), hot-dip galvanized (HDG), prephosphated or also organically pre-coated as well as aluminium panels are subjected to various drawing processes and partially extreme deformations in the body-in-white shop, i.e. prior to the application of paint. A local difference in the levels of roughness is therefore inevitable. On the other hand, there is a direct proportional relationship between appearance, i.e. smoothness, build and gloss of the coating, and the roughness of the metal panel (see chapter 3.2.4 and 4.1.2). The substrate differences mentioned can only be compensated by the paint materials and the coating process to a certain extent.

The length of a coating line, from transfer of the vehicle bodies from the body-in-white shop to delivery to final assembly, is usually between 2 and 3 km. This can also be considerably exceeded if substantial time is spent on making corrections in order to increase the first run ok ratio or meet extreme line speeds. “First run ok” means that a vehicle body passes through the paint shop without the need for any major corrective action and is accepted by final assembly in accordance with the quality agreement. The speeds of all lines on average are between 3 and 6 m/min so for cycle lengths of approx. 5 m per vehicle body about 40 to 70 vehicle bodies are coated per hour. The dwell time in the paint shop is then about 8 – 11 hours. However, American vehicle manufacturers often prefer higher-speed lines of up to 12 m/min.

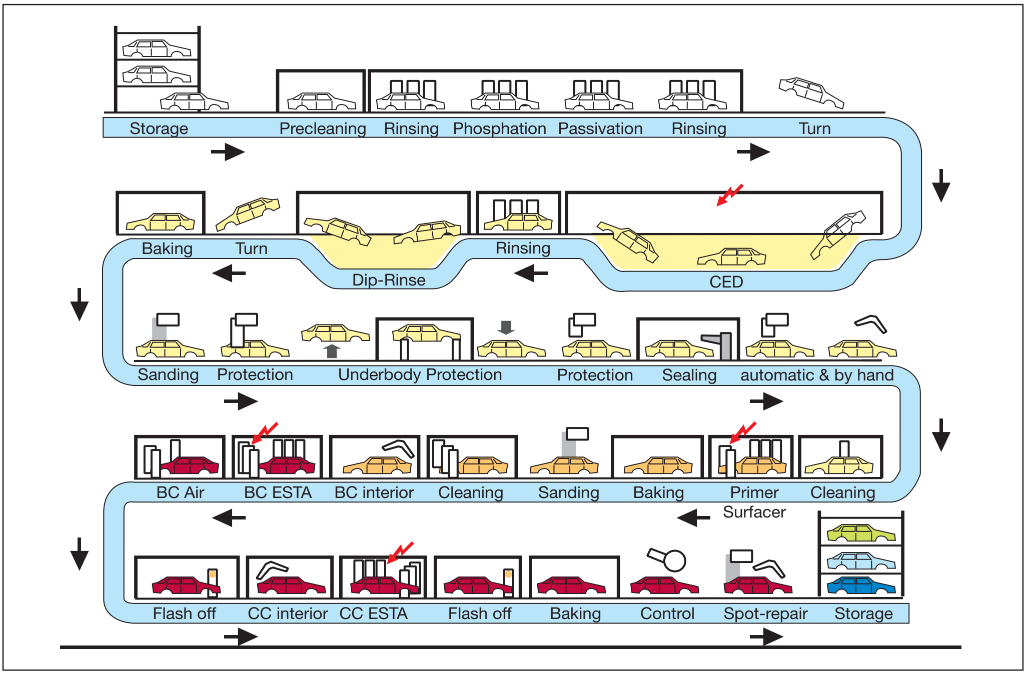

Fig. 7.1.4
Typical steps of a coating line in the automotive industry (BC = basecoat; CC = clearcoat)

The environmental problems which have to be solved with coating lines that operate more and more efficiently involve solvent emissions and waste, which takes the form of paint sludge and is due to overspray when applying primer surfacer and topcoat. In terms of solvent emissions, paints have undergone substantial improvements, particularly over the last 30 years (see figure 5.3.3).

Apart from the coating units at all the stations paint has to be supplied to a large number of outlets via so-called circulation systems. Here the paint is pumped out of a supply vessel, the size of which is between 200 litres and 1,000 litres, circulated and thus fed to the spray guns or spray bells (see chapter 4.2.1). The size of the supply vessels depends on outlet speed. For logistical reasons they are together in one room, the so-called “paint kitchen” or “paint mixing room”, which has to meet the regional storage and safety regulations (see chapter 5.2.2). The tasks of paint kitchen staff are not only to supply paints but also to conduct quality control, keep documentation and support the process of localizing and avoiding defects.

To obtain a defect-free surface one endeavours to work under clean room conditions in the coating zones. Cleaning stages and corrective stages also have to be integrated into the sequence, depending on experience. Preventive measure to keep vehicle bodies and ambient conditions clean in paint shops are becoming increasingly important [7.12.3].

The spraying units are chiefly electrostatic high rotation atomizers which perform paint application with roof and side machines, the reciprocators. In special coating stages such as rocker panel coating, or when coating other areas where access is difficult, the pneumatic spray atomizer is used on robots.

High energy costs are incurred for ventilating the spray booths and in the curing ovens. The overspray due to spray application is fed to the flood sheet fluids under the installation through air ducts in the spray booths. The water is treated in reasonable cycles and coagulated paint is removed (see chapter 4.2.1).

Any necessary repairs to defective spots in the surface of the coating are performed by ejecting the vehicle body in booths with so-called spot repair equipment. In the event of any major defects or a large number of defects the vehicle body is usually repaired by running through the coating line again.

7.1.1 Pretreatment

In the body-in-white shop special attention is paid to the type of anticorrosion oils and drawing greases used which penetrate voids and grooves formed on the body panels by the drawing process. Their ability to be easily removed in pretreatment baths and a good level of compatibility with the paints improve the efficiency of coating lines substantially.

Pretreatment of the vehicle bodies delivered from the body-in-white shop to the paint shop is organized by the various vehicle manufacturers in different ways. In some cases the cleaning process is the responsibility of the body-in-white shop and in others it is the full responsibility of the coaters. At all events the sequence of pretreatment consists of the following stages: cleaning, phosphating and rinsing.

Cleaning and phosphating are chiefly performed in dip baths, the size of which depends on the number of vehicle bodies/h. At quantities of less than 15/h cycle tanks are used, otherwise continuous baths with a capacity of 150 to 450 m^3.

To avoid bubbles of air in the interior and cavities on continuous lines tilting motions are performed inside the baths by routing the conveyor belt accordingly. Recently new concepts have been used incorporating rotary motions during passage through the line, in the form of the “Rodip” processes [7.12.4].

Cleaning

In practice, a weakly alkaline degreasing solution of aqueous mixtures consisting of salts, wetting agents and emulsifiers has become standard. The application temperatures are 40 °C, and up to 60 °C in individual cases (see chapter 4.1.2). The process is usually a combination of spray and dip treatments followed by rinsing stages with deionized water in order to avoid salt residues. The dip stage allows optimum cleaning of drawing and anticorrosion oils as well as good cleaning of the internal areas but it calls for longer throughput times than with spray cleaning.

The cleanliness of the entire vehicle body is essential to ensure that the coating lines operate efficiently. By efficiency we mean the so-called “first run ok ratio” of a vehicle body passing through the entire line without the need for significant corrective action.

Phosphating

Phosphating is an important stage for increasing the durability of a body coating under the aspects of corrosion protection and adhesion. The uniformity of the application of the conversion coat, which is about 1 – 2 µm thick, is an important factor affecting the quality of the coatings as a whole. It takes place in two stages, firstly activation of the surface and secondly build-up of the conversion coat in the form of phosphate crystals. Modern materials have the ability to treat different substrates like steel, galvanized steel, aluminium and magnesium jointly to a limited extent. In particular, the increasing proportion accounted for by aluminium attachments calls for greater attention. The figure was about 1.1% in the year 2000 in relation to the total surface area of vehicles and the forecast for 2005 is 1.5% [7.12.5].

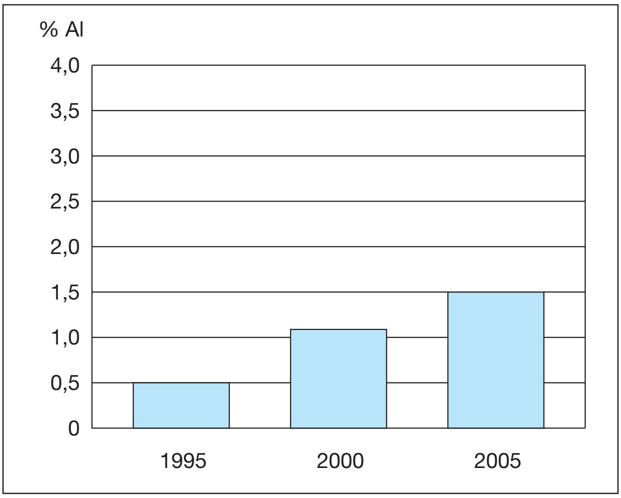

Fig. 7.1.5
Growth of the relative share of aluminium on automotive body construction

On the usually horizontal continuous lines the high quantity of sludge which occurs owing to the pretreatment of aluminium makes it necessary to conduct more stringent process control, more intensive rinsing at bath exit and a specific adaptation of pretreatment materials [7.12.6].

The state of the art nowadays includes zinc phosphating processes containing manganese. They have superseded ones containing nickel. Furthermore, less and less accelerators containing nitrates and nitrites for activating the surface are being used; they are being replaced by environmentally compatible active amino compounds as well as peroxides. In the case of aluminium substrates fluorides are also used (see chapter 4.1.2).

With respect to the ensuing electrocoating process the rinsing zones downline of the phosphating zones are sized so that as much of the phosphating solutions as possible is rinsed off. That minimizes contamination of the electrocoating bath by salts or other substances on the one hand, and on the other, flaws are avoided in the deposited electrocoating film which may be caused by salt residues on the surface of the workpiece. This is particularly necessary with even surfaces where the appearance has to meet high standards.

In some cases there is also a so-called passivation zone upline of the rinsing zones. This improves the adhesion and corrosion protection properties of the electrocoat primer. The materials containing chromium used in the 1980s have nowadays been replaced by environmentally compatible, toxicologically safer chromium-free products such as titanates. Very often passivation steps are already abandonned.

After the last rinsing cycle, which is conducted with deionized water, it is advisable to install a hot blow zone with air temperatures of between 50 °C and 60 °C in order to completely dry the surface of the workpiece. Otherwise there is a risk of marks appearing during immersion into the electrocoating bath under tension, which would lead to considerable sanding work on the coated object.

Over the last few years the dip coating process has become more common than spraying. The better development of conversion layers in cavities proved to be the deciding factor. So-called slipper-dip processes combine dipping and spraying by immersing the vehicle body up to the waistline and spraying the upper section. The advantage is that the tanks are smaller and hence easier to control. For space reasons the Vertak process was used for some time. Here the vehicle bodies are dipped vertically into several cycle baths at each stage and treated. The "Rodip" process can also be performed as a cycle process by rotating the vehicle body into the bath in order to finally pretreat it horizontally, albeit upside down. In this process the advantages are that the visible surface to be coated is not contaminated by any sediments from the baths.

Owing to the large number of treatment steps, not least on account of the high demands in terms of vehicle body cleanliness when immersing it in the downline e-coat bath, the size of pretreatment lines is astonishing. Depending on the configuration there can be tunnels up to 200 m long made of stainless steel sheet, through which a vehicle body has to pass. The effluent of a pretreatment line requires careful attention, although it can usually be disposed of in the normal sewage treatment plants.

7.1.2 Electrocoating

Nowadays electrocoating has become the most widespread process for evenly applying a corrosion protection primer to all metal mass-produced products such as vehicles (see chapter 4.2.1). Consequently, practically all vehicles throughout the world are primed by the electrocoating process.

Anodic electrocoating introduced at the end of the 1960s was a revolutionary process for parts of complex design with major advantages of improved utilization of paint and hence improved economy and environmental friendliness compared to the dip processes used up to that point in time. This was substantially improved once again by introducing the ultrafiltration technique. The ultrafiltrate produced in ultrafiltration installations is used as a rinsing medium in a counter-current system in order to wash off the electrocoat clinging to the surface and return it to the tank. In this way material efficiencies of over 99% are achieved.

The chemical basis of the first anodic primers was maleinized linseed oil, which was later replaced by maleinized polybutadiene. They were self-curing binders which were hardened with the aid of catalysts at approx. 160 °C. Then, in the middle of the 1970s

Parameter	Unit (conditions)	Anodic ED 1965	Anodic ED 1975	Cathodic ED 1975	Cathodic ED 2000
Solids	(1 h/130 °C)	8 – 15 %	12 – 18%	15 – 20%	15 – 20%
Solvents in tank	%	10 – 15	5 – 10	3 – 5	0,5 – 2
Film thickness	µm	30 – 40	25 – 35	15 – 20	18 - 22
Lead	Yes/No	Y	Y	Y	N
pH		7 – 9	7 – 9	6 – 8	5 – 7
Bath temperature	°C	20 – 25	20 – 25	25 – 30	28 – 35
Deposition time	S	120 – 200	120 – 200	120 – 200	120 – 200
Voltage	V	150 – 250	150 – 250	250 – 350	300 – 450
Electr. equivalent	mg/C	60 – 80	50 – 70	30 – 50	30 – 40

Fig. 7.1.6
Technical data of product generations for electrodeposition (ED) coatings

the anodic systems were superseded by cathodic electrocoats and the latter have remained state-of-the-art to the present day. The latest generations are characterized by very low solvent contents, no lead and a high level of reliability.

The reasons for the rapid switch from anodic to cathodic electrocoats despite conversions costing several millions of euros were as follows:

- 3 – 4 times better protection against corrosion in conjunction with a suitable pretreatment on steel, prevention of iron dissolving and enhanced crosslinking by new film forming agents
- Much improved throwing power, i.e. better coating of cavities like in rocker panels
- Greater process reliability due to compensation with two components made consisting of neutralized and pre-dispersed binder as well as a pigment concentrate and greater chemical stability of the components in water
- Smaller film thicknesses
- Greater alkaline resistance of the film at the points of contact in zinc/iron hybrid designs

These advantages are of various significance depending on the industrial application. In all cases process reliability plays a crucial role because for industrial mass production the homogeneity of the products used is vital. Since a coating line handles up to 1,500 vehicle bodies a day with an area of approx. 60 – 90 m^2 to be coated by each unit, this places high demands on formulation and production of the coating materials. That also applies to process control and plant engineering at the user's. Both physical and analytical parameters serve as control criteria in order to always keep the electrocoat bath at the same level of quality with regard to coating results. Nowadays there are control circuits based on power consumption, e.g. in order to maintain the bath solid content. Another important contribution to process reliability has been made by the mentioned subsequent adding of fully neutralized coating material and the splitting into two components. The subsequent feed of already dispersed material means that this process is simplified by reducing it to simple addition. However, the nonseparated acid becomes concentrated during the process in the tank and has to be withdrawn from the system via an anolyte circuit (see chapter 4.2.1).

Improvement in the corrosion protection of the cathodic electrocoats in comparison to the anodic ones can be verified by conducting various tests.

Depending on the quantity of items per hour the tanks operate in a cyclic or continuous system, in a similar way to pretreatment. Cyclic systems achieve tank capacities of 100 m^3 whilst continuous systems achieve up to 450 m^3.

Properties/Tests	**Unit**	**Anodic 1975**	**Cathodic 2000**
Film thickness	µm	30	20
Salt spray test ASTM B117 (480 h)	mm[1]	2	0
Climate change test VDA 621 (10 cycles)	mm[1]	destroyed	< 2

[1] rust creepage

Fig. 7.1.7
Comparison of corrosion protection anodic versus cathodic electrodeposition coatings on zinkphosphated steel panel as rusting at the scribe

The actual electrocoating process commences upon transfer from pretreatment [7.12.7]. The vehicle body can be wet or dry when it is dipped into the tank. With cyclic systems a variable voltage programme can be set with one rectifier in order to achieve optimum coating results in terms of surface quality, film thicknesses and throwing power. In the case of continuous systems the voltage programme is set with at least two rectifiers. The input rail is separated from the main rail for the central dipping area and the emerging zone. This is necessary in order to reduce high current peaks which can cause surface defects on account of high local heat development and excessive gas development (see chapter 4.2.1 and 6.2.2).

Fig. 7.1.8
Dipping a body into the electrodeposition tank

To keep the quality of coating constant one must take care to ensure that bath temperature maintains set levels within close limits of approx. ± 0.5 °C. Heat exchangers must be designed in such a way that they can dissipate the heat generated by the flow of current. Since the highest flows of current occur in the entry area, that is where one should endeavour to achieve a high velocity of flow in order to dissipate the heat quickly. For this reason and in order to prevent the pigmented electrocoats from settling the bath contents must be circulated continuously. As a rough guide when sizing the pumps one should aim for circulation of about five times per hour (see chapter 4.2.1).

In many coating shops in the automotive industry there is now only one tank supplying a number of topcoat lines owing to the reliability of the electrocoating process. In this way it is possible to prime up to 1,500 units a day. At such a throughput it becomes particularly important to regularly compensate with replenishing material in order to achieve a consistent level of quality. The automatic subsequent addition linked to power consumption is particularly expedient for this (see chapter 4.2.1).

Bath material still clings to the film compacted by electro-osmotic effects during precipitation and adhering firmly to the substrate when exiting the tank and it has to be removed by rinsing. Since this material can still be used, the vehicle body is rinsed by the countercurrent method with the ultrafiltrate produced from the tank and the rinsing water is returned to the coating bath (see chapter 4.2.1). This takes place in at least two cascades. Modern electrocoats no longer require any further rinsing with deionized water after the rinsing stage with pure ultrafiltrate.

When designing the rinsing zones care must be taken to ensure that paint is prevented from drying onto the coated object. The first rinsing process, usually conducted with a spraying cycle, should therefore be completed by the vehicle body in less than one minute after emerging from the tank. Once paint runs have dried on they can only be removed afterwards by sanding and they otherwise lead to considerable disruptions in the overall set-up of vehicle coating. In a similar way to pretreatment the main rinsing zones take the form of dip tanks. Depending on the quantity of ultrafiltrate fed in with < 0.6% solids these baths have solid contents of less than 1% in order to ensure efficient rinsing (see figure 4.2.19). Material efficiencies of over 99% are achieved under such conditions.

Deposition of the electrocoat and the rinsing process are followed by a pass through the baking oven. There the residual water of approx. 5% present in the coating is first of all removed and good flow is achieved along with crosslinking to create the corrosion protection film. Baking takes place at an object temperature of between 160 °C and 190 °C for a least 15 minutes depending on the type of electrocoat. During the crosslinking process organic substances are released which can lead to deposits in the oven. To comply with most legal regulations they have to be sent for thermal after-burning. In view of both aspects an optimum supply and circulation of air must be set in the ovens, which are usually of type A design (see chapter 4.3.1).

An electrocoating process can be chiefly used in a closed circuit without any significant environmental pollution due to waste materials. In terms of environmental pollution four sources of emissions have to be taken into consideration:

1. Emission of volatile compounds in the tank and rinsing zone areas
2. Emission of organic compounds in the oven due to crosslinking reaction and increased paint film temperature
3. Waste water in the form of ultrafiltrate of rinsing water
4. Anolyte overflow with organic acids.

The solvent contents of the latest generation of cathodic bath material are less than 0.5%. Together with the usual air ducting via the tank, which is directed into the baking ovens, this causes the concentration of organic compounds to be below the ‘MAC’ maximum allowable concentrations at the workplace. The air with the minimal load is then treated by thermal after-burning together with the cleavage products from the crosslinking reaction in the baking ovens.

Quantities of ultrafiltrate that have to be disposed of occasionally can be fed directly to the sewage treatment plants because the biodegradability of the composition is perfect and decomposition takes place in relatively short dwell times. The same applies to the

substances in the anolyte circuit. Here one has to consider that the pH is about 4, whilst the ultrafiltrate is within the working range of the electrocoat, i.e. 5.8.
Before the primed vehicle body is transferred to the next station, the surface is inspected and repair steps may have to take place, usually in the form of sanding defective surfaces. To reduce the level of dirt and dust caused by such sanding operations it is recommended that sanding be conducted by the wet method. Apart from that, there has to be a very careful cleaning procedure prior to application of the primer surfacer.

7.1.3 Seam Sealant and Underbody Protection

In most paint shops the vehicle body is sealed with sealing materials when electrocoating has been completed and provided with underbody protection materials. In individual cases soundproofing materials are also inserted at this stage of the coating process.
The electrocoat primer is a suitable substrate for the materials made of plastisols (e.g. PVC or PUR). Sealing materials considerably improve the protection against corrosion in cavities with poor accessibility for CED, whilst the underbody protection coating of approx. 1 mm film thickness protects against stone chipping. In many cases underbody protection coating has meanwhile been replaced by plastic panels because application of these materials involves considerable contamination of the coated surface and the efficiency of the paint shop declines.
Application of seam sealant is performed with airless spray guns at high temperature with the aid of robots (see chapter 4.2.1). Manual adjustments may still be necessary in individual cases if the seams do not always have the same gap width and if the seam has to be coated where there are awkward joints with several body parts.
Application of the underbody protection coating is also performed by the airless method with the vehicle body jacked up. In this case the precision of the spray jet is higher and manual corrections are rarely necessary.
The pieces of soundproofing material are chiefly inserted by hand.
They are thermally treated together with the seam sealing and underbody protection materials in the downline primer surfacer oven. In the case of PVC the emulsion particles become dissolved in the plasticizer. When it has cooled down the material gels to form a film, which is highly resistant to physical stress caused by abrasion and stone chipping. For quite a while some automotive manufacturers also used to provide the visible exterior of the vehicle body with special stone chipping protection coatings or plastisols in the lower area, e.g. at the door sill or front spoiler. Modern primer materials have now made the use of such materials superfluous.

7.1.4 Primer Surfacer

As opposed to electrocoating the primer is essentially applied by spraying to the exterior, in the entrance area of vehicle bodies, in the engine and luggage compartments. As a result the vehicle body is given its second external coating, which not only provides extra corrosion protection and stone chipping protection and protects the electrocoating from possible attacks due to ultraviolet radiation but also serves as further preparation for a smooth surface and a bright coating.
Owing to their multi-functionality the formulation of primer surfacer is a difficult task. Nowadays polyurethane-modified polyesters in conjunction with epoxy resins have

become the most popular film forming agents. The appropriate coating formulations are rounded off with crosslinkers based on melamine or blocked isocyanate. In Europe they are chiefly aqueous coating materials and are generally characterized by a high level of pigmentation. Consequently the solid content is between 50% and 65% and the binder/pigment ratio is between 1 and 0.5. Approx. 10% of all vehicle bodies throughout the world are coated with powder primer surfacer nowadays. With a film thickness of 0.1 mm and a high material yield due to recycling at the line they constitute an economical and ecological alternative to aqueous primers, which already fulfil all their functions at a film thickness of about 25 µm. With most formulations the crosslinking conditions are > 150 °C object temperature over a period of 15 minutes but they can be about 130 °C for the liquid ones.

As the name says, primer surfacer have the task of filling out and smoothing unevenness in order to level the substrate for the following layers of topcoat. Apart from the good build, good sandability is another important quality criterion even the goal of modern coating lines is to make the sanding of primer surfacer superfluous. On the other hand, the levelling of substrates has become more important nowadays because more and more different substrates such as steel, galvanized steel, aluminium and plastics have to get a homogeneous appearance on the vehicle body despite the fact that there are considerable differences in surface properties in some cases.

Over the last few years special attention has been devoted to the primer surfacer on account of the aspect of the hiding power of the colored topcoats. Consequently, the color of the primer surfacer is extremely important in order to minimize the film thicknesses of the next basecoats for any given range of topcoat colors. Many vehicle companies have decided in favour of the "color keyed primer surfacer" concept. Here between 3 and 7 primer surfacer colors are supplied to the spray booths, which are then applied, depending on the color of basecoat, in order to achieve maximum color agreement and minimum basecoat film thickness. Some automotive manufacturers have developed this further to create a so-called "color specific primer surfacer" concept in which each basecoat is based on a specific primer surfacer whose color is largely identical.

Whereas in the above analysis the emphasis is on the visual quality of the primer surfacer on the one hand, this intermediate layer has to fulfil crucial tasks in the area of physical/technological properties such as stone chipping protection on the other. Wherever protection of the substrate against corrosion is missing, e.g. after sanding through the electrocoating, the primer surfacer also has to fulfil corrosion protection functions.

To **prepare** application of primer surfacers the vehicle body is, in many cases, subjected to a cleaning process. In most cases this is first performed manually and is often completed with an automatic process similar to that of a car wash. Manual cleaning of the surface is conducted with special, lint-free and usually moist wiping cloths. Any seam sealant resulting from improper application also has to be removed. The automatic cleaning systems have rotary brushes which are provided with ostrich feathers in order to prevent any electrostatic charges and any accumulations of dirt caused thereby. All the measures serve to achieve as high a first-time ratio as possible (see figure 7.1.9).

On some coating lines the surface of the body is cleaned with air from air locks and precision air ducting. Air ducting is designed in such a way that the particles of dirt can easily be separated off.

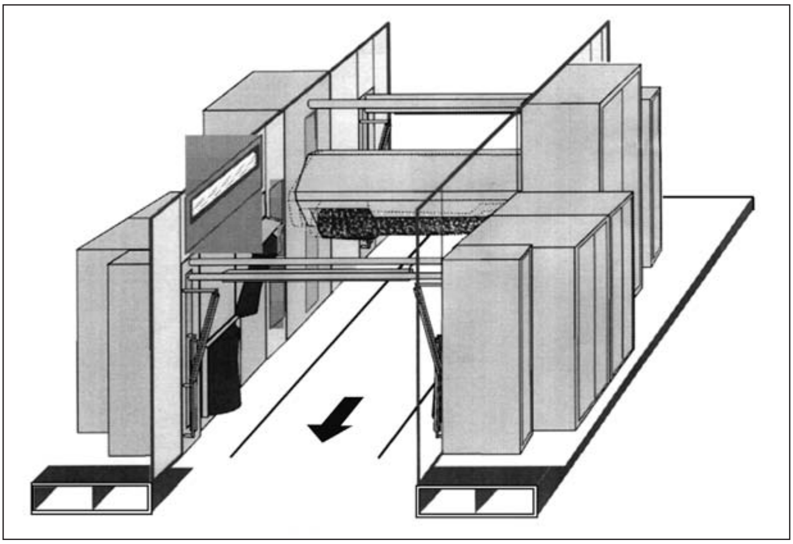

Fig. 7.1.9
Scheme of an automated cleaning station for preparing defectfree coatings in automotive painting process

Liquid paints can be applied to the body of the vehicle with the aid of an appropriate number of supply lines, the circulation system, without any substantial loss of material, via a spraying assembly. The circulation system is supplied from a central supply tank which usually has a refill tank. In the latter the coating material is adjusted to set viscosity levels as required. The circulation system pipes, which can be up to several hundreds of metres in length, are supplied from the supply tanks. The excess material not consumed flows back into the tank via a back pressure regulating valve. At the outlets of the approx. 7 to 10 spraying units per coating line there are pressure controllers which ensure that material pressure at the outlets remains consistent in order to achieve uniform film thicknesses. Owing to the rheologically more demanding aqueous coating materials volume forced systems have now largely superseded the pressure-controlled systems (see chapter. 4.2.1).

Whilst coatings used to be applied with compressed air, state-of-the-art application uses electrostatically assisted high-rotation atomizers. The necessary number of spray units largely depends on line speed and the film thickness of usually aqueous primer surfacers to be applied. To reach points with poor accessibility such as the door rocker panel in the interior, the first stage of the coating process usually consists of two robots with pneumatically atomizing spray units. For each one these are usually followed by two side machines and two roof machines (reciprocators) for overall coating. The spray jets of the latter can be programmed in such a way that they optimally follow the contours in order to ensure a uniform film thickness. When only one color is used internal charging has proved successful whilst if more than one color is being used external charging is more favourable in terms of the volume of investment. The two methods have slightly different levels of transfer efficiency, with external charging not quite so good.

Cleaning the spray booths is one of the important factors helping to achieve high first-time ratios. The frequency and the economy of overspray recovery from booth water [7.12.8] depend on the transfer efficiency which has to be achieved.

The environmentally-friendly and eco-efficient powder coating was first used at the beginning of the 1990s for primer surfacer with a preliminary stage as stone chipping primer. The large film thickness for good stone chipping protection, nonuse of solvents, high level of transfer efficiency by recycling the overspray directly in the application system, plus the lower cost of investment and lower running costs were the main reasons for the increase in the use of powder primer surfacers. Initial applications in the USA were implemented not least on account of legislation [7.12.9].

In 2006 about 3.5 million vehicles were coated with powder primer. In the commercial vehicles sector some manufacturers have switched to now only priming the all-galvanized cabs of commercial vehicles with powder and dispensing with electrocoating.

The switch in dispensing equipment, different handling of powder coatings compared to liquid coating materials on a large scale and the problems with color changes are reasons why penetration of the automotive industry by powder coating technology has so far only been slow.

For the application of powder primers as well it is important to take the same amount of care when cleaning the vehicle body to be coated as when applying aqueous primers.

Fig. 7.1.10
Application of powder primer surfacer in automotive painting

The low volumetric flow of powder and the large film thickness call for about double the number of spray units compared with liquid paints. The highest delivery rates in order to apply the powder with as high a transfer efficiency as possible reach those of electrostatically assisted rotary atomizers. The levels of first transfer efficiency only reach 60% depending on the type of body, so for recycling powder the cab has to be designed carefully. This involves suitable conveyance of the vehicle body, efficient air ducting and a high degree of cleanliness. In the case of primers larger film thicknesses in the underbody area are frequently used for reasons of quality. There it is the powder recovered which is mainly used. That way it is possible to achieve material transfer efficiencies of > 98%. The surfaces of powder layers with thicknesses of approx. 80 – 100 µm are just as good as with liquid coatings but they have the advantage that they present less “orange peel” on vertical surfaces but more on horizontal surfaces.

In the case of aqueous or solventborne primer surfacer, when the body has left the application zone it reaches the baking oven via a flash-off zone. Sizing of the ovens depends on the type of coating applied, the object and line speed. The heating curve plays a major role when ensuring defect-free, smooth surfaces (see chapter 4.3). After leaving the oven, passing through the sanding and correction zone and repeated cleaning of the surface the vehicle body passes into the topcoat application zone. The application of aqueous primer surfacer with aqueous basecoats without prior baking, that is, by the “wet on wet” process, is gaining importance [7.12.10].

7.1.5 Topcoat Application

Suitably high demands are made of the last coating layer, which determines the visual impression of the vehicle throughout its service life and which is subjected to enormous stresses in all parts of the world during that period. By interacting with the coating design as a whole the topcoat helps guarantee the standard of physical properties of the coating. Good adhesion between all coating layers and with the substrate, a harmonized level of formability and elasticity whilst providing the film surface with a high level of hardness are worthy of special mention. High gloss, good flow, resistance to ultraviolet radiation in combination with weather influences, resistance to chemicals and organic solvents such as fuels, are the requirements which a topcoat has to fulfil (see chapter 3.2 and 3.3).

At the same time it is the topcoat which provides the color. Under the conditions described it must guarantee a high level of surface uniformity, repair capability at the coating line and, during use of the vehicle and over the service life of the vehicle, consistency with regard to the visual and physical/technological properties.

Color styling nowadays plays a much more important role than about 20 years ago. This is evident from the fact that meanwhile entire departments of automotive manufacturers and coating manufacturers monitor color trends, develop new colors and special effects, and select them carefully for new models [7.12.11]. The regional aspects of the world of colors have gained profile. For example, the color frequencies in the three regions of North America, Asia and Europe are quite different in the year 2000 [7.12.12]. The importance of color styling is also supported technologically, on the one hand by new application processes and by new raw materials and pigments, on the other, which have created enormous scope for color variations. To satisfy the requirements described more fully there has been a considerable change in coating materials and application processes over the last 20 years. For instance, the topcoat is applied in two separate layers almost everywhere nowadays, by the “wet on wet” process. Consequently the two functions have been separated, i.e. color in the first coat and resistance in the second coat, the clearcoat. The paint formulations for both coats have been optimized in order to fulfil the functions described to such an extent that levels of resistance lasting over 10 years have been achieved, e.g. in gloss and color. An important formulation step was not only the use of UV-resistant acrylic resins but also the use of UV absorbers and at the end of the 1970s as well as development of pigments with a higher level of light fastness (see chapter 2.1.3).

Fig. 7.1.11
Example of a design supporting coating

With this two-layer topcoat it was also possible to create much brighter metal effects. Consequently, light/dark effects were achieved depending on the angle of view, as were hitherto unknown with single-layer topcoats. The entire quality level of such two-layer topcoats has led to the fact that the single-layer solid colors today are also applied in two coats. That made it possible to set up standardized coating lines which can meet customers' wishes more easily, irrespective of the popularity of various colors.

Experts refer to the first layer as the basecoat (BC) and the next layer as the clearcoat (CC).

Basecoat

Solventborne basecoat is a low-solid paint which can reach 45% solids for solid colors in North America and 35% solids in other countries. The effect coatings are much lower. The resulting high solvent emission has led to the fact that in Europe and to a certain extent in North America as well aqueous formulations of coating materials have become common. Compared to the solventborne basecoats they only have a solvent content of approx. 16%. Depending on color, basecoats are applied in films of approx. 12 to 30 µm dry film thickness.

		Solventborne BC	Waterborne BC
Metallic	NV	25 %	25 %
	Solvents/NV	3,0	0,5
Solid color	NV	40 %	35 %
	Solvents/NV	1,5	0,3
Total (1)	Solvents/NV	2,5	0,4
(1) Metallic/Solid color = 60:40			

Fig. 7.1.12
Reduction of organic solvents by waterborne basecoats (BC) related to the nonvolatiles (NV)

Before reaching the automatic coating machines such areas as are difficult to access are precoated with the aid of robots or by hand pneumatically. These include the doors sill and some zones of the engine compartment and of the luggage compartment. In the case of robot application the vehicle body is usually stopped briefly in so-called "stop and go" mode and the appropriate hoods and doors are opened so that coating can take place automatically. This may have to be repeated for clearcoat application. If applied

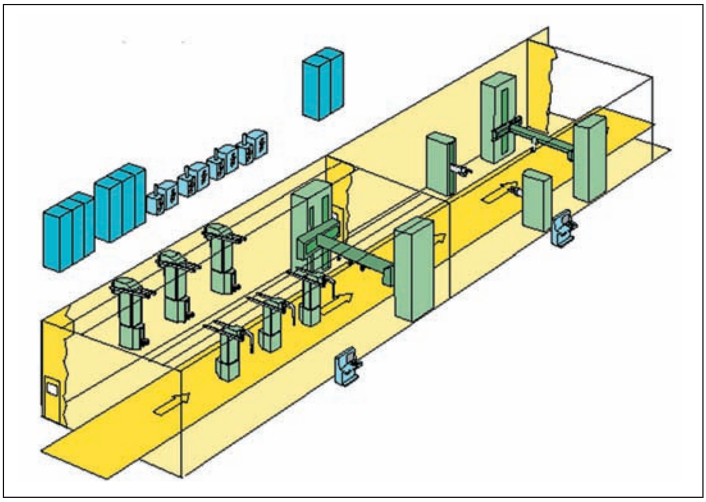

Fig. 7.1.13
Typical placement of bells for roof machines and side machines

manually there is no need for the "stop and go" mode.

Owing to the low solids content of effect coatings two applications are necessary at line speeds of about 3 m/min upwards. In the case of solid-color coatings there is usually only one application with electrostatic high rotation bells on account of the higher solids content.

Fig. 7.1.14
Application of automotive top coats with high rotational bells and external electrodes for charging

In the case of effect coatings the first coat is also usually applied with electrostatic high rotation bells whilst the second coat is often still applied pneumatically with about 30% of the necessary quantity of paint in order to achieve the desirable high effect in the orientation of the flake pigments and create easy reparability. To increase the efficiency of application and reduce costs high rotation bells, so-called micro-bells, are also being used nowadays for the second layer of basecoat. That achieves an effect in the coating which comes very close to that of pneumatic atomization.

Owing to the high conductivity of aqueous paints and on account of the many colors, usually more than 12, the electrostatic charging is performed with external electrodes. It helps to avoid elaborate isolation of the paint supply of the large number of many colors. However, development of the "cartridge" system is so far advanced that even direct charging systems whose technical arrangement has a perfect command of electrical isolation are used in production (see chapter 4.2.1).

The arrangement of the bells is usually selected in such a way that first of all the sides of the vehicle bodies are coated and only then does the roof machine start up. Both types of machine are capable of following the contours of the vehicle bodies within certain limits. Since the spray jet does not have a homogeneous material distribution, the roof machine performs motions at right angles to movement of the vehicle body in order to provide the coats with greater uniformity (see chapter 4.2.1).

Between the two application stages of effect coating there is a brief flash-off time of about 1 to 2 minutes. The purpose of this is to prevent the first coat from starting to dissolve, as a result of which the orientation of the effect particles is not lost. This is particularly important in order to ensure reliable reproducibility of the flop effects and the associated color perceived. The general rule is that the basecoat layers subjected to intermediate drying should have a residual water content of less than 10%.

When formulating such basecoats maximum flexibility should be obtained by optimizing the composition of all the paint components in order to guarantee a uniform color perceived in relation to application conditions. Owing to vehicle body shapes there are different distances and overlaps of spray jets. In the case of colors which are not very robust there are significant differences in color perceived and effect on a single vehicle body.

Effect paints for automotive coating may be divided up into classes of metal effect paints with brightness flop, pearlescent effect paints with slightly changing color flop and color flop paints with a considerable color change.

The colors perceived, which are dependent on the angle of viewing, are created by two physical principles. Metal effect paints reflect the incident light depending on the precision of the positions of the aluminium flakes more or less efficiently and thus create a light-dark effect. Color flop paints require flakes which are provided with two or more oxide coatings with a varying refractive index. This then creates an angle-dependent color on account of interference caused by certain wavelength components. Pearlescent effect paints have less effect, which comes about in a similar way to that of natural mother of pearl (see chapter 2.1.3). The combinations of all pigment classes permit a whole host of new colors perceived (see chapter 3.2.4).

For the necessary quality control and for maximum precision when defining the specification optical multiangle measuring instruments are meanwhile state of the art. Nevertheless, owing to the problems already described due to the shape of vehicle bodies and dependence on application, visual inspection is still performed at the vehicle manufacturer's (see chapter 3.2.4).

Clearcoats

After application of basecoats the vehicle body passes through a short intermediate drying zone, so-called “flash off”. The conditions are such that downline clearcoat application exerts no influence or only a minimal influence on color and effects of basecoats. Usually the parameters are as follows: 50 – 70 °C object temperature for 3 – 5 minutes. As is the case in most drying zones, infrared lamps are also used here to speed up heating and shorten the zones. Infrared lamps essentially heat up the coating and not the vehicle body so the cooling zones can also be smaller (see chapter 4.3.1).

The clearcoats chiefly and increasingly used nowadays are two-component acrylic resin-borne bases, which are cured with polyisocyanates (see chapter 2.1.1). The mixing of the two components in the proportion of 3:1 to 5:1 is performed in the gun or bell just before atomization. Together with the dried basecoat curing is performed at about 130 °C – 150 °C to create a durable film.

One-component clearcoats used in addition to the two-component ones are also acrylic resin-based and they contain melamine resins or blocked isocyanates as cross-linkers. The baking conditions are comparable with those for 2-component clearcoats.

The film thicknesses are 40 to 50 µm. They are crucial for the brilliance, smoothness and appearance of the coating applied. In particular, it is important to observe the film thicknesses on the vertical surfaces without tendency to sag. This is one of the important requirements for ensuring that the difference in orange peel is not too large between the horizontal surfaces (small) and vertical surfaces (large). Thixotropic agent or specific pseudoplastic behaviour constitute the formulation bases for clearcoats which can be applied reliably. This viscosity characteristic is achieved either with additives or with special resin combinations (see chapter 2.1.4).

The one-component and two-component types of paint are dissolved in solvent and as high solid systems they can reach a solids content of up to 65%, as achieved particularly in North America by optimising the resins and improving the dissolving power of all the paint components (see chapter 5.6.1). The North American coatings industry has been

		North America	Europe
2-component clear coats	NV	65 %	55 %
	VOC	250 g/l	350 g/l
1-component clear coats	NV	60 %	50 %
	VOC	300 g/l	420 g/l
VOC = volatile organic compounds			

Fig. 7.1.15
Solid content (NV) and VOC-numbers of actual clear coats

addressing the development of such high solids paints for approx. 25 years. For this purpose the molecular weight of the base resins and crosslinkers has been reduced by polymerization technology to such an extent that paint formulations with relatively high solids but identical viscosity can be achieved. The same applies to polyisocyanates and melamine crosslinkers.

The European coatings industry and paint-applying automotive industry decided in favour of aqueous basecoats and thus initially invested in flexibility in terms of application reliability, performance profile and emission of clearcoats. Owing to a self-commitment and legal conditions also being tightened up, users of solventborne clearcoats are now being forced to make a move. Aqueous, solvent-free products such as slurry and powder have found their first applications [7.12.13, 7.12.14].

The large film thicknesses of powder clearcoats from 60 – 80 µm provide a visible enhancement in the appearance of surfaces because they can create a so-called “wet look”. What is meant by this is a deep gloss intensifying the color perceived which is revealed provided the surface is sufficiently smooth.

Slurry technology provides a dispersion of very small particles in water without solvent. This product makes it possible to utilize conventional material metering systems for liquids and also achieves thinner film thicknesses than with “dry” powder (see chapter 5.6.3).

Color trends

The impression which a vehicle makes on a potential buyer is very heavily dependent on color styling. For this reason the design departments of the automotive industry keep a very close eye on trends in fashion, culture, art, furniture and social developments. At the same time they are in close contact with the paints and coatings industry in order to keep abreast of new possibilities for color and effect styling. So on the one hand colors follow trends in taste and on the other ideas for new color effects have to be heeded in order to achieve a stronger differentiation in the market and an increase in the attractiveness of vehicles,

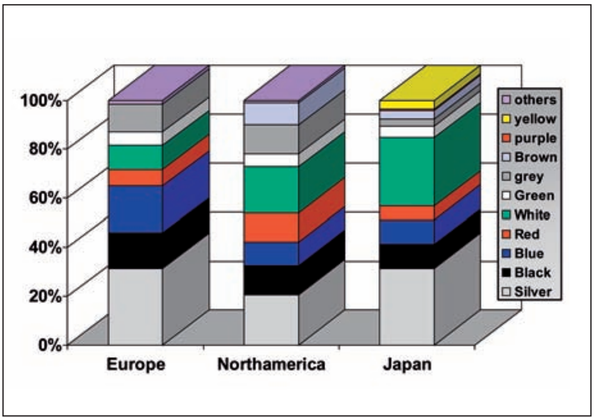

Fig. 7.1.16
Regional color population 2003 (source: Dupont)

which have been drafted or which are going to be drafted, amongst customers. Over the last few years there has been a distinct trend towards achromatic colors. Achromatic colors are black and grey shades as well as metallic ones with a slight tint of color. This is most evident in Europe. Although these colors provide a neutral impression, they emphasize the character of high-quality vehicles.

All in all, when a buyer purchases a new vehicle he has more and more colors to choose from, provided he is prepared to pay more. Some manufacturers even supply so-called “tie colors”, which means that vehicles are coated and delivered with colors according to the customer’s wishes like ties.

7.1.6 Repair in Automotive OEM Lines

Despite all precautions, sometimes even under clean room conditions, not all defects such as dirt contamination, pinholes and other coating abnormalities cannot be completely avoided. After leaving the cooling zone of the clearcoat baking oven the coated vehicle body is subjected to careful inspection. An appropriate work station with special illumination is set up for approx. 6 to 20 staff. This makes it possible for the trained member of staff to detect surface defects quickly and reliably (see chapter 6.2).

Fig. 7.1.17
Inspection line of coated automotive bodies

Minor defects, especially in the clearcoat, are remedied by sanding and polishing, others call for either a spot repair or a complete repair, whereby the vehicle body is prepared accordingly, usually with light sanding, and passes through the entire coating process a second time. The spot repair of rejected vehicle bodies is conducted manually in specially equipped booths. With special tools only the small defects are prepared by skilful light sanding, planing and cutting out and then they are refinished with special spraying units depending on the particular problem. The OEM-paints can be used for this purpose. The necessary crosslinking temperature is created locally by infrared lamps at the point of repair. This manual activity calls for a high level of manual skill in handling special application units and on average it takes about one hour. It means there is no longer any partial repair over a larger area, which used to be customary and involved considerable labour. When a whole body repair is performed the vehicle body passes through the normal coating process a second time after the defective areas have been prepared carefully. Normally the total coating surface has to be scuffed

Apart from the surface defects visible to customers the inspection zone also detect the objective quality pattern of the coating. In addition to the measurements of film thickness, gloss, haze and surface smoothness, which are conducted offline with transportable measuring instruments, gantries are meanwhile in use performing automatic quality control. These measure defined quality characteristics online by video remotely

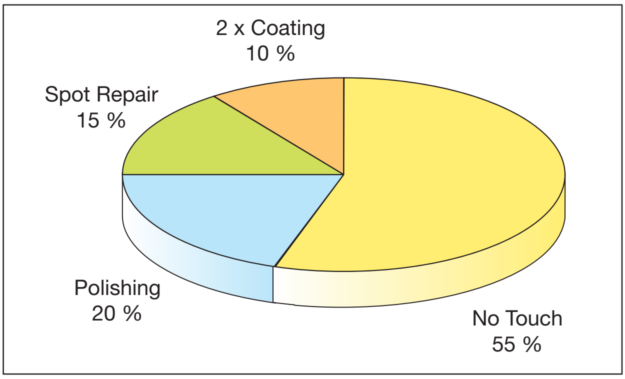

Fig. 7.1.18
Common share of processes for defect handling in effective paint shops of the automotive OEM lines

[7.12.15]. However, quality control is only able to intervene correctively in the process or the paint to a limited extent if there are nonconformities. The response time can, depending on the point of necessary intervention, be several hours and so a large number of vehicle bodies may not be reached.

Optimization of efficiency calls for an integral analysis of the coating line and paint quality, from conceptual design through to implementation. Especially the capacity of the coating shop and the cost per vehicle body are largely determined by this parameter. It fluctuates considerably from line to line. The so-called “first run ok” ratio is defined in a variety of ways. Coating lines designed to be a core process in which work is performed, for example, without underbody protection coating application creating any dirt, and carefully operated lines have “first run ok” ratios of about 92%, if first time capability, polishing and spot repair are considered jointly.

Total film build [µm]	90 – 130
Gloss at 20° [%]	> 90
Haze [log.scale] metallics	200 – 300
solid colors	< 20
Wavescan	
Longwave	< 10 (h)/< 15 (v)
Shortwave	< 20 (h)/< 25 (v)
h = horizontal, v = vertical	

Fig. 7.1.19
Common quality data of automotive OEM top coatings

Further coating work has to be performed in final assembly if carelessness or technical reasons create defects in the coating of the already completed vehicle. These are then repaired with conventional automotive refinish paints and cured at temperatures of around 80 °C locally.

Some automotive manufacturers dip the finished coated vehicle bodies half in baths of hot wax in order to achieve a further step towards improving corrosion protection, by flooding and wetting the cavities.

7.1.7 Outlook

The quality level of automotive coating has been raised continuously over the last 30 years. Owing to the increasing use of galvanized and other types of precoated panels, further improved pretreatment, cathodic electrocoating, flooding with wax in order to protect the cavities, and design measures, resistance to corrosion has been improved to such an extent that individual automotive companies give perforation warranties for over 12 years. It is no longer a privilege of expensive vehicles.

Another remarkable advancement in the durability of the automotive coating is the resistance to weathering due to the introduction of the basecoat and clearcoat system. Visible gloss deficiencies nowadays no longer occur before the 8th to 10th year of a vehicle’s life, depending on the region. This has been achieved despite declining paint consumption due to more efficient application equipment and despite a 20% reduction in film thicknesses.

Although the development potential of paints has still not been exploited to the full, the efforts towards further optimization are nowadays focusing on the coating process as a whole, and they will continue to do so. In addition, the main focus of attention is on introducing toxicologically safe substances, now that substances such as cadmium, lead and chromium compounds, which are regarded as highly critical, and some glycol ethers have already been largely eliminated.

For the current individual stages of the coating process there are many ways of optimizing procedures. This particularly applies if in addition to the coating no other production stages have to be performed on the vehicle body but the process of coating is designed as a core process.

For example, the primer can be replaced by a suitable electrocoat if the conductivity of crosslinked electrocoat films is sufficiently high. In the same way, a nonbaked but dried electrocoat film can be coated again with an electrocoat or an aqueous spray paint and baked together [7.12.16].

Ideas for reducing the product diversity and for increasing efficiency in the automotive coating process concentrate on basecoats which takes over the primer surfacer functions like stone chip resistance and UV-protection of the electrocoat and can be applied with the second basecoat ”wet-on-wet”. They are baked together with the clearcoat ceasing the use of a separate primer surface. These processes are already introduced under the term of ”Integrated Paint Porcess (IPP)” [7.12.17].

The attractiveness of radiation-curing paints due to the speed of crosslinking is supported by the high scratch resistance of such clearcoats. One endeavours to overcome the drawbacks of curing three-dimensional items, such as a vehicle body, with plenty of creativity in the technical environment and in material development [7.12.18]. What all the concepts have in common is the desire for a more efficient coating process. They will be judged by how efficient application is and by the quality level of the surface.

The increase in the number of hang-on parts mainly made of plastics for the outer skin of the vehicle leads to further considerations, which have their origins in color management. As a result of the fact that, as is normal nowadays, parts are purchased from five or more suppliers in the original color of the vehicle and hence considerable quality assurance costs are incurred, conceptual ideas are maturing in order to control this complex situation [7.12.19]. On the one hand, there are ideas for a coating technology based on appropriate materials with low crosslinking temperatures of 80 °C, which make it possible to coat plastic attachments on the vehicle bodies at the same time [7.12.20]. On the other hand, the concept of replacing paints with plastic films or coil coating gains interest, in which case the use and application of conventional coating materials no longer plays any role in color matching.

The development in coil coating has been pursued by the automotive industry for many years now because this coating technology is firstly the most efficient and fastest and secondly there is no longer any need for a coating process in manufacture of the vehicles (see chapter 7.4). The first organically precoated coils have now been used in the automotive industry. As a result there is no longer any need for expenditure on cavity sealing [7.12.21].

7.2 Automotive Refinishing

The main difference between automotive refinishing and OEM coating at the vehicle manufacturing plant is firstly that coating is not conducted on a conveyor belt under industrial conditions, and secondly it has to be performed on a finished vehicle with all its components. It is conducted by contractors on a small scale by means of manual spray application under drying and curing conditions which do not usually exceed 80 °C.

Higher temperatures, even if they only occur locally, can cause damage due to deformation or melting of plastic parts, deformation of tyres or irreversible damage to the electrics or electronic equipment of the vehicles.

From this requirement it can be easily inferred that for refinishing different paints are required from those in OEM coating. Whilst there is still sporadic use of physically drying or catalyzed reaction paints, on account of the excellent quality of coating there has in the meantime been a switch to polyacrylate-based or polyester-based 2-component technology with isocyanate crosslinkers, throughout the world (see chapter 2.1.1). The curing times of the 2-component systems are less than one hour with infrared-forced drying [7.12.22] and up to one day at room temperature. Waterborne products are gaining importance. They crosslink according to the same principles as solventborne 2-component paints except that water evaporates less easy (see chapter 5.6.2).

Refinishing is used for localized repair of defects in the coating but it can be also used in order to upgrade vehicles entirely by providing more attractive coatings. The refinishing process depends on the type and amount of damage to an automotive coating. In the case of minor dents coarse-grain body filler is used for smoothing purposes. On top of that a fine-grain body filler is usually applied, followed by primer and topcoat. When the filled areas have hardened they have to be sanded carefully before coating.

If repairs only involve scratches and similar damage, sanding may go down to the metal panel depending on the depth of the imperfection and the first coat to be applied is anticorrosion primer, followed by primer surfacer and topcoat. In many cases it is only the topcoat which is sanded lightly and the topcoat is usually made with a basecoat followed by clearcoat on the entire part of the vehicle. Depending on the equipment on the coating lines and the severity of the repair, refinishes take between one hour and one day.

Fig. 7.2.1
Refinishing cars is craftsmanship

At the automotive refinisher's all types of vehicle arrive in the workshop. They have various ages, various designs of OEM coating and various surface conditions. In order to recognize the respective prior history, select the appropriate process and suitable work materials for the repair, sound experience and manual skill are required. The quality criterion which is most visible to customers and hence the most important aim is matching the color of the repaired defect with the other areas of the vehicle. The increasing durability of the OEM coating causes the number of colors to rise continuously. Nowadays it is estimated that there are more than 40,000 different colors on the 400 million vehicles worldwide. Increasing vehicle exports ensure that all the colors can be found everywhere. This large number of colors in all regions can only be handled economically with intelligently designed mixing systems and well managed logistics.

Since refinishing constitutes a highly skilled manual activity, it is necessary to provide coaters with suitable training sessions. This is also handled by the paint suppliers because in addition to technical conditions it is also paint quality which has a major influence on coating parameters and the results of skilled work performed by coaters.

The specific factors influencing processing include the parameters of the spray guns, e.g. HVLP guns of electrostatic design or only pneumatic design, booth temperature and, in the case of aqueous products, humidity.

Special manual skills such as blending in call for careful handling of the spray gun in order to achieve a saleable refinish. The term blending in is the coating of part of an entire vehicle body such as a fender, on which the defective area is repaired without removal and the area surrounding the defect is coated with refinish and feathered out. This is especially to be recommended if there are color discrepancies between the original paint and the refinish paint until a tolerable difference in color has been achieved. This technique conceals the color discrepancy at the margin of the repair.

One very important component when adjusting paints is the reducer. Usually there is a whole host of solvents available, which mainly influence the rate of drying during and after application. The respective reducing solvents are termed “fast” for rapid evaporation and “slow” for gradual evaporation.

Furthermore, users have to have a good command of safe handling during storage and application of the materials and must be aware of potential hazards to people and the environment.

Fig. 7.2.2
Examples of high class effect refinish coatings

The quality properties of the various paints and the coating systems for refinishing are defined by most vehicle manufacturers themselves and certified in the form of material releases. The most common materials nowadays, accounting for more than 75% worldwide, are acrylic resins in conjunction with isocyanates as 2-component systems. In terms of film properties the repairs come close to the level of the first coating if the work is done properly. In particular, the longterm outdoor exposure of topcoats achieves the quality of the OEM coating owing to the use of light stabilizers (see chapter 2.1.4)

Defining the repair process

The average life of vehicles has increased continuously to approx. 12 years. At the same time the OEM coating processes have become more standardized worldwide. Nevertheless, in the case of veteran cars, for example, it may be necessary to characterize the original coating in order to define a suitable repair process. Figure 7.2.3 shows the main original coatings. In particular, paints and sanding requirements have to be selected according to type.

	Type of Coatings	Remarks/Characteristics
A	**Solid colors and 1-coat metallics**	
	baking enamel (alkyd/melamine)	crosslinked : no problems
	baking enamel (acrylic/melamine)	crosslinked : no problems
	thermoplastic acrylics	sensitive to solvents, swelling
	nitrocellulose coatings	sensitive to solvents, swelling
	PUR coating	crosslinked : no problems
	oxidatively hardened alkyd paint	crosslinked : no problems
B	**2-Coat-metallics**	
	baking enamel (acrylic/melamine)	crosslinked : no problems
	thermoplastic acrylics	sensitive to solvents, swelling

Fig. 7.2.3
Important types of OEM coatings before 1980 und their characterics

A simple process has become established for determining the type of paint used in the original coating. For identification it exploits the tendency of the various paint films to dissolve and to swell. To this end one soaks a white piece of cloth in paint reducer i.e. solvent and uses it to rub down an inconspicuous part of the surface. In the case of thermoplastic paints and nitrocellulose-based coatings the cloth becomes discolored or at least there is visible swelling.

Fig. 7.2.4
Comparison of colors for refinishing cars

Color check

Further preparation of a refinish on vehicles includes a color check. Each original coating undergoes a change in color depending on the type, age and stress, e.g. due to ultraviolet radiation as well as individual vehicle care (see chapter 3.3.1). This can be largely eliminated by polishing. Nevertheless, color adjustment of the refinish paint may be necessary. It is performed by comparison with a specimen made by spraying on a separate panel. The starting paint is the material manufactured according to the mixing formula for the color registered. If, after visual comparison of the panel with the coating to be repaired, a color adjustment proves necessary, the color is usually adjusted with the components of the mixing formula.

Repairing effect coatings is more problematical because according to the angle of viewing the color and intensity of the effect are heavily dependent on application technique and equipment parameters. These are:

1. Inside diameter of the nozzle and atomizer air temperature of the spray gun. Atomization is finer if the inside diameter of the nozzle is small and spray pressure is high, thus making the color lighter.
2. Reducing and spray viscosity. With a reducer which evaporates more quickly one can often make the silver effect brighter (i.e. the difference between light and dark is larger) than with a reducer which evaporates more slowly. The higher the viscosity, the coarser the particle distribution will be in the overspray and so the greater the tendency to cause mottling (i.e. large-area discrepancies in light/dark properties).
3. Method of spraying. If, for example, fast-evaporating reducers are used to spray dry or if there is considerable overspray, the color will appear lighter and more metallic. If, on the other hand, the paint is sprayed wet, the color appears to be heavier and darker. In between there are all the various shades of metallic effect and color. Mottling is avoided by allowing time for intermediate evaporation.
4. Spray gun distance. If the distance is short the film applied will be wetter, i.e. darker and more chromatic, whereas if the distance is large the film will be drier and the color will be lighter and more metallic.

Pretreatment

When the preparations described have been competed, the repair process can commence. Depending on the aims the process is divided into four categories which mean different amounts of work in order to achieve the appropriate end result and fulfil the customers' expectations:

1. New coating refinish. This is repair of a coating on a new vehicle and so it has to achieve the quality level of the original coating in terms of color matching, surface quality and adhesion to the substrate
2. Market value coating. This is a refinish on a relatively old vehicle. Depending on the state of the original coating body filler and sanding may be unnecessary for pretreatment.
3. Saleable or used vehicle coating. Usually a whole-vehicle coating which makes an unattractive vehicle attractive again. This coating dispenses with elaborate sanding and body filling work. Cleaning and rust removal are followed by application of an adhesive primer and the topcoat in a wet on wet process, i.e. without any lengthy intermediate drying of the two coatings.
4. Blending in is performed in the case of color discrepancy problems which cannot be solved or in the case of minor defects which are restricted to the topcoat.

The vehicle body is prepared for the respective refinishing process by masking surface areas not to be coated and detaching parts such as protective trims and spoilers. Furthermore, initial sanding work is conducted as far as necessary. That is followed by cleaning of the original coating, initially by washing thoroughly. After drying, tar stains, residues of wax and silicone are removed from the surface of the paint with silicone remover. If this is not done, these materials would prevent wetting and adhesion of the refinish. In some cases, particularly in the case of market value coating or used vehicle coating it may be necessary to strip off the original paint with paint remover. For this purpose, appropriate paint removers or paint strippers are usually applied with a brush. After a specified soaking time the original coating is scraped off with a scraping knife. Areas without sufficient stripping effect may have to be treated a number of times until the original coating has been completely removed. That is followed by thorough cleaning and careful removal of the stripper with mineral spirit or similar solvents.

Sanding

If the original coating has been cleaned but not stripped, the next stage consists of wet or dry sanding. Severely weathered or cracked coatings are sanded down until a perfect film has been reached, e.g. in the layer of primer or electrocoat. After sanding, dust must be removed from the surfaces thoroughly. In the case of wet sanding the surface is washed down with pure clean water afterwards and the edges and folds are rubbed dry properly. Sufficient time is left for the remaining moisture to evaporate. In the case of dry sanding the surface is blown with compressed air and cleaned with a dust-binding cloth afterwards. Areas of rust are sanded down to the bare metal.

Application	Grit	Type of Machine
Derusting, coarse sanding	P16 – P80	Angle grinder
Putty	P40 – P120	Vibrating grinder
	P40 – P80	stick
	P80 – P120	Excenter grinder
Fine putty	P24 – P360	Sanding by hand
	P80 – P120	Excenter grinder
	P80 – P120	Vibrating grinder
Primer	P400 – P800	Sanding by hand
	P120 – P180	Excenter grinder
	P120 – P320	Vibrating grinder
Filler (primer surfacer)	P400 – P800	Sanding by hand
	P180 – P220	Excenter grinder
Top coat	P400 – P800	Sanding by hand
Old coatings	P180 – P220	Excenter grinder
2-Coat refinishing	P600 – P1200	Sanding by hand

Fig. 7.2.5
Sanding materials and sanding machines for the different steps of a refinish job

Depending on the grit the sandpaper is used for the stages described above and below. The rule is: the higher the number, the finer the sandpaper.

The types of abrasives mainly used are aluminium oxide or silicon carbide. Original coatings and hard substrates are chiefly treated with aluminium oxide paper whilst relatively soft substrates are sanded with silicon carbide paper.

One must bear in mind that beads and edges should be sanded manually because with power tools it happens too easily to sand through to the substrate. A fast procedure is to perform sanding with emery cloth by the wet method.

Applying body filler, i.e. putties

Damaged areas such as small dents and irregularities are corrected with body filler after removing any rust. After hardening, sanding is performed so that the defects are levelled off. It may be necessary to apply a second layer using a special fine body filler in order to achieve the good topcoat appearance of the original coating.

1-component body filler based on nitrocellulose/alkyd resin mixtures take about 2 hours at room temperature to harden whilst 2-component body fillers based on unsaturated polyester have already hardened after 15 minutes. The main constituents of the hardener of a 2-component body filler are peroxides which accelerate the radical hardening of the unsaturated polyester (see chapter 2.1.1).

Primer

When the surface of the body filler has been sanded and cleaned for the last time a primer is applied for high-quality coatings. This can be aqueous or dissolved in solvent and is usually a 2-component coating system. Drying takes about 2 hours at room temperature or 30 minutes at 60 °C. The formulations are chiefly oriented towards smoothness, sandability and the rate of drying.

Primers are also used on areas where sanding has gone through to the bare metal if no body filler is required. Such primer fillers are usually 2-component systems based on epoxy resins with amine crosslinkers (see chapter 2.1.1). They provide optimum protection against corrosion and guarantee good adhesion on metal substrates such as steel, galvanized steel and aluminium. If in the case of the primer the emphasis is on stone chipping protection, 2-component polyacrylic or polyester-PUR systems are an advantage.

Topcoats

The topcoat system and application procedure are defined according to the type of color. Topcoats in solid colors make the least demands of paints and the coating process, metal effect paints make medium demands and pearlescent and color flop paints make the highest demands (see above).

Effect paints are applied in two coats during OEM coating, i.e. with a basecoat that provides color and effect, wet on wet with one clearcoat.

The paint used is either the original refinish paint made on the basis of the mixing formula for the OEM color or, usually in the case of relatively old coatings, paint which has been adjusted to the color to be repaired by conducting spray tests and making appropriate corrections.

In most refinishing shops the original refinish paint has to be made with mixing paints on the basis of distinct formulas. These are to be found in mixing machines, in which approx. 40 – 50 different colors are stocked. Depending on the OEM color of the vehicle to be repaired the paint is either mixed manually or even automatically using the components of the paint formula predeveloped for it. These mixing formulas are worked out by coating manufacturers and administered electronically. They are an essential part of using the mixing machine.

Fig. 7.2.6
Collection of samples of mixing colors to identify the color and a mixing machines

Since solventborne basecoats have high solvent contents for the purpose of orienting the aluminium particles in order to achieve bright effects and therefore constitute a burden on the environment, there are aqueous products available nowadays which achieve the same effects at much lower solvent levels with a pseudoplastic or thixotropic adjustment. In conjunction with spray guns using the so-called HVLP technique this has brought about a declining paints market in this industry because it was possible to increase the transfer efficiency of the paint by 30%.

Repairing plastic parts

Bumpers, spoilers, so-called “front ends”, fenders as well as trunk lids and tailgates have been increasingly manufactured from plastics since the 1970s. On some models plastics in the outer skin meanwhile account for more than 30% of the area. A whole host of different types of plastic are used in pure form and in blends. They are tailored to the relevant requirements profile (see chapter 4.1.3 and 7.3).

Most of the plastics used are thermoplastics, and so-called SMC (sheet moulding compound) plastics are being increasingly used for large parts on account of their rigidity and hardness. The latter are duromers based on unsaturated polyesters, which are frequently reinforced with glass fibres. SMC indicates the process by which the plastic parts are manufactured, where the part is made by thermoforming, hardening and reinforced prefabricated mats.

Among this diversity of types the most common ones are polypropylene (PP) thermoplastics. This material is used for bumpers by almost all the automotive manufacturers and in Europe it is pretreated for the coating process during OEM coating by flaming the surface or in North America by means of special adhesion promoters based on chlorinated polyolefins (CPO). When refinishing appropriate parts special adhesion primer is applied thinly to the PP thermoplastics, possibly after sanding and cleaning the surface, and subjected to further treatment after about 20 minutes at room temperature, as with the standard refinish already described. The other thermoplastic and duromeric plastics can be easily coated in production after cleaning the surface and possibly tempering at 60 °C and refinished accordingly. Good cleaning is extremely important in order to remove from the surface any surfactant release agents resulting from the process of manufacturing the plastic parts. Tempering is particularly necessary in the case of polyamide (PA), PMMA, PC and PUR plastics.

In certain cases topcoats may have to be provided with elasticizing additives. Otherwise the elasticity or notch impact resistance of the plastic may be affected by coating.

Generally speaking, it is important not to exceed a total film thickness of 100 µm in the refinish system.

7.3 Automotive Supply Industry

Over the last few years the automotive supply industry has gained considerable importance. Worldwide turnover came to 350 billion euros in 1999. This is due to the global strategy of the automotive manufacturers endeavouring to reduce the production depths of their products (cars) and shift the development of components and their assembly to the supply industry. Production depths in German car manufacture, for example, were only about 30% in the year 2000. In the USA GM and Ford have divested themselves of their subsidiaries Delphi and Visteon. At the same time the number of direct suppliers has fallen drastically so a pyramid of first, second and third tier suppliers has formed for the automotive industry. The wave of consolidation which thus took place at the end of the 1990s has nowadays led to large global suppliers with turnovers of up to more than 50 billion euros.

The diversity of products in this industrial segment is enormous. It has bound to lead to the fact that practically all coating processes are used. For example, there is the entire range of eco-efficient processes such as powder coating, electrocoating and coating processes based on radiation curable paints. The use of new application techniques and coating materials often begins in that market segment.

The industry can be divided up into the following segments:

- Exterior plastic attachments
- Interior plastic attachments
- Wheels
- Axles
- Engine blocks
- Mirrors
- Head lamps
- Door handles
- Other parts

Exterior plastic attachments

The most important plastic attachments for the exterior on all car models nowadays include the bumpers, which are moulded from a very wide variety of thermoplastics but and are coated predominantly. There are also tailgates, such mainly PP lids, sliding roofs, fenders, trims and outer mirrors, which are already coated when delivered because they are fitted to the vehicle body later. Furthermore, these attachments such as the outside mirrors are put together as assemblies with all the electrical equipment so they can no longer be coated at the car plant [7.12.23].

Since there have to be further reductions in weight and cost the trend towards using plastics continues to be on the increase.

The plastics used are primarily tailored to the necessary functionality on the vehicle body. Consequently most bumpers are made of highly flexible, impact-resistant and low-cost polypropylene (PP) blends.

The coating of these parts is performed on specially designed coating lines. On many lines throughout Europe the procedure initially provides for aqueous cleaning in the "power wash" process, then flaming in order to improve adhesion, an aqueous primering followed by application of aqueous basecoats and solventborne 2-component clearcoats. Between the primer and topcoat application there is a short intermediate drying process which takes 2 to 3 minutes. The crosslinking temperatures are 80 – 90 °C and they require dedicated paints for primer and clearcoat application. The trend towards eliminating primer is on the increase because owing to flaming there is no longer any need for special-purpose, adhesion primers. Moreover, the cost advantages achieved by eliminating a coating stage are significant. In North America and Asia flaming is often replaced by applying an adhesion primer (promoter), which is usually formulated with chlorinated polyolefins [7.12.24]. The crosslinking temperatures are then slightly higher at approx. 120 °C. Aqueous products are still not very common in those regions.

On many coating lines application is performed by robots and pneumatic spray guns, which achieve a maximum transfer efficiency of 40%. For an electrostatically assisted coating plastics have the crucial disadvantage that they are usually nonconductive. This can lead to the fact that electrostatic charges on the workpiece repel the charged paint and affect the quality of the coating. This disadvantage can be eliminated if conductive primers are used. With good grounding and use of electrostatically assisted high rotation atomizers good results are achieved in the downline application of basecoat and clearcoat [7.12.25]. On account of the high conductivity of aqueous paints the charging is performed after spraying by means of external electrodes (see chapter 4.2.1). The levels of transfer efficiency for the coating materials reach 60% – 70% under the conditions described.


Fig. 7.3.1
Coating of bumpers

The efficiency of the coating lines, measured by first time capability, is not as good as in automotive OEM coating because owing to the low conductivity of the plastics there is a risk of electrostatic charge effects. As a result, particles of dirt are attracted. Efficiencies of 60% – 70% are good levels for a coating line handling plastic parts. The low material and production costs for bumpers mean that it is not necessary everywhere to rework all defective parts. In addition, production of new parts is less expensive and it is easy to recycle the thermoplastics [7.12.26].

The definition of a color specification with respect to visual or colorimetric aspects is firstly important for the success of the supplier. Secondly, the ability to make corrections for coating bumpers quickly is necessary because first-time body coating color discrepancies can occur or the coating does not conform to the specification of the color. Different concepts provide for parallel, harmonized paint development and production as well as an intensive exchange of test results and empirical results [7.12.27].

Furthermore, the coating of plastics may only have a minimum negative influence on the mechanical properties of the substrate (e.g. impact resistance at –30 °C). For this reason the paints used in automotive production coating are not always suitable for plastic coating. In particular, the primer surfacers and clearcoats for plastic coatings are formulated with highly flexible resins and isocyanate crosslinkers. Nevertheless, it has so far not always been possible to ensure that on account of the crosslinked coating properties such as impact resistance of the plastic at low temperatures in particular are not affected.

Fenders are made of a very wide variety of plastic blends, depending on the specification requirements made by the vehicle manufacturers. Usually they are merely primed at the manufacturer's and then coated on the respective vehicle manufacturer's production coating line after electrocoating. The reason for this is that it is possible to achieve a much higher level of integration for mounting the attachment in the vehicle body assembled from the various materials. The fenders not made of thermoplastic polyolefins (TPO) such as polyamide merely require good surface cleaning, e.g. with a "power wash" process, so that they can then be coated with a primer. The same applies to the outer skin of the tailgates to be coated, which, on account of the rigidity requirements of such an attachment, are increasingly being made of "sheet moulding compounds" (SMC), e.g. based on unsaturated polyesters (see chapter 4.1.3).

Interior automotive attachments

In order to upgrade interior plastic mouldings or the housing of the dashboard as well as many other parts in the passenger compartment of vehicles coating is required in many cases if low-cost plastics are used. The coating is such that the layer of paint not only improves the surface visually but also creates a certain amount of grip (feel). In English-speaking countries such coating materials are termed "soft feel" coatings.

Such modern coatings are mainly applied with 2-component, polyurethane-based systems which are also available in the aqueous form. The latter are starting to become more common. With the usual film thicknesses of 20 – 40 µm highly specific requirements are also fulfilled, e.g. laser engravability, low surface reflection in the form of "velvet" coatings, high flexibility at low temperatures, e.g. in the case of airbags, the triggering of which has to take place at low temperatures without creating any splinters. The avoidance of emissions from the plastic parts is also included.

Most recently colored coatings have been used in order to following fashion trends for small vehicles. All in all, this market is growing very significantly because with this coating the acceptance of plastic as a material is considerably enhanced and helps to avoid the "cheap" image [7.12.28].

Fig. 7.3.2
Different coated plastic parts inside of a car

Application is performed on lines similar to those used for exterior coating. However, for the plastics chiefly used in this segment, e.g. PA, PC, ABS, polybutylene tere-

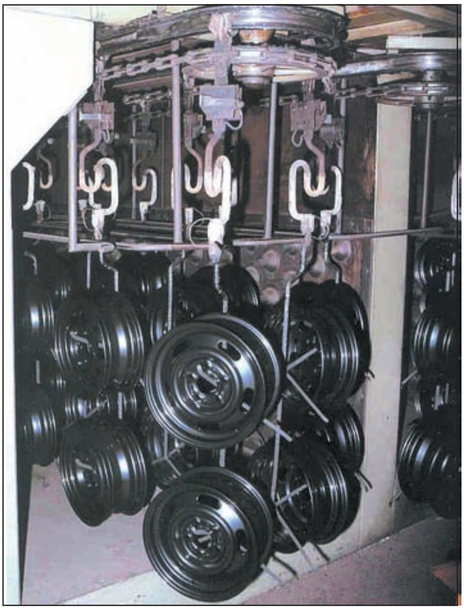

Fig. 7.3.3
Steel wheels primed by cathodic electrodeposition process

phthalate (PBT), pretreatment by flaming is unnecessary (see chapter 4.1.3). Careful cleaning in the “power wash” process is usually sufficient.

Wheels

Throughout worldwide vehicle production, amounting to approx. 57 million units annually, more than 300 million wheels are produced. Steel wheels are still in first place. However, owing to the reduction in weight and design options available the proportion of aluminium wheels has been showing a continuous increase for years now.

Wheels made of steel have been standardized more and more in design. They are adapted to the various types of vehicle with plastic hub caps featuring custom coating. The purpose of the coating is particularly to protect the metal against corrosion. Only a few steel wheels for cars are provided with topcoat, and then mostly in silver metallic. This does not apply to wheels for commercial vehicles, much higher percentages of which are provided with topcoat.

Most steel wheels are initially cleaned, then pretreated, primed with electrocoat and possibly provided with one layer of topcoat as described. As with automotive coating the pretreatment consists of zinc phosphating in order to achieve maximum protection against corrosion. The state of the art in priming is the electrocoat which is deposited cathodically. It provides a high level of edge protection at film thicknesses of 15 – 18 µm. Wheels in particular have a high edge-to-area ratio. Since the edge is the most frequent starting point for corrosion, it constitutes the most important quality criterion for the coating. The importance of anodic electrocoat with the silver metallic effect, which still used to be standard only a few years ago, and the red cathodic electrocoats has declined.

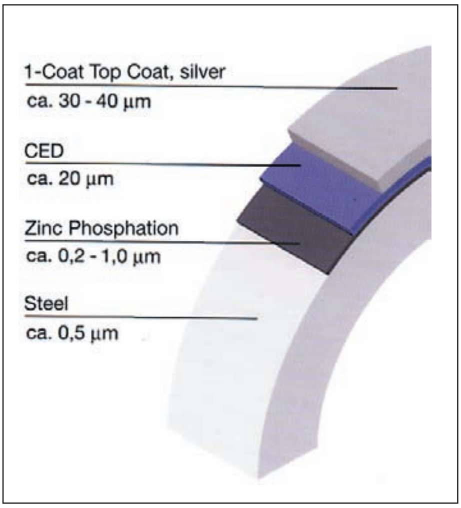

Fig. 7.3.4
Multilayer coating of a steel wheel

Coating requirements are dominantly specified by corrosion protection tests such as the ASTM salt spray test and the VDA climate change test (VDA 621-415), adhesion and chemical resistance to brake fluids, fuel and engine oil (see chapter 3.3.2).

Cost pressure in this field of business has for some time been promoting optimization of the entire manufacturing process by furthering cooperation in a spirit of partnership between suppliers and customers. This situation has meant that in many cases nowadays supply contracts are negotiated in cost per square metre. In some contracts other common saving potentials are agreed, which have to be achieved by reductions in process costs or paint costs, depending on the situation.

Production of aluminium wheels has been increasing above average for years now so it is gaining shares of the total volume of wheel production. In the retail business in particular aluminium wheels are highly popular on account of their attractive design.

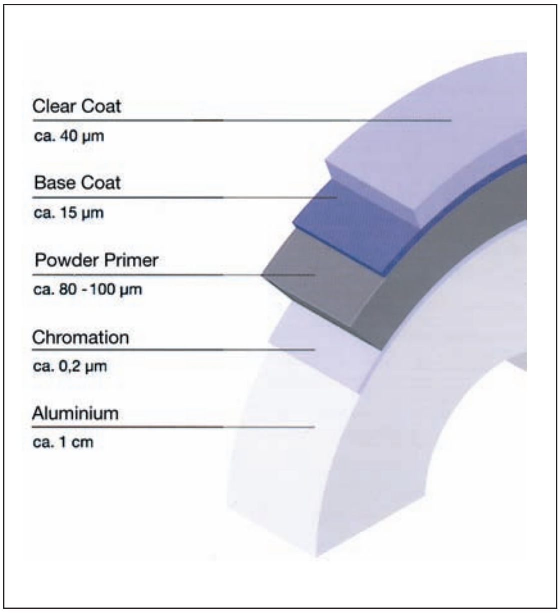

Fig. 7.3.5
Multilayer coating of an aluminium wheel

They are usually manufactured by the die-casting method. All wheels are coated with a standard paint system, some are “turned off” for design reasons and then provided with clearcoat. “Turned off” means that the coating is milled off at certain points and the aluminium surface is sanded or treated specially.

Application of the standard paint system initially means the surface has to be degreased and chromated carefully. The coating consists of an epoxy-based or epoxy-polyester-resin-based powder primer, which is crosslinked at temperatures of 160 – 190 °C. It is followed by application of topcoat with basecoat and clearcoat. In Europe the two topcoats are solventborne systems, whilst in the USA clearcoat is much more frequently a powder coating. Topcoats are crosslinked at about 130 – 150 °C.

The specifications for the coating of aluminium wheels are based, amongst other things, on the CASS (Copper Accelerated Salt Spray) test in accordance with DIN 50021 as well as tests for levels of weather resistance and chemical resistance, as with steel wheel coating.

Axles

Axles for cars and heavy trucks are being increasingly manufactured as components and delivered as complete units to the automotive industry for final vehicle assembly. Usually the parts required for this are primed by the electrocoating method prior to assembly. Owing to high demands in terms of protection against corrosion pretreatments comprising zinc phosphate and almost only cathodic electrocoats are used (see chapter 4.2.1). Some automotive manufacturers specify high build electrocoats, which can be applied up to a film thickness of 35 µm.

The high energy consumption for heating the heavy parts has promoted the development of electrocoats for some time, which crosslink at object temperatures of less than 150 °C. However, the paint and coatings industry has still not succeeded in developing a product which leads to protection against corrosion at such temperatures, which the usual, commercial products can achieve at 180 – 200 °C. In special cases the electrocoat primer is coated with powder, e.g. for manufacturing colored coatings. There are also primers made of powder coatings which are applied after pretreatment.

For these pretreatment and coating stages standard processes are used. The sizing of the coating line is essentially determined by geometry of the parts and throughput.

Engine blocks

Engine blocks are cast from molten aluminium scrap and any necessary alloying constituents. After cleaning residues out of the mouldings a black matt layer of powder paint is usually applied with a film thickness of 100 µm and cured at approx. 230 °C. The powder paints are based on epoxy resins in order to ensure good protection against corrosion. In addition, the levels of chemical resistance, good adhesion and high abrasion resistance as well as high thermal resistance must also be achieved.

Mirrors

Mirrors are highly complex modules, the design and manufacture of which is meanwhile the sole responsibility of the supply industry. Interior mirrors are not usually coated. The exterior mirror, though, is predominantly delivered in the color of the vehicle for design reasons.

The housings required for exterior mirrors are made of various types of thermoplastics coated in the color of the vehicle. A small percentage remains black and uncoated. The plastic types vary from polyamide (mainly in North America) and ABS to PC/ABS and PC/PBT blends in Europe.

Coating is initially performed after cleaning the housings using primer, followed by an application of basecoat and clearcoat “wet on wet”. The paints are chiefly based on solventborne systems. Only in the case of the basecoat are aqueous products being used increasingly. Clearcoats are 2-component coating materials made of acrylic resins and isocyanate crosslinkers. The crosslinking temperatures for the primers and topcoats used in Europe are 80 – 90 °C whilst in North America they are 120 °C.

Application is conducted pneumatically and is only supported electrostatically in a few exceptional cases.

Headlight systems

In the course of the 1990s most headlight systems were switched from steel and glass to plastics. This step achieved a reduction in weight, on the one hand, and new possibilities in design on the other. Headlight systems are entirely developed, assembled and delivered to the automotive industry as a finished component by the supply companies.

They consist of two main components: the reflector and the lens.

The reflector is increasingly being made of “blow moulding compound” (BMC) plastics according to the appropriate process and it is replacing the formed, die-cut metal panel, which was cathodically electrocoated to prepare for metallization. This step is no longer required with the dishes made of BMC. Both types of reflector are spray-coated with pigmented, UV-curable primer in the next process step. UV paints have the advantage of not shrinking during the curing process so they create extremely smooth surfaces. This is an important requirement for defect-free formation of the reflector surface in the downline vapour-depositing process with aluminium in autoclaves.

The lens is made of thermoplastic PMMA or PC. In order to increase the weathering resistance the lens is coated externally. In this area there are currently two types of paint available. On the one hand, scratch-resistant clearcoats are used curing at 120 – 140 °C, and on the other UV-curable clearcoats are used. Both types of paint are applied by spraying.

Door handles

Door handles are complete modules, the handle and handle recess of which are usually coated in the color of the vehicle for design reasons. Use of raw materials is tending to move away from cast aluminium towards plastic.

The coating is applied on suitable lines, usually with a basecoat-clearcoat system and brief intermediate flash off. Aqueous paints are being used more, as with the other coatings of plastic parts.

Other parts

Other parts, most of which are coated, include trim strips, windscreen wipers, radiator grilles, heat exchangers, airbags and seat frames.

For windscreen wipers, heat exchangers made of aluminium and seat frames electrocoating constitutes the most important method of coating. Windscreen wipers are also provided with a topcoat in order to increase weathering resistance. In the case of seat frames the process used is occasionally autophoresis (see chapter 4.2.1). Radiator grilles and airbags are made of plastic and are often spray-coated in the color of the vehicle. In this sector there are many job coaters.

7.4 Coil Coating

The term coil coating refers to the continuous coating of metal coils, usually with liquid coating materials. Slightly over 40 years ago this coating technology, which was new in those days, was implemented with a coil coating line 200 mm wide [7.12.29].

The importance of this efficient coating process has seen a constant increase since that time. Even modern-day prospects suggest that growth will be above average over the next few decades. Coil coating allows the user to usually dispense with coating lines in production entirely and transfers the cost structure of producers to the variable category by reducing fixed costs.

The most important substrates for coated coils are steel, galvanized steel and aluminium. At the moment the growth of the surface area accounted for by aluminium coils is higher than that of steel. The respective coating market is about 500 kt worldwide.

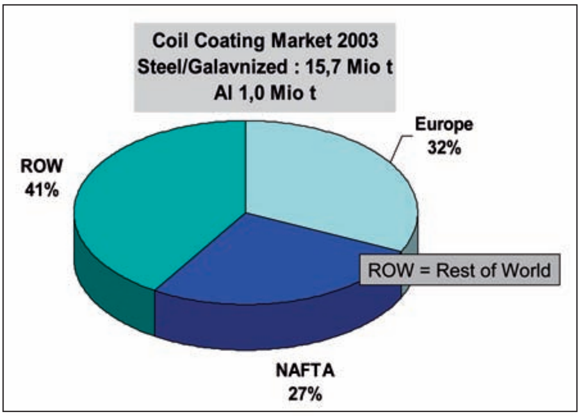

Fig. 7.4.1
Regional share of the worldwide coil coating market (source: ECCA)

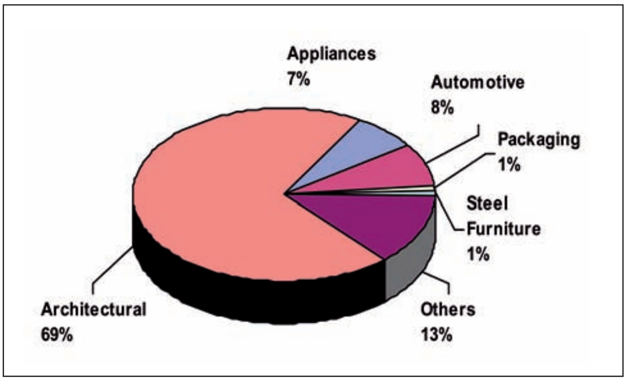

Fig. 7.4.2
European application of coil coating in the different industrial segments 2003 (source: ECCA)

The number of coating systems and the number of colors is showing a considerable increase for all applications. Almost all industrial sectors nowadays use coil coated panels. The main customers are the construction industry in the case of outdoor and indoor paneling, the packaging (cans) industry, household appliances industry, the commercial vehicle sector including motor caravans and trailers as well as industrial lighting systems amongst other applications. There are regional differences in the focus of application. For example, in Europe the construction sector accounts for nearly 70% in the year 2003 and is thus above the world average of 54%.

On the coil coating lines operated by approx. 60 coaters coils of metal are processed with thicknesses of between 0.2 mm and 2 mm. Materials used are cold-rolled coils made of soft grades of steel or general-purpose structural steel, electrolytically galvanized thin sheet, hot-dip galvanized coil or aluminium with its forgeable alloys. Maximum coil widths are about 1,800 mm for steel coils and 2,000 mm for aluminium coils. Line speeds for steel coils go up to 200 m/min and average between 80 and 140 m/min. The speed for aluminium coils reaches more than 200 m/min.

Fig. 7.4.3
Storage of coated coils

The lines consist of a coil feeder, the necessary coil storage unit (strip storage), a pretreatment zone, the first coating station plus baking oven and a downline cooling zone, a second coating station with oven, laminating station and cooling as well as a coil storage unit and coiler (see figure 7.4.4). Most lines are equipped for two application steps, firstly for applying a basecoat, secondly for applying a topcoat on the front and a protective coat on the back or topcoat on both sides of the coil. To this end, two baking ovens are necessary. As with any industrial coating of metal substrates the coil coating process also calls for a perfect coil surface to achieve a high quality of coating. For this purpose chemical and physical cleaning steps are applied. To perform the pretreatment dip and spray methods are used nowadays as well as application by roller. Roller application, a so-called “no rinse” process, is becoming more and more common on new lines. For many appli-

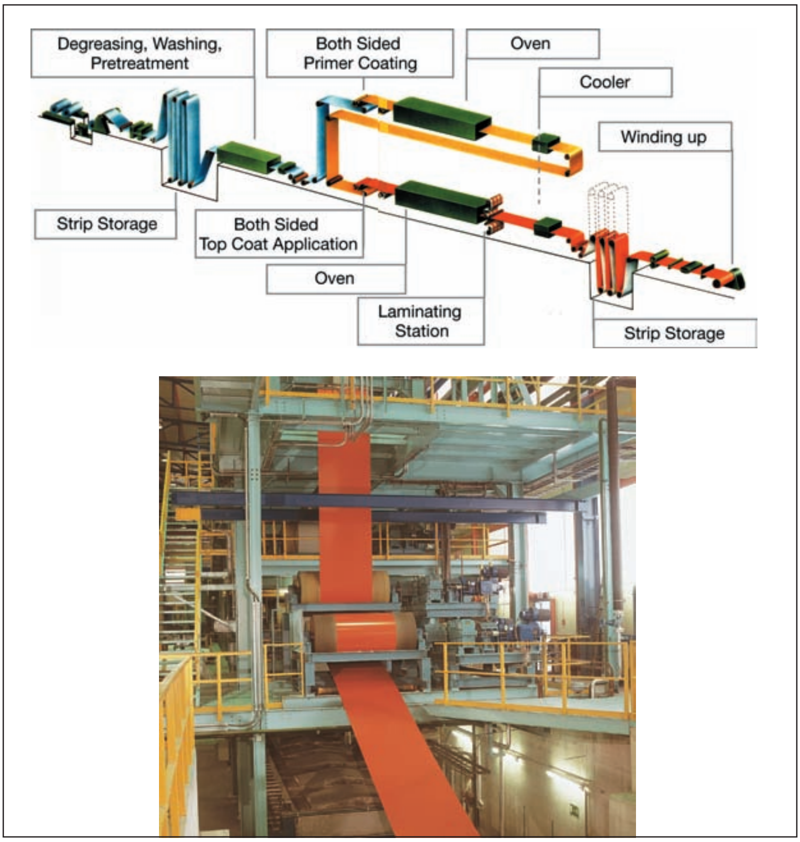

Fig. 7.4.4
Process flow and picture of a coil coating line

cations materials which contain chromium have meanwhile been replaced by chromate-free formulations, both for pretreatment and for priming.

Up to 98% of the application of primers and topcoats is nowadays performed by roller (rolling process). This allows a high level of productivity, coupled with a high level of transfer efficiency, so the coil coating process is probably the most efficient method of coating in terms of the amount of area coated per unit of time. In addition, the short time between application and crosslinking allows highly efficient reduction of solvent emissions by thermal after-burning of the emission sources from the applications zone and the oven. The merging of the two emission sources leads to such high levels of concentration that after-burning requires no additional support in terms of energy.

Coating Layer		Solid Content (1)	Film Thickness	Baking Conditions
Primer		45 – 55%	5 – 8 µm	20 – 60s/200 – 240 °C
Top coat	- polyester	55 – 65%	20 – 25 µm	20 – 60s/200 – 250 °C
	- PVC-plastisol	> 95%	100 – 300 µm	20 – 60s/180 – 220 °C
Backside coating		50 – 60%	8 – 10 µm	20 – 60s/200 – 240 °C
(1) 30 min/180 °C				

Fig. 7.4.5
Technical data of important coil coatings

The dry film thicknesses of the primer are about 5 – 8 µm, those of the topcoat are 15 – 25 µm and those of the protective coat are approx. 8 – 10 µm if crosslinkable coating materials are used. If plastisols are used the film thicknesses can be up to 300 µm.

At high coating rates high demands are placed on the coating materials with regard to rheological properties. Since the oven zone begins about 3 to 10 s after roller application, the coating applied has virtually no time to flash off. Therefore, to achieve faultless surfaces formulation calls for special knowledge of the composition of the solvents and additives.

Property	Unit	Total Coating
Film thickness	µm	25 – 40
T-Bend		0 – 2
Hardness (Buchholz)		90
Gloss (20°)	%	20 – 90
Exposure in Florida (5°)	Years	> 3

Fig.7.4.6
Film properties of coil coatings

The curing or crosslinking of the organic coating materials takes place in continuous ovens with several zones. These are designed as induction ovens, most of which are forced-air ovens. Owing to the high line speed they can be extremely long in order to allow a curing time of 20 to 60 seconds at object temperatures of up to 250 °C. The heat transfer in such a short time must be as even as possible over the width of the coil.

Amongst the test methods for coil coating the cupping test and the T-bend test are specific methods which are designed to forecast whether the requirements will be fulfilled in practice. The cupping test is a modification of the Erichsen cupping test and the T-bend test is a variation of the mandrel bending test. In accordance with the test method recommended by the European Coil Coatings Association (ECCA) under T 7 in 1996 the cracking and/or the pick-off of the organic coating of a coil is examined by bending the test panel parallel to the coil coating processing direction. Various devices are allowed. Bending must always take place within 1 – 2 seconds. The value of the bending radius is stated at which no cracks occur. T 0 therefore means that the smallest possible radius has been reached.

Owing to the versatility of coil coating in various industries almost all paint raw materials are used. For façade applications it is mainly plastisols made of PVC and polyvinylidene fluoride (PVDF) which are used. Polyesters, acrylics, PUR and silicone-modified polyacrylics and polyesters are applied as topcoats. The primer is usually an epoxy-polyester mixture in order to achieve good adhesion and good corrosion protection. Carefully matched coating systems nowadays ensure coil formability, which is only restricted by the steel itself. This means that no damage must be caused to the surface during die-cutting, forming, profiling, trimming and deep-drawing.

The last section of a coil coating line, the laminating station, can either involve embossing the surface, applying laminates or applying protective plastic films. PVC coatings are embossed in the heated state by means of engraved rolls in order to create textured surfaces. Peel-off protective plastic films usually made of PE or PVC with a thickness of 70 – 150 µm protect the coated coil against soiling and damage to the surface during storage, transport and assembly. Adhesion of the plastic film to the coating must be adjusted so that on the one hand there can be no disruptions to further processing of the coated coils and on the other hand the plastic film can be easily peeled off the finished item.

Outlook

In Europe and Asia coil coating lines are chiefly located at the steel and aluminium manufacturers. That involves a distinct forward-looking strategy in the value added chain on the part of steel manufacturers. In the USA, on the other hand, the operators of color coating lines are chiefly job coaters. It is understandable that especially in Europe enormous efforts have been undertaken by steel manufacturers for years now to promote the use of coil coated panels in manufacturing industry and particularly in the automotive industry. The associated concepts are gradually advancing with the introduction of so-called "pre-sealed" coatings, which are weldable and initially only eliminate secondary corrosion protection precautions such as cavity sealing and other sealing on vehicle bodies. The next intended step will involve the entire replacement of pretreatment and cathodic electrocoating in the paint shops of the automotive industry. Such necessary "pre-primed" materials will also be weldable. That implies the task of achieving protection of the cut edges resulting from coil processing e.g. stamping in a different manner. For the future work is being conducted on also applying the colored automotive topcoat to the coils and thus making the entire coating line as it stands superfluous in automotive plants [7.12.30].

In the latter case the welding of parts stamped out of such coils for manufacturing vehicle bodies is an illusion according to the current state of knowledge. It will be necessary to develop a completely new production technique consisting of clinching, riveting and gluing for vehicle body manufacture. This is currently the greatest challenge to successfully introducing coil coating to vehicle manufacture besides the edge cover problem.

New surface structures and effects due to coatings will also support a broadening of the application of coil coating in a very wide range of industries. In particular, the possibility of applying thick films by powder coatings is helping to achieve such surfaces. The high line speeds must remain unaffected. This is only possible with conventional spraying units up to a certain limit. One variation of fluidized-bed coating, the so-called "cloud chamber" process, is currently being investigated for its ability to handle very high line speeds [7.12.31]. In addition, a process involving electromagnetic brushes (EMB), similar to that used in copying processes, is currently being developed [7.12.32]. It may enable line speeds up to 300 m/min for powder coating.

Further growth for coil coating is expected in the market for roof structures for houses. In this area the Scandinavian and the North American markets are serving as models for ecological building using coil coated panels [7.12.33].

7.5 Commercial Vehicles

The term commercial vehicles covers a large number of industries. Not only the manufacture of heavy trucks, buses, trailers, fork-lift trucks and agricultural machines can be attributed to the sector but also a whole host of products largely made individually such as special-purpose transporters and earthmoving vehicles.

In terms of coatings technology it is only possible to obtain a better picture of this production segment if one takes into account the nature of production and the associated size of vehicle. As a result the segment can be divided into two categories. In a similar way to vehicle manufacture, the first category, such as truck cabins, can be attributed to batch production whilst the second category can be attributed to manual work, for example, bodies for silo or refuse vehicles, and huge earthmoving vehicles.

Despite the size of agricultural machines such as harvesters, it may be possible to achieve a coating under production conditions by adapting the type of assembly, i.e. if many of the components are coated prior to assembly. Under production coating conditions efficient coating processes such as electrocoating and robot coating can be used. Appropriate sorting of the production parts then allows high crosslinking temperatures of up to 180 °C. Skilled manual production processes and the usually associated size of the items to be coated, on the other hand, call for coating systems which cure without the need for a baking step.

In many cases the number of relatively small production parts is so low that they are coated by job coaters on electrocoating lines for parts susceptible to corrosion and on flexible spraying lines, frequently powder lines for attachments to be given a color coating. Coil coating panels are used in bus manufacture and in trailer production.

Coating under production conditions

In cases where the quantity of products or components is high it is advisable to invest in a company paint shop. This is the case, for example, in heavy truck and bus production. The coating process starts with the cleaning and pretreatment stage. For this purpose the lines are configured to a cycle. In a continuous process the bath size will lead to an excessively long dwell time for the coating materials. Alternatively it is also possible to use the spray method. The methods in use are mainly environmentally-friendly zinc/manganese pretreatments.

Directly after that the electrocoating is performed with cathodic materials, which on account of the excellent throwing power and the good corrosion protection have also become common with the hybrid design usual in this industry and the high level of stability. Baking temperatures are 180 – 200 °C and film thicknesses are 20 – 25 µm.

Prior to application of the usually aqueous primer, sanding is performed and body filler is applied in order to eliminate any defects in the body-in-white. Primer is chiefly applied with stationary spraying robots or spraying machines. Film thicknesses are 30 – 35 µm whilst curing takes place at 130 – 180 °C depending on the specification.

The topcoat is generally a single-coat, alkyd-melamine-resin-based baking enamel. It is applied in the same way as with primer application. The baking conditions are approx. 30 minutes at 130 – 150 °C object temperature, whilst thicknesses are 40 – 45 µm. On account of the greater resistance achieved some companies have switched to high-quality 2-component PUR topcoats.

To apply single-coat, colored topcoats or primers to galvanized steel powder coating is becoming more and more important. If powder coatings are used, there is no application of primer because owing to the large film thicknesses of the powder coating it is possible to achieve much better coverage of substrate defects compared to liquid topcoats.

Coating at coating contractors

If quantities are very small, it is unprofitable nowadays to have a paint shop which would be capable of coating all production parts. In such situations the coating task is frequently handled by job coaters.

In some cases, however, manufacturers use an electrocoating process and pretreatment which make it possible to prime a very wide variety of parts from the total range in an eco-efficient manner. On account of the diversity of materials one must select a pretreatment which provides the various materials with a perfect conversion layer. To this end the substrate has to be specially degreased and pre-cleaned or stripped in many cases. Owing to the reduction in weight many of the attachments are made of aluminium, whilst the bare skeleton and chassis are made of steel or galvanized steel. The wood which was used for bodies until some years ago has virtually disappeared.

Aluminium calls for just as appropriate pretreatment as steel. Although aluminium protect itself against corrosion by quickly forming a layer of oxide, it does not provide good paint adhesion under all conditions, which can be the cause of blistering and flaking. The whitish oxide layer, which is only difficult to see, must be removed by physical or chemical pretreatment. After that the item is sanded in order to increase the surface area. The sanding procedure and the sandpaper depend on the type of aluminium. For example, hard types of aluminium are used for road tanker bodies, medium ones for stake bodies and claddings, as well as soft to medium-hard ones for bodies. The basic rule is as follows: for hard alloys use mechanically assisted sanding with a fine grain of sandpaper and for soft alloys use skilled manual sanding with a coarse-grain sandpaper. If the surface is to be electrocoated afterwards it must be adjusted to suit the diverse materials in the application conditions.

Many manufacturers have manual coating stations in which primers and topcoats are applied either to the finished product or to selected attachments. Spray application is conducted with pneumatic atomization by spray guns, which can have electrostatic assistance [7.12.34].

All these skilled manual operations are becoming more and more superfluous owing to the use of pre-coated aluminium panels. However, these panels are also sanded and cleaned in case they are going to be re-coated.

If galvanized panels are used, very careful cleaning and pretreatment are also necessary. Although the zinc coat is passivated in a similar way to the aluminium by forming a layer of oxide, it is easily subject to chemical and physical attack so it does not provide any longterm protection and has to be removed before the coating process. Sanding must be avoided because the zinc layer is soft and is soon stripped off. This particularly applies to the electrolytically galvanized panel, which has a very small zinc film thickness of only 8 µm.

Fig. 7.5.1
Example of application by hand

The chassis of many of these vehicles are very large and bulky. In some cases it is not possible to integrate them into continuous processes. Coating starts with manual cleaning using jet equipment. It is followed by a rinsing process and application of primer, also by spraying. The primers or primer fillers used are 2-component epoxy-resin-based coating systems. They are cured at temperatures of 60 – 80 °C. After that a colored topcoat can be applied. The paint normally used is also a 2-component one based on polyacrylics with isocyanate crosslinkers.

Apart from the conventional spraying equipment such as flow cup and suction cup gun other more powerful spraying techniques are used for spraying large vehicles (see chapter 4.2.1).

Pressure vessels with capacities up to 50 l and approx. 10 m of paint and air hoses are not uncommon. They have the advantage of adjusting paint and spray pressure separately in order to improve atomization and ensure a better supply of paint. The suction tube is immersed in the delivered vessel direct.

Shaping air-assisted airless spray guns also used in this industry. Such systems achieve fine atomization and prevent the overspray from being reflected. Overspray is reduced by approx. 50%, although the spray pattern is not as good as with standard equipment. Suitability is restricted to large areas where the standard of visual attractiveness does not have to be particularly high.

Coatings for fire brigade vehicles and other rescue vehicles call for a special paint system because the relevant coating formulations for daylight fluorescent paints are not opaque. On top of the primer a white filler is applied, usually in the color RAL 9010. Finally the daylight fluorescent paint is applied in a film of at least 100 µm and covered with clearcoat after intermediate drying. The colors are slightly different when exposed to sunshine. However, this is accepted on account of the high level of safety.

Vehicle lettering nowadays is chiefly made by applying prefabricated foils. This has almost entirely superseded the application of topcoats using suitable templates.

The self-adhesive foils may only be applied to well cured, solvent-free topcoats. The degree of curing can be established by conducting solvent resistance tests or scratch tests (see chapter 3.1.5; 3.2.5 and 7.2).

7.6 Mechanical Engineering

Mechanical engineering is a widely varied industry, the product diversity of which is so great that all kinds of coating materials are used. Textured and hammer finish effect paints round off the range available. The RAL colors which used to be customary are nowadays often replaced by company-specific colors.

The materials to be coated are chiefly metals such as steel, galvanized steel and cast iron. Light metals such as aluminium and plastics, usually in a dyed form, are becoming increasingly important.

The pretreatment can only be solvent degreasing or flash rust removal or an iron or zinc phosphating process. In the case of aluminium anodising may be sufficient. If necessary a color coating can be applied with the aid of 2-component PUR topcoats. In the case of other metals pretreatment is followed by priming with 2-component epoxy primers applied by spraying or with the aid of electrocoating. The color of the topcoat is nowadays predominantly obtained with powder coatings applied by electrostatic spraying.

Depending on the level of corrosivity expected and the functions of the parts some manufacturers classify the quality of the coating in three categories so various product classes of coating materials can be selected.

Parts which are too large for an oven are coated with automotive refinish products.

Construction plant and similar equipment is subject to such enormous stresses that its coating is ultimately only of a decorative nature. Therefore, after simply cleaning the objects only single-coat powder paints based on polyester-epoxy resins (= hybrid-powders) are used.

In the case of machine tools and metalworking machines there are so-called "wet runs" because they use aggressive coolants, drilling oil emulsions as well as lubricating duct oils and hydraulic fluids. Only high-quality coatings based on 2-component PUR primers and topcoats are resistant to these materials. Hydraulic fluid-driven machines also require a high-quality, highly crosslinked coating such as the 2-component PUR system. Although the coating softens when subjected to such oils, the process is reversible.

In the case of coatings for machinery in the food industry regulations imposed by the authorities have to be observed. The coating must in any case not be attacked by fats, water, alcohol or fruit juices.

The manufacturers of printing presses also make special demands for the coating. For example, the coating must not be weakened by acids, alkalis, inks, printing ink, solvent or chrome cleaner.

7.7 White Goods

The market for all kinds of household appliances is still covered by the term "white goods". The term "brown goods", which was used for self-evident reasons describing the segment of audio and TV industrial products, is no longer used nowadays. Although colors are playing an increasing role in the design of household appliances, white is still always predominant because many household appliances are integrated into kitchen furniture and they are no longer directly visible.

The manufacturing process for refrigerators, freezers, washing machines, dryers, dishwashers, microwave ovens and cooker hoods has been undergoing an upheaval for some years. On the one hand, new production lines have been designed especially for refrigerators, dryers and microwave ovens where coil coated and precoated panels can be used, so that there is no longer any need for a coating shop. On the other hand shares accounted for by liquid paint are on the

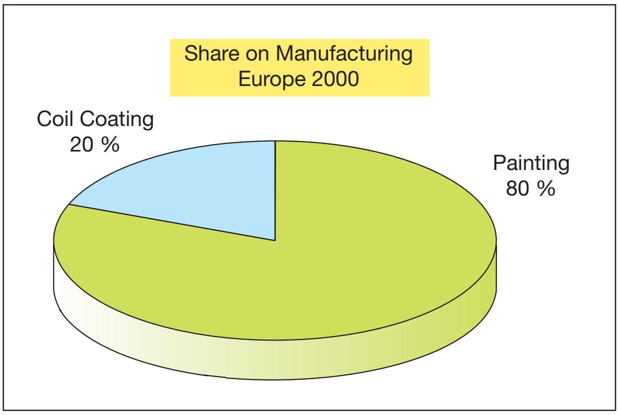

Fig. 7.7.1
Share of the coil coating at manufacturing of white goods in Europe 2000

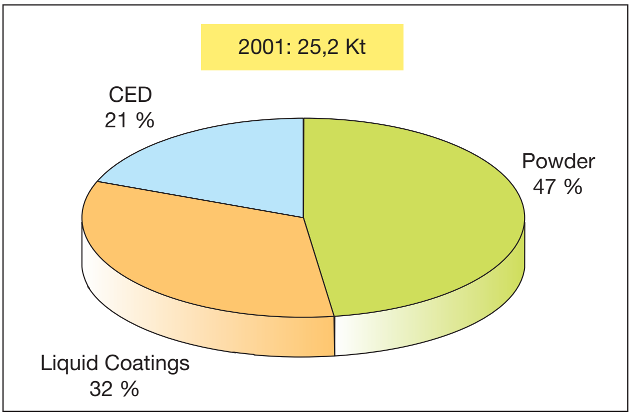

Fig. 7.7.2
Share of different coating technologies in the European market of white goods in 2001

decline and on traditional production lines they are being replaced by powder coatings. As far as paint consumption is concerned this means a shrinking market despite growth in the buyer's market in the East European countries. Apart from housings and structural parts of household appliances various components are still being manufactured and coated at the manufacturers. They include evaporators, compressors, heat exchangers and motors. Such parts merely require protection against corrosion because they are not parts of the appliances which are visible to the user. In most cases protection against corrosion is provided by an electrocoat primer in conjunction with iron or zinc phosphating.

In terms of coating technology the market for coating materials can therefore be divided into three product categories: electrocoats, liquid coatings and powder coatings.

For the so-called "low-temperature" product segments such as refrigerators and chest freezers merely a one-layer coating of the usually galvanized and pretreated parts is sufficient on account of the lower exposure to corrosion. This can be performed with powder coatings or liquid coatings. The "wet" segment comprising dishwashers, washing machines and dryers is frequently provided with a coating consisting of an electrocoated with cathodic or anodic paints and a topcoat of powder or liquid paints on account of the higher exposure to corrosion. Apart from the electrocoats there are also applications of aqueous dip coatings.

Many microwave ovens in the USA are provided with a single-layer electrocoat. The qualities used are based on acrylic resins and have a greater resistance to light than the traditional epoxy resin-based primers.

7.8 Building Supplies

It is mainly for industrial construction, but also for private housing construction, that a whole host of components are manufactured, coated and then supplied to building sites for installation.

They include exterior and interior plastic panelings, heating systems and radiators, industrial light fittings, doors and gates along with the frames as well as aluminium windows, to mention the most important components.

These products are generally produced in batches and coated by a very wide variety of processes in order to firstly match the geometry of the parts and secondly meet the various quality requirements for indoor and outdoor coatings. They mainly include a diversity of colors and weathering resistance.

Façade elements are chiefly coated by coil coating (see chapter 7.4). To a lesser extent so-called “sheets” or “blanks”, i.e. pre-cut panels, are powder-coated. This is usually performed at a job coater.

The same applies to interior plastic mouldings such as ceilings, etc., whereby the share accounted for by powder-coated panels (“sheets”) is much higher.

In the case of **heating systems** the steel panels covering the burners and boilers are coated. This is performed using powder coatings that are applied to the cleaned panels, which have usually been pretreated by iron phosphating. The production of relatively small heating systems, which are usually fitted to the wall in kitchens or bathrooms, is increasingly being switched over to the use of coil coated panels.

Radiators serve to transfer heat in the domestic and occupational areas of buildings. They are mainly used in Europe. With approx. 60 million units a year radiators account for about 10% of the area in vehicle manufacture and thus constitute the second largest steel surface to be protected in any product segment. Panel radiators, which are virtually the only type used nowadays, with convector plates, are therefore mass-produced. After leaving the fully automated welding lines they are degreased, pretreated and then coated. The pretreatment most frequently used is iron phosphating. Cathodic electrocoating, followed by powder coating, has become quite common, chiefly for quality reasons. In addition there are also coating lines with anodic electrocoating particularly for radiators made of aluminium and simple lines based on aqueous dip coatings (see chapter 4.2.1). Owing to the continuity and reliability of the process, invoicing in this market segment is being increasingly based on cost per m^2. Specially shaped, so-called design radiators are primed by electrocoats and afterwards given a topcoat using spray coatings according to the colors requested by customers.

For reasons of protection against fire and burglary **steel doors** are used especially in industrial construction. Fire doors and fire-retarding doors are made of sheet steel. After coating the inside surface with a corrosion protection primer a fire-retarding insulation panel is inserted and welded to the other half of the door. That is followed by treatment of the exterior with air-curing corrosion protection primers applied by spraying. The objects must be stackable after a short time and it must be possible to paint over them with the usual coatings.

Other metal doors are generally provided with a silky matt powder coating baked at 150 – 170 °C. The doors are prepared for this with wet-chemical pretreatment on spraying lines.

Door frames are mainly made of galvanized sheet steel and primed by electrocoating after phosphating. Garage doors are also made of hot-dip galvanized steel and powder-primed. This priming has good adhesion to zinc, is resistant to weathering for several years and can be painted over with standard coatings. Nowadays coil coated panels are also used in this segment.

As with ceiling elements industrial **extra-long light fittings** not only fulfil their real purpose but are also decorative. They constitute an integral part of modern ceiling cladding and are also chiefly made of coil coated panels. Apart from that, polyester powder coatings are used. Outdoor light fittings are subject to special requirements in terms of corrosion resistance. Suitable materials are aluminium alloys and galvanized steel. The coating is applied with powder paints.

Aluminium window frames are chiefly color-treated by an inorganic process (anodization) although to a certain extent they are also coated. For this purpose the frames are degreased, passivated or chromated and then provided with a single-layer color coating using powder paints.

Specially designed components made of a wide variety of materials are coated with powder paint at job coaters and electrocoated beforehand if a high standard of corrosion protection is required.

7.9 Rail Vehicles

Rail vehicles include railway wagons and locomotives for trains, underground railways and trams. They are of hybrid design. For the cladding and structural parts of the vehicle body it is chiefly aluminium that is used in order to reduce weight. Compared to steel, aluminium has become quite common, not least on account of the less effort involved in pretreatment and rework. Furthermore, glass-fibre reinforced plastic is the usual material for mouldings. Load-bearing components are made of steel.

The procedure when coating for the first time and applying a glossy refinish starts by descaling the surface by sandblasting, usually by hand. Chemical pretreatment has not been performed for some time now, for reasons of environmental protection. Preparation of a locomotive to be refinished, for example, means sanding the entire surface of the vehicle manually. Further preparation for the coating includes applying body filler to level off relatively large cavities. The body filler compounds are formulated on the basis of unsaturated polyesters.

The coating of such rail vehicles is usually conducted manually in suitably sized buildings using 2-component coatings which cure within a few hours at a temperature of 60 – 80 °C. Attachments such as doors etc. are coated separately.

In Germany there are meanwhile aqueous 2-component primers established whilst in other European countries it is still solventborne 2-component coating materials which are used. These are applied within 1 – 2 hours and cured at 60 – 80 °C in chambers of suitable size. The base film formers are combinations of epoxy resins with amine hardeners on account of the good corrosion protection. The usual film thickness of the primer is 50 µm for the outer skin and 300 µm for the floor area. Consequently it is necessary to use variously adjusted qualities of paint. Aqueous products are necessary on these coating lines because on account of the size of the coating space no other measures are economically expedient for reducing emissions.

In a second stage of coating an aqueous 2-component PUR primer surfacer is applied to the primer, especially in the case of trams and railways. It is applied with a film thickness of 100 µm and then manually sanded down to 50 µm. This is necessary for municipal vehicles in order to meet the high standards in terms of “appearance”. This layer too is dried at temperatures of 60 – 80 °C before the 2-component PUR topcoat is applied.

Application of primer and topcoat is performed with 2-component guns by the airless or airmix process (see chapter 4.2.1), and in many cases it is still conducted by coaters who are driven past the rail wagons or locomotives on appropriate mobile stages. Recently robot-assisted coating lines were put into operation [7.12.35]. Since meanwhile a whole host of different colors are being used, the distance between the mixing block and the

Fig. 7.9.1
Coating of rail vehicles in huge automated cabins

spray gun must be short in order to ensure a perfect color change with as little detergent as possible.

It is necessary for the entire coating system to have a high level of resistance to acids and alkalis, particularly so that graffiti can be removed with suitably aggressive materials.

For this reason the two-layer system of basecoat and clearcoat is used for the topcoat especially on railway wagons and underground railways. The anti-graffiti properties such as weak adhesion or wetting of the graffiti paints by specially formulated clearcoats can be exploited [7.12.36]. The standards of appearance, weather resistance and chemical resistance are similar to those required for automotive coating. The coating of a locomotive or rail wagon by this process takes about one day.

The life of locomotives and rail wagons is frequently more than 20 years. Depending on the amount of stress, a new coating is applied at least once during the life cycle. Similar or identical lines are used as for the original coating, the difference being that the process is preceded by a stripping stage. This is designed so that all organic coatings are completely removed.

7.10 Wood Coating

Wood coating covers an extensive range of various coating measures and processes for the wood-processing industry. Methods can be divided into three segments:

- Direct processing of wooden products such as solid furniture, pianos, structural components, window frames, etc.
- Components made of wood, usually coated chipboards, for the furniture industry for example
- Floors.

The market for wood coatings in Europe was approx. 377,700 t in 2003. Italy and Germany play the most important role. A whole host of products and processes are used. Spray application is still the most common. In terms of materials PUR coatings account for by far the largest share, followed by nitrocellulose coatings. Environ-mentally-compliant water base materials and radiation-curing coatings account for 30% of the

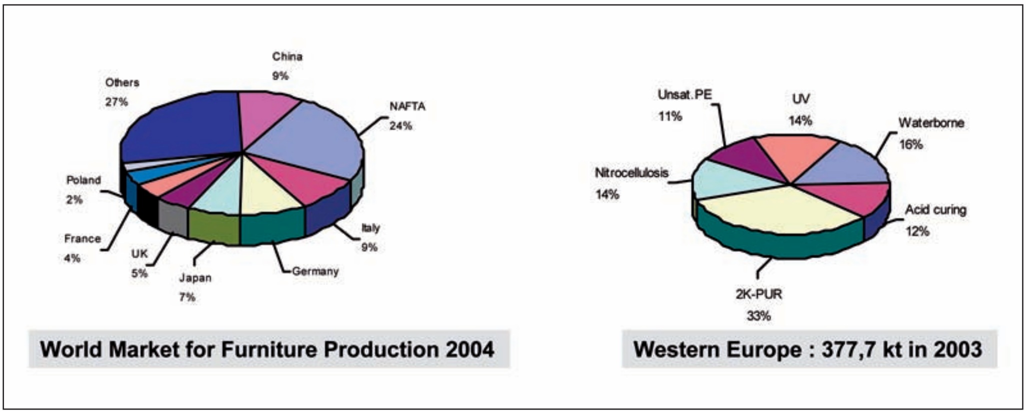

Fig. 7.10.1
Worldwide furniture production and European technology shares for wood coatings

market [7.12.37]. The distribution of coating technology is quite different in North America [7.12.38]

Direct processing of wood
In the coating of wood the texture and properties of the various types of wood play a major role. Wood ranks among the naturally regenerative materials and its structure is not as standardized as metals or plastics for example. Its type and diversity are virtually unsurpassed. Almost all types of deciduous and coniferous wood such as pine, larch, fir, spruce, alder, birch, koto, gabun, cedar, anigre, cembra pine, wenge, oak, beech, teak, walnut, mahogany, macassar ebony, limba, yew, cherry, Indian rosewood, elm, makoré, mansonia, ash, pear, abachi, afrormosia, zebrano and ramin are used.

The inhomogeneous texture of the wood exerts a major influence on its physical and technological properties. For example, “summer wood”, which chiefly grows in late summer and autumn, has a much higher density than “spring wood”, the main growth of which is in spring (e.g. pine trees). The reasons for this are the varied formation of the wood fibre and the varying thickness of cell walls depending on the flush (see chapter 4.1.1).

Building timber is impregnated with preservative at the manufacturer’s under pressure, particularly prior to use outdoors. The thus pretreated parts can usually be easily coated at no great expense. Solid wood that has not been pretreated is used in the window industry and for high-quality furniture. In the case of chairs and tables up to 90% is accounted for by solid wood.

The coating system on wooden surfaces is expected to cope with many different requirements depending on the particular application. Generally speaking, they can only be met by combining different coats of paint. What all the coating systems have in common is that they must have an attractive appearance, good adhesion to the substrate and good adhesion between the individual layers of the coating. In the case of interior applications such as furniture and doors chemical resistance to household substances such as coffee, red wine or detergent is also important. Exterior applications such as window coatings, on the other hand, call for a high level of weathering stability and resistance to physical forces such as hail.

The coating frequently consists of pretreatment, staining, priming and finally the topcoat.

For all applications nowadays there are aqueous coatings available, and the market share is increasing accordingly at the expense of solventborne products.

Application is conducted by spraying or flood coating.

The requirement of good adhesion to the wood is best fulfilled by using an aqueous adhesion primer. The adhesion-enhancing effect is achieved by causing the material to swell and penetrate the wooden surface. The wood fibres turn up, are fixed in drying and can then be sanded down. This not only guarantees optimal adhesion but permits very smooth surfaces.

Fig. 7.10.2
Coated pianos

For high-quality coated surfaces nowadays 2-component PUR coatings are used which have the optimum performance profile in terms of weathering resistance, gloss and resistance to chemicals. In the case of large-area geometries UV-curable coatings are being used increasingly.

Special effort is put into piano coating. The usually three-coat system consisting of U.P. filler, a black PUR-based coat and a U.P. clearcoat is applied by spraying. The individual coats, which can be up to 100 µm thick, are sanded carefully after each application and finally polished.

Manufacture of components made of wood composites

Boards either in the form of blockboards for high-quality furniture such as shop fittings or even pianos, as chipboards or as wood fibre boards for all segments, are extremely important in the furniture industry (see chapter 4.1.1).

Many of these boards are covered with foils which are made of impregnated paper after appropriate wood patterns have been applied and finally they are sealed with clearcoat. This is performed from roll to roll, i.e. by the coil process, at speeds of up to 200 m/s.

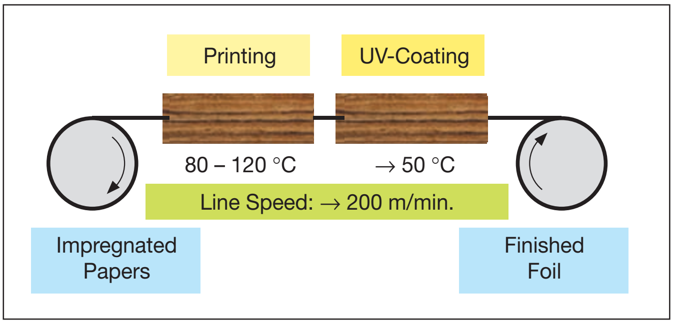

Fig. 7.10.3
Scheme of foil coating process

The most appropriate clearcoats are coatings which can be cured by ultraviolet radiation because on account of the high speeds in production a good performance profile is obtained with regard to scratch resistance and chemical resistance.

Fig. 7.10.4
Coating boards for the furniture industry

Solid or even wood veneer flat components for the furniture industry are also sealed with UV clearcoats. The latter can also be aqueous UV coatings depending on the particular application and performance profile. In recent years UV-curable powder coatings gained in importance [7.12.39]

The coating of wooden components for outdoor applications such as windows is gaining importance because the use of more weatherproof tropical woods is declining. The service life of coated woods is about 5 years. To increase performance in competition with aluminium and plastic windows UV coatings are also recommended [7.12.40].

Other applications for outdoor applications use the traditional coating systems for woods, whereby the topcoat has a high level of weathering resistance.

Floors

Particularly high standards are expected in terms of the adhesion and abrasion resistance of coatings on industrially manufactured parquet. Owing to the rapid production process and the geometrically uncomplicated parts UV coatings became established in this product segment at a very early stage. They are applied by roller. Originally their formula was based on unsaturated polyesters (UP) with styrene as reactive diluent. In the meantime they have been largely replaced in European clearcoats by unsaturated, urethane-modified acrylic systems [7.12.41]. Compared with paint formulations based on UP resins they offer the following advantages:

- Faster curing reaction, which allows higher line speeds
- Less inhibition on some wood substrates such as exotic woods
- No swelling of the rubber lining on application rollers.

The sequence of coating can consist of up to three priming stages. Prior to the subsequent application of clearcoats a sanding process must be conducted. The primers can still be based on unsaturated polyester resins. To improve abrasive strength the clearcoat is enhanced by adding approx. 10% fine-particled corundum. The addition of silicone-modified polyester resins increases abrasion resistance. The unsaturated acrylic resins are formulated as so-called 100% solids systems using reactive thinners such as hexane dioldiacrylate (HDDA), tripropylene diacrylate (TPGDA) or dipropylene glycol diacrylate (DPGDA).

For all wood products for indoors one must pay increased attention to smells because the production and delivery times have been reduced considerably. With this aspect in mind, aqueous UV coatings offer advantages [7.12.42].

7.11 Other Fields of Application

The number of manufacturing industries is so large that no coating manufacturer can be equally successful in all the industries. Many of the market segments call for substantial specialization in terms of coating and application technologies. To provide an overview of the most important segments the following fields will be described briefly, most of them not being covered by BASF Coatings activities at present.

7.11.1 Protection of Structures

Large steel structures have appropriately large surfaces which have to be protected against corrosion if there is to be no detrimental effect on their functions. They include road bridges, railway bridges, steel masts, wind turbines, all types of tank and tank facilities, cranes, exploration installations such as drilling rigs as well as buildings and production installations of all kinds.

Basic protection is largely provided by inorganic coatings such as galvanization and zinc dust paints [7.12.43, 7.12.44]. Most structures are protected with coatings in order to guarantee a service life of more than 30 years in many cases. Last but not least, colored coatings are also applied for decorative reasons. A recommendation for so-called "duplex systems" has been issued by the relevant associations in Germany [7.12.45]. In accordance with the requirements of DIN EN 12944 the major factors for a reliable coating of hot-dip galvanized substrates with organic paints are described in order to achieve a high level of guaranteed durability.

Although many of the structural components are delivered to the construction site already coated, the topcoat usually has to be applied on site. Parts require careful treatment of the substrate. If structures are new, the steel surface is often covered with firmly adhering scale. Efficient methods for removing it are sand-blasting, flame blasting, staining and grinding, depending on the size and accessibility of the item. The coatings consist of a thin dust primer approx. 100 µm thick, a 2-component intermediate layer with a film thickness of approx. 100 µm and a colored 2-component topcoat with a film thickness of 50 – 70 µm [7.12.46].

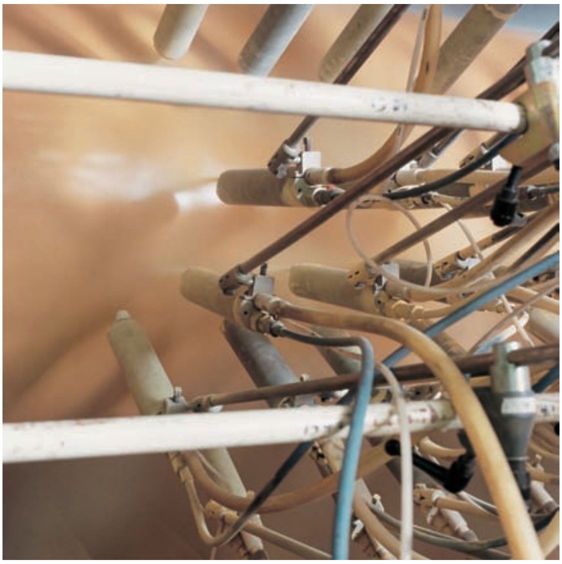

Fig. 7.11.1
Powder coating of pipe lines

For commercial and ecological reasons these operations are frequently performed directly at the steel component manufacturer's plant. Here it is possible to perform fully automatic blasting on equipment in which the abrasive is recycled. After that the parts are provided with an antirust primer in order to prevent damage due to corrosion during transport to the construction site and storage. It is formulated in a variety of ways depending on further use. These are a high-build primer when bolting together and a weldable primer offering only temporary protection against corrosion during welding operations. Further coating with primers and topcoats should then be conducted as soon as possible.

This also applies to the large structures of off-shore platforms which have to be dried as quickly as possible with special drying techniques, usually after degreasing and blasting with steam, with 2-component PUR coatings for an efficient coating sequence. For this purpose, preconditioned air is used in many cases [7.12.47].

One special application of structural protection is the coating of oil and gas pipes. The exterior of pipelines laid in the ground or in the sea has to be prepared for a long service life. A large number are coated with special powder paints to a film thickness of between 350 and 500 µm. This is conducted either on coating lines at the pipe manufacturers' or on site in rarer cases. This is possible because the standards required for the surface are understandably low. The pipe is heated to approx. 230 °C and in this way the unusually thick coatings are achieved with a sequence of several spray units. The residual heat is sufficient for curing purposes. In other cases a powder coat 100 µm thick assumes the role of a primer for coating with polyolefine foils. For the service life of 50 years and longer the pipe system is protected cathodically during operation of the installation. The epoxy powder coatings are therefore specially optimized for resistance to alkalis [7.12.48].

7.11.2 Steel Furniture

Steel furniture chiefly comprises lockers, wardrobes, tool cabinets, office furniture and fittings, shelves for shop construction, vending machines, as well as furniture for doctors' surgeries and hospitals.

On account of the low exposure to corrosion indoors the materials used are chiefly plain steel, frequently black plate and steel tubing. For higher protection against corrosion galvanized material or even aluminium is used.

As far as furniture for doctors' surgeries and hospitals is concerned, requirements have to be fulfilled in terms of resistance to disinfectant and hot steam sterilization.

Pretreatment depends on the stresses to be expected. For example, lockers and cabinets are merely degreased whilst steel furniture for offices, doctors' surgeries and hospitals are also phosphated. Depending on the production programme this is performed automatically in cycles or continuously.

Coating is almost always conducted with powder paints, which are used both as primer to protect against corrosion and as single-coat, colored coatings in addition to coloring. For high-quality, smooth and glossy surfaces liquid coatings are used in some cases.

In a few applications it may also be expedient to conduct an electrocoating process on account of higher standards required for protection against corrosion.

7.11.3 Aviation Industry

In this market segment there are three important areas:
- Commercial aircraft construction
- Military aircraft construction
- General aviation industry.

The first segment currently consists of Boeing and Airbus as the world's largest aircraft manufacturers for passengers and cargo. This segment has the largest potential of the world market for aircraft coatings, with a sales volume of approx. 200 million euros [7.12.49]. A civil aircraft like a Boeing 777 or Airbus 330 with about 2000 m^2 surface area needs about 13 km of tape, 2 km of paper and about 750 kg paint to be coated taking about 4 days time.

The technical requirements for coatings for military aircraft are regionally much more specific than those for commercial aircraft [7.12.50].

In all cases the two-film coating has to provide not only good protection against corrosion on components made of aluminium, magnesium and titanium as well as their alloys but also withstand extreme conditions and cope with the following stresses:
- Abrasiveness associated with high velocities
- Intense ultraviolet radiation at altitudes between 10 km and 14 km
- Extreme and frequent temperature fluctuations from +100 °C on the ground to –60 °C in flight
- Expansion of components at altitudes between 10 km and 14 km
- Resistance to
  - hydraulic fluid
  - de-icing agent
  - kerosene
- Easy paint removal using ordinary paint stripper

This must be guaranteed at minimum film thicknesses because weight is an extremely sensitive parameter for utilization and energy costs, particularly in aircraft construction.

The structural components for an aircraft are pretreated separately and in the case of aluminium they are anodized or chromated. In some cases so called active primers containing phosphoric acid or other corrosion inhibiting pigments with a film thickness of 6 – 8 µm are applied after cleaning.

The corrosion protection primer is based on an epoxy resin which cures with amines or isocyanates at room temperature. On account of the high standards of safety required in terms of component resistance chromate-containing active pigments are still used today in order to prevent dangerous filiform corrosion.

The topcoat is made with a 2-component PUR paint and has high gloss, color fastness and weather resistance. Application of the two coats is performed in suitably large hangars by manual spraying in a predefined sequence. Curing then takes place at room temperature.

After approx. 5,000 flying hours a complete overhaul of the aircraft is necessary, including a repainting of the outer skin, one of the reasons being the high stresses involved. For this purpose the aircraft are stripped manually in the large hangars, cleaned, inspected for defects and fatigue, and finally recoated. As with the original coating this is conducted manually using conventional spraying.

A large segment is accounted for not only by exterior coating but also the coating of the interior. Although wall linings, window frames, doors and luggage shelves are partially made of dyed plastics, these and the nondyed components can be provided with appropriate coatings depending on the airlines' design specifications. The coatings used for this have good adhesion to plastics as well as high flammability. For this segment 2-component PUR systems mainly are used.

The high emission of solvents which is bound to occur when applying exterior coatings is leading to the increased use of aqueous products on account of legislation. One major challenge is also chromate-free formulations, which must not affect the important protection against corrosion.

7.11.4 Electrically Insulating Coatings

Electrically insulating coatings have the task of insulating electrically conductive substrates so they assume a special role amongst the various coatings. Decorative aspects are virtually negligible although protection is increasingly desirable in the field of electronic parts and components.

For example, the items to be coated are either, as with wire enamels, homogeneous materials, live parts of electric motors and transformers as with impregnating agents, or electronic parts and components as with casting materials.

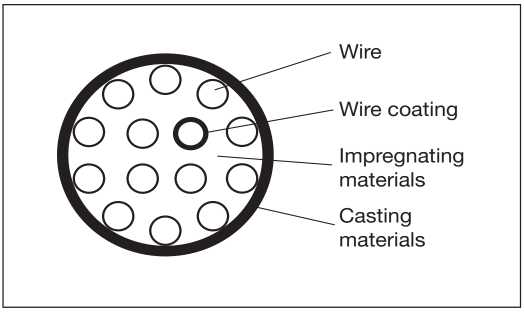

Fig. 7.11.2
Different coatings and their functions on the example of electrical windings for electric motors

In the case of electric motors it is important to match all types of paint with one another in order to create an optimally effective electrically insulating system.

Electrical insulation is a vital function in order to make electric motors and transformers operate properly. Thermal resistance is also crucial to safe continuous duty. For this reason you will find imide structures in most of the coating systems described.

Wire enamels

Wire enamels provide an insulating coat for wires which are used in electric motors, transformers and coils. They are not to be confused with wire insulation for wires which are used for electric cables.

The wire enamel is continuously applied by a dip process in several thin layers and baked at temperatures of 400 – 500 °C. Solderable wire enamels permit direct tinning without the coating having to be removed. Other wire enamels feature high thermal resistance. The latter are formulated on the basis of polyesterimides.

Impregnating materials

Impregnating materials have the task of filling cavities in windings and strengthening them physically. Consequently the penetration of harmful substances, e.g. water, is prevented, heat dissipation is improved and the risk of wire breaks when switching on as well as the occurrence of imbalance during rotation is avoided.

Impregnating materials are applied either by flooding, dipping, vacuum impregnation or trickle impregnation with trickle coatings. The latter process prevents coating of the housing because a thin jet of trickle coating is directed at the end winding of the rotating object. The coating then flows inside and is distributed inside the winding by the centrifugal forces of rotation.

Impregnating materials are generally baked at 120 °C. Impregnating materials used are based on unsaturated polyesters which are activated by peroxide hardener. Application is conducted within the pot life. Solvents of the formulations are styrene and similar unsaturated compounds. To a certain extent phenol-alkyd resin-based impregnating materials are still used. Modification with imide structures improves thermal resistance. Long drying times constitute a drawback though.

Casting materials

The use of casting materials ranges from additional surface protection for electrically conductive winding parts and complete casting of electrical components such as high-voltage coils to solid casting as an insulator and mechanical load-bearing structure.

The casting materials are based on polyester resins, polyurethane resins or epoxy resins depending on performance requirements. They are usually pigmented with extenders and activated by hardeners so curing takes place rapidly at room temperature.

Application is performed by processes ranging from simple casting, as is usual with cable connection components, to the vacuum process, which adjusts electrical insulation optimally by preventing cavities.

7.11.5 Communication Equipment

Apart from the coating of television sets and computer cases, which are coated on conventional lines depending on the selection of substrate, applications worth mentioning are the coating of printed circuit boards with photoresist, the sealing of CDs or DVDs and the coating of fibre-optic cables [7.12.51].

Cabinets for television sets, personal computers and peripheral equipment such as printers and scanners, as well as cameras and mobile phones are chiefly made of plastics. Many of these items are not coated because they are manufactured with appropriately dyed plastic granules. This is possible because there are no high stresses due to light, temperature or moisture. Cameras and mobile phones, on the other hand, are subjected to higher stresses and increasing design requirements so these are often coated. The very different plastic materials must be pretreated specifically (see chapter 4.1.1). Their

Fig 7.11.3
Examples of coated handies

coating is performed on standard coating lines by the spray application process. The number of coats depends on the requirement for the quality of the surface of the respective item. For this reason two-layer topcoats are usual for effect coatings, e.g. on mobile phones.

In the manufacture of printed circuit boards no durable coatings are required, only temporary ones, which cure selectively by ultraviolet radiation and then create appropriate structures on electrical microscopic conductors by means of washing, etching and metallization stages. These coatings can be both electrocoats and conventional solvent-borne coatings.

The high production speed of compact discs based on PMMA or PC plastics calls for an appropriately fast sealing process for the aluminium film. It is usually provided by UV-curable coatings which are applied by the spin-coating process owing to the circular shape of the information storage device. For this purpose droplets of coating are applied centrally whilst the disc rotates at an appropriate speed and the resulting film cures by means of ultraviolet radiation.

To cover long transmission distances fibre-optic cables require an external coating with a much higher refractive index than that of the substrate. For this purpose UV-curable clearcoats are also used.

7.11.6 Road Marking Paints

Road markings have to fulfil the following specific requirements:

- Daytime visibility with durable high degree of white
- Nighttime visibility due to reflecting body
- Nighttime visibility under wet conditions
- Good adhesion to road surfaces
- Slip resistance
- Permanent elasticity
- Abrasion resistance.

They are based on studies which constitute a scientific basis for the safety aspects of road markings. In 1998 the European Standard EN 1436 was introduced which has since led to a significant improvement in the quality of markings.

Easy application and very rapid solidification and curing are essential properties of materials in order to ensure a smooth road marking procedure without unacceptably obstructing traffic with road blocks.

Depending on the requirements and appropriate compositions the marking materials can be divided up into ones for thin-layer road markings and ones for thick-layer road markings.

Thin-layer markings with wet film thicknesses of between 0.5 and 1.5 mm have virtually been phased out as purely physically drying single-component coatings because the time between application and usability is too long. The present base is usually a VC copolymer (see chapter 2.1.1). In the case of two-component systems a more rapid curing process takes place after adding the curing component, directly before application. Despite the high cost of raw material isocyanate crosslinking has become established on account of its speedy curing.

Thicker-layer markings are applied with hot-melt plastics, i.e. thermoplastics, whereby these materials are heated to 180 °C for application [7.12.52]. When the markings have cooled down vehicles can drive over them. The most important resin base in Europe is hydrocarbon resins and esters of colophonium (see chapter 2.1.1). Maleic acid-modified natural resins account for two thirds of the total market in North America and are gradually gaining importance in Europe on account of the higher pigmentability and wetting of glass beads providing better visability [7.12.53].

In addition, so-called cold-setting plastics are used which are designed as solvent-free 2-component systems and also feature rapid curing. However, they are much more expensive than hot-melt plastics.

In Germany road markings are applied with materials which are approved in accordance with the regulations imposed by the Federal Road Research Institute ("BASt"). Conditions and specifications are defined in the "TPM" or "Technical Provisions for the Testing of Marking Materials for Trunk Roads". According to these the materials are classified according to load capability and service life.

7.11.7 Shipbuilding

The coating of ships can be divided into in two segments:

- Commercial ships such as container vessels, tankers and cruisers
- Yachts and other boats for leisure.

Commercial ships are of steel design and require good corrosion protection by paint coating because the constant effect of salt, particularly in marine transport, seriously increases the corrosive effect on steel. To assist corrosion protection, particularly under water, most ships are also cathodically protected by active anodes or extraneous current. The resulting hydroxyl anions create an alkaline environment, which the ship's coating has to withstand by means of saponification resistance [7.12.54].

Furthermore, the paints and coatings must be resistant to algae growth and deposits of other seawater organisms. This growth not only contaminates the anticorrosive coating but also constitutes an economic problem. The surface of the hull, which is rough on account of clinging mussels, reduces the speed of ships and increases diesel fuel consumption by up to 10%. Resistant coatings extend the intervals between ship maintenance in dock by 30%. Consequently, in relation to the world fleet approx. US $ 1.5 billion a year can be saved if appropriately resistant coatings are used. Tin compounds in addition to copper oxide in the appropriate formulations are state of the art at the moment for the biocidal action of underwater coatings. These formulations, which are termed "antifouling" coatings, emit their inorganic compounds more or less quickly during the course of their functional life and thus cause the algae in the direct vicinity of the coating to be destroyed. The toxicological risk of organic tin compounds such as TBT (tri-butyl tin compounds) has prompted enormous development efforts in order to search for new substances and other solutions (see chapter 2.1.4) [7.12.55]. Suitable coatings are also used in the growing market for drilling platforms.

Further requirements for the coating ships have to be observed depending on the section of the ship involved. Upper deck coatings must be durable for walking on, slip-proof and hard-wearing. For this purpose solvent-free 2-component liquid plastics are particularly suitable. Deck superstructures such as command bridges, masts, container brackets, hatches, railings, etc. are given coatings with a quality which is equivalent to those used on the shell plating, often in different colors.

Coatings in the engine room must have a low level of flammability and conform to the specifications issued by the Seamen's Accident Prevention and Insurance Association. This also applies to the interior finish of passenger ships.

Special coatings based on epoxy resins and combinations of epoxy resins with hard coal tar are necessary for the oil bunkers of tankers. The same coatings are suitable for oil ballast water changing tanks. However, for transporting nonreactive hydrocarbons zinc silicate coatings are also used. Generally speaking, the coatings for tanks transporting chemicals are particularly critical. For example, they call for careful coordination of paint formulation, quality assurance test methods, manufacture, surface pretreatment and monitored application and inspection of the coating. Coatings are generally applied by the airless process. Poorly accessible surfaces are prepared manually and coated by brush.

For storage rooms 2-component systems based on epoxy resins with isocyanate cross-linkers have proved successful.

In technical terms, the coating of yachts and other boats for the leisure sector must be assessed differently because many boats from this sector have plastic hulls. However, one still finds wood being used as a material, chiefly in the luxury class. Coating is conducted with primers for plastics and colored underwater coatings with an "anti-fouling" function.

7.11.8 Miscellaneous Coating Applications

A major segment for the application of coatings is the **packaging industry**. In this market segment one differentiates the field of cardboard boxes and tubes, which is essentially served without printing inks, and consumer packaging. In the latter segment, beverage cans share the market with food cans. They are made of tinned steel (tin plate) or aluminium whilst the interior and exterior are coated. In addition, the exterior is printed with the necessary product information to comply with food legislation as well as advertising.

The per capita consumption of beverage cans is very different throughout the regions. For example, in the USA it is approx. 330 a year and in Germany it is only about 50. The situation as regards food cans is similar. In North America almost only aluminium cans are used whilst in Europe tinplate still accounts for a considerable share. The manufacture of beverage cans is performed by subjecting the can body to a deep-drawing process. After that it is spray-coated inside and primed outside with rollers, usually white. This can body is then provided with a prefabricated lid in a combined pre-forming and bonding process. This "2-piece" process has largely superseded the "3-piece" process, in which the bottom, body and lid are manufactured separately and then soldered together.

Beverage can coating in particular is a high speed process which can handle up to 3,000 cans per minute. The interior lining applied by spray heads, requiring 100 mg to 300 mg per can, must be absolutely void-free. Either one or two coats are applied, depending on the load exerted by the filling. The coatings used in North America are chiefly aqueous based. On the other hand, establishment of a thermal after-burning installation, especially in Germany, also permits the use of solventborne coatings. The curing process takes only a few minutes at more than 180 °C.

Whilst beverage cans are made of a single sheet of metal, apart from the lid, the food can, especially for relatively large volumes, can only be made as a three-piece welded can. It is important to systematically protect the welded seams of the parts made of coated plate. This is chiefly performed using powder coatings. The cans, which used to be internally coated chiefly using gold lacquer, a yellowing epoxy coating, are nowadays frequently provided with an opaque white coating for visual reasons.

Coatings for beverage cans and food cans have to be approved by the food monitoring authorities. The American Food and Drug Association (FDA) is accepted throughout the world. Coatings are mainly based on epoxy resins.

Drum coating is another market segment in which some coating companies have specialised. Epoxy/phenolic resins constitute the basis for the highly solvent-resistant coatings with a thickness of about 20 – 40 µm inside, which are increasingly being applied with aqueous coating materials by spraying [7.12.56]. The outside coating is applied in one layer. Gas cylinders are protected with powder externally [7.12.57].

The coating of **bicycles** is chiefly performed using powder paints. High-quality effect coatings are achieved on a powder primer with subsequent topcoat using liquid basecoat/clearcoat layers. Some manufacturers uses powder clear coats based on acrylic resins [7.12.58]. **Motorcycles** are coated taking the aspects of automotive coating into account, whereby 2 to 3-coat systems are applied depending on the substrate. In the USA powder clearcoat is being used on steel components.

Spray can lacquers for DIY applications, which are also used as graffiti coatings, have gained a certain amount of importance. The formulations based on mixed color systems, similar to automotive refinishes, have to be compatible with propellant gas, propane and butane. Spray ability and hiding power are the vital quality criteria. The creation of special effects such as "granite" or hammer finish are important for this segment.

Various **sports articles** such as skis, snowboards, rollerblades, protective helmets, etc. are coated for design reasons. Articles with simple geometries are usually given a clearcoat based on UV coatings, which achieve a high level of scratch resistance.

Flame retardant coatings based on brominated polymers are of distinct importance for fabric back coatings, carpetings and paints (see chapter 7.11.7) [7.12.59].

Lettering on vehicles, signs or other coated items has almost solely switched to decal technology, i.e. sticking on prefabricated plastic films. Coating is no longer of much significance.

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8 Industrial Standards

8.1 General Information on Standardization Work

The standardization of products, processes as well as methods of measurement and testing promotes rationalization and quality assurance in industry, technology, academic research and administration. It serves to provide safety for people and property and improve quality in all spheres of life.

Standardization is the planned unification of material and immaterial items, performed jointly by interest groups, for the benefit of the general public. Internationally accepted industrial standards eliminate trade barriers and promote cross-border trade. For this reason they are of major economic importance.

Industrial standards are designed to be introduced as recognized rules of engineering. They constitute a benchmark for quality and quality consistency. This benchmark is of importance as far as legal regulations are concerned. Standardization also serves to regulate sensibly and provide information in the various technical fields.

The standardization body in Germany is Deutsches Institut für Normung e.V. (DIN) in Berlin. It is an institution of self-government by all groups interested in standardization. DIN is the round table at which manufacturers, trade, consumers, craftsmen, service companies, academic researchers, technical monitoring bodies, the government and anyone who has an interest in standardization, meet in order to determine the state of the art and place it on record in German standards. Its work is based on 10 basic policies:

1. Voluntary participation
2. Disclosure to the public
3. Participation by all interest groups
4. Unified approach and freedom from contradiction
5. Objectiveness
6. Consensus
7. Orientation towards state of the art
8. Orientation towards economic circumstances
9. Orientation towards general benefit
10. Internationalism

Many German standards and draft standards are currently available for reading on the internet (see chapter 9.2). All German, European and international standards can be obtained from the publishers, Beuth-Verlag, which is associated with DIN. The Association of the German Paint and Coatings Industry (VdL) also publishes regular overviews concerning the current state of standards for members.

In the field of coating materials and coatings it is chiefly a question of the harmonization and standardization of test methods and properties as well as technical terms. This harmonization is desirable because in the course of time a whole host of “company standards” have become established which have been developed from the usually specific requirements of paint users and the high value of experience in dealing with these standards and test methods. The verification of standards and test methods, as required by quality management systems, has recently dispensed with a large number of test methods on account of inadequate repeatability and measuring inaccuracies (see chapter 6.5). Furthermore it regulates handling of paints taking safety aspects and environmental compliances into account. An essential guide has now been published concerning the terminology of standards, in German, French and English [8.3.1].

Standards which are concerned with coating materials and coatings are summarized in a DIN handbook entitled “Paints, Coating Materials and Similar Coating Materials”. It consists of a collection of loose leaves which is updated twice a year by the standardization committee responsible, NAB (standardization committee for coating materials and coatings). This committee celebrated its 50th anniversary in 2002. At the time when this book goes to press the committee’s sphere of competence covers 131 DIN standards, 53 DIN EN ISO standards, 36 DIN EN standards and 8 DIN ISO standards. 143 standardization projects are currently under way.

Apart from this committee there are other standardization committees which are relevant to the paint and coatings industry. They include:

- Standardization committee for principles of environmental protection (NAGUS)
- Standardization committee for personal safety equipment (NPS)
- Standardization committee for materials testing (NMP)
- Standardization committee for pigments and extenders (NPF)
- Standardization committee for quality management, statistics and certification principles (NQS).

A DIN standard is therefore a standard drafted by Deutsches Institut für Normung and issued by it bearing the DIN logo. This can be done in the form of a pre-standard which is still subject to reservations about application and which can be used on a trial basis for the time being. A supplement contains information about the standard but no additional standardized definitions. A draft standard is the provisionally completed result of standardization work which is presented to the public for opinions.

Like industry, standardization work is also subject to trends towards globalization. Consequently, efforts are being made to develop standards jointly for the paint and coatings industry in Germany, Europe and throughout the world. Although DIN standards still exist, now only country-specific standards are filed under this classification which are not subject to European or global acceptance or significance. European standards are filed under DIN EN if they have been introduced by Germany and verified by CEN (Comité Européen de Normalisation) with regard to competitive advantages and have been passed by that body.

The European standardization committee collaborates closely with the ISO, the International Organization for Standardization which is based in Geneva. Accepted standards are given the designation of DIN EN ISO if they originate in Germany and have been passed in Europe. In addition to these there is a whole host of DIN ISO standards. This standardization system is mainly used by the Asian region.

In Germany also the Association of Engineers (VDI) as well as the association of Automotive Manufactureres (VDA) develop their own directives and standards including those for coatings.

Almost for all countries exist specific standards and norms for the defense and military aerospace industry.

The United States has many organizations that comprise the US standardization system including government and non-government organizations. Mandatory standards are set by government and can be either procurement or regulatory standards. A procurement standard sets out the requirements that must be met by government suppliers. Regulatory standards may set healtch, safety or environmental criteria. Some of the major players in the US standard development system are The American National Standards Institute (ANSI) and The National Institute of Standards and Technology (NIST). While ANSI is a non-profit, non-governmental organization and just coordinating US positions in the worldwide standardization world NIST is a US government agency and has to assist the US industry to advance performance in technology.

Apart from that there is the ASTM, the American Society for Testing and Material, in West Conshohocken, PA, which works on standards and standardization processes for the North American market, more or less in parallel with the ISO, CEN and DIN. The renaming as ASTM International in 2001 demonstrates that this organization is also taking due consideration of the globalization of markets. Harmonization of inspection and test methods is also a common goal of ISO and ASTM [8.3.2]. ASTM surveys almost 11300 standards and works similar to DIN in several subcommittees for the industrial and technological sections. The subcommittee D01 with several more subgroups deals with paints and coatings. Other groups of interest are D07 ”Wood”, D20 ”Plastic” D34 ”Waste Management”, E12 ”Color and Appearance”, E42 ”Surface Analysis”, E50 ”Environmental Assessment”, G01 ”Corrosion of Metals” and G03 ”Weathering and Durability” to name a few.The voluntary participation and work needs to be recognized by the industry [8.3.3]. As an example for industry group standards it is worth to mention IEEE-standards for the electronic industry which also have impacts to the respective coating development.

Regional significance only is for the JIS-Norms of Japan, the British standards and for the SNV-Norms of Switzerland.

Ultimately paint and coatings companies with global operations currently have to find their way about both standardization systems in all markets because, for example, American manufacturers in Europe often specify ASTM standards.

A rather globally operating organization of great relevance to the coating industry is the CIE (International Commission of Illumination) headquartered in Vienna, Austria. The CIE is a technical, scientific and cultural non-profit organization dealing with all matters of light including the development of standards and procedures of metrology in the field of light and lighting. It is based on actually 38 national committies, which cover almost the whole highly developed countries. Each major subject of interest is dedicated to the seven divisions working for the Board of Administration:

Division 1 : Vision and Color
Division 2 : Measurement of Light and Radiation
Division 3 : Interior Environment and Lighting Design
Division 4 : Lighting and Signaling for Transport
Division 5 : Exteror Lighting and other Applications
Division 6 : Photobiology and Photochemistry
Division 7 : Image Technology

Each national Committee is entitled to have a voting member in each division. Standards are published. Joint publication include ISO/CIE Standards.
To keep pace with the continuous improvement of all standards from all sources some service companies have been established, so that the actual status of the world of standards can be kept more efficiently (see chapter 8.2).
Apart from harmonization of standardization work for inspection and test methods another area of standardization focuses on quality management systems and environmental standards (see chapter 6.3). One interesting investigation is a study which demonstrates that there is virtually no reference to environmental aspects in current standards [8.3.4].
Nevertheless, the management standards developed to date are well accepted and widespread throughout the paint and coatings industry.

8.2 Actual Industrial Standards and Specifications for Coatings

The latest, most important standards and specifications of customer segments for the paint and coatings industry are hard to keep up with for each single company. This is why today the electronical updating from service companies like Beuth Verlag for standards or Information Handling Services for specifications and standards via the internet (see chapter 9.2.2) is more and more accepted and in use. The task of those companies is to keep updated with the selected standard series and provide access to actual versions by downloading or ordering for each customer. Furthermore the companies provide the latest status of specifications e.g. for the automotive industry. This service costs money, but seems to be the only and most effective way of being on top of specifications and standards throughout the world from case to case for worldwide operating paint manufacturers.

8.3 Literature

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9 Appendix

9.1 List of Physical Constants

9.1.1 Latin Symbols

A	Area, Hamaker-Constant
a	Electrodeposition Equivalent in g/C
a*	Distance on Red-Green-Axis from Zero in CIE-Lab-System
Ä	Electrodeposition Equivalent in C/cm^3
Ä’	Electrodeposition Equivalent in C/g
B	Magnetic Flux
b	Barometric Reading, Factor of Interference in Formula for Sedimentation
b*	Distance on Blue-Yellow-Axis from Zero in CIE-Lab-System
C	Throw Number, Electrical Capacity
C*	Chroma (Colorfulness) in CIE-Lab-System
C_w (Re)	Friction Factor
c	Concentration of Mass, Specific Heat, Acoustic Velocity
c_p	Specific Heat of Gases at Constant Pressure
c_v	Specific Heat of Gases at Constant Volume
c_s	Irradiance Number of Ideal Black Source
c_{gr}	Irradiance Number of Real Source
D	Diameter, Cumulating Sum, Diffusion Coefficient, Dispersity, Velocity Gradient (Shear Rate)
D_v	Hiding Power, Volume Based
D_m	Hiding Power, Mass Based
d	Diameter
d_{32}	Sauter Diameter
d’	Average Particle Size According to RRSB-Method
E	Elastic Modulus, Electric Field Strength, Indentation Coefficient, Initial Weight
E_s	Area Related Irradiance
E’	Storage Modulus
E’’	Loss Modulus
ΔE_a	Activation Energy
ΔE^*_{ab}	Color Distance in CIE-Lab-System
e	Elementary Charge
e_a	Sum of Acid Equivalences
F	Force, Faraday Constant
F_{rel}	Relative Color Strenght
F_w	Resisting Power
f	Frequency, Form Factor
G	Free Enthalpy, Shear Modulus
ΔG	Change of Free Enthalpy
g	Accelaration due to Gravity
H	Enthalpy, Adhesion Power
H_K	Hardness According to Hertz
H_V	Hardness According to Vickers

H_n	Universal Hardness According to Martens
h	Height
h*	Hue in CIE-L*C*h*-System
I	Ionic Strength, Intensity, Electrical Current Density
j	Electrical Current Density
K	Absorption Coefficient
k	Boltzmann Constant, General Constant
L	Power, Length
L*	Lightness in CIE-Lab-System
l	Length
M	Torque
$\overline{M}_n$	Number Average of Molecular Mass
$\overline{M}_w$	Mass Average of Molecular Mass
m	Mass
m_0	Sum of Mol Numbers
m	Mass Flow
$\dot{N}$	Power Dissipation
N/V	Power Dissipation Density
Ne(Re)	Newton Power Index
n	Refraction Index, Mol Number, Rotational Speed, Number,
O	Surface Area
O_m	Mass Related Surface Area
O_v	Volume Related Surface Area
Ohz	Ohnesorge Number
p	Pressure, Turn Over
Q	Electrical Charge, Thermal Energy
$\dot{Q}$	Heat Flow
$\dot{q}$	Area Related Heat Flow
R	Radius, General Gas Constant, Degree of Reflexion, Electrical Resistance
R_s	Gloss Peak
Re	Reynold Number
Re_M	Reynold Number for Stirring Processes
r	Radius
R_a	Average Roughness
R_t	Roughness
S	Entropy, Scatter Coefficient, Film Thickness
S_D	Film Thickness
s	Standard Deviation at Limited Number of Values, Distance, Wet Film Thickness
T	Temperature, Oscillation Time
Tg	Glass Temperature (= Glass Transition Temperature)
T_c	Ceiling-Temperature
ΔT	Difference of Temperatures
t	Time
$t_{\frac{1}{2}}$	Half Life
t_i	Induction Period at Electrodeposition Process
t_{rel}	Relaxation Time
t_{ret}	Retardation Time
$t_{S,N}$	Student-Factor
t_{Fg}	Flash Point, measured
t_{Fn}	Flash Point, standardized

U	Electrical Power, Inconsistency
u	Velocity
u_A	Peripheral Speed
V	Volume
V_T	Potential Surface Energy
V_A	Potential of Attraction
V_R	Potential of Repulsion
V_{Pi}	Volume of Pigments
V_{Bi}	Volume of Binder
$\dot{V}$	Volume Flow
W	Work, Probability
W_K	Adhesion Force at Häsiometer Test
W_p	Adhesion Force at Peeling Test
We	Weber Number
X,Y,Z	Standard Color Values
x,y,z	Share of Standard Color Values
$\bar{x},\bar{y},\bar{z}$	Standard Spectral Values
$\bar{x}$	Arithmetic Average
z	Valence

9.1.2 Greek Symbols

α	Contact Angle, Number of Heat Transfer, Polarizability, Correction Factor for Calculating the Hiding Power
β	Mass Transfer Number
γ	Shear Angle, Volume Dilatation Coefficient
δ	Thickness of Diffusion Layer, Loss Angle, Solubility Parameter
Δ	Difference
ε	Dielectrical Constant, Relative Irradiance Number, Relative Elongation,
ζ	Zeta-Potential (= Electrokinetical Potential)
η	Dynamic Viscosity
κ	Specific Electrical Conductivity
λ	Wavelength,
λ(Re)	Specific Proportion Factor for Pressure Drop in Pipes
μ	Dipole Moment, Poisson Number, Damping Coefficient, Average Number at Unlimited Numbers of Values
ν	Kinematic Viscosity, Frequency
θ	Required Space of N_2-Molecule at Adsorption
ρ	Density, Spezific Electrical Resistance
ρ_T	Dry Film Density
σ	Surface Tension
Σ	Sum
τ	Shear Stress
φ	Electrochemical Potential, Fluidity
φ_0	Electrochemical Normpotential
Φ	Good Factor, Magnetic Flux
ψ	Specific Surface Charge
χ	Exponent in Hückel-Function
ω	Angular Speed
Ω	Electrical Resistance

9.2 Web-Addresses of Interest for the World of Coatings

9.2.1 Organizations

The American National Standards Institute	www.ansi.org
American Society for Testing and Materials, (ASTM), West Conshohocken, PA, USA	www.astm.org
Association for UV-/EB-curing Technology, The Hague, NL	www.radtech-europe.com
Association of Paint Manufacturers of Czech Republic, Prag, CZ	www.avnh.cz
Australian Paint Manufacturers Federation (APMF), Sydney, AUS	www.apmf.asn.au
Brasilian Association of Paint Manufacturers (ABRAFATI), Sao Paulo, BR	www.abrafati.com
British Coatings Federation(BCF), Leatherhead, UK	www.coatings.org.uk
British Colour Makers Association, Shawclough Rochdale, UK	www.bcma.org.uk
Bundesanstalt für Materialprüfung, Berlin, D	www.bam.de
Canadian Paint&Coatings Association (CPCA), St.Laurant, CAN	www.cdnpaint.org
Can Manufacturers Institute (CMI), Washington, USA	www.cancentral.com
China National Coatings Industrial Association (CNCIA), Beijing, C	www.chinacoatingnet.com
Danish Color and Paint Industry, Kopenhagen, DK	www.fdlf.dk
Deutsche Forschungsgesellschaft für Oberflächenbehandlung eV (DFO), Düsseldorf, D	www.dfo-online.de
Deutsches Institut für Normung eV, Berlin, D	www.din.de
Deutsches Lackinstitut (VdL), Frankfurt, D	www.lacke-und-farben.de
European Coil Coating Association (ECCA) – Secretary, Brussels, B	www.eccacoil.com
The Electrocoat Association, Cincinnati, OH, USA	www.electrocoat.org
Environmental Protection Agency, USA	www.epa.gov
Europäische Gesellschaft für Lackiertechnik eV, Düsseldorf, D	www.egl-online.de
European Commission for Standardization, Brussels, B	www.cenorm.be
European Council of Paint, Printing Ink and Artist’s Colours Industry (CEPE), Brussels, B	www.cepe.org
European Coil Coating Association, D	www.ecca.de
European Isocyanate Producers Association, Brussels, B	www.isopa.org
European Solvents Industry Group (ESIG), Brussels, B	www.esig.org
European Union	www.europa.eu
Fachgruppe “Anstrichstoffe und Pigmente” (APi) der GDCh, Frankfurt, D	www.gdch.de/fachgrup/api.htm
Fachverband der chemischen Industrie Österreichs, Vienna, A	www.wk.or.at/fcio/

Federation of Societies for Coatings Technology (FSCT), Whitpain, PA, USA	www.coatingstech.org
Gesamtverband der Aluminiumindustrie, Düsseldorf, D	www.aluinfo.de
Industrial Association for Paint and Coatings (IVP), Brussels, B	www.fedichem.be
Indian Small Scale Paint Association, Mumbai, IN	www.isspa.org
International Commission of Illumination, Vienna, A	www.cie.co.at
International Paint&Printing Ink Council (IPPIC), Washington, USA	www.ippic.org
International Organisation for Standardization, USA/CH	www.iso.org
Inter-Society Color Council (ISCC), Reston, VA, USA	www.iscc.org
Italian National Associations of Industrial Coaters (ANVER), Vimercate, I	www.anver.org
Italienischer Verband für Lack-, Klebe- und Dichtmaterialien (AVISA), Milano, I	www.federchimica.it
Japan Paint Manufacturers Association (JPMA), Tokyo, JP	www.toryo.org.jp
The Mexican Paint and Printing Ink Manufacturers Association (ANAFAPYT), Mexico City, MEX	www.anafapytmexico.org.mx
National Association of Corrosion Engineers (NACE), Houston, TX, USA	www.nace.org
National Association of Architectural Metal Manufacturers (NAAMM), Chicago, IL, USA	www.naamm.org
National Coil Coating Association, Chicago, IL, USA	www.coilcoating.org
The National Institute of Standards and Technology Gaithersburg, MD, USA	www.nist.gov
National Paint and Coatings Association(NPCA), Washington, USA	www.paint.org
The Oil&Colour Chemists Association, Wembley, UK	www.occa.org.uk
Optical Society of America, Washington, USA	www.osa.org
Paint Research Association, Teddington (London), UK	www.pra.org.uk
The Powder Coatings Institute, Alexandria, VA, USA	www.powdercoating.org
Radtech International North America, Chevy Chase, MD, USA	www.radtech.org
Schwedische Vereinigung der Farbenhersteller (SVEFF), Stockholm, SE	www.sveff.se
Stahlinformationszentrum, Düsseldorf, D	www.stahl-info.de
The Society for Protective Coatings (SSPC), Pittsburgh, PA, USA	www.sspc.org
Society of Automotive Engineers, Warrendale, PA, USA	www.sae.org
Society of Dyers and Colourists and American Assoc. of Textile Chemist and Colourists, USA	www.colour-index.org
Spanish Association of Manufacturers of Paints and Printing Inks (ASEFAPI), Madrid, E and Barcelona, E	www.asefapi.es
Surface Coatings Association Australia, Victoria, AUS	www.scaa.asn.au
Surface Coatings Association of New Zealand, Inc. (SCANZ), Auckland, NZ	www.scanz.org.nz
Surface Engineering Assoc., Birmingham, UK	www.sea.org.uk

Verband der deutschen Lackindustrie, D	www.lackverband.de
Verband der griechischen Lack-, Beschichtungsstoff- und Druckfarbenhersteller, Athen, GR	
Verband der Industrie von Lacken, Farben und Klebern (FIPEC), Paris, F	www.fipec.org
Verband der Ingenieure des Lack- und Farbenfaches e.V., Düsseldorf, D	www.vilf.de
Verband der Mineralfarbenindustrie (VdMi), Frankfurt, D	www.vdmi.de
Verband Schweizerischer Lack- und Farbenfabrikanten (VSLF), Zürich	www.vslf.ch
Vereniging van Verf- en Drukinktfabrikanten (VVVF), Leiden, NL	www.vvvf.nl

9.2.2 Publishing/General Informations

Automobil Produktion, mi-Verlag, Augsburg, D	www.mi-verlag.de
Beuth Verlag (International Norms), Berlin, D	www.mybeuth.de www2.beuth.de
Chemical Week Associates, New York, USA	www.modernpaintandcoatings.com
Coatings World, Ramsey, NJ, USA	www.coatingsworld.com
Marcel Dekker, Inc., New York, USA	www.dekker.com
Ecomed Verlag, Landsberg, D	www.ecomed.de
Elsevier Science Publications, Orlando, FL, USA	www.elsevier.com
Progress in Organic Coatings/Metal Finishing	www.metalfinishing.com
Emerald, West Yorkshire, UK	www.emeraldinsight.com
Expert Verlag, Renningen, D	www.expertverlag.de
Fachinformationszentrum Technik, D	www.fiz-technik.de
Finishing Industry, Brick, NJ, USA	www.finishing.com
Carl Hanser Verlag, München, D	www.hanser.de
S. Hirzel Verlag, Stuttgart, D	www.hirzel.de
Information Handling Services, Englewood, CO, USA	www.ihs.com
Informations about German Paint Manufacturers and Suppliers, D	www.chemcompass.de
Jedermann Verlag, Heidelberg, D	www.jedermann.de
Journal of Coatings Technology, FSCT, Whitpain,PA,USA	www.coatingstech.org
Paintsquare, Information Platform of JPCL and PCE, Pittsburgh, PA, USA	www.protectivecoatings.com
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California Polytec State Univeristy, San Luis Obispo, CA, USA	www.calpoly.edu
Coatings Research Institute (CoRI), Limelette, B	www.cori-coatings.be
Dutch Organization for Applied Research, Chemistry, Appeldorn, NL	www.chemie.tno.nl
Eastern Michigan University, Coatings Research Institute, Ypsilanti, MI, USA	www.emich.edu
European Center for Coatings and Surface Technology, Enschede, NL	www.eccs-online.org
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Forschungsinstitut für Pigmente und Lacke, Uni Stuttgart, D	www.fpl.uni-stuttgart.de
Fraunhofer Institut für Produktionstechnik und Automatisierung, Stuttgart, D	www.ipa.de
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Institute of Materials Science, New Paltz, NY, USA	www.ims-np.org
Institut für Holztechnologie, Dresden, D	www.ihd-dresden.de
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Institut für Kunststoffprüfung und Kunststoffkunde, Uni Stuttgart, D	www.ikp.uni-stuttgart.de
Institut für Lacke und Farben, Magdeburg, D	www.lackinstitut-magdeburg.de
Institut für Lackprüfung, W.Keiner GmbH, D	www.institut-lackpruefung.de
Institut für Polymerforschung, Dresden, D	www.ipfdd.de
Laboratoire de Materiaux Macromoleculaires, Villerbanne, F (University Savoie)	www.univ-savoie.fr
North Dakota State University, Fargo, ND, USA	www.ndsu.nodak.edu
Paint Quality Institute, UK	www.paintquality.co.uk
Paint and Coatings Resource Centre (EPA), USA	www.paintcenter.org
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9.3 Acronyms/Abbreviations

AAS	Atomic Absorption Spectrometry (Analytic)
ABS	acrylonitrile-butadiene-styrene copolymer (Thermoplastic)
ACS	American Chemical Society
ADR	fr.: Accord Europeen relatif au transport international des marchandise dangereuse par route (European Directive)
AED	Anodic Electrodeposition (Coating Process)
AFM	Atomic Force Microscopy (Analytic)
ANSI	The American National Standards Institute (US Organization)
AQMB	Autospect Quality Measurement System (Surface Measurement)
ASTM	American Society for Testing and Materials (US Organization)
AV	Acid Value (Analytic)
BAT	Biologische Arbeitsplatztoleranz (German Law)
BASt	Bundesanstalt für Straßenwesen (German Authority)
BC	Base Coat (Colored Layer before Clear Coat)
BET	Brunauer, Emmet and Teller (Analytical Method to Determine Surface Areas of Particles)
BetrSichV	Betriebssicherheitsverordnung (German Law)
BImSchG	Bundesimmissionsschutzgesetz (German Law)
BIP	= GDP
BMBF	Bundesministerium für Bildung und Forschung (German Authority)
BMC	Blow Molding Compound (= Manufacturing of Plastic Parts by Blow Process)

BOD	Biological Oxygen Demand (Waste Water)
BONS	β-oxi-naphtoic acid (German : β-Oxi-Naphtoesaure)
BSB	= BOD
BSC	Balanced Score Card (Company Guidance)
BTLV	Biological Threshold Limit Value (Health & Safety)
CAA	Clean Air Act (USA Law)
CAB	cellulose acetobutyrat (Additive)
CAS	Chemical Abstract Service
CASS	Copper Accelerated Acid Salt Spray (Corrosion Testing)
CCD	charge-coupled-device
CD	Compact Discs
CED	Cathodic Electro Deposition (Coating Process)
CEN	Comite Europeen de Normalisation, Brüssel (= European committee for Standardization)
Cepe	Conseil Europeen de l'Industrie des Peintures, des Encres, d'Imprimerie et des Couleurs d'art (Union of European Paint Associations)
CIE	Comite Internationale d'Eclairage (=International Committee of Illumination)
CMC	Critical Micelle Concentration
CMI	chloromethyl isothiazolinone (Preservative)
cmr-substances	Cancerogenic, Mutagenic, Reproduction-toxic
CNSL	Cashew Nut Shell Liquid (Natural Raw Material)
COD	Chemical Oxygen Demand (Waste Water)
CPO	Chlorinated Polyolefines
CPU	Cost per Unit
CPVC	Critical Pigment Volume Concentration
CPWC	Critical Pigment Weight Concentration
CVD	Chemical Vapor Deposition (Surface Treatment)
CWA	Clean Water Act (USA Law)
DABCO	diazabicyclooctane (Catalyst)
DBTL	dibutyl tin dilaurate (Catalyst)
DETA	diethylenetriamine
DFG	Deutsche Forschungsgemeinschaft (German Organization for Research Funding)
DFO	Deutsche Forschungsgesellschaft für Oberflächenbehandlung eV, Düsseldorf (German Organization for Surface Research Funding)
DGSA	Dangerous Goods Safety Advisor (European Law)
DH	Dispergierhärte (Testing)
DIN	Deutsches Institut für Normung eV, Berlin (German Institute for Standardization)
DIY	Do it Yourself (Market Section)
DLVO	Derjaguin, Landau, Verwey, Overbeek (Theory of Stabilization of Dispersions)
DLS	Dynamic Light Scattering (Analytic)
DOA	dioctyl adipate (Platicizer)
DOI	Distinctness of Image
DOP	dioctyl phthalate (Plasticizer)
DPA	diphenolic acid
DPGDA	dipropyleneglykol diacrylate
DPM	dipropyleneglykol monomethylether
DPP	diketopyrrolopyrrole (Pigment)
DTA	Differantial Thermoanalysis (Analytic)
DSC	Differential Scanning Calorimetry (Analytic)

EB	Electron Beam (Radiation Curing)
ECCA	European Coil Coating Association
ECCS	European Center for Coatings and Surface Technology (Institute)
ECJ	European Coatings Journal (Paint Journal)
ED	Electrodeposition
EDA	ethylenediamine
EDP	Electrodeposition (Coating Process)
EDX	Energy Dispersive X-Ray Analysis (= SEM)
EG	Electro Galvanized (Electrolytically Deposited Zn-Layer on Steel)
EMB	Electromagnetic Brushing Process (Powder Application)
EMMA	Equatorial Mount with Mirrors for Acceleration (Testing)
EMS	Environmental Management System
EN	European Norm
EP	Epoxi or Epoxy Resin
EPA	Environmental Protection Agency (US-Authority)
EPC	Electro Powder Coating
ESCA	Electron Spectroscopy for Chemical Analysis (Analytic)
ESH	= EB Curing
ESTA	Electrostatic Application
EU	European Union
EX-RL	Explosionschutzrichtlinie (German Directive)
FDA	Federal Drug Administration (US-Authority)
FID	Flame Ionization Detector (Analytic)
F+L	Farbe und Lack (Paint Journal)
Flip-Flop	Difference in Lightness of coated surfaces at Various Angles of Spectators
FROK	First Run oK = Number for Efficiency of Coating Processes
FSCT	Federation of Societies for Coating Technology (US)
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography (Analytic)
GDP	Gross Domestic Product
GefStoffV	Gefahrstoffverordnung (Hazardous Substances Ordinance, German Law)
GGVSE	Gefahrgutverordnung Straße/Schiene (Ordinance for the Transportation of Dangerous Goods by Rooad/Rail, German Law)
GGVSee	Gefahrgutverordnung See (Ordinance for the Transportation of Dangerous Goods by Sea, German Law)
GMA	gylcidylmethacryl acrylate
GPC	Gel Permeation Chromatography (Analytic)
GTP	Group Transfer Polymerization
HALS	Hindered Amine Light Stabilizer (Additive)
HBB	Heated Black Box (Testing)
HDDA	hexane dioldiacrylate
HDE	Hochdruckentlackung (Paint Stripping at High Pressures)
HDG	Hot Dip Galvanized (Depositing Zinc-Layer by Dipping Process)
HDI	hexamethylene diisocyanate (Crosslinker)
HLB	Hydrophilic-Lipophilic Balance
HMDI	hydrated diphenylmethane diisocyanat (Crosslinker)
HMMM	hexamethoxymethyl melamine (Crosslinker)
HPLC	High Performance Liquid Chromatography (Analytic)
HS	High Solid
HVLP	High Volume Low Pressure (Spray Gun)

IEEE	Institute of Electrical and Electronic Engineers (USA)
ILB	Industrie-Lackierbetrieb (Paint Journal)
IMC	Inmoldcoating (Coating Process)
IPDI	isophorone diisocyanate (Crosslinker)
IR	Infrared
IRASER	Infrared-Laser
ISO	International Organization for Standardization (Located in USA and Switzerland)
JCT	Journal of Coatings Technology (Paint Journal)
JOCCA	Journal of Oil&Colour Association (Paint Journal)
JOT	Journal für Oberflächentechnik (Paint Journal)
JPCL	Journal of Protectic Coatings&Linings (Paint Journal)
JV	Iodine Value (Analytic)
1-K-	1-component
2-K-	2-component
KNV	katalytische Nachverbrennung (Catalytic Incineration)
KrW-/AbfG	Kreislaufwirtschaft- und Abfallgesetz (German Law)
KPI	Key Performance Indicator
LAMMA	Laser Microprobe Mass Analyzer (Analytic)
LC	Liquid Crystal Lethal Concentration (Health & Safety)
LCA	Life Cycle Analysis
LCD	Liquid Crystal Display
LCE	Life Cycle Engineering
LD	Lethal Dose (Toxikology)
LEPC	Low Emission Paint Consortium (Group out of DaimlerChrysler, Ford and GM for Testing Low Solvent Emitting Paints, Detroit)
MAC	Maximum Admissible Concentration (Health & Safety)
MAK	= MAC
MDF	Medium Density Fiberboard (Wood, Furniture)
MDI	diphenylmethane diisocyanate (Crosslinker)
MEQ	Milliequivalent (Analytic)
MF	Melamine-Formaldehyde-Resin (Film Forming Agent)
MFT	Minimum Film Forming Temperature
MO	Metalloberfläche (Paint Journal)
MS	Mass Spectrometry (Analytic)
MSDS	Material Safety Data Sheet (German : Sicherheitsdatenblatt)
NAB	Normenausschuss für Beschichtungsstoffe und Beschichtungen (DIN-Subgroup for Coatings)
NAD	Non Aqueous Dispersions
NAGUS	Normenausschuss für Grundlagen des Umweltschutzes (DIN-Subgroup for Environmental Protection)
NAFTA	North American Free Trade Agreement (Canada,USA,Mexico)
NCO	Isocyanate-
NEPA	National Environmental Policy Act (USA Law)
NIR	Near Infrared (Segment of Wavelength Spectrum)
NIST	The National Institute of Standards and Technology (US Governmental Agency)
NMP	N-methyl-pyrrolidone Normenausschuss für Materialprüfung (DIN-Subgroup for Material Testing)
NMR	Nuclear Magnetic Resonance (Analytic)

NPCA	National Paint and Coatings Association (USA)
NPF	Normenausschuss für Pigmente und Füllstoffe (DIN-Subgroup for Pigments and Extenders)
NPG	neopentylglykol
NPS	Normenausschuss für persönliche Schutzausrüstung (DIN-Subgroup for Personal Protection Equipment)
NQS	Normenausschuss für Qualitätsmanagement, Statistik und Zertifizierungsfragen (DIN-Subgroup for Quality Management, Statistics and Certifications)
NV	Non-Volatile (Solid Content)
OEM	Original Equipment Manufacturer
OEL	Occupational Exposure Limit (US)
OHV	Hydroxyl-Value (Analytic)
Organosol	see : Plastisol
OSHA	Occupational Safety and Health Act (USA Law)
PA	polyamide (thermoplastic Material), phthalic acid
PBT	polybutylene terephtalat (Thermoplastic Material)
PC	polycarbonate (Thermoplastic Material)
PCE	Powder Coating Europe
PDA	Phase Doppler Anemometry (Analytic)
PE	Polyester (Resin,Plastic)
PF	Phenol-Formaldehyde-Resin (Film Forming Agent)
pH	Negative Dekadic Logarithm of Hydrogen Ion Concentration
PIG	Paint Inspection Gauge (Measurement of Surfaces)
PM	methoxy propanol
PMMA	polymethyl methacrylate (Thermoplastic Material)
Plastisol	Dispersion of mostly PVC-Polymer in Plastisizer (eventually with Hydrocarbons as Diluents = Organosol)
POP	Persistant Organic Pollutant
Potlife	Shelf Life for Workability of 2K-Coatings after Mixing Both Components
PP	polypropylene (Thermoplatic Material)
PPCJ	Polymers, Paint & Colour Journal (Paint Journal)
ppb	parts per billion
ppm	parts per million
PPO	polypropylene oxide (Plastic)
PRA	Paint Research Organization (UK-organization)
PS	polystyrene (Plastic)
PSA	Phthalsäureanhydrid = phthalic acid anhydride, Peugeot SA
PTB	Physikalisch-technische Bundesanstalt, Braunschweig (German Authority)
PTFE	polytetrafluorethylene (Raw Material)
PUR	polyurethane
PVC	polyvinylchloride (PLastic) Pigment Volume Concentration
PVDF	polyvinylidene fluorid (Plastic)
QELS	Quasielastic Light Scattering (Analytic)
QMS	Quality Management Standards
RAL	Reichsausschuss für Lieferbedingungen (German Color Standards)
RBN	Rub-out-Number (Measurement Method)
REM	Rasterelektronenmikroskopie = SEM (Analytic)

R&D	Research and Development
RIM	Reaction Injection Molding (Manufacturing Process for Plastic Parts)
RRIM	Reinforced Reaction Injection Molding (Manufacturing Process for Plastic Parts)
SAN	styrene-acrylnitrile (Plastic)
SAM	Sustainable Active Microbiocidal Polymers (Biocide) Self Assembling Molecules
SB	styrene-butadiene (Plastic)
SD	Schichtdicke (Film Thickness)
SDB	= MSDS
SEA	South East Asia (without Japan)
SEM	Scanning Electron Microscope (Analytic)
SIMS	Secondary Ion Mass Spectroscopy (Analytic)
SMC	Sheet Molding Compound (Manufacturing Process of Plastic Parts)
SMP	Solvent Management Plan (EU Regulation)
SOP	Standard of Operation (QM)
Spot Repair	Small, local Repair of Defects of Coatings by Hand Operations
SV	Saponification Value (Analytic)
SZ	= AV
TA Luft	Technische Regeln zur Reinhaltung der Luft (German Directive for Air Emission)
TBT	tributyl tinoxide (Biocide)
TDI	toluylene diisocanate
TE	Thermische Entlackung (Thermal Paint Stripping)
TETA	triethylenetetramine
Tg	Glass Transition Temperature (Material Characteristics)
TG	Thermogravimetry (Analytic)
TGIC	triglycidyl isocyanurate
TMP	trimethylolpropane
TNO	dutch : Toegepast Natuurwetenschappelijk Onderzoek (Institute)
TNV	Thermische Nachverbrennung (Thermal Afterburning)
TOF-SIMS	Time-of-flight Secondary Ion Mass Spectroscopy (Analytic)
TPGDA	tripropylene glykoldiacrylate
TPM	Technische Bestimmungen für die Prüfung von Markierungsstoffen... (German Law)
TPO	2.4.6-trimethylbenzoyl phosphine oxid Thermoplastic Polyolefines
TQM	Total Quality Management
TRbF	Technische Regeln für brennbare Flüssigkeiten (German Law)
TRGS	Technische Regeln zur Gefahrstoffverordnung (German Law)
TRK	Technische Richtlinienkonzentration (Technical Directive on Hazardous Substances Concentration, German law)
TSA	trimellitic anhydride Thermosetting Acrylics
TSCA	Toxic Substances Control Act (USA)
TÜV	Technischer Überwachungsverein (German Control Office)
UBS	Underbody Protection
UF	Ultrafiltrate(ion) Urea-Formaldehyde-Resin (Film Forming Agent)
UMS	Umweltmanagementsystem (Management System for Environmental Protection)
UP	Unsaturated Polyester (Resin, Plastic)
US	Ultra Sound

USCAR	United States Council for Automotive Research (Governmental Funded)
UV	Ultraviolet
UVA	UV-Radiation with Wavelength of 360 – 400 nm
UVV	Unfallverhütungsvorschriften (German Directives for Prevention of Incidents by Berufsgenossenschaften)
VbF	Verordnung über brennbare Flüssigkeiten (Old German Law)
VC	vinylchloride
VCI	Verband der chemischen Industrie Deutschland, Frankfurt (Association of Chemical Industry in Germany)
VDA	Verband der deutschen Automobilindustrie, Frankfurt (Association of the German Automotive Industry)
VdL	Verband der Deutschen Lackindustrie eV, Frankfurt (Association of the German Paint and Coatings Industry)
Vertak	Vertical Dipping Process
VOC	Volatile Organic Compounds
WGK	German : Wassergefährdungsklasse (Water Endangering Class, German Law)
WHG	Wasserhaushaltsgesetz (Water Resources Act, German Law)
WOM	WeatherOMeter (Equipment for Short Term Weather Tests)
XDI	xylilene diisocyanate
ZWM	Zentrifugalwirbelbettmühle (Centrifugal Fluidized Bed Mill, Manufacturing)

9.4 Picture Sources

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