Poucher's Perfumes, Cosmetics and Soaps

10th Edition

Edited by

Hilda Butler
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KLUWER ACADEMIC PUBLISHERS
DORDRECHT / BOSTON / LONDON

Library of Congress Cataloging-in-Publication Data is available.

ISBN 0-7514-0479-9

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Sold and distributed in North, Central and South America
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 332, 3300 AH Dordrecht, The Netherlands.

Publisher's Note: This edition of *Poucher's Perfumes, Cosmetics and Soaps* is the tenth edition of what was formerly Volume 3 of the ninth edition of *Poucher's Perfumes, Cosmetics and Soaps* (ISBN 0-412-27360-8).

Printed on acid-free paper

First edition 1923
Ninth edition 1993 published by Chapman & Hall
Tenth Edition

Printed and bound in Great Britain by Antony Rowe Limited.

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Preface to the 9th Edition

Cosmetic Science has developed greatly since the publication of the 8th edition of this textbook in 1974. Although the first part of this volume still consists of chapters about product preparations in alphabetical order, each product category has been revised and updated by a specialist. An outline of the biology, structure and function of skin, hair, teeth and nails and the reasons for the need for cosmetics are given in those dealing with the relevant preparations. Throughout, the word Cosmetics includes toiletries and thus all products which protect, cleanse, adorn, and perfume the human body, and combat body odour and perspiration.

The 'f' spelling for the element 'sulfur' and its derivatives has been used following the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) and the decision taken by the Royal Society of Chemistry (RSC) and the British Standards Institute (BSI) to use 'f' instead of 'ph' in all their publications. This stems from the derivation of the use of the 'f' from Latin and its use in England until the 15th century.

Deionized water has been used in the formulations because many manufacturers standardize the water supply to the factory by removing cations and anions by exchange resin treatment. This lessens the variation in ionic content which can occur in the mains water. A typical design for a water supply of constant quality in factories, which can be tailored to fit local conditions, was described for the Max Factor Company by N. Wheeler and J. Kilsheimer in the Water Documentary issue of *Cosmetic and Toiletries* in 1983. The properties of the water supply and its treatment are also discussed elsewhere, especially in Chapter 15, page 403 and Chapter 21, page 595.

In most formulae the quantities for preservatives and perfume are indicated by 'q.s.'– *quantum sufficit*. It would be unwise to be more exact when the actual quantities depend on the results of research on each formulation where differing raw materials, methods and conditions of production will occur. In some formulae the main ingredients already add up to 100 and the preservatives and perfume appear as extras – q.s. When these two are determined as a result of tests and the two quantities are significant then an equivalent amount can be deducted from the largest ingredient present to maintain the total at 100.

These tests at the development stage will be described by the chapters in the second part and give an idea of the research needed to produce a safe, stable and successful product which is acceptable to Governments and Consumers alike. This would have been appreciated by Poucher who at the end of the preface to the 6th edition, advised: 'keep the formulations simple' and 'give the experiments long shelf tests, with frequent observations before finally approving a formula'.

In a previous volume Poucher included a historical sketch. This has been retained and brought up to date in the present edition, followed by a chapter of advice on perfuming products, and finally one on the psychology of fragrance. My thanks are due to the authors who have spent so much time and trouble in providing their contributions; and to all others who have helped to make this book possible.

Hilda Butler, Editor
1992

Foreword to the 9th Edition

There can be no doubt as to the importance of cosmetics and cosmetic science – this edition of *Poucher's Perfumes, Cosmetics and Soaps* is at once powerful evidence of the importance of its subject and of the detailed study of its applications. Cosmetics are as old as mankind itself. Even in the most primitive societies the use of deodorants and decorative cosmetics was universal, and the same basic objectives remain unchanged today although the means employed to further them are now far more complex and are scientifically based and controlled.

The importance of the subject fully warrants the increasing attention being paid to it in recent years and this new edition of Poucher illustrates both the advances made to date and direction of further progress. Mrs Hilda Butler is to be congratulated on her provision of a volume both practical and fascinating as well as comprehensive and I commend it not just to the practitioners of cosmetic science but to all chemists interested in the practical development of their science.

Lord Todd OM, FRS
Cambridge, 1992

Editor's note: Lord Todd retired as patron of the Society of Cosmetic Scientists in 1996 after giving his support for a number of years and died on January 10th, 1997.

Foreword 2000

Having been asked by Hilda Butler to write a forward to this tenth edition of my late father's *Perfumes, Cosmetics and Soaps,* I thought it would be instructive to re-examine my copy of the first edition of this work published in 1923 by Chapman and Hall entitled *Perfumes and Cosmetics.*

I was surprised to find that it contained seventeen advertisements, presumably to lower the cost of production, from suppliers of raw materials, machinery and a journal, *Perfumery & Essential Oil Record* (well known in the industry then and for many years after).

Although, in Poucher, the first part, a dictionary of raw materials, contained cosmetic as well as perfume materials (150 pages), the section (part 3) on cosmetics products with descriptions and formulae occupied 120 pages, while in the middle section 160 were devoted to monographs on essential oils, methods of extracting them and formulae for fragrances using them. A review in the *Chemist and Druggist* stated: 'The book is a good one. The matter is sound and practical, the get-up and illustrations are excellent, and it is quite free from gross errors, a thing that can hardly be said of nearly every book on perfumery that has appeared in late years. We cordially recommend it to all interested in practical perfumery.'

One of my late father's aims was to make cosmetics less costly so that they would be available to women in all walks of life, whereas at the time they were on the whole too expensive for all but the wealthier members in society.

It might surprise present readers that he was the author of another book on Cosmetics, titled *Eve's Beauty Secrets,* published in 1926 by Chapman and Hall, in which he explains in non-technical language what cosmetic products are suitable for various skin types and how and when women should use them to enhance their appearance. In a review that appeared in the *American Perfumer* I find the following extract very revealing: 'Copies of this little book should be in the hands of those who at present are seeking to restrict and hamper the toilet preparations industry by the passage of state legislation. A copy on file in the New York Department of Health for the use of certain officials in their leisure moments would do much to keep them out of mischief'.

I spent nearly forty years in the industry and, though not a perfumer myself, was taught by perfumers to identify the odour of essential oils and other raw materials. Neither am I a cosmetic chemist, and therefore the technicalities of

this branch of science is a closed book to me. However I do realise that the number of new raw materials coming on to the market and the global expansion of the industry has given rise, of necessity, to the increasing complexity of today's regulations on safety, quality etc., which means that it is imperative for the information in this treatise to be as up-to date as possible, and undoubtedly Mrs Butler has seen that it has been revised to meet this challenge.

I commend this new edition to all cosmetic chemists and others who are interested in the art and science of cosmetics.

John Poucher
Cockermouth, Cumbria
January, 2000

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Hilda Butler

INTRODUCTION

> *A Cosmetic: Any substance or preparation intended to be placed in contact with the various parts of the human body (epidermis, hair system, nails, lips, and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view to exclusively or mainly to cleaning them, perfuming them, or changing their appearances and/or correcting body odours and/or protecting them or keeping them in good condition.*
> (Definition of a Cosmetic, 6th Amendment (1993), Article 7a, *EU Cosmetic Directory*)

The legal regulations cover all the products named in this book whether classed as toiletries or cosmetics.

The reason for a new edition of Poucher's volume on cosmetics is that during the years that have intervened since the last one there have been important developments, not only in the cosmetic industry but in cosmetic science, which cover the research in maintaining standards of quality in the development and regulation of the marketing of safe, stable products which the consumer can use with confidence.

Young chemists using this new volume and benefiting from the information on cosmetic science and facts about the industrial side of marketing cosmetics must wonder who the writer was whose opus is being revised and enlarged for the tenth time.

Well, he was a man of great character with many interests which he followed with great energy. He was born in Horncastle in 1891 and named William Arthur Poucher, but was known to family and friends as Walter (he preferred it that way). He went to the local primary and grammar schools here. He was

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 3–11

apprenticed to a pharmacy, Carltons, then attended the College of the Pharmaceutical Society in Bath where he obtained his PhC (Minor in 1912 and Major in 1913), winning the Bronze Medal in 1914. He studied for a time at Charing Cross Hospital with a view to a career in medicine, but was persuaded to join the Royal Army Medical Corps. He was commissioned in 1915 and promoted to Captain in 1918. He served in France mainly with the 41st Casualty Clearing Station and was demobbed in 1919 as Captain and Quartermaster.

After the war as a Vice-president of the League of Ex-service Pharmacists, and at the request of the Council he visited branches round the country to arouse public opinion regarding the state of the Army Pharmaceutical Service. He joined the United Chemists Association Ltd and became their Works Manager and Chief Chemist. On leaving UCAL he worked as an independent consultant to the Perfumery and Cosmetic Industry. He bought the soapmakers, R.F. Wright, which he later sold, and became Chief Perfumer of Yardley. He remained with them for 30 years until his retirement at 65. In his later years with this company his unique contract with Yardley allowed him to work for them for six months leaving him to follow his other pursuits for the rest of the year. His major creation for them was his perfume 'Bond Street'.

1923: FIRST EDITION: PERFUMES AND COSMETICS

In the 1920s he believed that 'it was unfair that perfumes were only available to Royalty, actresses and prostitutes' and as a consultant he was able to introduce inexpensive perfumes that could be obtained by office girls and shop girls. He also created new developments for perfuming cosmetic products.

Cosmetic chemistry was closely allied in those days to pharmacy, and specialist books on cosmetics were not printed. His experience and aims enabled him to write and have published in 1923 the first edition of this book entitled *Perfumes and Cosmetics, with especial reference to Synthetics*; this was contained in one volume. It was only in later editions that *Soap* was added to the title, and later editions expanded to form three volumes. The reference to synthetic aromatic materials is interesting because in the intervening three-quarters of a century they have become exceedingly numerous with many more suppliers marketing them. The cost of collecting and processing the natural extracts of oils from natural flower leaf and root oils rose considerably as higher wages were demanded and obtained under trade union influence, through the decades.

In the 19th century perfumery was considered to be an art, totally; but in the preface to the work Poucher opens with the observation that 'The study of perfumes has a fascination unsurpassed by any other branch of chemistry. The researches of many distinguished scientists have gradually raised it from one of the minor arts to almost the level of a science.'

The analysis, isolation and identification of the component parts of the natural oils evolved and pure synthetic materials were made – some absolutely identical

in chemical composition to the natural isolates: the 'menthol molecule' is one. The result is a product which is 100% pure and exactly reproducible for each delivery made to the buyer. Unfortunately today the modern consumer, having an inordinate fear of anything 'chemical', demands natural oils, unaware that everything is 'chemical' and the application of science can offer many more guarantees of purity and safety for simple synthetics.

Still in 1923, Poucher goes on to say that 'Synthesis as a natural sequence follows analysis and while the synthetics may not exactly reproduce the fragrance of the natural flower they certainly attain a close approximation. Furthermore the wide range of synthetic chemicals enables the perfumer to create new odours.'

The volume was divided into three parts, each of which became a separate volume in later editions. The first part contained a 'Dictionary of Raw Materials and Miscellaneous Bodies, including pigments and dyestuffs of interest to the chemist–perfumer'. In the preface Walter considered it essential that the perfumer should know as much as possible about the raw materials he was using, and stressed that he had included the more important of them with their varieties, sources and properties, and mentioned standard works of reference for more detailed chemistry or analysis. He included in some cases formulae to illustrate their use. For cyclamen he included one giving a good imitation of the flower perfume.

There are several black-and-white photographs showing the cultivation of some of the aromatic plants including one of rosemary in England at Long Melford and several of clary sage, *Salvia sclarea*, which at that time was an indispensable ingredient of 'ambers, chypre, carnation, trèfle, foin coupé and orchidée'.

Part II is on Perfumes, and in spite of his interest in synthetics is devoted to the production of natural perfumes. There are a number of photographs showing the apparatus used to extract the oils and the storage vats in the factory. The labour intensity of some of the operations, especially for Enfleurage, was considerable. For jasmine, for instance, the petals placed on the fat to absorb the essential oil were not only placed on by hand but also lifted off in the same way after absorption. The marks made by the girls' fingers when lifting the petals off spoilt the surface of the grease and made it uneven for the next layer of flower petals. The Lautier Fils company solved this problem by using a machine with a high-speed revolving brush to remove the petals which fell to the floor as rubbish. There is photograph of such a machine with girls operating it. There are many glossy photographs throughout the book.

At the beginning of Part III on cosmetics Poucher quotes an American, Lilian H. Foster of New York (*The American Perfumer*, October 1922) as follows:

> Instead of propagating wallflowers the rouge pot has nourished the roots of many a family tree, for man has oft and anon been beguiled into matrimony by a pink cheek, and he doesn't really care whether it's the result of wind and weather or of a laboratory so long as it pleases him.

> As it serves as a worthy commodity of commerce and as an adjunct to beauty, a double function combining the useful and the ornamental, should not the make-up box receive its due and be accorded recognition as a valued member of society?

The section is quite small in comparison with today's volume but shows quite clearly those products used by men and women in the early years just after the First World War. There are typical products of the period in chapters in alphabetical order, but most of the groups appearing today do not occur; for instance there are no antiperspirants. Toilet waters had appeared in 'Perfumes' in Part II – they were not in those days recognized as deodorants.

The formulae themselves are extremely interesting. For instance bath products start with bath crystals formed from sodium carbonate and then a formula using borax, and their production, tinting and perfuming are described. These are followed by bath tablets and powders and bath fluids. Bath potpourri and water softeners finish the chapter.

There was a chapter on hair preparations which included brilliantines, pomades, lotions, tonics, hair-curling applications, hair restorers, shampoos and henna. The shampoos, except for the dry shampoos, are all based on soap, and formulated using soap powder or made *in situ* from alkalis and natural oils. The following appears: 'Cocoa-nut oil Shampoos frequently known as Emulsified, are made from saponifying *odourless* [sic] Cochin Oil with potash.' But since the commercial values of potash (x) varied considerably from 78% to 83%, Poucher goes on to give a numerical formula for calculating the way to arrive at the amount (y) needed to neutralize the oil. He describes how the potash should be

> 'dissolved in a 1000 grams of water heated to 75°C and added to the oil at the same temperature. The reaction can be controlled by using phenolphthalein as an indicator – if the liquid remains *white* further additions of alkali are necessary, whereas when it turns red more oil is necessary.'
>
> The formula now reads:

Cocoa-nut Oil	1000 grams
Potassium hydroxide	y grams
Distilled water	1000 c.c.
Potassium carbonate	30 grams
Distilled water to produce	5000 c.c.

> The liquid soap is left to deposit and the clear solution decanted as required.

There were no named 'detergents' to use to make the later so-called soapless shampoos. The same can be said for emulsifiers, although the physical action of 'emulsification' is recognized when borax is added to the beeswax/mineral oil cold cream described in the skin preparations chapter.

There was a chapter on lip salves and rouge sticks, and a separate one for theatrical make-up. It was some years before make-up was to be used by most women – developed commercially from the theatrical products and really popularized by the movie stars; but manicure preparations were included. The most amazing inclusion is a whole chapter on smelling salts! Face powders of different colours were included in toilet powders. Interestingly compact powders were already *in vogue* and information is given on manufacture by hand and/or machinery, and nursery powders are also included.

The book was a great success in its day and in 1925 the second edition was printed with a large expansion of Part I. To keep pace with the increasing size of the industry and use of cosmetics and perfumes generally by the public, subsequent editions appeared in 1928, 1930, 1936, 1942, reprinted in 1950, 1959, 1974, and again reprinted in 1976, 1979, and 1984 with an updated revised edition for Volumes 1 and 3, the 9th in 1993, and now the 10th. Poucher wrote them all until 1974 when he still wrote Volume 2 on perfumes, but Volumes 1 and 3 were revised by G.M. Howard.

I came to industry straight from college, having a chemistry degree with physics as subsidiary, and I used the 5th edition when a separate volume was first issued for cosmetics. I was totally ignorant of the knowledge needed for the specialized subject and found the volumes a fountain of information for formulation of the various products I was asked to develop. During the Second World War, when raw materials were in short supply or often non-existent, replacement formulations had to be manufactured on the spot. Poucher was invaluable. After the war when I changed jobs I had to leave the books behind, but I made sure that I replaced them – this time it was the 6th edition published in 1942 and reprinted in 1950.

In the preface Poucher again mentions the huge increase in new substances used by manufacturers, and enumerates the new finished products which have had to be added, i.e. bath oils, brilliantine creams (Beecham's hair cream for men was selling all over the world), hair lacquers, greaseless hair creams (gums were used: gum tragacanth, sodium alginate), a new type of hair dye, lipstick colours, mascara, eye lotions, skin food, deodorant sticks, complexion milk and powder sticks.

Poucher also says:

> I cannot impress on chemists too strongly the importance of *simplicity of formulation* in their experiments. Almost always a few well-chosen raw materials properly combined will give a more elegant and stable product than a long formula in which one ingredient may upset another and so spoil the balance of the finished product – the unsatisfactory result not always being apparent until after packing and despatch for sale.

Times have changed, and this last hazard is not likely to take place, as the following outline should demonstrate.

TENTH EDITION: POUCHER'S PERFUMES, COSMETICS AND SOAPS

Now 58 years after Poucher wrote that preface industrial suppliers are offering increased numbers of new raw materials. Many form specialist groups, which with slight changes in molecular structure inspire improved formulations of existing products or new types not previously marketed. The manufacturers are guaranteeing good quality, that the materials have been thoroughly tested toxicologically, accepted for use in cosmetics, and they supply specifications for each batch showing the results of physical and chemical analysis including their microbiological status. They offer considerable help in establishing the grounds for the use of their products and usually supply evidence of the claims that can be made for their beneficial use.

The new volume is in four parts. After a historical start the chapters in Part 2, which deal with different products in alphabetical order, include examples of these new materials, their properties and uses. There are materials for which claims can be made for the finished product's feel on the skin, e.g. groups of substances such as the silicone polymer derivatives, which may also increase stability.

On offer today are new antiperspirant compounds, new emulsifiers, new colours, new surfactants, new sunscreens and many others and, because the public believe that 'natural ingredients' are safer to use than 'chemicals', many new extracts of plants and those used in past centuries are being offered for use.

Of course it is not true that, because these preparations were used for many years by many people, they are or will be safe for repeated use, or remain stable in the new type of basic products marketed today. Mass production, and storage in warehouses and in shops before sale, are serious challenges for stability compared with concoctions which were prepared in the family kitchens in days gone by and not kept very long before being used up. Today's challenges are described, and solutions discussed, in Part 3.

Also in Part 2 the physiological and biological functions of the skin, hair, teeth and nails, which were touched on in earlier editions and covered more fully in the 9th edition, are still included, but that and any other information which is repeated is needed for those who are not familiar with that work. This also acts as an easy reference and reminder. Apart from the new raw materials there are new forms of products and new methods of manufacturing them.

The industry has always realized that the authorities have in the past considered cosmetics unnecessary and trivial compared with the need for pure food and safe medicines, so to keep pace with the changing times the industry instituted its own voluntary guidelines for the manufacture and sale of cosmetics, to ensure the maintenance of good quality and excellent history of safety-in-use which they have always enjoyed.

However, as there have been areas in other fields where serious mistakes have been made in consumer goods, it has been thought necessary to introduce Legal Regulations to safeguard consumer confidence. A chapter in Part 3 covers the

latest developments in legislation in Europe, the USA and Japan, but also each separately outlines the steps which should be taken to comply with them.

In Europe the 6th Amendment has been added to the 1976 Cosmetic Directory, and this means considerable control of cosmetics today. Although these controls or similar ones are spreading to other countries they are not yet in force worldwide. There have been attempts by international meetings to bring this about, but it remains an ideal to be aimed at for the future when a cosmetic can be purchased and used anywhere in the world with absolute safety.

The other chapters in this Part support the obtaining of the legal requirements. In Europe under the 6th Amendment a Product Information Package (PIP) must be kept on each product and made available for inspection by the authorities, when required. Records of the test results of formulation development, batch checking during production, raw material and finished product specifications showing test results which comply with them, long-term storage stability of product and its package, and consumer safety-in-use must be included.

The chapter outlining methods of analysis gives some traditional methods but 'emphasis has been given to chromatographic and spectroscopic instrumental techniques because they represent the biggest areas of application, and the instrumentation involved has become much more accessible in terms of cost, reliability and the expertise needed to analyse samples', to quote its author.

During the development stage substantiation of the claims to be made when marketed must also be included in the PIP. There is a chapter discussing the use of human volunteer panels to assess the efficacy of products. During these trials, of course, any obvious adverse consumer reactions can be noted and the product formulation changed if necessary. Consumer panels are also used in the chapters on safety, microbiological control, stability, and in assessing consumer acceptance in perfume and the manufacture of consumer products. In the latter there is a discussion on the ethics of how the panels should be formed, and their responsibilities.

Panel trials, when all the tests which have been carried out in-house and by consumers at home seem to ensure that the product is safe and stable, long-term, also give an indication of whether this is still so with repeated consumer use in a different environment. Consumer comments are useful in many ways; one is on the assessment of the type of packing, e.g. is it easy to replace the lid of a jar or cap of a tube after use?

Thus if the information and guidelines are followed in this part of the book, so that the results of the investigation at the development stage of a new product are satisfactory and it is possible to repeat the results of the tests when in production and marketed, then the recording of the results which appear in the PIP should show that from its initial planned development through its manufacture and sale the product will be stable in long-term storage and safe in consumer use until the end of the material in the bottle, tube, jar, sachet or aerosol – in fact any pack used by the industry.

So from his first pioneering work in 1923, which separated cosmetics and toiletries from pharmacy, and his production of updated editions, W.A. Poucher contributed greatly to the development of cosmetic science, which includes perfumery and soap.

As a result of his career in perfumery and cosmetics, in 1952 he became the first Honorary Member of the Society of Cosmetic Chemists of Great Britain (now the Society of Cosmetic Scientists) and in 1954 the US Society of Cosmetic Chemists awarded him their Medal for 'his outstanding contribution to the art and science of Cosmetics' (the first perfumer and the first person outside the USA to receive the honour). In 1956 he was elected Honorary Member of the USA Society of Perfumers in recognition of his distinctive service to the perfumery and cosmetic industries.

W.A. POUCHER'S OTHER CAREERS

Poucher once said that his 'life was a search for beauty in music, cosmetics and mountains', and he achieved much in pursuing this search.

As a child he wanted to be a concert pianist. He had a passion for Chopin's music and practised until all hours, so that 'his father had to turn out the gaslight in order to get him to bed'. In spite of not following this ambition he continued to play for pleasure until he sold his Steinway in 1958.

In his love of perfumes and the formulation of cosmetics he aimed to inspire men and women to beautify themselves, and this formed his main business career, but when he retired from Yardley at 65 years of age they presented him with a Leica camera. He then had plenty of time to increase and perfect his photographic records of the mountainous scenery he so loved and to develop his second career.

His love of photography began when he had a darkroom in a cupboard at the top of the cellar steps in his youth in his home in Lincolnshire, and through the years he had taken black-and-white photographs of the mountains and hills in the Lake District, Snowdonia, the Highlands of Scotland, the Pennines, Surrey, the West Country and Ireland, with in addition photographs taken during visits to the Alps, the Dolomites, and on the Riviera. The first publication was *Lakeland through the Lens* in 1940, which was followed by a further 20 books (13 published by Chapman & Hall and eight by Country Life), with many photographs in black and white covering the areas he loved best in the British Isles and the Dolomites.

He was elected first an Associate and then a Fellow of the Royal Photographic Society in 1942 and later Honorary Fellow in 1975, and donated to them his library of black-and-white prints in 1985. He changed to colour, and in 1980 Constable published his *Scotland*, and to date a further 15 titles have been published in coffee-table format, the last in 1997 some nine years after his death. This was made possible because Constable had approached his son to see

if the series could be continued. He agreed with the idea and compiled the last five titles using his father's photographs.

Poucher was a great Fell walker, a member of the Climbers' Club and the Fell and Rock Club, and wrote four guidebooks which were published by Constable: *The Lakeland Peaks* in 1960, followed by *The Welsh Peaks*, *The Scottish Peaks* and finally *The Peak and Pennines* in 1966. All are still in revised editions, namely 11th, 10th, 8th and 5th, respectively.

Apart from these activities he lectured at meetings arranged by societies as different as the Society of Cosmetic Scientists and the Fell and Rock Club.

He was also a keen golfer with a not-inconsiderable handicap of 10 for someone who was not aiming to be a world champion. He was a member of the Walton Heath Golf Club for 50 years. His other passion was fast cars, and he drove a Jaguar Mark II which appeared in many of his post-war prints!

My thanks are due to his son, Mr John Poucher, who now lives in Cockermouth in the Lake District, who supplied me with, and reviewed, the above information and sent me eight of the many obituaries. His father died in 1988 and obituaries appeared in the *Daily Telegraph*, *Guardian*, *Glasgow Herald*, *Horncastle News*, *Photographic Journal*, *Great Outdoors*, *The Fell and Rock Journal* and *Newsletter of the Society of Cosmetic Scientists.*

Among the tributes to his memory is one from Chris Bonnington, who said: 'As a youngster when I was starting to climb, his photography books were some of the most important ones around', and went on to say how useful the detailed sections on photographic technique in the guidebooks had been when he started taking photography seriously.

Walter used to combine his two interests by wearing make-up and perfume in the mountains, a habit which disconcerted some of his self-consciously masculine climbing companions. He found much mischievous amusement in their reaction, as he did in the horrified response that greeted his advocacy – on television when he was well over 90 – of the use of make-up for men; and now there is a whole chapter devoted to products for them alone.

ACKNOWLEDGEMENT

I am indebted to Mr John Poucher for providing me with so much background information about his father's life.

2

Cosmetics through the ages

Hilda Butler

2.1 INTRODUCTION

The story of cosmetics and perfumery forms a continuous narrative throughout the history of man, developing as he developed. The origins are associated with fighting, hunting, religion and superstition; later with medicine; then, as knowledge increased, becoming dissociated from medicine and allied to pharmacy. In the sixteenth and seventeenth centuries books omitting cosmetics and devoted to perfumery were printed; interestingly, the study and preparation of essential oils developed separately in the wine, cordial and beverage industry with the beginnings of the science of distillation, in the sixteenth century. Today cosmetic, perfumery and essential oil industries exist with technologies of their own. The scientific bases of these are supported by the many new researches in chemistry and especially in the biochemistry of the skin and bodily functions.

The word cosmetic derives from the Greek *Kosm tikos* meaning 'having the power, arrange, skilled in decorating', giving *kosmein*, 'to adorn' and *kosmos*, 'order', 'harmony', the latter used today for the universe having been applied to the world by the ancients from its perfect order, the repetition of the seasons and the movements of the stars [1].

2.2 PREHISTORIC TIMES – 3000 BC

2.2.1 Evidence of use of cosmetics

Thirty thousand years ago early man used colour in cave paintings, mostly of bulls and calves, apparently to attract the animals he wished to hunt. He survived by hunting and fighting and in both cases coloured his skin and adorned his body for protection, either as camouflage or to provoke fear in an enemy, whether man or animal.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 13–63

The Picts, a tribe in Northern Scotland already living there in 1000 BC, were so-called by the Romans from the Latin *pictus*, painted. Many such customs are still in use in South American and other primitive tribes today.

The Patagonians mumble incantations, sway their bodies and smear their faces with chalk. The Australian aborigines adorn themselves with wreaths of flowers and feathers worn over greased bodies and faces daubed with white clay. South Sea Islanders wear helmet-like structures into which are built masks of wood, reeds, tortoise-shell and even human skulls decorated with vegetable substances to represent hair. Some of them discard the masks and paint their faces red and bodies black. North American Indians used to decorate their bodies with brightly coloured war paints and their medicine men were dressed in the complete skin and head of wild animals such as elk, bear, wolf or panther. Chinese and Siamese actors of today use blue, green, ochre, vermilion and white for spirits and demons [2].

In early eastern civilizations cosmetics and aromatic woods and oils were used extensively in religious practices; in India, China and Egypt some of them persist. Although those first civilizations undoubtedly used indigenous tree resins, aromatic oils and fats from plants and animals, it is only from the mythical sagas of China and India that we can learn of their prehistoric use in those countries.

2.2.2 Egypt

The exceptional climatic conditions and religious beliefs of the Egyptians have enabled us to learn about their daily habits. They were a happy people who so loved living that they buried many of their possessions with them after death, to enable them to carry on their living standards in the after-life. Even in prehistoric predynastic times (before 3000 BC) simple graves preserved in the dry sand on the edge of the desert yield evidence of the use of make-up. Slate palettes in the form of animals such as the hippopotamus, hyena, bat, tortoise, and cuttlefish were found on which face paint was ground for use. One grave, now in the Oriental Institute, University of Chicago, contained small bags of powdered malachite and galena for making eye-paint and red ochre for painting the face. The palette with a pebble on it for grinding lay beside the skeleton. Traces of powder ground on the palette surface showed that it was much used in life. There are also stone and pottery jars which probably held oils and unguents [1,2,4].

Tombs developed from these Neolithic simple graves into brick structures for the kings of the First Dynasty (Thinnite). The first ruler, King Menes, united Upper and Lower Egypt, founded Memphis and built the temple of Ptah, in 3100 BC (modern dating methods). His tomb was opened in 1897. Others of the First and Second Dynasty have been opened and the British Museum displays many beautiful alabaster vases of this period, containers for unguents.

The Neolithic age ended in Egypt in about 4000 BC and copper working began; with the discovery of tin used to harden it, this led to the Bronze Age,

evidenced by the implements found: combs, hairpins, tweezers and small clamp-like instruments believed to be curling tongs, and beautifully made spoons and ladles. The ancients preferred to be clean-shaven and razors of hammered bronze and mirrors of the same material or sometimes polished copper were found. The pyramids were built by the kings of Egypt to protect the valuable objects but to no avail; the richer tombs, and those thought to be more important at the time, have been plundered through the centuries and only the less important ones yield secrets in the twentieth century. In 2600 BC the pyramid at Gizeh, attributed to King Khufu (Cheops) was built. His mother was Queen Hetephores and he had her tomb resited there, from Dashur. The contents are now in the Cairo Museum. The articles included thirty alabaster vessels, a large copper ewer with its copper basin and toiletry box, three gold cups and implements of gold, copper and flint. The toiletry box has been reconstructed from fragments found on the floor. Its original contents were eight alabaster jars and a copper spoon. Seven of the jars contained seven traditional perfumed ointments and the eighth contained kohl. Six of the lids have been preserved and are inscribed with the names of the contents while a single sign on the rim of each jar indicates the connection between each lid and its respective jar. The gold objects include two razors, three rectangular knives, a manicure implement with a sharp end for cleaning nails and a rounded end for pressing down the skin at the base of the nails. The copper ones consist of five razors, which with the two gold razors make a set of seven, and four rectangular knives which, with the three gold ones, make a set of seven. With these there is a set of extraordinary flint instruments which seem to be older prototypes of the metal ones, thirteen oval flints or flint razors and nine rectangular flint knives. There is also a very fine copper needle [5].

In earlier times the women painted the undersides of their eyes with green colour made from malachite, a copper carbonate ore, and the lids, lashes and eyebrows were painted black with kohl. These powders were pulverized on stone or metal palettes and the powder applied to the eyes by a finger dipped in water. Both eye-paints were found in various states in early graves; as lumps of ore; as stains on the palettes with pebbles by which the ores were ground; as powder in linen bags; and as compact masses of colour from which the binding agent had dried out. In later times the green eye-paint was used only in ritual offerings to the gods. It was superseded in ordinary use by the black kohl applied by an ivory or wooden stick. According to A. Lucas, of 61 samples of kohl analysed, 40 contained approximately 65% galena, a lead ore. Two contained a trace of antimony sulfide and four some carbon. Of the remaining 21 samples, two consisted of lead carbonate, one of black oxide of copper, five brown ochre, one magnetic oxide of iron, one antimony sulfide, four malachite, a copper ore, and one chrysocolla (a greenish-blue copper ore). There is some evidence that the women coloured their cheeks and lips with red ochre (red iron oxide) [5].

A plant which must have been used in Ancient Egypt much as it is today, is henna. The pungent odour of the flowers was probably used to perfume oils and

ointments. In modern times in the Eastern countries the leaves are used to redden the nails, the palms of the hands and the soles of the feet. This seems to have been the fashion in ancient Egypt as the mummies are similarly stained; but some historians believe that this could be largely discolouration from the embalming materials. We do know that the Romans used henna for dyeing the hair and they probably learned it from the Egyptians. Indeed, the brilliant red hair on the mummy of a royal lady of the 18th Dynasty (fourteenth century BC) was probably dyed with henna [1].

2.3 3000 BC–AD 200: NORTH AFRICA AND THE MIDDLE EAST

2.3.1 Egyptians

The Egyptians were fond of aromatics which they used in their temples to perfume the sanctuary in which offerings of food and drink and the preparing of sacrificial food and clothing were made; as part of the process of embalming the dead; and for aesthetic purposes during their lives.

Although it has been difficult even with modern techniques to identify the perfume materials from such residues as have been found, they are named in the earliest offering lists in the pyramid texts, as well as in tomb and coffin inscriptions and funeral papyri of much later periods. However it is not always possible to know what ingredient is meant by some ancient word. It is known that gum resins, oleo-resins and perfumed woods were available. These substances were made into small pieces and were volatilized by being thrown into glowing censers. At Heliopolis, where the sun-worshippers gathered, three different resins were burnt at dawn, noon and sunset. That at noon was myrrh, a gum from a small tree growing in East Africa and Arabia. The evening offering was Kaphi, believed to be a mixture of 16 aromatic resins [1,5].

At the fête of the god Isis it was customary to sacrifice an ox. The odour of burnt flesh was so obnoxious that the worshippers found it necessary to fill the carcass with aromatic gums and oils which, on volatilization, improved the atmosphere. The word incense has a basic meaning similar to perfume (*per fumen*) – the aroma given off with the smoke of any odiferous substance when burnt: oleo-resins, gum resins, wood barks, and flowers, fruits and seeds. Incense comes from late Latin *incensum*, thing burnt. Perfume has been extended to anything sweet-smelling but incense became restricted through the years to frankincense (*Boswellia* species), though later other gums were added to form a characteristic note. The 'frankincense' tree flourished in India and especially where the Buddhist religion was founded in AD 400 in the north [2]. In religious processions in Ancient Egypt there was always a lavish use of perfumes and no king was ever crowned without being anointed with fragrant oils by the priests. It is probable that the priests prepared most of the fragrant oils and unguents and were therefore much esteemed as the perfumers of their time,

guarding the secrets of a mysterious art. Alabaster and ivory were mostly used for containers but carved wood, onyx and porphyry were also used [2].

(a) Use of materials for embalming

In the prehistoric graves the dry sand preserved the bodies, but as civilization and consequent wealth developed, and large and airy stone tombs were made, decomposition took place. The prehistoric mummification led to the tradition that the body should be preserved to be able to continue the after-life; so from the early dynastic period to Christian times, in the third and fourth centuries AD, highly successful methods of embalming were developed, a process carried out by professional embalmers [4].

Those of the Old Kingdom were not able to preserve the body tissues but by the Middle Kingdom, around the 11th Dynasty (2000–1782 BC), the techniques had improved. The bodies were rapidly desiccated with dry natron, an indigenous naturally occurring salt composed of sodium carbonate (or bicarbonate) and sodium chloride or sulfate, and then the surface of the skin was coated with resin and the body wrapped in linen. It is interesting to note that there is evidence that at this time some princesses were tattooed, a Nubian practice, and it is known that there was Nubian blood in the royal family. No evisceration was practised but a turpentine-like oleo-resin was injected into the anus to dissolve the organs [2,5,6].

Superior preservation was attained in the New Kingdom (1570–1070 BC) when the internal organs were eviscerated and placed in natron, treated with hot resin, bandaged and placed in four distinctive canopic jars. The cavity left in the body was washed with palm wine, and spices stuffed with a temporary packing material, and the body placed in natron for up to 40 days, after which it was washed in the waters of the Nile to purify it. The cranium was stuffed with resin-soaked linen and the body cavity was repacked with linen bags containing myrrh and soaked in resin, then the abdominal incision was sewn up. The surface of the body was rubbed with a mixture of cedar oil, wax, natron and gum, and then dusted with spices. After plugging the nose and eyelids with pads of linen the whole body was then coated with molten resin to close the pores and protect the surface. The embalming process was probably over by the 52nd day after death. The mummification and funeral ceremonies took place over a period of 70 days; during the remaining 18 days after embalming, the bandaging of the body and each separate limb was accompanied by ritualistic incantations and spells. When in 1912 Elliot-Smith wrote about Egyptian mummies he reported that the body of Rameses V (reigned 1145–1141 BC) was stuffed with sawdust containing spices which still perfumed the body. In 1973 the resins from the mummy (coded PUM II in the Pennsylvanian Museum) were analysed and found to be oils of juniper, camphor and the gum-resin myrrh (see ref. 4, pp. 44, 58).

From the time of the 22nd Dynasty there was a decline in embalming. The viscera were replaced in the body and later placed between the legs, and the

body covered with a black resin-like 'bitumen' from which the word mummy is derived; in Arabic it means a 'bitumenized thing'. The embalming continued through to Roman times until the Christian era when it fell into disuse, as did the burning of incense, considered to be too reminiscent of pagan practices (see ref. 4, p. 48).

(b) Aesthetic uses of materials

There is ample evidence from papyri and murals not only that the wealthy Egyptians used make-up, but that they perfumed their hair and bodies with fragrant oils, unguents and ointments. The extremely dry, hot climate in summer with, in upper Egypt, very little rain, and the dry, cool winter air, makes it necessary even today to apply something to soften hands and face frequently. In ancient times soap for the body was unknown so that oils and ointments were effective cleansing agents. The black colouring of eyebrow and eyeshadow (kohl) probably served some protection against the glare of the sun and there was also a belief that the green paint for under the lids was prophylactic against the many eye diseases prevalent in a subtropical country. In the British Museum there is a statue of a goddess wearing golden eye masks, supposedly donated by a worshipper in grateful thanks for being cured of an eye disease.

Both men and women used make-up and wore wigs. The men preferred to be clean-shaven, the kings wearing artificial beards on ceremonial occasions. It was a courtesy to offer to a guest a cone of ointment to place on the head when in an Egyptian house. During the visit the heat of the body melted the nard which ran down the tightly curled wig and onto clothes. This practice is also seen in murals depicting appointments of viziers and other officials, and the shaven heads of priests in procession to the temple. In the Oriental Institute in Chicago there is a tomb painting of *c.* 1100 BC showing an all-girl orchestra with cones on their bewigged heads [1].

Alcohol was not known as a solvent, so that oil and fat (beside being emollient to the scalp, hair and skin) would be an excellent vehicle for the aromatic oils available. There were plant oils from sesame seeds, croton, saffron, pumpkin seeds, linseeds and olives. Animal fats were obtained from cows, sheep and goats, and sometimes, according to remedies found on papyri, from non-domesticated animals such as serpent, ibex and cat, to cure baldness. As most of these animals, like the lion, hippopotamus and crocodile, were sacred to the gods, they may be only symbolic mentions [6].

The fashionable skin colour was yellow, obtained by applying a piece of linen dipped in a suspension of yellow ochre in water, to face, neck and arms. Both men and women shaved their eyebrows and then long black heavy ones were drawn in just above the natural line. All the statues of the gods and the murals depicting them show this very impressive effect. Brownish-red pigment in perfumed ointment was worn on the cheeks, and rouge on the lips [7].

Most of the cosmetics were made in the home, but the raw materials were sold in the shops, and were traded with Assyrians, Babylonians, Persians and Cretans. They used not only indigenous minerals and aromatic woods, gums and plants, but also resins and woods imported from Arabia, India, the Far East and China. The Egyptians were excellent teachers, and their habits and customs were exchanged with these countries [6].

From a study of archaeology, tomb contents and ancient writings it seems that men used iron oxide, henna and litmus to colour the skin and white lead to whiten it; henna, indigo and rastic, a beautiful permanent black made from nut-galls, copper and iron filings roasted in a little oil, for hair dyeing; and kohl for eye make-up [6].

2.3.2 Sumerians

During excavations at Ur of remains from Sumerian times, Dr Kenneth Graham found in a tomb lipsalves believed to have been used by Queen Shub-ad around 3200 BC. In the British Museum there are small Sumerian sea-shells still filled with cakes of coloured paint for make-up.

According to Herodotus, writing in 500 BC, both young men and women in Babylonia painted their faces with white lead and vermilion. They curled and perfumed their hair, kept the skin smooth with pumice stone and used perfumed oils on their bodies. They used powdered manganese oxide and turquoise as black and green lining for the eye and eyebrows. The highly organized and civilized Medes used false hair, eye-paint and perfumes. The Scythian women used to rub on their bodies a mixture of frankincense, cedar, and cypress woods in water. When washed off the next day the body was left smooth and glossy [7].

2.3.3 Thracians

Thracian tombs from 300 BC to AD 20 have been excavated, and perfume phials found in them analysed, but even with the latest techniques for analysis only trace evidence of oxidation and polymerization products were recognized, which could not be used for the identification of specific aromatics. Evaporation and deterioration over the years destroys the evidence, which is only available in ancient writings [8].

2.3.4 Jews

Cosmetics were evidently used by the Jews because in the Old Testament 'When Jehu came to Jezreel, Jezebel heard of it and painted her face and tired her head, and looked out at a window' (2 Kings IX. 30). A further reference occurs in Ezekiel (Ch. 23, v. 40), 'Thou didst wash thyself, paintedst thine eyes, and deckedst thyself with ornaments.'

Ancient Jews used incense and aromatics for religious rites and political ceremonies, and anointed their bodies for aesthetic reasons. The first reference to trade in aromatic substances is about 1730 BC in the *Bible,* when the Ishmaelites came from Gilead with their camels bearing 'spices and balm and myrrh'. In Exodus the Lord commanded Moses to build an altar to burn incense upon; 'and Aaron shall burn incense upon it every morning' [9]. Later detailed instructions are given for compounding a holy anointing oil of myrrh, cinnamon, sweet calamus and cassia in olive oil; and another of sweet incense for the altar consisting of sweet spices, stacte, onycha, galbanum and pure frankincense beaten to a fine powder [10]. Pliny says that stacte was the gum extract from the myrrh tree, while others, citing the similarity of the Hebrew word and the Greek meaning 'dropping', say that it is storax. Onycha may have been labdanum; but Eugène Rimmel says that the general version is that it was ground fish shell, fragrant from the spikenard it lived on, found on the shores of the Red Sea [10]. It was strictly forbidden to use either the holy anointing oil or the incense for any other than sacred purposes; 'Whosoever shall make like unto it shall even be cut off from his people.'

The *Bible* confirms that the Assyrians and the Babylonians burned incense and aromatic gums on the altars erected to their gods. The Assyrians used perfumes lavishly, and although they produced vast quantities themselves they had to import a thousand talents of frankincense a year from Arabia. Saffron, cinnamon and fenugreek were among the aromatics used during their extravagant banquets and way of life described in romantic tales of the period; for example, Belshassar's Feast, which is supposed to end the Babylonian monarchy and the empire. Myrrh is frequently referred to in Assyrian and Babylonian cuneiform tablets as being useful, with other aromatics, as incense to exorcise the demons from the body of a sick person. It was believed to have cleansing and medicinal properties and thus its use was ordained by Jewish Law in the purification of women, which had to last for a year. Myrrh was used in the first 6 months and other sweet odours in the second 6 months by Esther before being presented to King Ahasuerus.

To enhance her attractiveness Judith 'anointed herself with precious ointments' before going to meet Holofernes. She also braided her hair 'and put a tire on it'. Jewish men and women were very proud of their hair and dreaded baldness; shorn locks were a sign of slavery. Josephus relates that, in grand ceremonies, King Solomon was preceded by 40 pages from noble families, whose hair, powdered with gold dust, glittered in the sun's rays with a most brilliant effect. The Queen of Sheba brought spices 'in great abundance to the court of Solomon'. These would naturally be included in her gifts because the region of Sabaea or Sheba was the spice centre of Arabia. The Sabaeans not only produced most of the myrrh and frankincense of the Middle Eastern nations but were on the trade route for the spices and aromatic gums from India and the Far East. These included sandalwood, incense, vetivert roots, musk, and resins and flowers of henna, jasmine, lotus and rose [2,11].

2.3.5 India

India had had a medical code since 1000 BC in the Ayurveda and used the native raw materials in medicine, also in religious rites and for aesthetic use to alleviate the rigours of the hot climate [2]. Excavations in the Indus Valley have yielded cosmetic pots of clay, stone, ivory, faience, and alabaster from the third millennium to the second millennium BC. They are believed to be kohl pots, and some to have been for perfumed oils and unguents. Galena and lamp-black were used for eye make-up and kohl sticks of copper, bronze and wood have been found; also polished bronze mirrors. Red iron oxide used for rouge in small shells seems to indicate an influence from Sumaria, while the practice of colouring the soles of the feet, the nails and palms of the hands was prevalent. Heavy perfumes were used lavishly, the most popular being sandalwood-perfumed body oils to give a long-lasting odour. Women painted their faces with suns, moons, flowers, stars and birds [7].

2.3.6 Persia – 600 BC

With the Persian conquests, in the sixth century BC, of all the countries from the Aegæan to the Indus, where the medical and cosmetic knowledge was largely linked with mysticism and superstition, the Asiatic customs were absorbed and respected, especially those of the advanced Medes.

2.4 EUROPE FROM 2000 BC

2.4.1 Crete

The first civilization in Europe developed in Crete in about 2000 BC. The Cretans were a nation of clever craftsmen who traded their bronze and later their fine pottery and glassware with Egypt and the Aegæan countries. There are examples of beautifully worked scent bottles in the British Museum. This Minoan culture was absorbed by the Mycenæans when the Greeks conquered the city of Knossus in 1450 BC [3].

2.4.2 Greeks

The Greeks loved perfumes. Perfumery was an art practised mainly by the women, and reflected in the beautiful pottery scent bottles manufactured in Athens in 400–350 BC. They represented their gods; for example, Kephalus with dog feet, and Eros. Others from Sicily, Corinth and eastern Greek cities can be seen in the British Museum: black glazed terracotta vessels with details painted on in black and white from sixth-century Rhodes, and later ones in bright colours, and not all god-like in shape [12].

With the conquest of the Persian empire by Alexander the Great of Macedon in the late fourth century BC there was further exchange of knowledge and trade

with countries as far east as Tashkent, south to India and west in Babylon and Egypt [3]. Medical schools had been established in Greece in the sixth century and the Greeks revered Asklepius (Aesculapius, *Latin*), the god of Healing. Hippocrates (460–400 BC), who is believed to have taught at the temple of Asklepius at Cos, is credited with the title of Father of Medicine. Little is known about him and although the Hippocratic Collection may not have been written by him, but made by his followers later, he did begin the dissociation of the principles of cosmetics and medicine from superstition and religion.

Aristotle, born in Stagira, Greece in 384 BC, was the source of the biological and physical scientific knowledge at this time [2]. Erasistratus established physiology as a separate study and distinguished between the hygienic and therapeutic care of the body, advocating exercise and bathing as the prime necessity for health [6].

Theophrastus was probably the earliest Greek writer on the subject of perfumery. He was born in 370 BC and lived to the age of 85. His principal work was on botany and is characterized by a peculiar and yet remarkable classification of plants [2]. His minor works on perfumery and the weather are equally interesting. For instance, he speaks of a compounded perfume (as distinct from a flower perfume) as one that is artificially and deliberately produced; thus the method of the makers of perfumed powders is to mix solid with solid, that of those who compound unguents is to mix liquid with liquid; the third method, which is commonest, is that of the perfumer who mixes solid with liquid. Concerning fixation, Theophrastus says:

> Now the composition and preparation of perfumes aim entirely, one may say, at making odours last. That is why men make oil the vehicle of them, since it keeps a very long time and also is most convenient for use.
>
> They use spices in the making of all perfumes; some to thicken the oil, some in order to impart their odour. The less powerful spices are used for the thickening, and then at a later stage they put the one whose odour they wish to secure. For that which is put in last always dominates even if it is in small quantity; thus if a pound of myrrh is put into a half-pint of oil, and at a later stage a third of an ounce of cinnamon is added, this small amount dominates [5].

Theophrastus also describes the raw materials from which perfumes are prepared:

> Perfumes are compounded from various parts of the plants: flowers, leaves, twigs, root, wood, fruit, and gum; and in most cases the perfume is made from the mixture of several parts. Rose and gilliflower perfumes are made from the flowers; so also is the perfume called *Susinon* made from lilies; also the perfume from bergamot, mint and thyme, named *Kypros*; and the saffron perfume. The crocus that produces this is best from Aegina and

Cilicia. Instances of those made from the leaves are the perfumes culled from myrtle and dropwort. This grows in Cyprus on the hills and is very fragrant; that which grows in Hellas yields no perfume being scentless.

From roots are made the perfumes named from iris, spikenard and sweet marjoram, an ingredient in which is *koston*; for it is the root to which this perfume is applied. The Eretrian unguent is made from the root of *kypeiron*, which is obtained from Cyclades as well as from Enboea. From wood is made what is called 'palm perfume'; for they put in what is called the 'spathe', having first dried it. From fruits are made the quince perfume, the myrtle and the bay. The 'Egyptian' is made from several ingredients including cinnamon and myrrh [5].

Another perfume mentioned by Theophrastus is one called Megaleion which contained burnt resin, oils of *balanos*, cassia, cinnamon and myrrh, alleged by him to have been very difficult to make [5]. He said that 'perfumers seek upper rooms which do not face the sun, but are shaded as much as possible. For the sun or a hot place deprives the perfumes of their odour, and in general makes them lose their character more than cold treatment' [5].

Although the early Greeks did not, apparently, use make-up, by the fourth century BC cosmetics were well established for the well-to-do. The women were painted rose colour and white. The white was mostly white lead, the rouge was vermilion or vegetable substances, such as mulberry, seaweed and paederos, a root similar to alkanet. Later mercuric sulfide was used as well as white lead. Orpiment, a compound of arsenic, was used as a depilatory. Fragrant oils were used in the hair and both men and women dyed grey hair. Eyebrows were painted black and brought fairly close together. The eyes were painted with both black and green make-up. Sometimes false eyebrows were worn. Both men and women liked blond hair. After washing their hair with a special Athenian ointment, they sat bareheaded in the sun by the hour so that their tresses turned a beautiful golden blond [10].

The men of Athens used different aromatics for different parts of the body. A poem by Antiphanes [10] says:

> He really bathes
> In a large gilded tub, and steeps his feet
> And legs in rich Egyptian unguents;
> His jaws and legs with thick palm oil,
> And both his arms with extract sweet of mint;
> His eyebrows and his hair with marjoram,
> His knees and neck with essence of ground thyme.

Another virtue the Greeks attributed to perfumes, even among the Epicureans, was that they were enabled to drink more wine. The wealthy and luxuriant Athenians used vast quantities of aromas at their banquets when, first, slaves

brought guests water for the hands, with a perfumed clay well mixed with oil (Grecian soap) for cleansing them; and then fine linen towels, and fragrant ointments; and finally garlands of violets. Odorous gums were placed round the room, and one poem of Alexis describes how one host 'slipped four doves whose wings were saturate with scents, all different in kind – each bird bearing its own appropriate sweets ... wheeling around ... drenching, bathing both clothes and furniture, and lordlings all. I deprecate your envy when I add that on myself fell floods of violet odours' [10]. One of the beliefs was that, 'The best recipe for health was to apply sweet scents unto the brain'; also that if the breast be anointed with unguents, being the seat of the heart, it was soothed by fragrant smells. Socrates, on being offered perfumes, declined them as being fit only for women; and the Spartans sometimes drove the perfume merchants from the state for wasting edible oils as solvents for perfumes. They also banished cosmetics at one time 'as a flatterer of the senses'. The Greeks cleaned their teeth carefully with twigs and sucked aromatic gums to sweeten the breath [10].

(a) Religious festivals

At all the religious festivals aromatics were consumed in large quantities. Sacrificial altars were erected in private homes as well as the temples decked with garlands of herbs and flowers where the animal consecrated to a particular deity would be burnt with frankincense and libations of wine. An ox was offered to Jupiter, a dog to Hecate, a dove to Venus, a sow to Ceres and a fish to Neptune. No Greek would embark on any enterprise without first placating the god most likely to be concerned. Greeks cremated their dead. At the funeral, friends and relatives threw incense and poured wine on the burning pyre; the bones and ashes were afterwards washed in wine, mixed with perfumed ointments, then stored in decorative urns. Fragrant flowers and sweet perfumes were placed on monuments to the dead as a mark of respect [10].

2.4.3 Romans

In their early history the Romans buried their dead but, after the expansion of the empire to include Southern Italy, where the Greeks had settled, they adopted the funeral rites practised by them. The urns were given Latin names and stored in family tombs by the rich, the costliness and quantity of the perfumes used depending on their wealth. According to Suetonius at the funeral of Poppaea, Nero used more incense than Arabia could produce in 10 years, though Pliny says one year [5]. Gradually the other aesthetic customs were absorbed and developed extravagantly, during the times of Otho, who was ridiculed by Juvenal for his effeminacy because he carried an arsenal of perfumes and cosmetics on a military campaign; and Caligula who spent enormous sums on perfume and plunged into perfumed baths after his excessive orgies. In Nero's palace, known as the Golden House, there were dining rooms with fretted

ceilings of ivory whose panels could turn and allow flowers to be showered down; and silver pipes that sprinkled the guests with perfumes.

The Romans devised all sorts of beautiful containers for their perfumes and unguents, of which there were three principal kinds:

1. solid unguents, or hedysmata;
2. liquid unguents, or stymmata;
3. powder perfumes, or diapasmata.

The solid unguents were generally of one specific perfume, such as almond, rose or quince. The liquids were frequently compounds containing flowers, spices, and gums, and followed very much on the lines quoted above from Theophrastus. The constituents were generally digested in one or other of the fixed oils, such as sesame, olive or ben. According to Pliny, resin and gum were added to fix the odour in solid perfumes; indeed, he says, 'it is apt to die away and disappear with the greatest rapidity if these substances are not employed'. He also notes that unguents improved with age and for that reason were stored away in lead containers. They were tested on the back of the hand and not on the palm, owing to the 'heat thereof having a bad effect on them' [5].

(a) Bathing

The Egyptians are said to have invented public bathing, though the practice may have been imported from the East, since pouring cold water over the body is very cooling in hot climates. There is evidence of baths in Egyptian palaces, though there are better-preserved ones in Aegæan buildings. Those at Knossus in Crete show an advanced system of water supply and drainage even from 1700–1400 BC; and at Tyryns in 1200 BC. Greek vase paintings show that they also had showers. Alexander the Great is reported to have admired the luxurious baths of the Eastern civilizations [2].

In India, where it is thought to be a dirty habit for all to immerse in the same water, age-old customs were still in use in southern India in the first quarter of this century. There the villagers would still rather squat by a tub of water or a tap and pour water over themselves. Oil baths perfumed with sandalwood and floral extracts since ancient times were considered to be a skin tonic, and physically and mentally refreshing. Steam baths were popular where the bather sits beside the tub of boiling water into which neam leaves have been thrown, under an all-enveloping blanket [11].

It was the Romans, however, who developed bathing to such an extent that baths in public buildings became like modern social clubs. The process was probably as follows. The bather undressed, was anointed with perfumed oil by a slave, then after a period of violent exercise went into a steam room. It was probably here that the body was scraped with a strigil, a curved metal instrument, used to remove accumulated oil, dirt and perspiration. A personal metal container

for a bronze oil flask, a strigil and a shallow bronze pan dated AD 200 can be seen in the British Museum. The bather then went to the warm room and thence to the cold one where there was often a swimming pool. The plan was often the same in large houses as it was in public baths [2].

(b) Soap

There is no mention of soap being used to wash the body, but a clay called *sapo* (from which the word soap comes) was found near Rome and used for general cleaning. Pliny the Elder mentions that the Phoenicians were making soap from goat tallow and causticized beech ashes in 600 BC. Salt was added to make a hard soap. Later, wood ashes were replaced by seaweed and kelp; an industry grew up in Germany and the seaports of Italy and was then introduced into France and Spain, and thence into England in the ninth century [2].

(c) Cosmetics

Both Nero and Poppaea used cosmetics. Amongst the many things they used were white lead and chalk to whiten the skin; kohl to make up the eyes, eyebrows and lashes; fucus, a red colour for cheeks and lips; psilotrum, a depilatory; barley flour and butter as a cure for pimples; and pumice stone for whitening the teeth [10].

In ancient Egyptian times kohl has been shown by analysis to have been almost always galena or lead sulfide and not antimony sulfide. The Egyptian word for kohl *(m)sdmt* passed into Greek as *stimmi* then into Latin as *stibium*. We use this word today as the Romans did, with its derivative, *stibnite,* to mean antimony sulfide. The use of *stibium* for kohl arose, according to A. Lucas, from the use of the antimony compound called by Pliny *stimmi* or *stibi*, which was applied to the corners of the eyes to make them more lustrous [2].

The Romans, like all peoples through the ages it seems, attempted to preserve youth and beauty by artificial means. They dyed their hair black or blond according to the prevailing fashion, used astringent mixtures, e.g. one made from large beans cooked in butter, to remove wrinkles, and wore false teeth, false eyebrows and eyelashes, and wigs. They curled the hair elaborately. Even the statues were supplied with different wigs to keep in fashion. Beauty spots were fashionable [7].

All this gave ample opportunity for the satirists of the day to ridicule these customs. Martial, in one epigram, says of a sleeping female: 'you lie stored away in a 100 caskets, and your face does not sleep with you – yet you wink with that eyebrow which has been brought out for you in the morning'.

(d) Roman literature

The scientific writers of the day strengthened the links between medicine and cosmetics. Celsus (7 BC–AD 53), a Roman physician, included a section on the conditions of skin and hair in his medical books. Pliny the Elder (AD 23–79),

writing on chemistry and botany, included matters of interest for perfumes and aromatics, and Discorides in a *Materia Medica* named practical uses for all the known animal, vegetable and mineral substances used in cosmetics; for example, mud packs and medicinal baths were recommended. In the second century AD Galen wrote on many branches of medicine including hygiene and pharmacy, his works remaining the supreme authority for the next 1500 years. As regards cosmetics he is remembered because he formulated *ceratum refrigerans*, literally, cooling wax. He added as much water as could be incorporated into a mixture of 1 : 4 of beeswax and olive oil in which rose petals had been steeped. This was an improvement on previous ointments in that it was easy to apply and produced, when the water evaporated, a cooling sensation. It was the forerunner of the modern cold cream. He also wrote the first scientific treatise on the human skin, called *Local Remedies* [2,6].

2.5 AD 600–900

2.5.1 Arabia and India

The unification of Arabia began when Mahomet founded a religious movement in AD 625 which finally linked Syria, Persia, Mesopotamia and Egypt with India where an advanced medical school was established at Junishapur and where the cosmetic hygiene of its people, especially the women, was very elaborate [3]. They rubbed the whole body with almond paste and other oils before bathing and used make-up and hair dyes. The Hindus used betel juice to darken the lips and teeth; vermilion and other colours in waxes for the face to denote caste; and quantities of aromatics for family celebrations such as weddings and births [11].

Thus, while barbaric tribes were over-running Europe from the north and east, and bringing about the Dark Ages, there was a spread of learning and a thirst for knowledge throughout Asia. The works of Pliny, Galen, Discorides many more were translated from Greek and Latin into Arabic, and advances in medicine, botany and pharmacy were made. The intellectuals of many nations were attracted to Baghdad and Alexandria. New spices and aromatic plants from India, China and Malaya were introduced, studied and added to *materia medica* [2,3,6]. Enlarged volumes based on the original text of Discorides were written. It was a time when good general health was aimed at by adopting good general hygiene. Cosmetics were used which corrected or were supposed to prevent disease, and not just to cover up blemishes [6].

During the eighth and ninth centuries important advancements in experimentation with materials, including the distillation of drugs, aromatic oils and flavours from India such as cassia, myrrh, cloves, nutmeg and rose, were made. In the tenth century an Arab doctor named Avicenna attempted to distil flower essences. He was able to isolate otto of rose and produced rose water which later became a considerable Arabian trade item [5].

Other Arabian, Persian and (with their influence) Spanish and Italian chemists developed methods of distillation and preparation of drugs. The distillation of alcohol was made in northern Italy in around 1100. With this discovery purer extractions were possible. Previously, perfumers such as the Romans had soaked flower petals in wine to obtain essences. Meanwhile, during the so-called Dark Ages in Europe, the growth of monasteries had spread the discovery of medicinal and other uses of many plants. The monks grew herbs in the monastery gardens and prepared remedies from them to treat the poor and sick. During the bubonic plague, which ravaged Europe in 542, their ministrations were much in demand. Walafrid Strabo (Strabus), a German Abbot, wrote a poem, *Hortulus*, dedicated to Grimald, which was an account of a little garden tended by his own hands; it consisted of descriptions of the various herbs he grew there, with their medicinal and other uses. Sage was most important; rue came next as an antidote to poison, and then came melons, fennel, lilies, poppies and finally rose; 'which in virtue and scent surpasses all other herbs and may rightly be called the flower of flowers' [2].

In the early Christian era most of the information about make-up comes from the clergy and, though it was undoubtedly used, they condemned it as fit only for harlots. In Britain the people dyed their hair blue with woad, a colouring used also by the men in war. This practice seems to have been discontinued after the Norman Conquest in the eleventh century. The Danes were the cleanest, most hygienic people in the north, and took great pride in their appearance.

2.6 AD 900–1200

In the tenth and eleventh centuries a medical school was established at Salerno in southern Italy, reputedly the first European university. It developed enormously in surgery, clinical treatments and the study of drugs when the centre acted as a hospital for crusaders returning from the Holy Land, from 1099 onwards. Some of the cleverest Christians of the times were attracted there to study and teach. One of them, Nicolae (Parvum), compiled the *Nicolae Antidotarium* giving the preparation and identification of 150 drugs. It is believed to be the first authenticated Pharmacopoeia. With the decline of the Mohammedan Empire in the eleventh century learning passed to Spain and then to France, and benefited from the Arabs who remained to continue their scientific studies and teachings [2,6].

A brighter side of the crusades were the perfumes and toiletry articles introduced into western culture from the eastern harems and as a result of the opening up of trade with Arabia, India and southern Asia. The knights brought back from the Holy Land pepper, cinnamon and many spices from Ceylon and the Spice Islands; Arabian attars of ambergris and musk; and African gold and ivory [3].

In the twelfth century the kings, nobles and ecclesiastics vied with one another in building new towns in Europe and setting up trade routes and fairs.

They fostered the perfume and cosmetic sales which were most lucrative, became rich and influential and interchanged their fashions and customs. Arts and crafts developed, such as jewellery, leather working, and weaving, glass-making and ceramics. Leather working, in particular, developed in Spain and passed to Italy and France. In 1190 Philip Augustus granted the master glove-makers, who had developed a method of perfuming gloves, a monopoly in the craft, and in dealing in perfumes [2,3,9].

2.7 AD 1200–1500

2.7.1 China and trade

From the sixth to the thirteenth century China was the world's greatest power and Chinese culture the world's greatest splendour. Science and technology were far more advanced than in contemporary Europe, but transport was bad and the sea as yet unexplored. In the thirteenth century conquests by the Moguls and the formation of their vast land empire stabilized the land route from China to the Black Sea and opened up exchanges of missionaries and travellers between East and West. The most important of the latter was Marco Polo, a Venetian, who described the wonders of the civilization he had experienced during the years he stayed with Kubla Khan in China [2,3]. A trade route developed bringing ginger, drugs, aromatic perfumes and porcelain overland to Samarkand and then either to Moscow, Novgorod and the Hanseatic League, or alternatively to Baghdad or Constantinople to Venice. The Hanseatic League traded in cloth and wool from London, cloth from Bruges, and furs from the Russias. Exchange of goods took place mainly in the periodic fairs which had grown up in the Middle Ages. One of the largest was the quarterly one at Lyons on a trade route through the Rhône valley. Cosmetics, soaps, and aromatic pourri and oils for women were a significant part of these fairs [2,3].

With the decline in the overland route from China and the Hanseatic League ports, other routes had to be found because Europe and China had become dependent on cosmetics, perfumes, drugs and spices [3]. After 1123 (the battle of Ascalon) Venice, and later Genoa, controlled a fleet of merchant ships which plied between the ports of the Mediterranean and through the Straits of Gibraltar to England. By the early fifteenth century Indian and Arab merchants sailed through the Red Sea to Alexandria. With the Spanish exploration in America and the Portuguese arrival in India and the Far East, trade became global for the first time in human history [3].

Universities were established all over Europe in the twelfth and thirteenth centuries and, to one of these, in Montpelier in southern France, intellectuals were attracted and its law and medical schools became the foremost in Europe, even though new ideas of medicine and surgery were introduced into France from Italy in the thirteenth century. An Englishman, known as Gilbert, working

in Montpelier, wrote a *Compendium Medicinae* on the care of skin and hair, and on hygiene. He advised all travellers to drink distilled water, and those at sea to eat plenty of fruit! [6]. It was in the thirteenth and fourteenth centuries that Henri de Mondeville distinguished between treatments for diseased skin and cosmetics for adornment. He realized that 'the favour of women cannot be overestimated, without it no-one can obtain the goodwill of men, and occasionally it is as useful as the love of the Pope or even of God'. He described treatments for burns and minor disorders, and ointments, soaps and paints to cover up the effects of age. His pupil Guy de Chauliac continued the separation of cosmetics from medicine, his influence being so great that medicine and surgery occupied the time of those dealing with disease, and cosmetics were left to others [6,7].

An apothecary in the Middle Ages, by definition, was a warehouseman, but by application the term became restricted to those who prepared and sold drugs. This remained so in Europe, Scotland and America [2]. In England by the sixteenth century apothecaries were granted the right to issue licences to practise medicine. The dealers in drugs on the other hand were included in the Guild of Pepperers formed in 1190. This in turn was amalgamated with the Spicers in 1345 to form the Fraternity of St Anthony. In 1373 the name of grocer first appears in the records, so that by 1500 the Guild of Grocers had full control of the drugs sold by apothecaries [2]. By the fifteenth century England had become dependent on spices from the East. Since the time of William I the floors of houses had been strewn with sweet local herbs, and rose water was offered to guests in noblemen's houses, with which to wash their hands after meals. Matilda, Queen of Henry I, received from France a beautiful silver peacock with a tail set in pearls and precious stones. The body was filled with water and it was used to fill finger bowls, the liquid issuing from its beak. The Duke of Burgundy owned a small statue of a child from which issued a jet of rose water [10]. Spices were used to flavour the salted and sometimes putrid carcase meat which was all that was available in winter. Margaret Paston, writing from Norfolk in 1453 to her husband in London, asks him 'to bring home half a pound of good cinnamon as she cannot buy any of good quality locally'. This was the main spice grown in, and exported from, Ceylon [13].

2.8 THE SIXTEENTH CENTURY

In Europe the demand for perfumes soon led in 1508 to the manufacture of native perfumes by the Dominican Friars in the monastery of Santa Maria Novella in Florence. The creations added to the fame of the Holy Order in other countries and, later on, Fra Angelo Paladini produced a cream and a toilet vinegar widely used by the ladies of the Tuscan court.

As the wealth of Europe increased, the international fairs gave way to more permanent markets where the sale of perfumes, spices and aromatics (they being

light and sale of them lucrative) became part of the centre of social life. The Medici family in Florence and Genoa controlled the finance of northern Italy [3].

Venice, however, besides becoming foremost in developing perfumes, became a centre for fine arts, and Titian's cousin, Cesare Vecellio, in the early fifteenth century describes how the ladies obtained the beautiful shade of hair called *capelli file d'ore* (golden thread hair) [10]. One formula consisted of 2 pounds of alum, 6 ounces of black sulfur and 4 ounces of honey distilled together with water. After soaking the hair in this preparation it was necessary to sit on the flat roof of the house and to allow the sun to act on it. To protect the complexion large hats with no crowns were worn, through which the wet hair was draped and allowed to hang over the brim until it was dry [10]. With increased trade the royal courts of Europe became rich and influential and their extravagant fashions were interchanged. Iron oxide and sometimes cinnabar (mercury sulfide) were used for rouge, and lead carbonate for face powder; but eye make-up was considered bad taste in western countries.

Catherine de Medici, a Venetian, married Henry II of France in 1533 when she was nine, but it was not until 1540 that she reached the age of puberty, by the aid, it is said, of pills of myrrh given to her by the famous Jean Ferrel. In 1554 she gave birth to Francis of Valois, later Francis I, husband of Mary Queen of Scots for a year, until his death at 17 years of age. He was sickly from birth and a weakling, conditions generally attributed to the many herbal remedies and potions taken before and during his mother's pregnancy. Eight other children followed but none was very robust. Two of them followed their mother in encouraging the use of cosmetics, perfumes and the lore of aromatic and herbal potions. Henry III, her third son, was very effeminate; he sometimes dressed as a woman at official functions and wore ear-rings, even though he was a brave and clever man, fond of literature and a good politician [6,14].

Catherine's daughter, Marguerite de Valois, who married Henry of Navarre, later Henry IV, also loved perfumes and cosmetics and introduced rouge and the Venetian method of bleaching hair at the end of the sixteenth century. Her sensitive nose may have been one of the reasons why she quarrelled with Henry IV. Though handsome and a womanizer he was slovenly in appearance, rarely washed, and 'smelt strongly of goat' [14].

The abuse of perfumes became so great that, among others, Nicholas de Montaut, in *Miroir des Francois* (1582), reproached ladies using 'all sorts of perfume, cordial waters, civet, musk, ambergris and other precious aromatics to perfume their clothes and linen and even their whole bodies'.

Catherine brought, in her entourage from Italy, her astrologer and alchemist, Ruggiero, and her perfumer, Renato Bianco, known as René the Florentine. He became famous and very successfully ran a shop in Paris dealing in perfumes, powders, pomades and cosmetics for the ladies of the court and the wealthy aristocrats, and it is said with more sinister concoctions when required. A drawing of his shop on the Pont au Change is used as a frontispiece in the 1865 edition of

Eugène Rimmel's *Book of Perfumes* [10]. An Italian named Tombarelli also came with her, and noticing the favourable climate in southern France at Grasse, started growing scented flowers, leading to the production of flower oils and perfumed waters. From this early beginning the famous modern industry has developed.

Mary Queen of Scots, who spent much of her childhood in the French court, learnt the recipe for a beautiful complexion. This was to wash the face first with hot water and then in wine, to make it glow. During her imprisonment in England she asked for an increased allowance of wine for this purpose, and it is believed bathed herself in buttermilk. She introduced many of the customs of the French court when she reigned in Scotland giving Knox, the Presbyterian, additional opportunity to preach against her. Interest in perfumes passed to England when Edward Vere, Earl of Oxford, presented to Queen Elizabeth I on his return from Italy a pair of embroidered gloves, sweet bags and a perfumed leather jerkin. Later she wore perfumed leather gloves and the habit became popular. She was very impressed and encouraged the women of England to grow flowers and herbs and to learn how to make scented washes, pomades and satchets for use in the household [6,7,9].

It was still the custom in the sixteenth century to strew the floors of houses with sweet-smelling rushes and pungent dried herbs, and Thommas Tusser in *Points of Good Husbandry* gives a list of 21 herbs suitable for strewing: 'Balm, baulm, camomile, costumary, cowslip, paggles, daisies of all sorts, sweet fennel, germander, hyssop, lavender, lavender spike, lavender cotten, marjoram, mandeline, pennyroyal, roses of all sorts, redmints, sage, tansy, violets and winter savory' [7,10]. With the increased wealth of the Elizabethan period leading to large houses, gardens were laid out called 'Knot' because complicated patterns were formed using trimmed hedges of box and lavender with herbs and flowers between, giving an attractive view from the windows [2].

After the Queen started to use a cowslip cream for her skin it became very fashionable. It was said to preserve, beautify and whiten it, to remove existing wrinkles and to prevent new ones. A milk of almonds, lemon and honey preserved and whitened the hands. A lotion of oils of rosemary, camomile, sage, thyme, southernwood and cloves made the hair grow thick and shining. An infusion of the eyebright plant made the eyes bright and sparkling [6].

Towards the end of the sixteenth century most large houses had a still-room where the ladies made their own concoctions [10]. The Queen loved the rose best of all flowers and derived much pleasure from the sprinkling of rose water on the floor of her room from a 'casting bottle' containing it. She carried in her hand the fashionable 'pomander', a small ball of a mixture of aromatics such as ambergris, benzoin and civet. She was 'mightily pleased' to receive a gift of a string of pomanders which could be worn round the neck [10].

To form the balls the gums were made very hot in a mortar and rolled in the hand, previously dipped in rose water. Holes were then bored in the beads which were then strung on string while hot. It was believed that they would ward off

infection as well as serving to cover bad smells [10]. Later in the century the separate aromatic substances were encased in silver or silver gilt vessels with perforations to allow the odours to escape. One from Germany was segmented like a cut apple, each segment being engraved with the aromatic substance it contained: Ziber, Ambre, Bisam, Zitroni BA, Rosmarin B and Angeio BA, linked together on a ring. The segments could be closed to form a ball and hung from a chain for carrying [12].

Many people carried prettily decorated silk or linen bags in their pockets or hanging from their belts, which could be held to the nose when necessary. They were highly perfumed with rose petals mixed with musk, storax, labdanum, gum benzoin, and calamus. They were also laid among clothes and household linens. A 'perfume pan' was used to burn juniper and other scented woods to fumigate a musty room instead of allowing in fresh air. Bed linen was fumigated with violets [15]. The animal odours, musk, ambergris and civet, being strong and heavy, were used as much by men as women. They had been used in Spain to perfume leather and with modifications this mixture has been known as Peau d'Espagne through the later centuries. In the nineteenth century, squares of perfumed leather were encased in silk or satin envelopes which were long-lasting and could be used to perfume gloves, writing paper, etc.

Frangipani was also introduced as an alcoholic liquid reminiscent of jasmine in the late sixteenth century by an Italian Count of that name who belonged to a distinguished Roman family. This had little to do with the West Indian flowers; *Plumeria rubra* or *Plumeria alba* were shrubs belonging to the NO Apocyanaceae. It was named Frangipani by a Frenchman, Tournefort, in honour of Charles Plumier, a Franciscan traveller, who discovered it and thought its odour very similar. The perfume revived in the nineteenth century, which became so popular, varied from the original [2,6,9].

2.8.1 Cosmetics

Elizabeth's attempt to present herself in the best possible way to her subjects meant that she spent many hours every day with her ladies on her toilette. Her face was covered with white and red paint, as were those of many of her subjects, in this prosperous age. The white paint consisted of white lead occasionally mixed with sublimate of mercury and ground orris. Rouge consisted of red ochre, vermilion or cochineal. Egg-white was used to give a fashionable glaze to the face. Most recipes to whiten teeth included ground brick, cuttle bone, red and white coral, egg shells, alum, mastic, sandarac, pumice and myrrh. Towards the end of her life the Queen used to stuff her cheeks with wool pads to hide the fact that she had lost many teeth [16].

Victims of spots and pimples treated them with sulfur and turpentine for an hour then rubbed them with fresh butter. Patches were used to cover pox marks and blemishes and gained in popularity among upper-class women and young fops.

2.8.2 Theatrical make-up

It was during this century that theatrical make-up became more natural. In the fourteenth century the players had worn masks or used symbolic paints. In the mystery play, Noye's Fludde, God appeared with a gilded face. In Paris, Gro Gallium, an actor in Henry IV's time, made up with a thick coating of flour and wore a lambskin beard. In Elizabeth's time masks were discarded, faces painted and beards and wigs worn according to character. The cosmetics were obvious, but little different from those used by the public [2].

2.8.3 Hair fashions

(a) Women

After the austerity of hairstyles of former centuries when foreheads were shaven, eyebrows plucked and every bit of hair hidden under wired caps (at least for married women), more hair was allowed to be seen arranged in tiny curls close to the head, from about 1540. Queen Elizabeth, who inherited her father's red-gold hair, set the fashion for various similar shades. The Venetian method of soaking in alum solution was followed by treatment with a solution made from the maceration of a mixture of rhubarb, turmeric, dogberry and barberry bark. Presumably this replaced the time spent by the Italians displaying their tresses in the sun. The Queen had a variety of wigs as she got older, not only to cover up the deficiency and greyness of her hair, but to save time in her busy court life. It became fashionable for women generally to do the same. One of the most pathetic sights at the execution of Mary Queen of Scots occurred when Bulle, the executioner, picked up her fallen head by the auburn hair, and her head with its short grey hair fell away, leaving Bulle holding the luxuriant wig [17].

(b) Men

Henry III of France (ruled 1574–1589) re-introduced the male habit of wearing false hair. He had treated his own hair with damaging chemicals and became quite bald in early life. He wore a turban or a velvet cap with tufts of hair round the brim, which led his courtiers to grow their hair long [18].

2.8.4 Literature

It was early in the sixteenth century that the first books appeared which were entirely devoted to perfumery. Surprisingly, the French astrologer, Nostradamus, published in 1555 in Lyons a book on perfumes containing 'Plusiers Exquisite Receptes'. Other early books devoted entirely to perfumery appeared in Italy and France. One, printed anonymously in Venice in 1525, describes the aesthetic uses of perfumes, while another by Raoul du Montvert, produced in Paris in 1521, combined the essence of flowers with the secrets of medicine [19].

In this century Ruscelli (Alexis of Piedmont), Cortese of Italy, Jean Libaut and André Fournier of France wrote books on cosmetics dissociated from medicine but included perfumery. On the other hand Giovani Marinelli, an Italian physician, tried to retain cosmetics as a branch of medicine [9].

The book by Signora Isabella Cortesa contained 'secrets' about 'every-thing under the sun' according to Edward Sagarin, and included the word perfumery on the title page. She was one-time president of a Venetian Society of Ladies, of which Catherine de Medici was a member. Its aims were to learn about and test new recipes for cosmetics [7].

2.8.5 Development in essential oil production

Aristotle (384–322 BC) described the distillation of sea water to give pure water, and Pliny (AD 23–79) wrote about the collection of oily condensate from heated resin on wool in the upper part of a still. The Alexandrians placed a head on the still and prepared oil of turpentine by distilling pine resin. The Arabians cooled the tube leading from the head, or *alembic*, and discovered a number of essential oils by distilling plants and plant juices [2].

A book published in 1500 by the surgeon and pharmacologist, Hieronymous Brunsschwick in Strasbourg, Germany, collated all the previous work on alcohol and distillation, giving illustrations of all the types of apparatus then in use, and describing how to obtain flower oils. It was reprinted and enlarged by others through the century. During this period other writers on essential oils also appeared. One Jacques Besson linked the oils with medicine and healing [6,19].

2.9 THE SEVENTEENTH CENTURY

2.9.1 Cosmetics

It was in the seventeenth century that medicine dealt with disorders of the skin, hair, teeth and nails, and no longer with decorative cosmetics. James I gave official recognition to the Apothecaries Guild in 1617 and the first British Pharmacopoeia was published in 1618 with subsequent publications at intervals controlling the formulation of medicines [2]. Various countries introduced laws controlling the use of the most obvious poisons. One such was made in Italy, where a woman called Teoffania ran a school training women poisoners. She prepared a cosmetic wash which not only whitened the skin but could be used to dispose of one's enemies; it contained arsenic, the favourite poison of the Medicis. She was hanged in 1633 after 600 murdered husbands had been accounted for. A law was soon passed requiring the registering of the sale and use of poisons. In France in 1682 a similar act was passed after the Marquise de Brinvilliers, the poisoner, was guillotined as a mass murderer [2,6,7].

In the first half of the century women were using cosmetics openly and usually prepared them themselves. Ceruse – a white, pale pink, or flesh-coloured

paint consisting of white lead – was used thickly to cover wrinkles on face and neck; alternatively some women used white lead powder. The first gave a shiny appearance and the second a matt look, the contrast being very obvious. Vermilion was used for rouge. Occasionally the eyebrows were darkened, and a cream eyeshadow in blue, brown or grey was sometimes worn on the upper lid and sometimes reached to the eyebrow. The Greeks and Turks, along with the Middle- and Far-Eastern ladies of the harem, used kohl for emphasizing the eyes and eyebrows, which met in the middle to form one line [7].

John Bulwer wrote in 1653 that 'there is a venomous quality in the paint, which wrinkles the face before its time; it dims the eyes, and blackens the teeth' [7]. It was noted that after a time the white lead turned grey or even black. In spite of such warnings given to all nations, and writings by satirists and moralists, obvious use of cosmetics continued. Black patches were cut into fantastic shapes like ships, hearts and stars – even coach and horses! [5–7].

Early in the century men used make-up discreetly and unobtrusively, but in the second half they were just as blatant as the women. One such flagrant user was Judge Jeffries, whose portrait can be seen in London's National Portrait Gallery, painted between 1678 and 1680 [7]. By this time, full fleshy faces were fashionable with red lips and cheeks, prominent eyes, dark eyebrows, dark hair and double chins. Black or brown hair was in demand. The ladies of the court who wanted to give the skin a rosy glow drew the blood to the surface with a wash prepared by boiling gum benzoin in spirits of wine and adding fifteen drops of this tincture to a glass of water. James II favoured the use of cosmetic washes and he was recommended a skin lotion consisting of coriander, vanilla pods, nutmeg, cloves, storax, benzoin, lemon rind and honey. He insisted that his wife Mary of Modena use rouge, which she did, even though she disapproved [7].

2.9.2 Bathing and soap

Hygiene and sanitation, especially in the larger cities, were not very advanced; indeed the conditions contributed to the plague epidemics in the seventeenth century. Ordinary houses did not have bathrooms but wooden tubs were brought by the servant into the bedrooms, along with the hot and cold water, so the achievement of keeping clean was very tedious. The Laws of Gallantry in 1640 had recommended that the entire body be bathed occasionally, that the hands be washed at least every day, the face almost as often, and the head from time to time. The imposition of an excise tax on the soap manufacturers of Cheapside, London, in 1741, certainly afforded no encouragement to follow this advice. At the time that it was 3d. per pound the tax was more than the cost of the soap.

2.9.3 Hair

Early in the seventeenth century Louis XIII of France started the fashion of wearing a wig, which later spread to all Europe, though not in England during the time

of James I, who disliked painted faces and distrusted long hair as part of 'an alluring beauty' which boded no good for the male sex. Charles I and his Cavaliers did allow the hair to grow long and curly, a fashion which accentuated the habits of Cromwell's Roundheads, though there were plenty of those (like Cromwell himself) whose hair reached below their ears. The Cavaliers took to wearing false hair and wigs to supplement hair loss [18]. As the wearing of patches for decoration by artisans and aristocracy alike developed so that this became 'the century of patches', Cromwell proposed laws (though they were not passed) condemning 'black patches, painted faces' and what was vaguely described as 'immodest dress'.

This repressive policy during the Inter-regnum under the Puritans was reversed with the restoration of Charles II, who brought the luxuriant and extravagant French fashions to the English court, and they passed to all classes as never before. The Frenchman's type of wig passed quickly into England. It was extremely difficult to keep long hair clean and free from nits. As it was easier to wash a shaven head and engage a barber to supply and care for one's wigs, the fashion developed; and this was Pepys' reason for adopting periwigs from 1663.

King Charles II adopted a more sober dress to lead the court away from the extravagant fashions of the French and Spanish courts. The Spanish women looked double the age of their English peers because the former used so much paint to cover up their pallidness [7].

2.9.4 Perfumery

In the 1660s London, the richest, most important city in the world, covered an area forming only the small loop at the eastern end of today's Circle Line of the London Underground. Yet in this coal-blackened city it is estimated that half a million people lived, rich and poor in close proximity and in unbelievable contrast. Even a large dwelling, in which 60 servants might be employed, had no proper lavatory, only a stinking 'house of easement'. Servants, however, were cheap so that there was plenty of labour to clear away the filth. Houses had no gutters, and rain and traffic made gunnels in the narrow streets. Into these went all kitchen waste and other garbage, to be carried away by the next downpour of rain. These were conditions in which disease spread [20]. After the Restoration, following the French and Italian fashions, perfumes were used in abundance to cover obnoxious smells. The courtiers held perfumed handkerchiefs to the nose, and the ladies had posies of flowers. Pomanders were carried to ward off infection and aromatic gums were sucked to cover bad breath. Home-made wash balls were scented with storax, benzoin, calamus, labdanum, cloves and arras. During the Great Plague cinnamon, juniper, lavender, cassia and cardamon were burnt in the streets and houses in the belief that the infection was air-borne [20].

In the late seventeenth century royalty and aristocrats of the French court were fond of 'scents'. Henry XIV watched the celebrated perfumer, M. Martial,

compose his odours, and the Prince de Condé supervised the perfuming of his snuff [10]. The first prototype named perfume was made for Madame la Maréchal d'Aumont, around 1675, as an alcoholic wash and a powder, afterwards popular as Poudre a la Maréchal. Its popularity depended on its fragrance and long-lasting persistence. The crushed natural materials such as cloves, dried lemon peel, dried orange flowers, and dried iris rhizome, together with rose and musk, etc., resulted in a fragrant long-lasting note. Though the name continued to be used modifications were made by professional perfumers. In 1777 a formula was given by Dejean, and in the nineteenth century it became very popular, used as a basic mixture to be added to lavender, for example. Itinerant pedlars always included a 'Marshal' (Maréchale) in their wares.

2.9.5 Literature

A century after Nostradamus, de Montvert and the anonymous writers, Giovanni Roseto in Italy in 1678, and Simon Barbe in France in 1693, wrote exclusively on perfumery. Barbe described the raw materials of perfumery and gave instructions on blending them and also on perfuming snuff [19]. Meanwhile, in England in 1675, Robert Boyle reported on the Mechanical Production of Odours; other references appeared in pharmacopoeias [19]. Several books contained, apart from recipes for cookery and beauty preparations, those for perfumed washes, wash-balls and lotions, for these items were still prepared in the still-room at this time. The latter had been built into large houses; they were not now used by the mistress of the household as a hobby, but everything was done by still-room maids.

2.9.6 Beginnings of organic chemistry

Boyle also advocated that chemistry should advance by experimental observation and factual conclusions [2]. Nicholas Léméry in his *Cours de Chemie* (1675) was the first to adopt the division of compounds in the animal and vegetable world as organic and those in the mineral world as inorganic [2]. In 1685 he published a book of very precise recipes, a simple, intelligent and practical handbook called *Curiosities of Art and Nature*, containing mixtures for lotions and pomatums.

2.10 THE EIGHTEENTH CENTURY

2.10.1 Cosmetics

Towards the end of the seventeenth century, fashion in the West dictated an oval look to the face with, preferably, a long aristocratic nose, high forehead, shaven if necessary, with hair in short ringlets and piled high under a wired lace

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head-dress; eyebrows were darkened. Early in the eighteenth century the pale porcelain look was adopted, though the reddening of lips lasted until the French Revolution. Women continued to paint themselves heavily and satirists, moralists and husbands continued to decry the ageing effect of the fashion [7]. In England it was mainly prostitutes who were highly rouged with full red lips, but in France the respectable women were reported by travellers to paint their lips, cheeks, eyebrows and shoulders, and the prostitutes were pale. A Turkish ambassador when asked his opinion of French women replied 'that he was no judge of painting' [7]!

By the 1760s men used rouge, blackened their eyebrows and used perfume. Children were rouged and painted as well, and dressed up to look like adults. At this time the rouge was applied in round blobs in the centre of the cheek and was surrounded by white lead paint. In 1753 the once-beautiful Lady Coventry ignored her husband's warning against excessive use of white lead paint and died at the early age of 27. Lady Fortrose, and Kitty Fisher, who posed for Reynolds, also died young from this cause. During this century bismuth subnitrate began to be used because it was whiter than the oxides of tin or lead.

The Greeks still accentuated the eyes with soot collected on a plate held over burning coals on which gum laudanum had been thrown. They cleansed their skin thoroughly, whitened their teeth and painted their cheeks with *sulama*, which reddened the skin and gave it a marvellous gloss; the mercury content of the paint caused the teeth to blacken [7].

In Queen Anne's reign patches were reduced in size and no longer appeared in such fancy shapes, but were used to denote political favour: the right-hand side for Whigs and the left-hand side for Tories. They continued to be worn throughout the century, giving rise to the use of small, beautifully worked gold and silver boxes to be carried around, and enamelled ones with gold and silver mountings were added to the pomatum jars and powder and rouge containers on the dressing table. Some tiny boxes held both patches and rouge [7].

2.10.2 Hair

The full-bottomed wig for men was still fashionable in the early eighteenth century, but when young men chose to bleach them it became fashionable and simpler to powder them instead. Physicians continued to wear them until well into the century, and judges do so even today on certain occasions, as do the Lord Chancellor on the Woolsack and Counsel when pleading in the House of Lords [18].

Shorter, stylized wigs, such as the tye, the queue, and the bag, were developed in time until there were over 120 different named styles, but in the 1760s men started to wear their own hair and frightened barbers petitioned the King to bring back the wig and save their trade [6,7,18]. This was saved however because women's fashions claimed their services. For the first part of the century the

women had not worn wigs but had followed the style of men's wigs in dressing their own hair and powdering it. Then, about 1760, when the dandies or Macaronis began to wear wigs 18 inches high, women's hair rose off the forehead and was dressed over pads of horsehair and greased wool. The whole was plastered with fumed paste and pomatum to make the perfumed powder which was then applied by stick. By the 1770s the head-dress was widened and heightened to 2–3 feet with decorations of all kinds including, sometimes, whole frigates. The doors of Versaille Palace were raised to accommodate Marie Antoinette's creations and those of the ladies of the court.

Tallow, beeswax and plant oils were used in ointments and brilliantines, and white flour was used for powdering. In England in 1795 the shortage of flour became so serious that a tax on its use for the hair was introduced. This and the fact that so many powdered heads had fallen in the French Revolution led to a decline in the outrageous fashions. Indeed the extensive use of cosmetics and other adornments by nearly all classes led in 1770 to the introduction of an Act of Parliament (though it was not passed) to protect men from deception by beguiling women. The proposed Act read as follows:

> That all women, of whatever age, rank, profession, or degree, whether virgins, maids, or widows, that shall, from and after such Act, impose upon, seduce, and betray into matrimony, any of his Majesty's subjects, by the scents, paints, cosmetic washes, artificial teeth, false hair, Spanish wool, iron stays, hoops, high-heeled shoes, bolstered hips, shall incur the penalty of the law against witchcraft and like misdemeanours and that the marriage upon conviction, shall stand null and void [5].

In the last decades of this century the neo-classical fashions based on Ancient Grecian styles were led by an opponent of Napoleon, Madame Récamier, in Paris. The natural hair was cut close to the head and dressed with masses of tiny ringlets, around which a bandeau was wound [21].

2.10.3 Perfumery

Although pharmacists throughout Europe, including the 'druggists' in Germany, were selling the raw materials and some plant oils and perfumes, not all the cosmetics and toiletries were made in the home. Itinerant pedlars sold all manner of perfumed beauty products claiming extravagant properties for them, each with different aromas, in market towns and villages throughout Europe. Eugène Rimmel describes how they conned the crowds 'in gorgeous red coat, with gilt lacings', with patter about their wares delivered from an 'elegant equipage', and 'with musical accompaniment' [10].

The Italian pedlars who roamed through France selling inferior products and given the name 'charlatan' from the Italian *ciarlare*, to chatter, were banned

from the country by Louis XVI some years before the Revolution. Perfumery then became more respectable [10]. As in Paris, shops for perfumery alone were opened in other European cities. Charles Lillie in 1708 opened a shop at the corner of Beaufort Buildings in the Strand in London, occupied in the next century by Eugène Rimmel. He prepared scented snuffs and perfumes, especially one called 'Ambre, Orangeflower, Musk and Civet Violet' [10]. His manuscripts written around the 1730s were not published until 1822, when they were edited by Colin McKenzie and entitled *The British Perfumer*. Earlier publication of his secret recipes would no doubt have been detrimental to his business while perfumes were still prepared in the home [19].

In 1710 a formula was devised by an Italian, Femini, with a shop in Cologne on the Rhine, and named by the relative who inherited it Eau de Cologne. Originally marketed as a pharmaceutical 'cure-all' and 'elixir of life' it became popular as a perfume mainly because it was refreshing; it used herbal extracts and citrus oils described in 1563 by della Porta [6,9]. Other mixtures became popular in the eighteenth century such as Millefleurs, Bouquet D'Esterhazy, Jockey Club and Rondoletia [9]. These were all based on a restricted number of essential oils from flowers, gums and resins which were well known commercially, and with which professional perfumers rang the changes when compounding. Notable perfume houses founded in this century were: Antoine Chiris in 1767, J.F. Houbigant in 1775, and Lautier Fils in 1795 in France; Floris (1730), Yardley (1771) and Pears (1789) in England; and Geigy in Switzerland in 1755. In the United States E. Schieffelin (1794) took over from E. Lawrence (1781); and in New York an Englishman named Robert Bach founded the firm which later became Dodge and Olcott in 1816 [6,22].

2.10.4 Essential oils – technical development

In 1753 Antoine Hornet gave instructions for obtaining flower oils and gave formulae for perfumes as well. One of these was a variation of Bouquet Maréchale given in 1770. He was known by the pseudonym, Dejean. Abbé Polycarpe Poncelot, in 1755, linked flavours with pleasant odours in a work which was printed again with additions during the next 50 years; and Jaques Francois Demarchy described the equipment to be used to distil essential oils. However, it was Ambrose Cooper who in 1760 and in 1810 combined in one book the methods of obtaining extracts from malt, raisins, molasses, and sugar with the preparation of rose water, orange flower water and cinnamon water; and included all 'the compound waters and rich cordials so largely imported from France and Italy, as, likewise those now made in Great Britain' [19].

2.10.5 Advertising

Advertising of the sale of products was at first by hand-bills, until around the 1700s newspapers and magazines became established both here and in America.

In *The Tatler* for 14 September 1710, a contributor writes that advertisements have three uses and the last of these is 'to inform the World that it may be furnished with everything that is necessary to Life. A man may be cured of Pains in the Head, Cholic in the bowels, Spots in his clothes, recover his Wife or his Horse ... if he wants anything else let him look for it here'[7].

By 1758 Dr Johnson in *The Idler*, 20 January, was writing that 'advertisements are so numerous that they are but negligently perused ... it has therefore become necessary to gain attention by magnificence of promise and by eloquence sometimes sublime and sometimes pathetick, I remember a wash-ball that had a quality truly wonderful – it gave an exquisite edge to a razor! The trade of advertising is now so near to perfection that it is not easy to propose an improvement' [7]. Surely he must have had a vision of the later extravagant claims for cosmetics. One such appeared in *The Times* for 7 February 1793 for Bear's Grease, then popular for sticking powder to the hair:

> Just killed an extraordinary fine fat Russian Bear at Ross's Ornamental Hair and Perfumery Warehouse, No. 119 Bishopgate Street (late Vickery's) three doors from the London Tavern. The excellent virtue which the Bear possesses has been experienced by both sexes, and of all Ages, in the Metropolis. To those who have used the real Bear's Grease, it is evident no Grease whatever beside, retains its moisture so long upon the head, it being the only thing possible to make the Hair grow thick and long, recover it after illness, prevent it falling off, or turning grey, during life, being the most efficacious remedy for making hair grow on Horses' knees when broken or chafed.
>
> It is sold at 1s per ounce or 16s per pound, to be seen cut off the Animal in the presence of the purchaser [7].

2.10.6 Beginnings of modern chemistry

In the last quarter of the eighteenth century many learned men followed Boyle's precept of a century before, discarded abstract theory and too much philosophizing and turned to careful observations of laboratory experiments. Lavoisier, Priestley, Scheele and Bertollet advanced the theory of combustion and respiration and a clear definition of an element was established. In 1789, 33 were listed and by the early 1800s John Dalton had put forward the Atomic Theory of Matter. Thus, by the end of the century chemistry was diverging from medicine which was still concerned with herbs and resins [2].

(a) Development of organic chemistry

From his studies on combustion Lavoisier concluded that animal and vegetable compounds contained carbon, hydrogen, oxygen and nitrogen and sometimes sulfur and phosphorus. Then in 1778, a Frenchman, Paul Barthez, serving Louis XVI, propounded the theory of the 'vital principle' (*vis vitalis*) being

necessary for life. Thus, while inorganic compounds could be prepared in the laboratory, organic ones could only be formed in the living organism under the influence of this life force [23].

2.11 THE NINETEENTH CENTURY

2.11.1 Technical and industrial progress

For convenience, organic and inorganic chemistry remained separate branches even though the 'vital force' theory was shattered in 1828 when Wöhler prepared urea, synthetically, in the laboratory, from cyanic acid and ammonia, compounds previously believed to be inorganic; and shortly afterwards acetic acid was formed from carbon, sulfur, chlorine, water and zinc. In 1832, jointly with Liebig, he published work on oil of bitter almonds, identified the benzoyl radical and showed that it formed an unchanging constituent of a chain of compounds including benzoic acid [2].

The mechanical phase of the Industrial Revolution occurred with the development of the steam engine in Britain, and other inventions. Not only was there an increase of raw materials available but economic production was greatly improved; and the results of chemical researches led to its chemical phase. For example, in 1785 there were 791 small soapmakers in the UK making an average of 16 tons of soap each year, but by 1830 there were only 309 with an average annual output of 170 tons each. This was partly owing to the development by James Muspratt in 1822 of the Leblanc soda process, first used in France in 1791 on a scale larger than ever before seen in England. War with France and the ceding of the American colonies curtailed imports and provided the impetus for increased British manufacture [24].

The chemical nature of soap was elucidated by a Frenchman named M.E. Chevreul, following his work from 1811 to 1823 on fats and oils; the observation made in 1741 by C.E. Geoffroy that 'fats' were different after reaction with mineral acids: they were soluble in alcohol (fatty acids); and that of Scheele in 1794 of a sweet substance (glycerin) produced when a soap-boiling was made [2]. William Colgate, who started a factory manufacturing soap and candles in 1807, was among the first to benefit from Chevreul's work, and later coconut and palm oils were used to supplement tallow. Other raw materials became available which enabled cosmetics to be produced in greater variety and more cheaply.

Hydrogen peroxide was discovered in 1818 but it was not used to bleach hair until the Paris Exhibition of 1867. [2,6]. Several dyes were prepared in this century: Robiquet and Colin in France in 1826 isolated alizarin from madder, a plant used for colouring since Egyptian times, later synthesized by Perkin in 1869.

During the first part of the century such men as Berzelius, Gay-Lussac, Dalton and Avogadro were furthering the study of the nature of matter which led in 1838 to Cannizarro establishing the distinction between atoms and

molecules [2]. Gay-Lussac and Humboldt in 1805 found that water consisted of hydrogen and oxygen in the ratio of 2:1 and that ethyl alcohol consisted of water and one ethylene radical. Lavoisier had earlier determined this information qualitatively and in 1808 de Soussure reported the quantitative value. Its synthesis was carried out in 1826 by K. Hennel, a Frenchman. It is interesting to note that the use of the word alcohol for the OH class of organic substances and ethyl alcohol in particular is fairly recent. The word is of Arabic origin, being derived from the particle, 'al' and the word 'kohl', the powder used for eye-paint. For many centuries the word was used to designate any fine powder. Paracelsus and Libavius used it in this way. The latter mentions an alcohol derived from antimony. Paracelsus also used the term to denote a volatile liquid and *alcool vini id est vini ardente*. It later came to mean any pure substance [2]. Wines and spirits had for some time been subject to excise duty but in 1855 a non-dutiable product containing 10% wood naphtha was allowed for use in industrial processes, the first industrial methylated spirits.

The work of Thomas Graham on colloids and emulsion formation which he published in 1861, and the discovery of borax in California in 1856 and a purer deposit in Nevada in 1871 gave rise to an improvement in cold cream manufacture. As already mentioned, Galen in the second century had added water to wax and rose-scented olive oil, the result giving a cooling effect on the skin, but the mixture was unstable [6,25]. Towards the end of the century the alkali, borax, was added which, by forming a soap with the beeswax fatty acids, stabilized the product. Then in the 1890s an American, V.C. Dagnet, replaced the vegetable oil with refined mineral oil and waxes from petroleum sources. The creams were then white, did not go rancid and could be reproduced exactly from batch to batch. The Pond's version was launched in 1907.

Petroleum had been discovered in Pennsylvania in 1845 and 10 years later M. Berthelot discovered isopropanol, the first of a number of compounds to be isolated from petroleum raw material. It was fractionated to give different oils of differing viscosity and petrolatum used in medicine [2]. The Chesebrough Company was formed in 1858 and marketed a proprietary form as 'Vaseline'.

Pharmacies opened in Europe and America selling drugs, perfumes and raw materials for home-made products. Gradually they included cosmetic powders, rouges, soaps and lotions in their wares. They used the raw materials manufactured by the new industrial companies, preparing fats, oils, waxes, minerals, dyes and fine chemicals primarily for other industries, such as paints and textiles [6].

Later in the century pharmaceutical companies were formed which also made cosmetics. In 1846 Pond's Witch Hazel Extract was introduced and a company formed in 1857 in the USA, coming to Europe in 1877. Among other developments in England, Eugène Rimmel was the first to employ women in his perfume factory [10]; and with the introduction of the collapsible tube in the 1870s Colgates launched toothpaste in 1873, in the USA [6].

2.11.2 Cosmetics

Historians have noted that often, throughout history, in a period after a war, there is a general air of permissiveness and loosening of morals.

This occurred when the neo-classical fashions passed from France to England in the Regency era and during the reign of George IV. Corsets were discarded and dresses became loose and flowing; they became high-waisted and diaphanous and few underclothes were worn. The neckline was low, 'exposing more bosom than was covered', and as cosmetics were fashionable some women even painted their nipples. Gradually, the use of cosmetics lessened and though most women used rouge to enhance a pale complexion they did so deceptively. It was mainly the older women who still overdid it, like Queen Caroline, George's consort, who rouged excessively, as can be seen from her portrait by Thomas Lawrence, and Mrs Fitzherbert, George's morganatic wife 'was rouged to the very eyes', according to a contemporary book on etiquette.

By now, cochineal from the 'Spanish' beetle in Mexico, and later the carmine made from it in 1857, was being advertised as harmless, and writers for women continued to decry the use of the toxic 'vermilion'. George IV loved show and dressed in bright colours, was corseted and used perfume profusely. His friend, Beau Brummel, introduced dark clothing with white shirt, cuffs and well-tied cravats and advocated cleanliness and elegance in man's apparel. The 'dandy set' who followed the Macaronis used corsets to obtain small waists, oiled their hair and used heavy perfumes. Older men used rouge and continued to wear wigs until later in the century.

There was further sombreness during the reign of William IV and Queen Adelaide, who were not interested in high fashion but preferred a quiet home life.

By Queen Victoria's time men had adopted the traditional trousers, waistcoat and frock coat for daytime and tails for evening, which lasted until the end of the century and into the next. Hair was cut short, and faces were clean-shaven until beards and moustaches became fashionable in the 1860s and onwards. Macassar oil was used to control unruly hair, which gave rise to the use of 'anti-macassars' on the backs of chairs [18].

For women, small waists at the natural level, 'leg o' mutton' sleeves, and full skirts made up in serviceable materials, were 'in' [2]. So was the pallid look arrived at by covering the face with white enamel or powder and enhancing the effect by outlining the veins in blue. One blue preparation was made by mixing talc with a solution of gum tinted with Prussian blue. Lip pomades were introduced by Guerlain in 1828 but the use of such aids in England in Victorian times became more and more discreet. Most books and articles gave hints on maintaining natural beauty though some artifice was allowed. Elderflower water and rosewater were popular washes with pearl powder to whiten the skin. (Seed pearls were dissolved in acid and the powder precipitated with alkali [7].)

In Europe and in America ladies could be enamelled with white paint to 'last for a day or a year' [7]! Lead and mercury paints were still used because they gave a brilliant white finish, lacking in starch, rice powder and chalk, which were other ingredients used in powders. Some of the better manufacturers had replaced lead oxide with bismuth sub-nitrate, which was less toxic, but unfortunately after the introduction of general gas lighting around 1833, though lead powders turned yellow, the bismuth ones turned grey and complexions darkened as an evening wore on. In 1865 an American, H. Tetlow, replaced bismuth sub-nitrate with zinc oxide in his 'Pussywillow' powder, which overcame the problem.

Tetlow later packed finely ground talc (magnesium silicate), suitably perfumed, into tins and sold it throughout America where it became the first large-selling cosmetic in the States. It was used all over the body and its popularity as a dusting powder in the hot climate was assured [6].

2.11.3 Hair

The short styles of men and women necessitated a sleek, glossy look to the hair. G.W.S. Piesse, in his book *The Art of Perfumery* (1862), gives recipes for hair washes, 'bandolines', and a hair gloss.

The hair washes were either alkaline solutions of rosemary or tincture of bay and otto of bay, or other perfumed waters with alcohol. The bandolines were fixatives using gum tragaganth, perfumed with rose water or otto of almonds. The gloss was glycerin, perfumed with jasmine and tinted with aniline [9].

Since Victorian women were restricted in their use of cosmetics they concentrated on hair as their 'crowning glory'. Perfumed bear's grease was still a popular pomade and at least one firm, Atkinson's, sold it in pretty jars until early in the next century. There were wax pomatums for fixing whiskers and moustaches, dyes for hair and whiskers, and wigs for men. After 1870 'puffs' and 'bangs' for thinning hair, or to augment current fashions, and even full wigs, were used by women; not forgetting toupées and moustaches to be wired on for men [7].

2.11.4 Advertising

By the 1890s advertising was appealing to a mass market, especially in America. Extravagant claims were made for beauty preparations, hair restorers and hair colour restorers. In England the Koko-Maricopas company showed a woman with hair flowing over her shoulders and reaching in luxuriant tresses to the ground, with the caption 'Now stop your hair from falling out with Koko for the hair'. This appeared in a penny paper called *Pick-me-up* of 20 June 1891. Other captions for the product claimed that it was 'All done by Koko', and 'Ensures Magnificent Tresses'. The preparation was a solution of cantharides in glycerin and water and was still selling in the 1960s (though the cantharides were not included from the 1950s).

Cosmetics and toiletries, having been promoted in advertisements by royalty or the aristocracy, were now advertised using prominent people from stage and opera. Mrs Langtry was a favourite.

2.11.5 Essential oils

The study of essential oils was increased by the development of the botanical classification of plants, more of which were being cultivated. Books were written solely dealing with essential oils, culminating in a major work of the century, *The Volatile Oils*, by Gildemeister and Hoffman, translated into English in 1913 [19].

2.11.6 Perfumery

The soft-drinks industry became dissociated from that of perfumery when the chemical nature of materials, together with their chemical and physical properties, were analysed, and the industrial uses of vacuum, steam and fractional distillation were developed.

In 1833 Joseph Dumas gave empirical formulae for camphor, anethole and similar compounds; and in 1853 the very important discovery by Bertagnini and Pirie of the nature of the aliphatic aldehydes, some of which were odiferous, suggested to perfumers that they could be used mixed with natural flower oils so that the resultant perfume did not resemble any particular flower [22].

In the second half of the century the commercial production of specific chemicals allowed for further variations. Among those were linalol, and linalyl acetate; coumarin discovered by W.H. Perkin; and vanillin by de Laire, Tiemann, and Haarman. New distinctive odours were developed by creative perfumers. In 1882 Houbigant, a company formed in 1775, launched 'Fougére Royale', a fragrance based on bergamot and coumarin, also presented in a soap.

In 1896 they followed it with 'La Parfum Idéal', the first perfume which did not resemble any specific flower. Both these were the creations of Paul Parquet, their perfumer and later owner [22].

2.11.7 Literature

Eugène Rimmel, who in 1834 started selling perfumes in the shop in London once occupied by Charles Lillie, wrote an interesting and beautifully produced book in 1865 entitled *The Book of Perfumes*. He won an award for perfumery in the Great Exhibition of 1851.

A series of exhibitions did much for industry in this century and in the next London one, in 1862, G.W.S. Piesse wrote a useful report on the 221 perfumery exhibits now shown in their own class. He also won an award [6].

In this year the third edition of his book *The Art of Perfumery* was published, with the subtitle 'And the Methods of Obtaining the Odours of Plants'. In

addition, it contained instructions for the manufacture of perfumes for the handkerchief, scented powders, odorous vinegars, dentifrices, pomatums, cosmetics and perfumed soap, thus giving an indication of what was in use at this time [9] (see below).

2.11.8 Soap

Piesse had introduced in 1850 a number of medicated soaps and named them in the book, giving formulae. The soaps were named sulfur, iodine, bromine, creosote, mercurial and croton oil. A clear juniper tar soap was made from almond and olive oil and weak soda lye. This, mixed with a little water, was to be applied to the affected part at night and washed off in the morning. He also gave recipes for 'emulsines' or 'milks' using scented soft-soap solutions (which he explained would not keep) for cleansing the facial skin 'in Town' to keep it 'healthy and to brighten it'.

2.11.9 Nails

Care of the nails was advised, and powdered tin oxide perfumed with lavender and tinted with carmine was advocated. (Tin oxide was used to polish horn and tortoiseshell.) This was sold in wooden boxes, to be applied by means of little leather squares on the ends of sticks.

2.11.10 Teeth

Tooth powder recipes were given, one based on milk sugar flavoured with mint, aniseed and orange flower oils; another on chalk with powdered orris root and camphor; and another on charcoal and powdered Peruvian bark.

2.11.11 Cosmetics industry

In the years 1869–1890 cosmetic firms expanded enormously, especially in France and America. Max Beerbohm in 1896 in his *Defence of Cosmetics* reported on one that had increased twenty-fold in 5 years.

Beauty salons opened up all over America and, in spite of Victorian prudery as regards make-up, a Mrs Hemmings opened one in London selling Cyclax preparations in 1886. This company was the first to manufacture only cosmetic products [6].

2.12 THE TWENTIETH CENTURY

2.12.1 Early development of cosmetics

In 1900 Paris was once again the fashion centre and the Great Universal Exhibition of that year its focal point. Jaques Doucet, a man of great culture and impeccable taste, was foremost among men and Madame Paquin set the fashion for women. At

5 o'clock tea in her salon, ladies could view model gowns in flowing styles, with hats decorated with feathers and flowers, following the fashions for decor furniture and architecture of the Art Nouveau period [21]. This atmosphere passed to the relaxed, uninhibited decade in England during the reign of Edward VII.

Make-up was used very discreetly and not by the general public. Even Poudre de Riz was frowned upon as not quite respectable, although a dusting of talcum powder was allowed. Gradually everything became less subdued. Queen Alexandra was known to use a little rouge, and advertisements appeared everywhere for beauty creams, lotions and tinted products. In 1907 Helena Rubinstein moved from Australia to London, opened her beauty salon and started a line of treatment cosmetics; she moved to America in 1915 and introduced fine, richer-toned face powders and cream rouge in her range of make-up products. She commented that the extremes of climate in that country necessitated their use to enhance the appearance even of young girls [7]. In 1910 Elizabeth Arden started her business in America.

2.12.2 Face powder

In France in 1903 satin-covered booklets of fine papers impregnated with white, cream or pink powders were available and were still being made in 1923 when W.A. Poucher gave a method of manufacture in his book on modern cosmetics [26].

In 1913 the Dorin line of make-up was introduced to England and America from Paris. A complete pack suitable for a lady's handbag contained face powder in little boxes with a choice of four flesh-coloured tints and a puff for application; rouge in several tints; and, as dark and arched eyebrows were in fashion at this time, wax crayons [6].

In 1912 a liquid non-sticky face powder was advertised in *Vogue*, and powder compacts were first introduced in 1917. By 1923 formulae were being given of cake make-up to be applied with a wet sponge [26]. This was followed by a greasier form which was not so drying for the skin.

During the Second World War liquid make-up was applied as a substitute for silk stockings, which were available only on the black market in England. Stick make-up was a most acceptable development for those who preferred a heavier type, and is being used today therapeutically to cover up birth-marks and blemishes [27]. Rouge followed the same divergence of products but in a larger variety of colours.

2.12.3 Lipsticks

Roget and Gallet in 1910 produced a lip salve which consisted of a pink or white soft wax in a cylinder of light cardboard. The first metal case to be patented for a coloured stick was a push-up one made by the Scovill Manufacturing Company in 1915. Cheap plastic push-up types were still being sold in

the 'Nothing-over-sixpence store' (Woolworths) in England in 1939. The lipsticks (wedge-shaped) were of good quality in three shades – light, medium and dark. The same mass with a more expensive perfume and in a metal swivel case was sold in pharmacies and departmental stores for 8s 6d.

By this time lipsticks were known as 'indelible' because they used eosin, first introduced by manufacturing company Louis Philippe in 1916. The pigmented waxy mixture wore off in use, leaving the soluble eosin staining the lips. Eosines as the acid derivatives, the bromo acids, were later used, which gave different tints to the lipstick mass but which, under the action of saliva, all gave the same red dye. G.W. Luft introduced Tangee, a changeable translucent stick which contained no pigments, was orange-coloured and dyed the lips a brilliant red. One advantage of this was that it did not come off on crockery.

After the Second World War the staining effect was lessened, softer sticks were the vogue and many more applications had to be made to maintain a satisfactory coverage.

Lip gloss was developed which could either be in the form of a stick, a salve paint or paste for finger application, or a liquid for roll-on or brush application. These, with or without pearl, could be bought by the customer and used over a pigmented colour. Manufacturers began to include pearl and gloss into their colour ranges. Paint-box lipsticks have been introduced which allow for a mixture of colours to be chosen to vary with different clothes or moods of the wearer. The products on offer today are discussed in Chapter 6.

2.12.4 The cinema and other influences on the growth of cosmetics

The fashions adopted by the stars of the silent screen were copied wherever films were shown. For example, the 'bee-stung' lips of Mae Murray, and the flappers who, with their short skirts, long cigarette holders and rolled-down stockings, tinted their knees pink. The vamp, Theda Bara, and the flamboyant actress Pola Negri started the fashion for eye make-up with mascara on eyelids and lashes, prevalent from 1921. The Empress Eugenie of France had been the first to use mascara in the western world in the 1860s [7].

Max Factor advised the Hollywood film stars from 1908 to 1938 on make-up and thereby helped to create the personalities of the stars copied by both men and women all over the world. Thus, plucked eyebrows, and the dyed hair, called 'platinum blonde', followed the appearance on the screen of Jean Harlow. Max Factor's company was therefore very successful when it marketed make-up 'as used by the stars'. Panstick and pancake make-up in varying shades were extremely popular.

2.12.5 The cosmetics industry

Between the wars the cosmetics and toiletries industries flourished in America in spite of the belief that French cosmetics and perfumes were the best. In these

favourable conditions some European companies expanded and set up in the USA. The availability of raw materials was a great advantage there. When new ingredients were discovered in other industries the potential for their possible use for cosmetics and toiletries in such large markets made their purification for human application economically feasible, and cheap enough for importation to Europe. For instance, soapless detergents used in textiles were improved and developed so that the first soapless shampoos were marketed, such as 'Drene' by Procter and Gamble in 1934. They were manufactured in England from imported surfactants, but Marshall Aid ceased in 1950 so that economic necessity was the stimulus for European production, especially in Germany and England in the 1950s.

By the 1980s a large industry produced a vast number of surfactants with special properties, and it is now nearly always possible to choose one which improves the formulation of any product. Examples are as diverse as shampoos for babies, and every condition of adult hair; bubble baths; wetting agents for pigments in make-up products; thickeners; emulsifiers for all types of creams, lotions and milks, even those incorporating the most intractable materials.

2.12.6 Shaving and shaving preparations

In 1901 the Gillette Company was formed in Boston, USA, and in 1903 marketed the safety razor. For the first quarter of the century it grew in popularity, although older men still used the strop or cut-throat type. Shaving preparations took the form of ordinary soap with masculine-type perfume in bar or stick form, or in a bowl. This type of stick was still selling in England in the late 1930s, cost 1s 6d, and lasted about 18 months with daily use. Superfatted lather shaving cream consisting of soft soap with excess unsaponified vegetable oils sold in flexible metal tubes for about 2s 6d and lasted for about 9 months. In the 1940s brushless non-lathering shaving cream was introduced. It was based on vanishing cream formulation, needed a new blade for each shave, cost 3s 6d and lasted 6 months. Then in the 1950s came the aerosol cream which cost 8s 6d and was supposed to last 3 months, though early ones sometimes did not. Prediction that this expensive luxury would not be successful were proved wrong. In the rising prosperity of the 1960s 65% of all shaving preparations sold in the USA were in aerosol packs, its convenience and speed of use being most important to the busy male [28].

In the late 1920s basic research was carried out on the science of shaving and its effect on the hairs and skin. Thus, in the 1920s and 1930s oils and lotions were available which were meant to soften the beard before shaving with soap, safety razor and water. When the electric razor was introduced later, the sale of shaving soaps of all kinds declined but pre-electric-shave lotions became popular; to be effective these had to free the hairs from moisture and allow the razor to slide easily over the face. Two forms became available – talcum powder

in stick form or alcoholic lotions which were astringent and lubricating. After-shave lotions, creams and powders were used with all types of shaving and formed the basis of the discreet use of cosmetics by men which has developed since 1945.

2.12.7 Hair

The other development in men's toiletries was in the grooming of the hair and scalp. Before the Second World War these products were purchased by women for men. This changed in the following decades when the number and variety increased considerably. Between the wars women visited hairdressers but men used barbers; wealthy women and others for a special occasion visited beauty 'parlours'. In the 1970s men's beauty parlours appeared and in the 1980s both sexes were catered for in the same establishments.

(a) Hair dyeing

The paraphenylamine dyes had been prepared by A.W. Hoffmann in 1854 and used for permanent dyeing of hair in the 1890s. Patents were granted in Paris and Germany. Hairdressers introduced them into the UK and USA, mixing their own colours; but the first commercial standard product was Inecto by Gaston Bardou, Emile Rousseau and Raimond Sabouraud in London and Paris in 1910, in 11 reproducible shades. By 1917, 18 shades were available, coded from 1 to 9 with fractional numbers for intermediate shades. These sufficed for 25 years when the range was increased by some manufacturers to more than 30. Inecto was introduced into the United States in 1919. Cases of dermatitis caused by the use of these chemicals resulted in the replacement of the *p*-phenylene derivatives by the *p*-toluene diamines, standardized methods of application, and control of the raw materials, including the hydrogen peroxide used. In 1926 Dr Evans of Columbia University, who carried out this research, established an institute for instruction in 'hair and hair dyeing', and trained staff, who travelled about the country demonstrating their safe use in beauty culture schools and hairdressers [6].

Until the 1920s metallic dyes had been in general use. They were not absorbed as were the organic dyes, only coated the hair shaft and were limited to black, brown and red shades. Repeated use caused the hair to become stiff and brittle. The new organic dyes were therefore on the whole preferable. The modern products are mixtures containing antioxidants, stabilizers and conditioners and are used by 90% of the potential market because such natural effects can be obtained.

(b) Hair-styling

In the first decade of the twentieth century Marcel waving grew in popularity as a result of a number of French hairdressers moving to New York and, being

unable to find employment, they visited women in their homes and dressed their hair the French way. It had been devised by Marcel Grateau in 1873, who used hot irons to set hair in waves on either side of the head. It was practised in the home and in hairdressing salons on both sides of the Atlantic in the 1920s and early 1930s. It was extremely suitable for the new bobbed hair of the 1920s.

Meanwhile there were many contributions to the techniques of permanent waving, beginning with the cumbersome method of Charles Nessler, a German, in London in 1905, which he took to America in 1915. In 1932 Eugene Sutter, a Swiss hairdresser, modified the apparatus and introduced the use of ammonia as the curling medium. In the middle of the decade a Czechoslovakian, Joseph Mayer, and Robert Bishinger of Pennsylvania reversed the method of winding the hair on the curlers by starting from the ends and finishing on the scalp. Sartory of London, in 1927, used a chemical reaction to heat the cylinders surrounding the curlers, and after that it was not long before the overhead apparatus was no longer necessary because the rollers were preheated on rods. In 1932 the Zotos method was introduced in which the heat was produced in chemical pads wrapped round the curlers, and was known as 'machine-less' [6].

In 1934 the cold wave was devised, which used ammonium hydrosulfite. This was so unpleasant that it was replaced by mercaptans, and this led to the successful 'home perm' marketed in 1944 by the Toni company in America, which became a subsidiary of Gillette in 1948.

(c) Other hair products

After the Second World War even the married women went out to work. They had begun work in munitions during the war and continued in factories, shops and offices afterwards. They had money to spend on their appearance and the manufacturers competed to capture the mass markets. Products for the hair proliferated in the following decades as its biology was researched and knowledge of its reactions to treatment increased. Developments in bleaches, colouring gels and rinses, setting gels and lotions, lacquers, temporary colourings, conditioning tonics, oils and creams, and shampoos for every variety of hair type and condition were made. Hair products in aerosol packs, such as lacquers, formed one of the largest sales in the 1960s and 1970s.

2.12.8 Aerosols

The word 'aerosol' was originally a colloidal term to describe the dispersion of a mist or fog and later fine solid particles smaller than 50 μm in size and usually less than 10 μm, in a gas.

As early as 1862 the first patent was filed and there have been many more, mainly in the USA, in the development of the techniques.

- 1862: N. Lynde, for a valve and dip-tube for dispensing a liquid from a bottle.
- 1889: H. Helbing and G. Pertsch, for the use of liquefied gases, methyl and ethyl chloride, as propellant.
- 1901 and 1902: G.L. Gebauer, an apparatus for the ejection of the liquid in the form of a spray or stream.
- 1903: R.W. Moore for a perfume atomizer using propellant.
- 1921: L.K. Mobley for the application of antiseptic liquids using carbon dioxide as propellant.

In 1940 the US army made large-scale use of the aerosol in the form of a 'bug bomb', to fight malaria. This was based on research by Goodhue and Sullivan. This led, in 1945, to the first civilian use in America. In 1947 low-pressure aerosols in thin-walled containers were introduced leading to the launch of the first shaving cream in 1950. In 1953 colognes in coated glass containers were available at '10 p.s.i.g.'. Drawn steel cans, followed by expensive extruded aluminium containers, suitable valves and various propellants were introduced for different types of products. By 1955 hair lacquers accounted for 23% of the pressurized product market.

Compressed-gas systems were found suitable for certain products, such as pastes and creams to be dispensed unchanged. Thus, after 1958, when special valves had been devised, nitrogen was used to propel toothpaste, and other viscous products such as hand and hair creams. During the next 25 years a vast industry grew up of which toiletries, cosmetics and perfumery formed a large part. However, many other commodities were also packed into some kind of convenient aerosol. A whole new science was needed and intense research was stimulated in valve, container and propellant developments and in corrosion problems.

Eventually, by separating the product and propellant and using mechanical actuators to improve the spray, bi-aerosols and tri-aerosols were possible. In these, two products could be mixed at the time of dispensing and hair bleaches and multi-component products could be contained in a single pack. Hot shaving creams and hair dyes were achieved with co-dispensing valves. The introduction in 1977 of the Aquasol, which used a vapour tap system, enabled dry sprays to be produced which were suitable for feminine hygiene sprays.

Alongside the aerosol developments, plastic squeeze bottles and mechanical pumps activated by the pressure of a finger were marketed; the latter first in 1946, but it was not until 1970 that the first fine-spray pumps were available. By 1975 hair sprays were fairly common in this pack in the United States, and in the middle of the 1980s this type of spray system became more universally popular. In 1968 the world sale of aerosols was 4000 million, in 1978, 6000 million, and in 1980 this had risen to 6500 million of which half were personal products, mainly hair-sprays and deodorants and antiperspirants [29].

These large sales continued to grow each year with increasing populations and increasing standards of living worldwide. The large numbers of products

were releasing a significant amount of volatile chlorofluorocarbons (CFCs), which were used as propellants, into the upper layers of the earth's atmosphere. Environmentalists believe that their reactivity could be a contributory cause of the observed reduction of the ozone layer which protects all living things on earth from excess of the high-energy ultraviolet rays of the sun. Since 1987, when a number of countries signed the Montreal Protocol to reduce the manufacture and use of CFCs, the cosmetics industry has replaced them with hydrocarbons, e.g. dimethyl ether and other gases. This has also increased the popularity of pump-packs that recirculate air.

2.12.9 Deodorants and antiperspirants

In 1969 there were 3000 million unit sales of antiperspirants, of which 60% were in aerosol packs. These figures largely reflect the increased purchase by men of these aerosol toiletries because they are so convenient to use. Antiperspirant aerosol sales grew in subsequent years at the rate of 10–15% a year. Deodorants sold to teenage boys and girls increased this market still further.

It was in 1916 that A.W. Stillian reported that a 25% solution of aluminium chloride in water reduced under-arm sweating when dabbed on the part. This is still the most effective chemical to use but in the 1940s aluminium chlorhydrate was mixed with it to render the product less acidic and so less irritant, but unfortunately less effective. From 1955 to 1975 patents were filed for the use of zirconium complexes, but when used commercially some doubt arose about their long-term ill-effects when used, especially in aerosols. In 1977 the FDA banned their use in aerosols but allowed them in preparations applied directly to the skin. In 1978 three of the top four leading American roll-on types used zirconium complexes. In the United Kingdom Cosmetic Products (Safety) Regulations for 1984 aluminium zirconium chloride hydroxide and chloride hydroxide glycine complexes are restricted to 20% as chloride hydroxide, 5.4% as zirconium, with the ratio of aluminium atoms to zirconium atoms between 2 and 10, and that of (Al+Zr) atoms to chlorine atoms between 0.9 and 2.1; all are banned from aerosol dispensers. These restrictions were still in force in 1991.

2.12.10 Suntan, sunburn and sunscreens

At the turn of the century there was a revival of the idea of the healing powers of sunlight for rickets and anaemia, etc., recalling the theories of the Herodotus school in Ancient Rome, and those of Fauré and Chauvin in the eighteenth century, who treated damaged skin and neurasthenic conditions, like apathy, with sunlight. Gradually, in the twentieth century, there was a reversal of the Victorian passion for modesty when every part of the body was covered up and, at least during the first decade, writers on aids for a beautiful skin advised women to keep out of the sun.

Between the wars the number of holidays in the Western world taken by families increased, and sunbathing became a national pastime, even in the UK. In the late 1930s a richly tanned body was a sign of good health. Gradually more and more exposure of the body became permissible and fashionable until, in the 1980s, controlled treatments under ultraviolet light became available in beauty parlours and clinics equipped with 'sunbeds'.

Inevitably sunburn was a serious drawback to the fashion and in the 1940s, in addition to medical remedies, many cosmetic creams were sold to relieve the condition, and oils were advertised to prevent peeling of the skin and to preserve a glossy tan. In 1936 the first successful sunscreening agent, menthyl salicylate, was introduced by F.E. Stockelbach.

It was shown by A.H. Roffo in papers published between 1933 and 1936 that there was a relationship between malignant growths and sunlight; and in 1938 R.D. Passey observed that sailors who travelled in sunny parts of the world contracted cancer of the skin more often than those who sailed in northern parts.

Subsequent intensive research produced a number of active ingredients which aim to alleviate sunburn and screen out the harmful UV rays and yet allow a tanning effect. As more people sought a healthy tan the incidence of skin cancer increased; the types of products containing the different actives increased, and the manufacturers introduced a scale of numbers to indicate their respective efficiency, and this represents a Sun Protection Factor (SPF). Originally the methods of testing for these factors varied from company to company and from country to country. COLIPA published in 1994 a new and pan-European method, 'The COLIPA SPF Test Method', which became widely used so that harmonization of the various procedures is increasing worldwide.

In view of the irritant nature of some of the active ingredients of sunscreen products and their breakdown products, and the unsupported claims by some manufacturers, strict regulations have been introduced under the Federal Drug Administration of America and the EC Directive in Europe. Positive and restrictive lists of sunscreening chemicals exist in both countries.

Brown and Fardell in Chapter 16 cover the whole subject of sun damage very comprehensively. They also list the newly introduced INCI names for all the active sunscreen agents mentioned.

2.12.11 Other product areas

Similar research and developments, too numerous to outline here, have occurred in other product areas which have been followed in the different editions of Poucher. The competition in mass markets for tooth, nail and foot care products stimulated research in the structure, biology, pathology and requirements for protection and beautification of all parts of the human skin. Similarly, new markets were discovered in teenage requirements when their purchasing power increased in the 1960s and 1970s. In baby toiletries during the baby boom after

the Second World War, and again in the 1980s and the late 1990s, new products in this area have been marketed. These consider the delicacy of a baby's skin as do the numerous products for the sensitive adult skin.

As most of the cosmetics, toiletries and foods contained perfume or flavour, either to cover up or blend with ingredient odour or taste, and to enhance the product's acceptability, the perfume and flavour industry flourished in the second half of the twentieth century.

2.12.12 Perfumery

In 1900 the preparation of pure hydrocarbon solvents allowed 'concretes' to be made by maceration with ether or benzene and evaporation of the solvents. Different and better absolute oils were obtained when further processing of the concretes with alcohol and its evaporation at reduced pressure gave products of a waxy consistency soluble in alcohol [22].

At the turn of the century the perfumer had, therefore, more natural oils, absolutes and isolates, together with synthetic chemicals, than ever before with which to create new compound odours. When romantically named and artistically packed both the prestige and status of the perfumer and the companies marketing them were enhanced. F.W. Wells and M. Billot in their book *Perfume Technology* (1975), give a comprehensive list of these famous names, the perfumes and types that they created and the date they were launched [30].

Between the wars, chemical and physical examination, plus olfactory assessment, were all that were used to control aromatic raw materials for the buyer's selection and for the quality controller. This consisted of chemical tests such as acid and ester numbers, chemical detection and content of constituents, and physical tests such as appearance, solubility in alcohol, density, optical rotation, refractive index and boiling range, etc.; but above all the comparison of the material's characteristic odour with that of the standard required. In 1959, however, Langenau and Rogers [30] reported that instrumental analysis of essential oils was widely used, in America at least, and by the 1980s the development from gas–liquid chromatography to high-resolution mass spectrometry had enabled the identity and purity of the constituents of essential oils, isolates and perfumes to be determined much more quickly and accurately.

Thus, in the second half of the twentieth century perfumery has become more of an exact science since it requires a thorough knowledge of modern techniques, but at the same time it is an artistic craft requiring flair and experience, because as Freddie Wells says, 'Vital decisions about which components are important as odorants and which are not, and what to omit and what to introduce, still require the attention of a skilled perfumer' [22].

As an aid to formulation many attempts have been made to classify odours. The first to be published was by A.F. de Fourcroy in 1798 [31]; in the nineteenth century Eugène Rimmel classified odours of similar character together and

obtained 18 different types, and G.W.S. Piesse arranged odours in octaves exactly like music, and suggested that fragrant blends could be obtained by using harmonious chords. He thus arrived at bass notes and top (or treble) notes. The numerical basis used by Crocker and Henderson in 1927 [32] was not nearly so useful, but none was completely satisfactory.

W.A. Poucher first began to classify fragrant materials in 1924, and in 1955 published a list of 300 in order of their volatility, eventually sub-dividing his materials into those with coefficients 1 to 14 as Top Notes; those from 15 to 60 as Middle Notes; and those from 61 to 100 as Basic Notes [32].

Although Edward Sagarin had written 'On the inherent invalidity of all current systems of odour classification' in 1950 [33], on the grounds of scientific reproducibility, W.A. Poucher pointed out the practical use of a chart showing that volatility grouping enabled an initial choice of top, middle and basic notes for a simple perfume – lilac for example [32].

Subjective assessment by persistence of materials (A. Ellmer) [34] and by volatility (J. Carles) [35] showed how personal such classifications were and, though a perfumer may find a classification useful, each must select his own. This was pointed out by Henry Roberts in 1962 [36]. There have been many more attempts at grouping specific materials; but Marcel Billet in 1948 used a simple division of eight groups of similar odour types, e.g. floral and woody. He elaborated on this in association with the Groupement Technique de la Parfumerie (later the Societé Technique de Parfumerie de France) to give ten groups including all aspects of odour. This was approved and published in 1966 [22].

Harper, Bate Smith and Land discuss in their book a few examples of classification put forward by perfumers, but agree that in the end they prefer their own grouping [37].

To help solve the problem for students Curtis and Williams, in their book *Introduction to Perfumery*, divide odours into families, e.g. floral, animal, green, spicy, etc., and suggest a vocabulary of odours for each family [38]. Such a scheme, if standardized, would help product manufacturers and aid everyone concerned with fragrances in their quest for day-to-day communication of odour impressions; especially, of course, manufacturers of finished products and suppliers of perfumery materials.

It is advisable for a perfumer to know the current recommendations of the United States Research Institute for Fragrance Materials (RIFM) and the International Fragrance Research Association (IFRA) who give lists of materials said to be potential sensitizers, and those which should be restricted to low levels of use. The United States 'Generally Regarded as Safe' (GRAS) grading is a positive list which must be observed when marketing a product in that country.

In the twentieth century separate industries exist for flavours and perfumes with a Society for Perfumers formed in 1963 and a Society for Flavourists in 1971. There are corresponding International Federations. The flavour industry has a separate association attached to the EU but the perfumery industry is

included in the CTPA and the CTFA presentation for regulation in the EU and the USA respectively.

2.12.13 Cosmetic regulations

(a) Voluntary guidelines

Large-scale manufacture of creams, liquid emulsions and other aqueous products meant that problems of stability in storage and safety in use arose. The industry was well aware of its responsibilities and enjoyed an exceptionally good record of acceptance. In the 1930s manufacturers employed chemists in quality control and development laboratories.

The industry was so well established in the 1940s that the war-time British government recognized its importance in maintaining morale by licensing toiletry and cosmetic factories as 'essential works', and allocated a quota of raw materials to allow them to function. Key personnel were in a reserved occupation for a limited period depending on the age of the employee, male or female, and the increasing needs of the armed forces. Retail pharmacists were allowed to sell a monthly quota of cosmetics which they could make on the premises. As early as 1940 the Perfumers and Toiletry Preparation Manufacturer's section of the London Chamber of Commerce had worked with the government in these arrangements. The Toilet Preparation and Perfumery Manufacturers Association was formed in October 1945, and became the Cosmetic Toiletry and Perfumery Association (CTPA) in 1978.

(b) Consumerism

Consumerism grew in the 1960s and 1970s in the USA, and to a lesser extent in the UK and the rest of Europe, and forced the governments to replace by legislation the earlier Voluntary Codes of Good Practice which had been prepared by the Toilet Goods Association, subsequently named the Cosmetic Toiletry and Fragrance Association (CTFA) in the USA and the CTPA in the UK.

(c) Legal requirements

It was the cooperation of these trade associations and the voluntary submission of scientific data on materials and products which was the main factor in allowing the industry to influence the bureaucrats. In 1976 the EC Cosmetics Directive and its Annexes became effective [39]. In Britain the Cosmetics Products Regulations became law in 1978, and the subsequent Statutory Instrument: Cosmetic Products (Safety) Regulations in 1984 [40]. There have been a number of amendments since then.

In Europe the Comité de Liaison des Associations Européennes de L'Industrie de la Perfumerie, des Produits Cosmètiques et de Toilette (COLIPA) was formed

from all the European Associations corresponding to the CTPA, to deal with the European Commission and to prepare submissions to its specialist committees. Positive lists exist for some classes of raw materials and further information is required on those provisionally listed ingredients, such as sunscreens, cosmetic colourants, hair dyes, and preservatives, before a decision can be made on whether or not to include them in the positive lists. As the industry is not otherwise represented in the Directorate-General XI, whose terms of reference include Consumer Protection, COLIPA is essential in helping 'to prevent the acceptance of unsubstantiated and hostile views' [41].

In 1993 a major revision in the regulations governing the manufacture and sale of cosmetics in the form of the 6th Amendment to Article 7a of the EU Cosmetic Directive was passed and became effective in the UK at least, at the end of 1998. The legal requirements are discussed in Chapter 20, and the other chapters in Part 3 of this book deal with analytical tests for raw materials and finished products, and methods of testing efficacy claims, safety and stability, including one on microbial control. These build up a survey of the research, development and hygienic manufacture needed to comply with the latest EU regulations when marketing cosmetics. Companies complying with the information found in them will be able to provide a comprehensive record of tests needed for the Product Information Package (PIP) required to be kept on a product in the EU, or the dossier in the USA under their legislation.

The USA, Japan and many other countries have similar regulations, which Wilkes describes in Chapter 20.

2.12.14 Research and development

Even before these legal developments a separate science was being formed. Original research was carried out in many universities and in companies such as Beecham, L'Oreal, Gillette and Unilever. In 1935 Maison de Navarre proposed the formation of a Society of Cosmetic Chemists in America, which became a reality with 12 members in 1945, and reached 3000 members in 1980. The Society of Cosmetic Chemists of GB followed in 1948. Until 1979 these produced jointly the *Journal of the Society of Cosmetic Chemists*, now published in the USA. The British and French Societies launched the *International Journal of Cosmetic Science* in 1979. The German Society contributes articles to the American publication and Japan has its own journal, and six societies in South America produce their own journals. Thus the latest results relevant to a specialist science are published and collected together in databases. With the increased knowledge of physiology and biochemistry of the skin, and of microbiological and toxicological aspects of the industry, graduates in these and other disciplines, including chemistry, formed the membership of the British Society which numbered nearly 800 in 1978; for this reason the name was changed to the Society of Cosmetic Scientists in that year. To date the numbers have risen

to over 1000. In 1969 the International Federation of Societies of Cosmetic Chemists (IFSCC) was formed at a meeting in London of representatives from eight societies. During the ensuing decades societies were formed in many countries, the latest in China in 1999 and in this year the number was 37, many using 'Scientists' in their title, showing that the members are not only chemists. Every two years a different society hosts an International Congress for the IFSCC in its respective country, and international conferences are held at other times. In 1998 the first volume of the IFSCC journal was inaugurated.

2.12.15 The status of cosmetics today

In the last quarter of the twentieth century there has been a search for new chemicals and plants which might prove beneficial to the human body. Some of these, such as the plant oils, have been proved by scientific investigation to contain fatty acids essential to human health, and some contain specially useful ingredients, e.g. azulene in camomile, and gamma-linolenic acid in evening primrose and borage. It can be seen, however, from the history of natural products use, that it would be unwise to revert to their use without proving safety and efficacy with modern methods of analysis and clinical testing. Also, as W.A. Poucher pointed out as early as the 1920s, materials of molecular identity with natural ingredients can be synthesized with guaranteed purity and thus ensure reproducible, standard, finished products; indeed, some synthetic materials not found in nature can be proved to be beneficial.

A movement towards natural products has been accompanied by excessive and violent pressure from Animal Rights groups. For years the industry has joined in research on alternative tests for safety in humans and there is an increasing use of non-animal tests, for example for carcinogenicity for new raw materials and products. The results of these tests are continually improving and confirming the animal tests; the aim of industry to persuade the Regulatory Authorities in Europe, America and elsewhere to accept them as acceptable replacements has at last achieved success in that animal tests for cosmetics are now banned in the EU.

Many people consider cosmetics to be trivial items. Throughout history, however, men and women have used cosmetics to cleanse, adorn and protect themselves. We care about food for healthy living and medicine during illness; cosmetics, which encompass all products applied to our bodies, daily, throughout our lives, deserve equally serious scientific consideration.

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PART 2
COSMETICS FOR EVERYDAY USE

Notes on formulations

1 INGREDIENT NAMES

Ingredient labelling of cosmetic products is now required by law in the USA, Europe and many other countries of the world. To ensure that consumers are given clear information on product composition a unique labelling name is assigned to each material used, and this also enables free movement of goods around the world. The EU Commission and the Cosmetic Toiletry and Fragrance Association (CTFA) of the USA devised the International Nomenclature for Cosmetic Ingredients (INCI) names, based on the International Cosmetic Dictionary officially accepted by the FDA in the USA and updated with frequent new editions. It is therefore imperative to check the latest list before marketing a product.

This especially applies to speciality compound chemicals. Suppliers apply for a descriptive name to be used for their proprietary products, and will be able to supply them. These names are to be used for **labelling finished packs** at least by any company marketing cosmetics in the EU and the USA – and many other countries such as Canada and Australia who are adopting them. A full review of cosmetic labelling is given in Chapter 20.

In the formulations in Part 2 the current (1999) names are used. In some chapters the INCI names are listed separately. The capital letters for each part of a molecule and American spelling of words like 'Aluminum' reflect the American source and are a legal requirement.

To aid recognition in many languages some Latin words are allowed for common ingredients, e.g. 'Aqua' for 'Water' and 'Paraffinum Liquidum' for 'Mineral Oil', and for natural products the Linnean System as long as the part of the plant (flower, root, leaf or seed) or whether oil, or liquid extract etc. is mentioned; e.g. Sunflower (Helianthus Annuus) Seed Oil. Note that italics are not used and both the genus and the species have capital letters.

It must also be remembered that under EU legislation C I numbers (Colour Index) must be used for the labelling of colours.

2 WATER

Deionized, demineralized, or distilled water is prescribed because any one of these treatments helps to lessen the ionic content of the mains water which can originate from different sources and vary in quality. It is often the largest ingredient in a product and one of the most likely sources of microbial contamination. This can occur in intermediate storage tanks, pipework joints and the resin beds of demineralizing plant. The CTPA, in the *Limits and Guidelines for Microbial Quality Management* (MQM) publication in November, 1996 have

itemized Pre-treatment, Anti-microbial Systems, Water Design System and Effective Flow Rate. In addition there are five sections on Water Treatment Systems with five subsections for Sampling, Testing and Interpretation of Results including Warnings and Actions, Levels and Documentation for Process Water. Chapter 21 in Part 3 of this book discusses sterilization and antimicrobial methods, and tests and outlines other places where 'clean' water is required, such as hygienic cleansing.

3 REPRESENTATION OF MATERIALS FOR WHICH EXACT QUANTITIES ARE DECIDED BY EXPERIMENTATION

In most formulae the quantities for preservatives and perfumes are indicated by 'q.s.' *quantum sufficit*. The actual quantities depend on the results of research on each fomulation where differing raw materials, methods and conditions of production will occur. In some formulae the main ingredients already add up to 100 and the preservatives and perfume appear as extras – q.s. When these two are determined as a result of tests and the two quantities are significant then an equivalent amount can be deducted from the largest ingredient present to maintain the total at 100.

4 SPELLING STYLE

The word 'formulae' is used throughout for the plural of formula.

This is because it is in general use among scientists who follow the usage given in dictionaries which say: '... formulas for popular use and politicians, but formulae for scientists.'

3

Antiperspirants and deodorants

Philip Klepak and Jack Walkey

> Quam paene admonul ne trux caper iret in alas ...
> (Need I warn you to keep the rank goat out of your armpits ...)
> Ovid, *The Art of Love*

At the International Federation of Cosmetic Chemists (IFSCC) Conference in London in 1958, Dr Middleton proposed a definition of cosmetics as products which made people nice to be near, and this is a good description of the products now known as antiperspirants and deodorants. In marketing terms, it is a phenomenon of the second half of this century. The problem of odour and excessive perspiration has been around much longer, as indicated above. About 200 years ago, John Wesley said 'Cleanliness is indeed next to godliness.' Until this century, efforts to combat the problem were confined to the use of soap, astringents and masking perfumes.

3.1 INTRODUCTION

Underarm antiperspirant and deodorant products make up one of the largest segments in the health and beauty aids industry today. This segment has grown so quickly that it now has sales volumes of well over $2.4 billion in the United States and well over £300 million in the UK (a figure that has more than doubled in 8 years). In general, across the globe there is an ever greater consumer awareness of products that can prevent body odour. Most of the adult population in the developed world uses an antiperspirant or deodorant product every day.

Underarm products comprise a variety of formulations dispensed in many different ways, including (in order of introduction): creams, powders, sticks, squeeze bottles, roll-ons, aerosols, pump sprays, suspension solids, suspension roll-ons, soft solids and gels.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 69–100

3.2 FIRST PRODUCTS

There have been several stages in the development of the underarm products market. From the late 1800s, actors and actresses started experimenting with solutions of aluminium chloride to make them nicer to be near under the spotlights in their heavy theatrical costumes. In 1888, MUM was launched in Europe using zinc oxide as an antimicrobial ingredient in a cream base. This product controlled odour but not wetness. By the early 1900s, the first aluminium-containing antiperspirant was introduced, based on a very astringent aluminium chloride solution having a pH range between 2.5 and 3.0. This acidity caused irritation of the skin and considerable fabric deterioration.

The consumer market started to develop in a limited way in the 1920s and 1930s, mostly in the USA. Such products as ODO-RO-NO and ARRID CREAM were launched, based, respectively, on aluminium chloride and aluminium sulfate. These products were effective antiperspirants, but with acidic properties yielding unacceptable side-effects. These undesirable factors led to the development of self-buffered aluminium chloride compounds known as basic aluminium chlorides or **aluminium chlorohydrates**. This complex, introduced in the 1940s, had an internal buffer that maintained a pH of approximately 4. It was formed by neutralizing some of the acidity of aluminium chloride with aluminium. Aluminium chlorohydrate with an empirical formula, $Al_2(OH)_5Cl \cdot 2.5H_2O$, had advantages of being less irritating with less fabric destruction than aluminium chloride, yet it was easily formulated and still effective as an antiperspirant. Aluminium chlorohydrate (ACH) quickly became the ingredient of choice and stimulated the development of safe and effective underarm products. It is still widely used today.

In the mid-1950s, a neutral pH **sodium aluminium chlorhydroxy lactate complex** was introduced which was stable in a sodium stearate-based deodorant stick. Although this material provides deodorant properties due to its antibacterial action, it has insufficient antiperspirant effectiveness, and is not an approved active per the Antiperspirant Drug Products Monograph of the Food and Drug Administration (FDA).

In 1966 alcohol-soluble ACH (aluminium chlorohydrate propylene glycol complex) was introduced for non-aqueous liquid formulations, so allowing the introduction of quick-dry alcohol-based products.

The need for increased sweat reduction properties has stimulated the development of more effective antiperspirant salts such as:

1. aluminium sesquichlorohydrate;
2. aluminium dichlorohydrate;
3. aluminium zirconium chlorohydrates;
4. aluminium zirconium glycine complexes;
5. enhanced efficacy aluminium chlorohydrates;
6. enhanced efficacy or 'activated' aluminium zirconium chlorohydrates;

7. enhanced efficacy or 'activated' aluminium zirconium chlorohydrate glycine complexes.

Today, the two principal active ingredients used are activated aluminium chlorohydrate (ACH) and activated aluminium zirconium chlorohydrate (AZCH) which have both proved to be safe and effective.

As customers and marketers seek greater efficacy, AZCH in a variety of Al : Zr ratios, have increasingly become the preferred active ingredients for non-aerosol products worldwide.

3.3 ANTIPERSPIRANTS *vs.* DEODORANTS

Most people use the terms 'antiperspirant' and 'deodorant' interchangeably, although they have quite distinct actions.

An **antiperspirant** actively reduces the amount of underarm perspiration. In the USA, an antiperspirant is classified as an over-the-counter (OTC) drug, since it has an effect on a bodily function, namely, eccrine sweating. Therefore, such products are regulated by the FDA. In the UK, an antiperspirant comes within the definition of a drug, in that it has a physiological action, but in practice these products are not subject to 'medicines' legislation at the time of writing.

A **deodorant** masks and/or reduces axillary odour through the use of an antimicrobial agent or a fragrance. Deodorants have a non-therapeutic effect only and are regarded as cosmetics, not subject to regulatory control in the UK or in the USA. It should be noted that a 'deodorant' is not an 'antiperspirant', but an 'antiperspirant' is automatically a 'deodorant'. The reason for this is that aluminium salts have bactericidal properties (Section XVI in the FDA Monograph), rapidly reducing the indigenous bacterial population when applied regularly. Accordingly, the labels of antiperspirants display the dual description 'antiperspirant/deodorant'.

3.4 SWEAT GLANDS

Commercial antiperspirants are formulated to reduce the secretion from eccrine sweat glands, and the level of body odour which develops as a result of secretions from the apocrine glands. Eccrine glands are present at birth and can be found all over the body (estimated at 3–5 million glands), although they are most abundant in the skin of the palms, soles and head. They function continuously and are known as the true sweat glands since their main function is to respond to thermal stimuli and cool the body/control body temperature. They can produce up to 2 litres of perspiration per day in excessively hot and humid conditions. The secretion is directly onto the skin surface and consists mainly of water (approximately 99%), sodium chloride, urea, glucose, and potassium and lactate ions. The axillary area can contain 20 000–30 000 eccrine glands.

Apocrine glands develop during childhood and function with the onset of puberty. These glands are present in the axillae and urogenital regions of the body. Their excretory ducts open into hair follicles. The secretion from the apocrine glands is the result of emotional stimuli such as excitement, anger and fear. It is a milky substance that primarily consists of fatty amino acids, cholesterol, and various steroids, and produces odour when decomposed by micrococci and diphtheroid bacteria naturally present on the skin surface. The presence of hair increases axillary odour since it acts as a collection site for secretions and bacteria. Scientists at the Monell Chemical Senses Center in Philadelphia, Pennsylvania, USA, have identified a main malodour compound as 3-methyl-2-hexenoic acid.

3.5 MECHANISM OF ANTIPERSPIRANT ACTION

Many different theories have been proposed to explain the mechanism involved in the reduction of sweat after the topical application of an antiperspirant product. Several hypotheses are listed in the FDA's *Tentative Final Antiperspirant Monograph* in the section 'Pharmacology of antiperspirants'. Today, the most widely accepted theory of the antiperspirant action is that of diffusion of the soluble antiperspirant active ingredient into the sweat duct coupled with the slow neutralization of the acidic metal salt. This produces a gelatinous and insoluble polymeric aluminium hydroxide–protein gel which acts as a partial obstruction at the orifice of the sweat gland so reducing, but not stopping, the flow of axillary perspiration. This reaction happens at, or below, the natural physiological pH of the skin surface.

3.6 CLASSIFICATION OF ANTIPERSPIRANT ACTIVES

USP XXIII has established 28 official monographs covering antiperspirant actives. Some of the actives included are:

1. Aluminum Chlorohydrate
2. Aluminum Chlorohydrate Solution
3. Aluminum Sesquichlorohydrate
4. Aluminum Chlorohydrex PG
5. Aluminum Zirconium Trichlorohydrate
6. Aluminum Zirconium Trichlorohydrex Gly
7. Aluminum Zirconium Tetrachlorohydrate
8. Aluminum Zirconium Tetrachlorohydrex Gly
9. Aluminum Zirconium Tetrachlorohydrex Gly Solution
10. Aluminum Zirconium Pentachlorohydrate

The above terminology is also used in the CTFA and INCI nomenclature.

3.7 FDA AND EC COSMETIC DIRECTIVE: REGULATORY STANDARDS OF SAFETY AND EFFICACY

3.7.1 USA – 'The Monograph'

In 1972 the US FDA published in the *Federal Register* a document establishing procedures for categorizing OTC drugs and appointing advisory review panels to evaluate safety, efficacy, benefit-to-risk ratio, active ingredient combinations and proper labelling. The FDA's purpose was to assure consumers that OTC drugs on the market are safe, effective and properly labelled. The *Tentative Final Monograph (TFM) for Antiperspirant Drug Products* for OTC human use was issued by the FDA in August 1982. It lists allowed active ingredients, labelling claims, minimum effectiveness requirements, and warning statements. The Monograph allows the use of aluminium chlorohydrates or aluminium zirconium chlorohydrates at levels up to 25% and 20%, respectively, calculated on an anhydrous basis where buffering components, such as glycines, are omitted from this calculation. However, aluminium zirconium chlorohydrates are not permitted in aerosol forms because of a possible inhalation risk. Most products now use either aluminium chlorohydrate or aluminium zirconium chlorohydrate actives in their formulations. On an equal-weight basis, aluminium zirconium salts are roughly a third more effective than aluminium chlorohydrate. There is a strong possibility that the TFM will be granted final status shortly.

3.7.2 EEC Cosmetic Directive

Antiperspirant products are regulated as cosmetics within the European Union. Certain substances can be used with restrictions.

The status of aluminium zirconium chlorohydrates in the European Economic Community was defined in the *EEC Cosmetics Directive*, June 1986, Annex III, Part 1, Page 9, Reference No. 50. Aluminium zirconium chloride hydroxide complexes and the aluminium zirconium chloride hydroxide glycine complexes are allowed at the following maximum authorized concentration in the finished cosmetic product: 20% as anhydrous aluminium zirconium chloride hydroxide, or 5.4% as zirconium; not to be used in aerosol dispensers. There are no restrictions on the use of aluminium chlorohydrate.

3.7.3 Efficacy standards

The Monograph states that in order for an antiperspirant to be labelled as such it must meet a minimum of 20% sweat reduction in at least 50% of the test population. The test is commonly referred to as a 'hot room' study or an antiperspirant effectiveness study where perspiration is stimulated by high levels of heat and humidity. The basic protocol indicates that gravimetric measurement of

axillary perspiration rates be conducted in a hot room at 100°F (37.5°C) and 35% relative humidity.

In the UK the Independent Television Companies Association (ITCA) has issued a protocol for antiperspirant effectiveness by direct comparison of products using gravimetric measurement under conditions of thermal stress. The benchmark for efficiency is a 20% minimum sweat reduction as specified in the FDA Monograph. Most roll-ons and sticks based on approximately 20% of ACH exceed this standard. The introduction of aluminium zirconium chlorohydrates in the 1970s produced a sharp increase in effectiveness. Roll-ons and solids based on 20% AZCH provide a 25–40% increase in perspiration reduction compared to similar ACH-based formulations. Even higher levels of efficacy can be achieved with activated AZCH in powder form – solids, roll-ons or soft solids. Sweat reduction levels of 50–60% can now be achieved.

In the case of the aerosol, the original powder-in-oil suspension reduces perspiration by 20–30%, significantly lower than the companion ACH-based roll-on. At this level of efficiency the products only just reach the minimum requirement of the OTC antiperspirant Monograph. The introduction of activated ACH to the market at the Lugano Aerosol Congress, in September 1985, allowed the formulation of aerosol antiperspirants with efficiencies of 35–45%. These enhanced efficacy systems are now used by all leading marketers worldwide and have become the standard for APD aerosol actives.

3.7.4 Cosmetic Directive 93/35/EEC 6th Amendment 1993

Cosmetic Products (Safety) Regulations 1996

The 6th Amendment has had a very strong impact on antiperspirant products, principally the requirement to list active ingredients and that proof of effects claimed must be available as part of the Product Information Dossier which is now required for all personal products.

PROOF OF EFFECTS CLAIMED is a new requirement in Europe, but has been accepted in the USA since the publication of the Monograph. European marketers have made a detailed study of all advertising and label claims so that each can be supported. The far-reaching effects of this legislation are discussed in the following section 'Claims and Justification'.

3.8 CLAIMS AND JUSTIFICATION

The introduction of the 6th Amendment to the Cosmetic Directive, referred to previously, forced European marketers to be in possession of proof of any claims they make for their products. This has far-reaching effects for APDs (antiperspirants and deodorants). Claims are normally grouped into one of the following categories:

PERFORMANCE, MILDNESS, FEEL, ONSET.

3.8.1 Performance

If such claims as 'UNBEATABLE WETNESS PROTECTION', 'MOST EFFECTIVE FORMULA', 'NONE BETTER' and 'MAXIMUM PERFORMANCE' are used, they must now be supported by hot room efficacy trials *of the total formulation.*

3.8.2 Performance – duration

The claim of '24 hour protection' is made for products which use active ingredients at levels recommended in the Monograph. Antiperspirant testing at an independent laboratory such as Hill Top involves a final sweat collection approximately 24 hours after the final product application. So it is reasonable and justifiable to make a claim that an acceptably formulated APD product will provide effective antiperspirant action over a 24 hour period. On this basis, similar claims such as 'ALL-DAY PROTECTION', 'DAY-LONG FRESHNESS', 'WORKS ALL DAY', 'KEEPS YOU FRESH ALL DAY' can also be justified.

3.8.3 Mildness

Non-specific claims are usually justified by the exclusion of known irritants such as alcohol, the careful selection of non-irritant perfumes, and the inclusion of emollients or other known skin-friendly ingredients. If mildness claims include any reference to specific testing, then the results of such tests must be available.

One claim in this area is 'pH BALANCED', which may reassure the customer but has no scientific basis since all stable formulations are pH balanced and the pH of APDs is generally dictated by the pH of the active, and all the actives currently used have a pH between 3.8 and 4.4.

3.8.4 Feel

NON-STING. Alcohol is a primary irritant and is the source of the stinging sensation. Excluding alcohol from the formulation will reduce the level of stinging. The addition of emollients or aloe, allantoin, etc., will also help to reduce any stinging sensation.

3.8.5 Feel

NON-STICKY. Stickiness is a function of formulation and drying time. All water-based formulations will feel more or less sticky during the drying phase. In quick-dry formulations, alcohol and volatile silicones accelerate drying so it is almost instantaneous. Oil-in-water or water-in-oil emulsions are at the other extreme of slow drying, and do not go through a sticky stage. Anhydrous formulations where the active goes on dry – aerosols, solid sticks, soft solid suspensions – are truly non-sticky.

3.8.6 Onset – body responsive

This claim revolves around statements such as 'works when you need it most', 'body responsive', 'heat activated'. These claims centre around the fact that antiperspirant actives are inert in dry form and react with perspiration only when they are dissolved by it. Eccrine sweating is triggered by excessive body temperature and the resultant sweat dissolves the antiperspirant deodorant active.

3.9 VOCs – VOLATILE ORGANIC COMPOUNDS

The State of California has issued regulations for reducing volatile organic compound (VOC) emissions from antiperspsirants and deodorants. VOCs contribute to the formation of oxidants and photochemically generated particulate matter in the atmosphere. The volatile organic compounds in antiperspirants and deodorants can generally include propellants, solvents, and non-solvent/non-propellant volatile organic compounds.

Antiperspirants and deodorants manufactured, supplied or sold in California must adhere to the standards in Table 3.1 for percentage VOC by weight.

Ethanol, fragrances (2% max), and substances with vapour pressures of 2 mmHg or less are exempt from the regulations.

Other regions and/or states in the US, as well as the European Community, are considering similar control regulations. Alternative control plans based on 'chemical reactivity' of ingredients are under consideration.

Table 3.1 Percentage VOC by weight required for antiperspirants and deodorants in California

	Effective dates					
	31 December 1992		*1 January 1997*		*1 January 1999*	
	*HVOC**	*MVOC†*	*HVOC*	*MVOC*	*HVOC*	*MVOC*
Aerosol antiperspirant	60	20	40	10	0	10
Aerosol deodorant	20	20	14	10	0	10
Non-aerosol	0	0	0	0	0	0

* High volatility organic compounds, i.e. a compound that exerts a vapour pressure greater than 80 mmHg at 20°C.

† Medium volatility organic compounds, i.e. a compound that exerts a vapour pressure greater than 2 mmHg and less than 80 mmHg at 20°C.

3.10 PRODUCT FORMS

This chapter is concerned with antiperspirants and/or deodorants for the underarm. Body sprays are excluded because they are sold for all-over body application.

These products, first introduced in Scandinavia in the 1970s, have proved extremely popular and certainly supply a consumer need, but they do not tackle the particular problems of axillary perspiration – odour and wetness.

There are distinct demographic differences in the choice of a combined antiperspirant (A/P)/deodorant (DEO) or a deodorant only, as indicated by the approximate figures in Table 3.2. No-one has yet suggested a satisfactory reason for these differences. Physiology, diet, standard of living, climate, cultural and sexual attitudes, religion and medical opinion, all play a part.

Antiperspirants are unique among health and beauty aids in the variety of product forms which are available, and the speed with which consumers choose to change. Until recently the American consumer set the pace and was followed by the UK consumer, but this is no longer automatically the case, as shown by Table 3.3.

Table 3.2 Demographic differences in choice of product (percentages)

	USA and Canada	*UK, South Africa, Australia*	*Continental Europe*	*South America*	*Scandinavia*	*Japan and Pacific*
A/P and DEO	90	80	20	70	50	40
DEO only	10	20	80	30	50	60

Table 3.3 Differences between the USA and UK markets (percentages)

	The USA market				
	1960	*1970*	*1980*	*1990*	*1998 (estimate)*
Aerosols	0	75	35	23	17
Roll-ons	40	10	35	24	14
Stick/solids	40	3	25	52	56
Others*	20	12	5	1	13
	The UK market				
	1965	*1975*	*1985*	*1990*	*1998 (estimate)*
Aerosols	0	34	55	70	69
Roll-ons	70	64	44	22	21
Stick/solids	20	2	1	8	10
Others	10	0	0	0	0

*Includes clear gels and soft solids.

The great breakthroughs in marketing came with the introduction of the roll-on (1950s in the USA; 1960s in the UK), the introduction of the aerosol (1960s in the USA; 1970s in the UK), the introduction of the solid (stick) in the 1980s and the introduction of gels in the 1990s. In terms of marketing, the aerosol had the greatest impact because of its hygienic and shareable advantages. Ten million men in the UK were converted to using antiperspirants or deodorants in the early 1970s as a result of the introduction of 'family deodorants' and the launch of OLD SPICE and other male grooming aids.

The USA and the UK took different directions following the conversion to hydrocarbon propellants in the late 1970s/early 1980s. Certain aerosol formulation changes in the USA were not accepted by the consumer, who turned increasingly to solid forms, which now dominate the market.

In the USA it seems that customers like solids, gels and soft solids because there is no waste. They are practical, effective and not sticky. As a marketing tool, antiperspirant efficiency is a potent advantage on the US market. Suspension roll-ons, solids and soft solid forms have the potential to contain what are currently the most effective actives – ACTIVATED ALUMINIUM ZIRCONIUM CHLOROHYDRATES and ACTIVATED ALUMINIUM SESQUICHLOROHYDRATE, and this proven increased efficacy has powered the market to new heights.

In the UK, aerosol formulations based on hydrocarbon propellant systems have not lost their market share as they have done in the USA and are by far the most popular product form. The quick use-up rate of an aerosol compared to any non-aerosol form makes it a natural choice for advertising support. Gels and solids now have a 10% share of the UK market, but have not yet succeeded to the same extent as in the USA. This is probably due to cost. In the USA all product forms are similarly priced, but in the UK solids and gels are premium priced, and the roll-on and aerosol are perceived as the best value products.

The aerosol is the dominant product form in other European countries, such as France, Germany, Italy and Spain.

3.11 ACTIVE INGREDIENT FORMS

The physical forms of aluminium chlorohydrate and aluminium zirconium complexes are available in: (1) aqueous solution (concentrations up to 50% in water for ACH and 46% for AZCH), (2) all forms of powders (various particle sizes and shapes) and (3) propylene glycol solutions.

POWDER TYPES. ***Macrospherical*** powder is composed of relatively large, dense spheres and a minimum number of small particles (10% less than 10 microns) for aerosol use and low-residue solids. At the other end of the scale, super ultrafine particles of ACH and AZCH are used in suspension sticks and suspension roll-ons, where settling rate and surface area play a large role. Spray-dried powder which is micronized to 97.5% of particles below 325 mesh is widely used in aerosol suspensions.

3.12 ANTIPERSPIRANT ACTIVE INGREDIENTS

Since the original patent (Huehn and Haufe, Klepak, US, 1940) on the redox synthesis of basic aluminium complexes, the number of these water-soluble complexes is growing. They include aluminium dichlorohydrate (ADCH), aluminium sesquichlorohydrate (ASCH) and the most widely used complex salt produced commercially from this patent, aluminium chlorohydrate (ACH). Buffering agents, such as glycine and urea, along with alcohol solubilizing adjuncts, such as propylene glycol and polyethylene glycol, can be combined with ACH. A synergistic effect was found to exist when cationic zirconium compounds were linked to ACH. The aluminium compounds buffered the acidity of the zirconium, which in turn increased the effectiveness of the complex. A new series of products are now possible by varying the aluminium-to-zirconium ratio. These compounds are called aluminium zirconium chlorohydrates, or AZCH for short. Once this salt is complexed with glycine for its buffering, solubilizing and stabilizing effects, these compounds are referred to as aluminium zirconium chlorohydrex-glycine.

Basic aluminium chloride systems have the general empirical formula $Al_2(OH)_aCl_b$, where $a+b=6$. ACH, $Al_2(OH)_5Cl \cdot 2.5H_2O$ is a 5/6 basic aluminium chloride. This means that five out of the six negative charges are derived from hydroxy groups. The accepted definition of aluminium chlorohydrate is based on the aluminium to chloride atomic ratio of 2.1 : 1 down to, but not including, the 1.9 : 1 ratio. If the active ingredient has any other ratio, it is not an aluminium chlorohydrate by definition. If it has a lower atomic ratio of aluminium to chloride, it is called either an aluminium sesquichlorohydrate or an aluminium dichlorohydrate. The ratio range for each active is given in Table 3.4.

Aluminium zirconium actives are defined by total metals to chloride atomic ratio as well as Al : Zr atomic ratio. For example, if the ratio of Al to Zr is 2 : 1, the compound could be either a trichlorohydrate or a tetrachlorohydrate. The determining factor in this case is the total metals to chloride ratio. If this ratio was, for example, 1.7 : 1, then the compound would be a trichlorohydrate; if the ratio was 1.3 : 1, the compound would be a tetrachlorohydrate. This confusing

Table 3.4 Nomenclature for aluminium chlorohydrates

Active ingredient	*Empirical formula*	*Al : Cl Atomic ratio*
Aluminium chlorohydrate	$Al_2(OH)_5Cl$ 5/6 basic	2.1 : 1 down to but not including 1.9 : 1
Aluminium sesquichlorohydrate	$Al_2(OH)_{4.5}Cl_{1.5}$ 3/4 basic	1.9 : 1 down to but not including 1.25 : 1
Aluminium dichlorohydrate	$Al_2(OH)_4Cl_2$ 2/3 basic	1.25 : 1 down to and including 0.9 : 1

Table 3.5 Nomenclature for aluminium zirconium complexes

Ingredient name	*(Al+Zr):Cl Atomic ratio*	*Al:Zr Atomic ratio*
Aluminium zirconium trichlorohydrate (-drex)	2.1:1 down to but not including 1.5:1	2.0:1 up to but not including 6.0:1
Aluminium zirconium tetrachlorohydrate (-drex)	1.5:1 down to and including 0.9:1	2.0:1 up to but not including 6.0:1
Aluminium zirconium pentachlorohydrate (-drex)	2.1:1 down to but not including 1.5:1	6.0:1 up to and including 10.0:1
Aluminium zirconium octachlorohydrate (-drex)	1.5:1 down to and including 0.9:1	6.0:1 up to and including 10.0:1

but necessary style for nomenclature is most easily understood in tabular form (Table 3.5).

Activated ACH and AZCH compounds are the most recent advancements in antiperspirant technology. 'Activated' or 'enhanced' refers to proprietary or patented processes which modify the distribution of the active molecular species, thereby resulting in significantly increased sweat reduction capabilities when compared to the standard or inactivated product. Experimental evidence supports the fact that higher amounts of intermediate molecular weight species and greater bulk charge are present in 'activated' products. The activated antiperspirant salts have identical chemical compositions to the conventional actives. Most major antiperspirant marketers are currently producing products incorporating enhanced effectiveness actives. The present range of activated ACH and AZCH compounds includes activated aluminium chlorohydrate and activated aluminium zirconium chlorohydrate.

3.13 FORMULATIONS

3.13.1 Creams

The first products marketed in the 1920s and 1930s were simple solutions based on aluminium chloride or sulfate. The solutions were thin and drippy; the creams were a slight improvement, although the consumers had to apply them with their fingers to the axillae. These oil-in-water emulsions required acid-stable emulsifying agents and the selection of an acid-stable perfume oil was equally important. Formula I is an example of an early ACH-based emulsion. While Formula II is also ACH-based, it yields an aesthetically elegant cream.

Note Aluminium chlorohydrate is referred to as ACH and aluminium zirconium chlorohydrate is referred to as AZCH in all formulations that follow. SD alcohol 40 refers to a particular type of specially denatured ethanol which contains tert-butyl alcohol and brucine sulfate as the denaturant system.

Formula I

	% w/w
A. Oil phase	
Petrolatum (and) lanolin alcohol	24.0
Cetyl Alcohol	1.5
B. Water phase	
Deionized water	54.5
ACH	20.0
C. Fragrance	q.s.

Procedure

1. Heat A and B separately to 70°C
2. Slowly add B to A with continuous mixing
3. Cool to 40°C. Add C
4. Homogenize and pour into suitable containers

Formula II

		% w/w
A	ACH 50% solution	40.0
B	Glyceryl stearate (and) PEG-100 stearate	15.0
C	Cetyl alcohol	5.0
D	Sorbitol, 70% solution	3.0
E	Deionized water	37.0
F	Fragrance	q.s.

Procedure

1. Combine A and E, heat to 70°C
2. Add B, C and D
3. Cool to 40°C. Add F
4. Homogenize and pour into suitable containers

3.13.2 Squeeze sprays (packs)

World War II led to the development of plastics, which were used in the antiperspirant/deodorant field to make the squeeze spray bottle. This product had the advantage of eliminating direct contact with hands for application. However, the spray to the underarms was coarse and wet. The following original cologne squeeze pack composition could be considered today for a hydro-alcoholic manual pump formulation:

Formula III

		% w/w
A	SD Alcohol 40	50.0
B	Propylene glycol	3.5
C	ACH, 50% solution	40.0
D	Deionized water	6.5
E	Fragrance	q.s.

Procedure

1. Mix A and D using overhead stirrer
2. Add B. Mix for 10 min
3. Add C slowly
4. Add E. When homogeneous, pour into suitable containers

3.13.3 Sticks and solids

Deodorant sticks are typically based on sodium stearate as the gelling agent for either propylene glycol or alcohol. They also contain an anti-microbial agent, humectant and perfume. Historically, deodorants are more generally accepted by men. The following are typical deodorant formulas:

Formula IV

		% w/w
A	Ethanol	75.0
B	Sodium stearate	8.0
C	Deionized water	11.9
D	Sorbitol, 70%	5.0
E	Triclosan	0.1
F	Fragrance	q.s.

Procedure

1. Combine A and C and heat to 70°C
2. Add D, mix for 5 min
3. Add B and E, mix until clear
4. Cool to 65°C. Add F
5. Pour into suitable containers at 60°C

Formula V

		% w/w
A	Propylene glycol	50.0
B	Sodium stearate	7.0
C	Deionized water	42.9
D	Triclosan	0.1
E	Fragrance	q.s.

Procedure

1. Combine A and C and heat to 70°C
2. Add B and D, mix until clear
3. Cool to 65°C. Add E
4. Pour into suitable containers at 60°C

The first stick antiperspirant deodorants were based on sodium stearate/alcohol building blocks. To make aluminium chlorohydrate compatible with this base, it was necessary to buffer it to a similar pH, and this was done by the complexing

of ACH with lactic acid to produce sodium aluminium chlorohydroxylactate (CHLORACEL; Reheis). The following is a typical formulation:

Formula VI

		% w/w
A	CHLORACEL* 40% w/w solution	52.2
B	Alcohol, SDA 40	37.6
C	Sodium stearate	6.3
D	70% Sorbitol	3.1
E	Stearyl alcohol	0.8
F	Fragrance	q.s.

*Reheis

Procedure

1. Add B to A. Heat to 65–75°C
2. Add D
3. Add C, mix until clear
4. Add E, mix until clear. Cool to 60°C
5. Add F
6. Pour into suitable containers at 55°C

These formulations are aesthetically pleasant and have excellent application characteristics, but the antiperspirant efficiency is low.

In the 1960s, more effective stick antiperspirants were developed based on aluminium chlorohydrate propylene glycol complex (REHYDROL II; Reheis) which is alcohol soluble and has good antiperspirant and deodorant efficiency. The following is a typical formulation:

Formula VII

		% w/w
A	REHYDROL II (Reheis)	20.0
B	Propylene glycol	26.0
C	Stearamide MEA	26.0
D	Isocetyl alcohol	11.3
E	Alcohol SDA-40 anhydrous	14.5
F	Isopropyl myristate	2.0
G	Titanium oxide	0.2
H	Fragrance	q.s.

Procedure

1. Add B to A. Heat to 80°C
2. Add C, maintaining 80°C
3. When dissolved, add D, cool to 76°C, then add E, F, G and H
4. Continue mixing until homogeneous
5. Allow to cool to 61–63°C and pour into stick casings

In the late 1970s, antiperspirant sticks, commonly referred to as antiperspirant solids or dry deodorants, were introduced. These products are typically anhydrous and are largely composed of volatile silicones that function as carriers of the active ingredient to the skin. These are low molecular weight cyclomethicones that have measurably low vapour pressure at body temperature. As well as evaporating from the skin relatively rapidly, without imparting a perceptible cooling sensation, they also leave a light non-oily skin feel.

Almost all antiperspirant solids employ stearyl alcohol as the gelling agent. Emollients are often added to impart a softer feel and to add glideability. However, men's sticks are formulated to be less emollient because a harder stick is preferred. Most solids also contain talc and/or silica. Silica is an effective suspending agent that helps to keep the active ingredient homogeneously suspended throughout the stick. Miscellaneous ingredients often include colours, titanium dioxide (opacifying agent) and allantoin (soothing agent).

While sticks or solids look simple, they are really complex chemical systems. From the formulator's perspective, each stick formulation is a balance of ingredients designed to make the most of several performance factors. Payout, slip or lubricity, chemical stability, softening temperature, and of course, efficiency, are just a few. The following are two antiperspirant solid formulations:

Formula VIII

		% w/w
A	Volatile silicone	47.5
B	Stearyl alcohol	20.0
C	PPG-3 myristyl ether	5.0
D	PEG-8 distearate	2.0
E	Talc, 325 mesh	1.0
F	Silica	1.5
G	Polyethylene	3.0
H	ACH super ultrafine	20.0
I	Fragrance	q.s.

*REACH AZP-908; (Reheis)

Procedure

1. Heat A to 65°C
2. Add C and D with stirring
3. Add B slowly. Maintain 65°C
4. Increase stirring. Add H. Mix for 5 min
5. Add E, F and G
6. Cool to 60°C. Add I
7. Pour into stick casings at 54°C

Formula IX

		% w/w
A	Volatile silicone	53.8
B	Stearyl alcohol	14.0
C	Hydrogenated castor oil MP-70	5.2
D	PEG-8 distearate	1.0
E	Silica	1.0
F	Activated AZCH* super ultrafine	25.0
G	Fragrance	q.s.

Procedure

1. Heat A to 70°C
2. Add B, C and D. Maintain 70°C
3. When clear, add F. Mix for 10min
4. Add E
5. Cool to 60°C. Add F
6. Pour into suitable containers at 54°C

Aluminium chlorohydrate (ACH), aluminium zirconium chlorohydrates (AZCH) and the enhanced forms of ACH and AZCH can be incorporated interchangeably into these types of formulas, but certain particle-size requirements must be met. Settling of the active before the stick solidifies must be avoided because it would cause an uneven distribution or stratification of the active ingredient. Micronized grades of active ingredients should be used.

In the USA the opaque solid antiperspirant deodorants have demonstrated a high level of consumer acceptability and satisfaction. They are available in a variety of colours, shapes and perfumes and currently hold in excess of 50% of the market. This success has not yet been duplicated in the UK.

Clear sticks, which are essentially gelled solutions of special liquid actives in glycols, have been introduced on the US market. They need substantial refinement of their aesthetic properties before they are more broadly accepted by the consumer. A typical formulation which uses a self-buffered active is shown below. Surprisingly, these products demonstrate good efficacy for the relatively low active levels that they contain.

Formula X

		% w/w
A	REACH AZP-908 PG (30% Soln.) SB (Reheis)	50.00
B	Propylene Glycol	33.50
C	Dipropylene Glycol (low odour grade)	10.00
D	Glycine	1.00
E	Diisopropyl Sebacate	2.00
F	Dimethicone Copolyol	1.50
G	Dibenzylidene Sorbitol	2.00
		100.00

Procedure

1. Combine A and D and heat to 105°C while mixing until clear. Cool to 80°C. Use a Lightnin® mixer or equivalent
2. Separately combine B and C and heat to 115–120°C, and then add G slowly. Mix until clear. Cool to 90°C
3. Add Step 1 and Step 2 and mix well
4. Separately combine E and F. Heat slightly to make clear. Add to Step 3. Cool to 72–74°C
5. Pour into containers before gelling

3.13.4 Roll-ons

One of the most versatile and globally popular carrier forms of antiperspirant is the roll-on. The several types of roll-ons differ in their formulation base. Water, alcohol, hydro-alcoholic systems, esters and silicones have been used over the

years as vehicles in roll-ons. This form is well accepted due to its long history, ease of application and high efficiency.

(a) Water-based roll-ons (oil-in-water)

The water-based roll-on is usually an oil-in-water emulsion rather than a water-in-oil system due to the poorer efficiency of the latter. The oil-in-water emulsion presents the active ingredient in a readily accessible solution form in the external phase. Since the active ingredient ends up in the dissolved state, the formulator can use either a liquid or solid antiperspirant active. The following is a typical emulsion roll-on formulation, which exhibits excellent physical stability and application properties.

Formula XI

		% w/w
A	REACH 501 soln., 50% (Reheis)	40.0
B	Steareth-21	2.0
C	Steareth-2	2.0
D	Steareth-5 Stearate	1.0
E	Cyclomethicone (and) PPG-15 Stearyl Ether	5.0
F	Deionized Water	50.0
G	Fragrance	q.s.

Procedure

1. Combine B, C, D and E and heat to 70°C
2. Heat F separately at 70°C
3. Add B/C/D/E to F with agitation
4. Homogenize the mixture for 1–3 min
5. Add A to emulsion slowly with agitation
6. Homogenize the mixture again for 1–3 min
7. Cool to 35°C with continuous agitation
8. Add G
9. Fill into suitable containers

(b) Alcohol-based and hydro-alcoholic roll-ons

The alcohol-based roll-on allows for a shorter drying time and only actives with adequate alcohol solubility will work in this system. These include alcohol-soluble ACH, aluminium chlorohydrex propylene glycol, aluminium sesquichlorohydrate and aluminium zirconium pentachlorohydrate. If properly formulated, a clear anhydrous product can be made. Since the active ingredient is dissolved in the formulation, initial particle size is not important. The following formulations are examples of an alcohol-based roll-on and a hydro-alcoholic roll-on. Both of these formulae are more popular in Europe than the USA.

Formula XII

		% w/w
A	SD Alcohol 40	40.4
B	Propylene glycol	2.0
C	PPG-5-ceteth-20	2.0
D	Hydroxyethylcellulose	0.2
E	Deionized water	17.9
F	AZCH, 40% Solution (REZAL 67 Solution; Reheis)	37.5
G	Fragrance	q.s.

Procedure

1. Disperse D in E until clear, mix for approximately 2 h
2. Add F slowly. Mix 5 min
3. In a separate container, combine A, B and C. Then slowly add to batch with agitation
4. Add G, mix thoroughly and pour into suitable containers

Formula XIII

		% w/w
A	SD Alcohol 40, anhydrous	54.2
B	Stearic acid (triple pressed)	2.0
C	PPG-15 stearyl ether	2.0
D	Cyclomethicone	20.0
E	Hydroxypropylcellulose	0.8
F	Isopropyl myristate	1.0
G	Aluminium chlorohydrex PG (REHYDROL II, Reheis)	20.0
H	Fragrance	q.s.

Procedure

1. Dissolve G, then B in A, mix until clear
2. Add C, mix until clear
3. Add H, D and F then E, mix until clear
4. Pour into suitable containers

(c) Suspension roll-ons

In the late 1970s, suspension roll-ons were introduced in the USA. This formulation is anhydrous and basically a physical suspension of antiperspirant salt in volatile silicone. It is the most popular roll-on in the USA due to the dry application, non-tacky feel, and effectiveness. However, due to the expense of volatile silicone, this type of formulation is not as yet popular in Europe. An important factor to note is that the particle size of the active ingredient needs to be superfine. Since this product is a suspension, settling is a problem, hence 'shake well' labelling instructions are indicated on these packages. A typical formulation is shown below.

Formula XIV

		% w/w
A	Volatile silicone	66.0
B	Quaternium-18 bentonite or quaternium-18 Hectorite mastergel	13.5
C	Silica	0.5
D	Activated AZCH, superultrafine	20.0
E	Fragrance	q.s.

Procedure

1. Disperse B into A with an overhead mixer for 20 min
2. Add D, mix for 10 min
3. Add C and F, mix for 10 min
4. Use homomixer on batch for 3–5 min and pour into suitable containers

(d) Clear water-in-oil roll-ons

These compositions are relatively new on the market. They demonstrate superior aesthetics and leave no residue or deposit on the skin after application. Clarity is achieved simply by following the room temperature order of addition specified.

Formula XV

		% w/w
A	REACH 301 soln., 50% (Reheis)	40.00
B	Deionized Water	8.75
C	Dipropylene Glycol	3.00
D	PEG-7 Glyceryl Cocoate	18.20
E	Cyclomethicone (and) Dimethicone Copolyol	20.00
F	Cetearyl Octanoate	3.20
G	Polysorbate 20	1.00
H	Deionized Water	4.10
I	Isopropyl Myristate	1.00
J	Fragrance	0.75

Procedure

1. Combine A, B, and C with overhead mixing (medium agitation)
2. Slowly add D. Mix well
3. Slowly add E. Mix well
4. Slowly add F. Mix well
5. Premix G and H. Slowly add to the main batch
6. Premix I and J. Slowly add to the main batch. Mix until clear
7. Pour into appropriate containers

3.13.5 Pumps

In the mid-1970s, pump antiperspirants were marketed in response to the first ozone depletion scare and the declining aerosol market, although their success

was limited. The second generation of pump antiperspirants was launched in the UK in the late 1980s, again in response to consumer concern over aerosols. If a consumer is to choose a pump in preference to an aerosol, it must have comparable aesthetic qualities, and this is best achieved by quick-drying alcoholic formulations. A typical formulation based on Rehydrol II (aluminium chlorohydrate propylene glycol complex) is given below:

Formula XVI

		% w/w
A	Volatile silicone	15.0
B	SD Alcohol 40	61.0
C	Stearic acid (triple pressed)	2.0
D	PPG-15 stearyl ether	2.0
E	Aluminium chlorohydrex PG (REHYDROL II, Reheis)	20.0
F	Fragrance	q.s.

Procedure

1. Dissolve E, then C in B until clear
2. Add D until clear
3. Add A, then F
4. Pour into suitable containers

The emollients incorporated, volatile silicone and PPG-15 stearyl ether, retard the possible crystallization of the active. However, hydro-alcoholic pumps are also popular. The active of choice is ACH solution or aluminium sesquichlorohydrate. Since the pump is considered an aerosolized form in the USA, aluminium zirconium actives cannot be used. The following is a basic hydro-alcoholic pump formula:

Formula XVII

		% w/w
A	SD Alcohol 40	50.0
B	PPG-15 stearyl ether	5.0
C	ACH, 50% solution	40.0
D	Deionized water	5.0
E	Fragrance	q.s.

Procedure

1. Combine A and B with overhead mixer
2. Separately, combine C and D; when homogeneous add to Step #1
3. Add E and pour into suitable containers

A clear hydro-alcoholic pump formula with a relatively low content of volatile organic compounds is also feasible. The REACH 501 active is an enhanced effectiveness aluminium chlorohydrate with established compatibility in aqueous-based systems. This formulation provides quick drying, minimal tackiness and reduced residue properties and also contains skin conditioning agents.

Formula XVIII

		% w/w
A	Activated ACH (REACH 501 Solution; Reheis)	45.50
B	Laureth-2 benzoate	10.00
C	SD Alcohol 40, anhydrous	20.00
D	PPG-5 ceteth-20	5.00
E	Propylene glycol	3.00
F	Volatile silicone	1.25
G	Deionized water	13.65
H	Allantoin	0.10
I	Hydrolysed wheat protein	0.50
J	Fragrance	1.00

Procedure

1. Oil phase: add B to C with an overhead mixer for 5 min. Then add D, E and F sequentially and after each addition, mix for 5 min
2. Water phase: mix G and A together with an overhead mixer for 5 min. Then add H, mix for 5 min
3. Add the water phase to the oil phase and mix for 5 min. Add I and J, mix for 10 min and pour into suitable containers

3.13.6 Aerosols

The commercialization of the aerosol as a cosmetic dispenser in the 1950s attracted the attention of the antiperspirant formulators. The advantages of a delivery system which did not involve the container or the product coming in contact with the skin of the user were immediately obvious. There was the possibility of a family-oriented product which could be purchased by one but used by all members of the household. It would help the young and the old to get the habit. However, the problem of incorporating acidic aqueous aluminium solution in a metallic can delayed realization of this product for many years.

The first water-free antiperspirant aerosol was probably produced and marketed in Manchester in 1965, the formulation being a suspension of 2% ACH suspended in an oil. The first successful marketing of a true powder-in-oil suspension antiperspirant aerosol occurred in 1966 when Carter-Wallace launched ARRID EXTRA DRY based on the patented Spritzer and Small technology. The product form was an instant enormous success and has dominated the market for the past 25 years. The original patent specified the composition comprising an anti-perspirant salt, a bulking agent, a synthetic polymer gum (to prevent

dustiness), a non-volatile organic liquid and a liquefied hydrocarbon or halocarbon propellant. This must have been a good invention because it is simple and has stood the test of time with comparatively few changes for such a successful product. Aerosols marked in the late 1960s were of the following formulation:

Formula XIX

		% *w/w*
A	Aluminium chlorohydrate, micronized	3.5
B	Isopropyl myristate	6.0
C	Silica	0.3
D	Fragrance	q.s.
	Ratio: formulation : propellant (fluorocarbon)	10 : 90

Procedure

1. Add A to B in high shear mixer
2. Add C, then D. Mix for 30 min
3. Pass through colloid mill at 6000 p.s.i.
4. Pass through 60 mesh screen
5. Fill into can, charge with propellant

The technical disadvantages of this formulation were:

1. a proportion of the expelled product misses the target or bounces off it;
2. the hydrophobic nature of the formulation is in conflict with the fact that the efficiency of ACH is water-activated;
3. there is a billowing effect which can cause coughing;
4. the hydrophobic formulation can lodge in fabrics and cause staining.

In spite of these problems, consumers preferred aerosols, probably for two main reasons – ease of use and hygiene. The industry tackled the disadvantages one by one and, by formulation and packaging improvements, arrived at a product which minimized the disadvantages and optimized the advantages. Bounce-off and billowing were reduced by valve/pressure modifications. Insolubility and staining were reduced by the replacement of isopropyl myristate with volatile silicones. The second generation of aerosol antiperspirants introduced in the 1970s were of the following general formulation:

Formula XX

		% *w/w*
A	ACH, micronized	3.5
B	Volatile silicone	6.0
C	Quaternium-18 bentonite or quaternium-18 hectorite	0.3
D	SD Alcohol 40	0.2
E	Fragrance	q.s.
	Ratio: formulation : propellant (fluorocarbon)	10 : 90

Procedure

1. Add A to B in high shear mixer
2. Add C, then D, then E
3. Pass through colloid mill at 6000 p.s.i.
4. Pass through 60 mesh screen
5. Fill into can, charge with propellant

There still remained one disadvantage – inferior antiperspirant efficiency when compared to non-aerosol dispensers. This problem was solved in the mid-1980s by the introduction of **enhanced efficiency aluminium chlorohydrate** in which the molecular species is changed and an increase in efficiency of 30–40% is achieved, simply by replacing standard ACH with the enhanced efficiency grade in the above.

The next challenge from the early 1980s was the necessity to phase out the use of fluorocarbon propellants. First in the US, and later in the UK, formulators changed to a hydrocarbon propellant system, and adjusted the formulations so that the same amount of active ingredient was deposited on the skin in the same spray time, so that no efficiency was lost. The following basic formulation is now widely used:

Formula XXI

		% w/w
A	Activated ACH (REACH 101 or REACH 103; Reheis)	10.0
B	Volatile silicone	13.4
C	Quaternium-18 hectorite	0.8
D	SD Alcohol 40 anhydrous	0.8
E	Propellant A-46	75.0
F	Fragrance	q.s.

Procedure

1. Disperse C into B in high shear mixer and mix for 15 min
2. Add D. Mix for 30 min
3. Change to low shear overhead mixing; blend in A gradually. Mix for 15 min
4. Pass the suspension through a Manton-Gaulin homogenizer at 6000 p.s.i.
5. Add F, mix for 15 min
6. Fill into cans, charge with E

These formulations tend to be more billowing than fluorocarbon-propelled systems, and in the US, as described previously, the aerosol has lost substantial market share to the stick. In the UK, however, hydrocarbon-propelled antiperspirant aerosols have been well received by the consumer and are still the dominant product form.

3.14 CONCENTRATED AEROSOL

The concept of a concentrated aerosol formulation has attracted attention for many years. Now this is a reality with the introduction of formulations containing ratios of product concentrate to hydrocarbon propellant of 1.5 : 1 (60 : 40) with an activated ACH level of 20%. Higher levels of silicone oils are necessary to prevent valve clogging. Spray rates are reduced to 0.35–0.45 g/s so that the same amount of product is applied to the skin in the same spray time.

A typical low VOC formulation is shown below:

Formula XXII

		% w/w
A	REACH 101 MicroDry	21.0
B	Bentone Gel VS-5 PC	18.5
C	Cyclomethicone (pentamer)	10.2
D	Dimethicone, 50 cst	8.5
E	Isopropyl Myristate	1.5
F	Fragrance	0.3
G	Isobutane	40.0

Procedure

1. Combine B, C, D and E. Mix well for about 10 min or until homogeneous using Lightnin® overhead mixer or equivalent
2. Add A slowly and mix until homogeneous (10–15 min)
3. Add F and mix 5 min
4. Place mixture into a suitable container and charge with G as specified.

3.15 SOFT SOLIDS

Soft solids are a recent product form introduced in 1993 in the US by Procter & Gamble. They are anhydrous creams in which the powder active is dispersed in volatile and non-volatile fluids, and the entire composition is then formed into a semi-solid using thickening agents. These products rub in quickly, are non-tacky, leave little or no visible residue on skin, and deliver high levels of antiperspirant protection. A formula with excellent stability (no syneresis) is shown below:

Formula XXIII

		% w/w
A	Octyldodecanol	16.0
B	C20–40 Pareth-40	0.5
C	C20–40 Pareth-10	1.5
D	C20–40 Alcohols	0.5
E	Stearyl Alcohol	1.5
F	Cetyl Alcohol	0.5

G	Cyclomethicone (pentamer)	43.5
H	Di(hydrogenate) Tallow Phthalic Acid Amide	10.0
I	N-Acyl Glutamic Acid Diamide	2.0
J	REACH AZP-908 or REACH 301 SUF	24.0

Procedure

1. Combine A, B, C, D, E and F and heat to 110°C until clear. Add I slowly and heat to 120°C until clear
2. Cool to 70°C and add G which has been preheated to 65–70°C
3. Add H and mix well until batch is homogeneous
4. Slowly add J and mix well until batch is homogeneous
5. Pour into appropriate containers at 50–55°C before gellation occurs

3.16 CLEAR GELS

Consumers equate clarity in a formulation with purity and hygiene. Crystal-clear antiperspirant gels have long presented a challenge to formulators. Recently, this has been accomplished beginning with Gillette in the US in 1993. These products are water-in-oil emulsions in which the refractive indices of the continuous and dispersed phases are identically matched. A silicone surfactant is also required to achieve stability. Clear gels have now established their own market sector and the product category will probably continue to grow. Formulation XXIV follows:

Formula XXIV

		% w/w
A	Cyclomethicone (and) Dimethicone Copolyol	9.70
B	Cyclomethicone (Tetramer)	3.40
C	Dimethicone, 50 cst	3.88
D	Isostearyl Palmitate	2.42
E	Rezal 36G Solution (35%)*	57.14
F	Dipropylene Glycol	19.51
G	Deionized Water	3.55
H	Fragrance	0.40
		100.00

Procedure

1. Combine A, B, C, D and H and mix until uniform
2. In a separate vessel, combine E, F, and G and mix until uniform
3. Match the refractive indexes of phases 1 and 2
4. Slowly add the aqueous phase from Step 2 to the oil phase from Step 1 and homomix at slow speed. The viscosity will slowly increase
5. Homogenize vigorously (5000 rpm) until a firm gel is obtained (typically from 1 to 5 min)
6. Fill into airtight containers

*Rezal 36G conc. (46%) can also be used. In both cases, adjust exactly to 20% active solids in the formula.

3.17 FRAGRANCE

Perfumery has always played an important role in antiperspirants and deodorants. Essential oils and plant extracts have been made available which combine deodorant action with perfume odour. Most antiperspirants include a perfume to define the product and give it a unique character. We all have a natural body odour, no matter how much we wash our skin or our clothes. A perfume initially masks this odour but eventually becomes indistinguishable to the user after regular use. Users then fear the product is no longer working. For this reason, and uniquely among toiletries, many brands offer a choice of perfumes in the same range and this choice is emphasized by a different colour to match the different perfume.

In recent years perfume levels have risen to achieve greater impact at time of purchase and to define more clearly the intended market in terms of age, sex and activity. Most recently there has been a trend to add so-called natural ingredients to formulations such as plant extracts, either for efficiency, emolliency or emotional appeal. If these additives are included in reasonable levels they could add to the staining potential of the formulation, and it is difficult to see what real benefit they bring. Antiperspirant fragrances must be formulated to be stable in highly cationic, acidic environments. Experience has shown that phenol-containing materials, natural oils, and unsaturated alcohols and aldehydes are unstable, while ketones, nitriles, esters, saturated aldehydes, and saturated primary and secondary alcohols are stable. It is of interest to note that aldehydic fragrances dominate the antiperspirant market. It is important to work closely with a fragrance supplier to ensure that the fragrance is not detrimental to the final product.

3.18 STAINING BY ANTIPERSPIRANTS

Some incidence of staining of clothing by antiperspirant products is unavoidable. Cotton and linen fabrics are most susceptible to stain formation, while polyester, nylon and wool are significantly less susceptible.

When an antiperspirant product comes in contact with fabric, several means of discolouration can occur. Some dyes used in clothing may be acid-sensitive, and will change colour when in contact with an antiperspirant or an antiperspirant mixed with perspiration. This change of colour is often reversible and can be corrected by sponging the area with a dilute solution of ammonia.

Another type of staining occurs when washing clothing which contains a deposit of aluminium salt combined with perspiration and body oils. When alkaline soap or laundry detergent contacts the fabric, an insoluble aluminium soap, or aluminium hydroxide, may form within the fabric matrix which is yellow in colour and somewhat sticky. Repeated ironing/pressing and/or exposure to heat in a clothes dryer will further set the stain. Blueing agents (violet dyes) or coloured detergents may also combine with the aluminium salt to produce a blue or grey stain. Optical whiteners used in some laundry detergents may also increase the discolouration. Dry-cleaning solvents will remove the oily and

waxy portions of an antiperspirant product residue, but will generally leave the aluminium salts in the fabric. Most stains on washable clothing can be reduced (if not entirely removed) by first rinsing the fabric in cool, soft water with no detergent present, and then followed by the standard detergent washing procedure.

Iron present as contaminants in antiperspirant formulations has been implicated in both fabric staining and fragrance incompatibility. For this reason the use of active ingredients in which the iron content has been purposefully reduced during synthesis is recommended.

3.19 DEODORANTS

Deodorants, as mentioned earlier, reduce underarm odour by exerting an antibacterial action on the organisms which decompose apocrine axillary secretions. The earliest formulations were based on zinc oxide, boric acid and, later, benzethonium chloride. During the period from 1942 to 1972 hexachlorophene increasingly replaced all other bactericides and was used successfully until it was banned from non-prescription products by the FDA in that year. After the ban, hexachlorophene was largely replaced by triclosan and zinc phenolsulfonate. The most popular product forms of deodorants are sticks and aerosols, with the active ingredient dissolved in alcohol.

A so-called natural deodorant based on sodium bicarbonate (baking soda) was launched in America in the 1970s and has been copied elsewhere but without much commercial success. At about the same time, essential oils with bacteriostatic properties were also marketed with a fair level of success as deodorant perfumes or deofragrances, which aimed to combine the properties of an axillary deodorant with a general body perfume. This in turn led to the all-over deosprays referred to earlier. Satisfactory *in vitro* test methods for deodorants are readily available, but these need supplementing by human sniffing tests because of the differing individual responses to finished formulations.

Deoperspirants have been launched on the UK market. These are deodorants which include a cellulosic plant fibre to absorb perspiration. The products were found to be sticky, had low consumer acceptance and were withdrawn from the market.

3.19.1 Deodorant properties of ACH and AZCH

ACH was first introduced as an antiperspirant, but in 1957 Blank *et al.*, published results of tests showing that aluminium chlorohydrate, chloride and sulphate are effective in preventing growth of microorganisms on hydrated skin. The OTC antiperspirant Monograph concluded that it was 'highly probable that the principal deodorancy effect of antiperspirants is a result of antibacterial actions', although deploring the lack of published data to support the statement.

This deficiency was made good in a paper given at the Wiesbaden Cosmetic Ingredients Europe Symposium in March 1990: '*In vitro* killing time studies of antiperspirant salts'. The primary conclusion from this work is that low concentrations of aluminium chlorohydrate and aluminium zirconium chlorohydrate, i.e. 4% and 6%, respectively, result in faster antimicrobial kill rates of the organisms responsible for axillary odour, than do relatively high levels of triclosan, i.e. 0.2–0.4%. This offers a cost-effective formulation option for marketers of deodorant products to consider.

An increasing number of deodorant products marketed in Continental Europe now include ACH and enhanced-effectiveness ACH as the active deodorant ingredient. These products are marketed as **dry deodorants** which combine full deodorant effectiveness with mild antiperspirant effect.

3.20 BATH AND SHOWER PRODUCTS

There is increasing interest in the deodorant and antibacterial properties of ACH and AZCH for bath and shower products, as a result of the above research. Levels of 1–3% are considered suitable to give antibacterial action without impacting on eccrine gland function.

3.21 THE FUTURE

In the past 40 years, through refinements in formulations and dispensers, antiperspirants have been transformed into an essential and socially necessary grooming aid used daily by the majority of the adult population of the developed world.

Antiperspirants have moved from the dressing table to the bathroom shelf – everyday necessities for most people, like soap or toothpaste, but it is still a market of innovation and fashion, so new or improved product forms will be developed. The US market now dominated by the stick/solid form, and the UK market still dominated by the aerosol form, will change in time as new generations of consumers select their preferred lifestyle product. The market will continue to expand as new and even more effective active ingredients, and individually tailored formulations, are developed. These could provide optimum effectiveness for a particular age, sex, or ethnic group, physical activity or environment.

In the US and the UK there will be a continuing switch to the use of enhanced-efficacy actives, and new products will continue to emphasize reduced residue properties and greater niche marketing. In Continental Europe there will be a rapid switch to antiperspirants from purely deodorant products, and pan-European branding from multi-nationals will become more evident. Eastern Europe may provide a significant future growth opportunity.

APPENDIX

Materials	*INCI*	*Supplier*
(1) Amerchol CAB	Petrolatum (and) Lanolin Alcohol	Amerchol
(2) Cetyl alcohol	Cetyl Alcohol	Croda Oleochemicals
(3) ACH	Aluminum Chlorohydrate	Reheis
(4) ACH 50% solution	Aluminum Chlorohydrate	Reheis
(5) Arlacel 165	Glyceryl Stearate (and) PEG-100 Stearate	ICI Surfactants
(6) Cetyl alcohol	Cetyl Alcohol	Croda Oleochemicals
(7) Sorbitol, 70% solutio	Sorbitol	Merck KGaA, Lonza
(8) Deionized water	Water, Aqua	
(9) Fragrance	Fragrance	Quest Int. Fragrances USA
(10) SD Alcohol 40	SD Alcohol-40A	
(11) Propylene Glycol	Propylene Glycol	BASF, Dow Chemical
(12) Ethanol	Alcohol Denat.	
(13)	Sodium Stearate	Stepan Company
(14)	Triclosan	Ciba
(15) CHLORACEL *40% w/w solution	Sodium Aluminum Chlorohydroxy Lactate	Reheis
(16) Alcohol, SDA 40	SD Alcohol-40A	
(17)	Stearyl Alcohol	Protomeen or Henkel
(18) REHYDROL II	Aluminum Chlorohydrex PG	Reheis
(19)	Stearamide MEA	Witco Surfactants GmbH
(20)	Isocetyl Alcohol	ISP, Van Dyke
(21) SDA-40 Anhydrous	SD Alcohol-40	Eastman Chemical
(22)	Isopropyl Myristate	Croda Oleochemicals
(23) Titanium oxide	Titanium Dioxide	Degussa
(24) Volatile Silicone	Cyclomethicone	Whitco Organo Silicones
(25) PPG-3 myristyl ether	PPG-3 Myristyl Ether	Croda Oleochemicals
(26) PEG-8 distearate	PEG-8 Distearate	Stepan Company
(27) Talc, 325 mesh	Talc	Whittaker, Clark & Daniels
(28) Silica	Silica	Degussa, Kolb
(29)	Polyethylene	Allied Signal Inc.
(30) ACH super ultrafine	Aluminum Chlorohydrate	Reheis
(31) Hydrogenated castor oil MP-70	Hydrogenated Castor Oil	CasChem, Henkel
(32) REACH AZP-908	Aluminum Zirconium Tetrachlorohydrex GLY	Reheis
(33) REACH AZP-908 (30% Soln.) SB	Aluminum Zirconium Tetrachlorohydrex GLY	Reheis

APPENDIX (*Continued*)

Materials	*INCI*	*Supplier*
(34) Dipropylene Glycol (low odour grade)	Dipropylene Glycol	BASF
(35) Glycine	Glycine	A & E Connock
(36)	Diisopropyl Sebacate	A & E Connock
(37)	Dimethicone Copolyol	A & E Connock
(38)	Dibenzylidene Sorbitol	Milliken
(39) REACH 501 soln., 50%	Aluminum Chlorohydrate	Reheis
(40)	Steareth-21	ICI Americas Inc.
(41)	Steareth-2	ICI Americas Inc.
(42)	Steareth-5	ICI, Croda
(43)	Clyclomethicone (and) PPG-15 Stearyl Ether	ICI Surfactants
(44)	PPG-5-Ceteth-20	Croda Oleochemicals
(45) Stearic acid	Stearic Acid	Croda Oleochemicals
(46) Hydroxyethyl Cellulose	Hydroxyethylcellulose	Aqualon
(47) REZAL 67 Solution	Aluminum Zirconium Pentachlorohydrate	Reheis
(48) Stearic acid (triple pressed)	Stearic acid	Croda Oleochemicals
(49) Hydroxy Propyl Cellulose	Hydroxypropylcellulose	Aqualon
(50)	Quaternium-18 Bentonite	Rheox
(51) Quaternium-18 Hectorite mastergel	Quaternium-18 Hectorite	Rheox
(52) Activated AZCH, superultrafine	Aluminum Zirconium Chlorohydrate	Reheis
(53) REACH 301 soln., 50%	Aluminum Sesquichlorohydrate	Reheis
(54)	PEG-7 Glyceryl Cocoate	Henkel
(55)	Cyclomethicone (and) Dimethicone Copolyol	Amerchol
(56) Cardamol CAP	Cetearyl Octanoate	Croda Oleochemicals
(57) Tween 20	Polysorbate 20	ICI Surfactants
(58)	Laureth-2 Benzoate	Bernel Chemicals
(59)	PPG-5-Ceteth-20	Croda Oleochemicals
(60)	Allantoin	A & E Connock
(61)	Hydrolyzed Wheat Protein	Croda Oleochemicals
(62) Aluminum Chlorohydrate micronized	Aluminum Chlorohydrate	Reheis
(63) Activated ACH Reach 101	Aluminum Chlorohydrate	Reheis

APPENDIX (*Continued*)

Materials	*INCI*	*Supplier*
(64) Activated ACH Reach 103	Aluminum Chlorohydrate	Reheis
(65) Propellant A-46	Propane/Isobutane/Butane	
(66) Bentone Gel VS-5 PC	Cyclometicone (and) Quaternium-18 Hectorite (and) Propylene Carbonate	Rheox
(67) Dimethicone, 50 cst	Dimethicone	A & E Connock
(68) Cyclomethicone (Pentamer)	Cyclopentasiloxane	Dow Corning
(69)	Isobutane	
(70)	Octyldodecanol	Henkel
(71)	C20–40 Pareth-40	Petrolite
(72)	C20–40 Pareth-10	Petrolite
(73)	C20–40 Alcohols	Petrolite
(74)	Di(hydrogenate) Tallow Phthalic Acid Amide	Stepan
(75)	N-Acyl Glutamic Acid Diamide	
(76) REACH AZP-908	Aluminum Zirconium Tetrachlorohydrex GLY	Reheis
(77)	Cyclomethicone (Tetramer)	Dow Corning
(78) Rezel 36G Solution (35%)	Aluminum Zirconium Tetrachlorohydrex GLY	Reheis
(79)	Isostearyl Palmitate	A & E Connock

4

Bath and shower products

Anthony L.L. Hunting

4.1 INTRODUCTION

For centuries bathing has been performed not only to cleanse the body but also for the therapeutic and relaxing properties of hot water and steam, particularly at spas and springs where the water contains dissolved minerals. Home bathing, and the consequent development of bath products, is comparatively recent: except for the well-off, bodies were washed communally in rivers and lakes or, as in the case of the Romans and the Victorians, for example, in specially built public baths.

The industrial revolution made regular bathing for all both a perceived necessity, because of a growing awareness of the need for personal hygiene, and possible, because of the availability of enamelled metal baths and home plumbing. The detergent used was soap, and it was not until the invention of modern foaming and cleansing agents (commonly known as detergents but more correctly described as surface-active agents, or surfactants) that this section of the toiletry industry developed rapidly. Later, a much faster method of body cleansing – showering – was developed which capitalized on the availability of modern surfactants to produce a variety of effective washing products.

Modern bath and shower products are used to cleanse the hair and body, anoint the skin with emollients and fragrance and soften the water, in particular to eliminate the hard-water 'ring' formed around the bath at water level. They are produced in solid (crystal and powder), semisolid (gel and paste) and liquid form. Each of these preparations will be discussed individually.

The recipes provided below are intended to be the starting point for formulators to produce their own variations according to the restraints and requirements set by their own organization. As with all toiletry products, the formulator must take full responsibility for the safety as well as the efficacy of the intended

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 101–149

product. It is essential to bear in mind that bath products come into contact with almost the whole of the body, including the sensitive anogenital region.

Formulations for bath soap are not supplied since soap is the subject of a separate chapter (see p. 453).

4.2 BUBBLE BATH PRODUCTS

Products which produce foam or bubbles when added to bath water are called bubble bath, foam bath, creme bath (when the product is opacified), herbal bath (or similarly, where the product contains a herbal or natural additive) and foaming bath oil. For convenience, they will all be referred to here as bubble bath.

A bubble bath is a dispersion of a highly foaming material in water. Soap, the oldest and cheapest foaming agent, is neither very soluble nor effective in the bath because, in the presence of hard water, soap molecules (usually sodium salts) are converted by double decomposition to insoluble, non-foaming soaps (i.e. lime soaps, calcium and magnesium salts of fatty acids). These deposit on the water surface to produce scum and on the bath surface at water level to produce, in association with soil and other insoluble matter, the well-known bath 'ring'. At bath dilutions, soap also partially hydrolyses to produce insoluble fatty acids which contribute to the scum and which are defoaming agents.

The advantages of using a properly formulated bubble bath are: it is safe on skin and mucous membranes, can produce copious foam (even in hard water areas), will leave the skin with a soft, velvety feel, and will fill the bathroom with a pleasant aroma. It also prevents or reduces the formation of the ring of scum around the bath.

Hair shampoo, although similar in composition to bubble bath, is not designed to cleanse the whole body, requires film-forming or humectant conditioning agents and is expected to foam in the presence of high levels of sebum, a factor not relevant to bubble baths. It also contains less fragrance than bath products. For these reasons the formulations for shampoo and bubble bath are slightly different, although based on similar ingredients.

4.2.1 Ingredients

It is not possible here to write more than a few words on each of a selection of substances from the vast range of surface-active agents, and to give more than a very elementary and generalized explanation of the physical chemistry of foaming agents. Further information is supplied with the formulations which follow (see Section 4.2.2). The interested reader seeking even more information is advised to consult the books recommended in the Bibliography.

4.2.1.1 Surfactants (foaming agents)

Surfactants can be classified ionically as anionic, cationic, nonionic or amphoteric. In *anionic* materials the large, organic, oil-soluble, portion of the molecule

contains a negative charge; in *cationics* this portion of the molecule carries a positive charge. The counter-ions are small and water-soluble. Sodium stearate (soap), $RCOO^-Na^+$, is an example of an anionic surfactant and benzalkonium chloride, $C_6H_5CH_2N^+(CH_3)_2R\ Cl^-$, a cationic surfactant. In both formulae *R* represents a fat chain. *Nonionic* surfactants carry no charge, their water-solubility resulting from the hydrogen-bonding of water molecules to hydroxyl or ether groups. *Amphoteric* surfactant molecules carry both positive and negative charges. The principal foaming agents used in bubble baths are invariably anionic, since cationic surfactants are expensive, frequently irritant and poor foamers, while nonionic surfactants, although inexpensive and non-irritant, are also poor foaming agents. Amphoteric surfactants are also used to some extent in bath products, but usually only where there are specific requirements, such as low irritation.

Organic materials which contain a long fat chain and one of the above-mentioned polar groups are surface-active or *surfactant*. Their ability to congregate at surfaces, so reducing surface tension, varies with the nature and length of the fat chain: lauric (with twelve carbon atoms, written C_{12}) and myristic (C_{14}) chains, found in coconut and some other oils, make good foaming agents; longer chains are more effective as emulsifiers, while shorter chains produce wetting agents. Surface activity is also affected by the position on the fat chain, and the nature, of the ionic group. All surfactants, of whatever ionic class, above a certain concentration form aggregates, or working units, known as micelles. This concentration, which is specific for each structure, is known as the critical micelle concentration (CMC).

The anionic surfactant sodium lauryl ether sulfate (Sodium Laureth Sulfate*) containing an average of three moles of ethylene oxide, $CH_3(CH_2)_nO(CH_2CH_2O)_mOSO_2O^-Na^+$ (where *n* is usually 11–13, and *m* averages 3), is the most widely used foaming agent found in bath products. It is inexpensive, colourless, almost odourless, very stable at normal pH ranges, is easily preserved, foams profusely in soft and hard water and in the absence of sebum (the situation pertaining with bubble baths) and, in particular, produces high 'flash foam' – the amount of foam generated when bath water is poured. It is compatible with any likely bath product ingredient and dilutions can easily be thickened very simply and cheaply to any viscosity including a gel. It is marketed as a 30% liquid and as a high active (60–70%) paste, but not as a powder. It is, however, slightly irritant (although not as much as Sodium Lauryl Sulfate), and is harsher on the skin

* Throughout the text and in formulations (but not in the key to formulations) the invidious use of trade names for chemical ingredients has been avoided wherever possible, as has the use of lengthy chemical names. Instead, the names originally devised for product labelling by the American organization the Cosmetic, Toiletry and Fragrance Association (CTFA) but now used (with minor changes) throughout the European Union and in some other countries, have been used. These names (known as International Nomenclature Cosmetic Ingredient [INCI] labelling names) are published in the CTFA *International Cosmetic Ingredient Dictionary and Handbook*, 7th edn [1]. In this chapter they are given initial capital letters to help distinguish them from standard or informal chemical names.

than some of the specialist surfactants mentioned below. Sodium lauryl ether sulfate produced from a 2-mole lauryl alcohol ethoxylate, is a common shampoo ingredient but the 3-mole ethoxylate is preferred in bubble bath for its superior foaming power and skin-friendliness. Both materials have the same INCI name, Sodium Laureth Sulfate. Magnesium lauryl ether sulfates are also effective foaming agents and are more skin-friendly. There has been concern over the use of ether sulfates in personal-care products because ethoxylated materials can, under sulfation conditions, produce 1,4-dioxane which is a potential carcinogen. Techniques have been developed to remove or minimize the presence of this material.

The use of Sodium Lauryl Sulfate, $CH_3(CH_2)_nOSO_2O^-Na^+$ (where n is usually 11–13), in bubble bath has declined. It is a good foaming agent but is less water-soluble and produces less flash foam than ether sulfates. It is also an excellent cleansing agent, particularly in the presence of dirt (or sebum), but is defoamed by soap, particularly in hard water, is irritant and leaves the skin with a slightly dry feeling, unless emollients or conditioning agents are also present. Ammonium and magnesium lauryl sulfates are slightly more soluble that the sodium salts, and more skin-friendly. The monoisopropanolamine (MIPA) salt is even more soluble but more expensive. The triethanolamine (TEA) compound was once a standard material in liquid foaming products but is now little used, mainly because of cost. Lauryl sulfates are available as 30–40% liquids and, in the case of the sodium and magnesium salt, as a paste and as a highly active powder.

Sulfosuccinates are surfactants which contain both a carboxylic acid (soap) group and also a sulfonate group. They are the neutral salts of monoesters of sulfosuccinic acid condensed with either a fatty alcohol, an ethoxylated fatty alcohol or with an alkanolamide. An example is Disodium Laureth Sulfosuccinate, $R(CH_2CH_2O)_{2-4}OCOCH(SO_3^-Na^+)CH_2COO^-Na^+$, which may be compared with Sodium Laureth Sulfate. It too is usually based on a 3-mole ethoxylate of lauryl alcohol, is colourless and odourless but milder than the ether sulfate. However, it is less easily thickened than the sulfate and is a less effective foaming agent. For this reason sulfosuccinates are often used in combination with ether sulfates.

Sometimes an alkanolamide is used as the base for a sulfosuccinate preparation: for example, oleic acid monoisopropanolamide produces Disodium Oleamido MIPA-Sulfosuccinate. It is very mild and a good foaming agent, but is coloured and has a slight odour which may require masking.

As a class, half-ester sulfosuccinates are very mild, leave the skin with a pleasant feel and can, in some cases, reduce the irritation caused by other ingredients. Some varieties produce copious amounts of foam. They are not defoamed by soap (important if the foam is not to collapse when the bather reaches for the bar of soap). The major disadvantage of sulfosuccinates is that they are pH-sensitive and can hydrolyse easily. They are available as liquids, varying in colour from colourless to amber, and, less frequently, as powders.

Sarcosinates are also related to soap, being $RCON(CH_3)CH_2COO^-Na^+$ where R is a fat chain. They share a number of properties with sulfosuccinates, being also very mild, soap-stable, high-foaming materials with good lime-soap dispersing properties. They are available as 30% liquids and as high active powders. They are one of the few surfactants available in a stable acid form.

Sulfonates differ from sulfates in that the former contain the $-C-SO_3$ group, while sulfates are sulfuric acid esters and contain the hydrolysable group $-C-O-SO_3$. Alpha-olefin sulfonates, typified by $RCH=CHCH_2SO_3^-Na^+$ (although other entities are present) and where R represents a C_{11}–C_{13} chain, are milder than alkyl sulfates and alkyl ether sulfates but not as good foaming agents as the two last-named. They have good pH stability but are not easy to thicken, which is one reason why they are frequently used in combination with alkyl and alkyl ether sulfates. Alkyl aryl sulfonates (for example, Sodium Dodecylbenzenesulfonate) are not regarded as suitable materials to use in the bath because they leave the skin with an unpleasant sticky feeling and have been suspected of causing irritation to the lower urinary tract [2].

The materials discussed so far have all been anionic surfactants. Some other surface-active agents used in bubble baths are not anionic and their use is often in a complementary or secondary role because their foaming properties are insufficient. They are employed because they are very mild and they can, in certain circumstances, reduce the irritant effects of other materials. In many cases they leave the skin with a pleasant silky feel. They are available in liquid and occasionally in powder form. Some of the more important of these secondary surfactants are described briefly below.

The description *amphoteric* is usually applied to a substance which contains at least two ionically functional groups of which one can ionize as an anionic and another as a cationic group, the ionic state achieved depending upon the pH. At acid pH the molecule is cationic, at alkaline pH it is anionic and at an intermediate pH (seldom exactly pH 7.0) it carries both charges – the zwitterionic state. Those amphoteric surfactants derived from fatty acid imidazolines are the most important for bath preparations, the INCI nomenclature for these substances containing either the expression *amphoacetate* (sometimes *amphodiacetate*) or *amphopropionate* (or *amphodipropionate*), as in Sodium Cocoamphoacetate or Disodium Lauroamphodipropionate. There are other types, but usually those based on coconut, lauric or oleic fatty acids are employed because they are extremely mild, reasonably good foaming agents and can reduce the irritation of alkyl and alkyl ether sulfates.

Betaines, derivatives of trimethyl glycine, are of two types: alkyl betaines, for example, Coco-Betaine, $RN^+(CH_3)_2CH_2COO^-$ and alkyl amido betaines, such as Cocamidopropyl Betaine, $RCONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$. These materials are mild, liquid foaming agents which leave the skin with a pleasant feeling. They can form gels and high-viscosity products in combination with alkyl sulfates and alkyl ether sulfates. Sultaines, or sulfobetaines, are similar materials

and contain a sulfonate group. Betaines and sultaines are cationic at acid pH and form zwitterions at any alkaline pH.

Materials that contain an ethoxylate chain are not pH-dependent for their solubility because, as has been mentioned, this is due to the affinity of the chain for water molecules attracted by hydrogen bonding. At certain temperatures, however, specific for each nonionic surfactant, the water molecules are shaken loose and the material becomes insoluble. A solution of nonionic surfactants above such a temperature becomes turbid (it has an inverse cloud point) unless other surfactants are present to solubilize it.

Substances containing an ethoxylate chain and a terminal carboxylate group are nonionic but, in alkaline conditions, anionic. Sodium Laureth-13 Carboxylate, a typical example, is nominally $CH_3(CH_2)_{10-12}CH_2(OCH_2CH_2)_{12}OCH_2COO^-Na^+$ but contains considerable amounts of unreacted ethoxylate. It is a mild, clear liquid which has excellent lime-soap dispersing properties. Calcium and magnesium ions can react with the carboxylate group but, because of the long hydrophilic ethoxylate chain, the molecule is still water-soluble.

There are very many surfactants that are completely nonionic. They can often be distinguished by INCI labelling names which begin with 'PEG-*x*' (indicating an ethoxylate chain containing *x* units of ethylene oxide), or 'PPG-*x*' (similarly, but with a propylene oxide chain), or end with '-eth'. For example, Laureth-6 and PEG-6 Cocamide, which are, respectively, six-mole ethoxylates of lauryl alcohol and Cocamide DEA, and PPG-12 PEG-50 Lanolin, which is obtained when lanolin reacts with 50 moles of ethylene oxide and 12 moles of propylene oxide. Alkoxylation reactions, however, produce many by-products and these names are somewhat notional.

Polysorbates are ethoxylates of fatty acids esterified with anhydrosorbitol. For example, Polysorbate 20 is sorbitan laurate (the ester of lauric acid and anhydrosorbitol) reacted with an average of 20 moles of ethylene oxide (for polysorbates the final number does not necessarily correspond to the number of moles of ethylene oxide; it happens to do so in this example). As a class, nonionics do not foam very well, but are mild and used for their solubilizing properties. They are usually liquid or soft solids and are nominally 100% active.

4.2.1.2 Thickeners and foam stabilizers

Some surfactant dilutions are thickened easily in the presence of electrolytes and others form high-viscosity products in certain combinations with other surfactants. For example, sodium lauryl ether sulfate dilutions thicken easily with the addition of small amounts of soluble electrolytes, such as sodium chloride and magnesium sulfate; combinations of betaines and fatty alcohol sulfates can often produce high viscosities. There are, however, some materials that are specifically used to increase viscosity so that the product appears to the uninitiated to be more concentrated. It is also the case that pearly products are more stable if the product

has a high viscosity. However, from the point of view of the functioning of the bubble bath, a thin product is likely to dissolve more quickly in the bath water.

Cellulose that has been modified by reacting it with either ethylene or propylene oxides (or both) produces cellulose ethers. A typical example is Hydroxypropyl Methylcellulose. It is a white, odourless powder which is soluble in cold water but insoluble in hot. As with most cellulose ethers, various grades are available, producing a range of viscosities when the material is dispersed in water.

Some synthetic water-soluble gums require neutralization with triethanolamine (or other base) after dissolving in water for the product to thicken. Examples include materials known by the INCI name of Carbomers, which are acrylic acid polymers. There are also some natural gums used to thicken: Guar Gum and Xanthan Gum, for example.

Fatty acid alkanolamides are prepared by condensing a fatty acid with an alkanolamine. They do not foam in solution but improve the stability of foam generated by alkyl and alkyl ether sulfates, and in such formulations they often enable the viscosity of the product to be easily controlled. The most frequently used are coconut diethanolamide (Cocamide DEA) and lauric diethanolamide, $RCONH(CH_2CH_2OH)_2$, but other fatty acids, such as oleic acid, and other alkanolamines, such as monoisopropanolamine, are frequently employed as starting reactants. Compounds based on diethanolamine are viewed with suspicion because of the possible presence of N-nitrosodiethanolamine (NDELA) in such materials. Some nitrosoamines have been shown to be potential carcinogens [3] and this fear has reduced the use of alkanolamides in personal-care products, particularly in bubble baths which have a great skin-contact area. [The issue of the safety of Cocamide DEA has again been raised in the US media – see *Cosmetics & Toiletries* **113**, May 1998.] Amine oxides, such as Lauramine Oxide $RCN(CH_3)_2\rightarrow O$, are sometimes preferred to alkanolamides because they do not form nitrosamines.

4.2.1.3 Miscellaneous additives

Pearly products can be prepared by adding small amounts of molten glycol stearates to the hot formulation and allowing the mix to cool under controlled conditions. Glycol Stearate and Glycol Distearate are frequently employed for this purpose. These materials are white or off-white waxy solids, usually sold in flake form, or they may be obtained ready crystallized and predispersed in a surfactant base. Their use may be desirable if the bath product is to be sold under a name that suggests pearliness or opacity, such as 'creme'. It must be remembered that glycol stearates have some defoaming action which, although not usually significant in a hair or body shampoo, is undesirable in a bubble bath. Also, they do not always crystallize properly, and hence do not produce a sheen, when sulfosuccinates are the only or main surfactant or when high levels of superfatting and emollient agents are added.

Sequestering agents such as citric acid or ethylene diamine tetra-acetic acid (EDTA) and its sodium salts are usually employed in small quantities to prevent metal ions, particularly iron, from precipitating as insoluble hydroxides. This allows the product to remain sparklingly clear. They also have an auxiliary preservative function because trace metal ions catalyse ultraviolet radiation degradation, which produces rancidity in oils, and cause inactivation of some antimicrobials. By tying up lime-soap ions, sequestering agents also prevent the formation of scum and can improve foaming power. Citric acid, being inexpensive and very safe, is therefore a versatile material to use if small pH adjustments are required.

Preservatives should preferably not be volatile, for the bather is immersed in a steamy atmosphere. Formaldehyde, for example, is therefore contraindicated. Parabens (for example, methyl *p*-hydroxybenzoate, Methylparaben) and the propyl homologue (Propylparaben) are commonly employed, frequently in combination. It must be emphasized that the final pack and contents should be tested according to the microbiological guidelines or regulations of the country in which the product is to be marketed to assess the efficiency and safety of the preservatives used.

Since bubble bath preparations are neutral, or nearly so, almost any cosmetically acceptable water-soluble colour can be used, provided it is compatible with the ingredients. Fragrance is usually used at a level of 1–2%, a higher level than for shampoos because part of the luxury of having a bubble bath is to indulge in an exotic aroma. However, some fragrance compounds depress the foam level. It is an essential feature of the product that a fragrance should be used that will linger for the entire period of the bath.

Few other additives are required although many are used, probably for their sales appeal. For example, protein derivatives and many other natural or naturally derived materials such as herbal extracts, vitamins and minerals are frequently found in bubble bath products. When adding minerals it must be remembered that electrolytes can play havoc with the viscosity of the product, as can oily materials, such as essential oils, which some formulators may want to include in 'aromatherapeutic' products.

4.2.2 Formulations

Note Most surfactants and some other materials contain water, and the correct INCI name for such ingredients should be 'Aqua (and) – ' [or, in the USA, 'Water (and) – '] but for conciseness only the active ingredient is given in the formulations below. All amounts are weight/weight unless otherwise indicated.

The simplest and cheapest formulation for a bubble bath is a coloured and perfumed solution of sodium lauryl ether sulfate in water. It is recommended, however, that other materials are added to improve the product, as in the following examples.

4.2.2.1 Clear liquid and gel bubble baths

	I [4]	*II* [4]	*III* [4]	*IV* [4]	*V* [5]	*VI* [5]	*VII* [6]	*VIII* [7]
1. Ammonium Lauryl Sulfate	–	–	–	–	–	–	30.0	13.0[a]
2. MIPA-Lauryl Sulfate, 75%	–	–	–	–	–	–	–	27.0
3. Sodium Laureth Sulfate, 70%	24.0[b]	–	57.0[b]	70.0[b]	–	–	–	–
3a. Sodium Laureth Sulfate, 28%	–	60.0[c]	–	–	45.0[c]	40.00[c]	–	9.0[c]
4. Sodium Olefin Sulfonate, 40%	–	–	–	–	–	–	10.0	–
5. Lauryl Betaine	5.0[d]	5.0[d]	–	–	–	–	–	–
6. Cocamidopropyl Betaine	–	–	–	5.0[e]	5.0[f]	15.00[f]	–	–
7. Cocamidopropyl-amine Oxide	–	–	–	–	–	4.00[g]	–	–
8. Cocoyl Sarcosine	–	–	–	–	–	–	3.0[h]	–
9. Cocamide DEA	–	–	–	–	3.5[i]	–	–	4.5[i]
10. PEG-6 Cocamide	–	–	10.0[j]	5.0[j]	–	–	–	–
11. PPG-5-Ceteth-10 Phosphate	–	–	–	–	–	–	–	4.5[k]
12. PEG-7 Glyceryl Cocoate	–	–	–	–	2.0[l]	–	–	–
13. Laureth-2	–	–	2.0[m]	–	–	–	–	–
14. PPG-15 Stearyl Ether	–	–	–	–	2.0[n]	–	–	–
15. Oleth-5	–	–	–	–	–	–	–	5.0[o]
16. PPG-12-PEG-50 Lanolin	–	–	–	–	–	–	–	1.0[p]
17. Decyl Oleate or Isopropyl Myristate	–	–	–	5.0	–	–	–	–
18. Lauryldimonium Hydroxypropyl Hydrolysed Soy Protein	–	–	–	–	–	1.00[q]	–	–
19. PEG-60 Almond Glycerides	–	–	–	–	–	2.00[r]	–	–
20. Hydrolysed Collagen	–	–	–	–	–	–	–	1.0[s]
21. Alcohol (ethanol)	–	–	1.0–1.5	–	–	–	–	–

	I [4]	*II* [4]	*III* [4]	*IV* [4]	*V* [5]	*VI* [5]	*VII* [6]	*VIII* [7]
22. Horse Chestnut (Aesculus Hippocastanum) Extract (powdered)	–	–	–	–	–	–	–	0.3
23. Herbal extracts	–	–	q.s.	q.s.	–	–	–	–
24. Sodium Chloride	–	–	4.0	2.5	–	–	–	–
25. Ammonium Chloride	–	–	–	–	–	–	3.0	–
26. Citric Acid/ Sodium Hydroxide, to pH	6.5–7.0	6.5–7.0	6.5–7.0	6.5–7.0	–	6.5	–	–
27. Triethanolamine	–	–	–	–	–	–	–	0.3
28. Parfum/Fragrance*, dye, preservative, buffer	←			q.s.				→
29. Aqua/Water† (deionized)	←			to 100				→ 34.4

* In the EU the term *Parfum* is to be used on product labels to indicate materials used to produce or mask a particular odour; in the US the equivalent term is *Fragrance.*

† In the EU water is to be indicated on product labels by the term *Aqua;* in the US the corresponding name is *Water.*

Sources (generic except for the following)

(a) Empicol AL30T; (b) Empicol ESB 70; (c) Empicol ESB 3/M; (d) Empigen BB; (e) Empigen BS/P (all Albright & Wilson); (f) Incronam 30 (Croda Oleochemicals); (g) Incromine Oxide C (Croda Oleochemicals); (h) Hamposyl C (Hampshire); (i) Empilan CDE (Albright & Wilson); (j) Empilan MAA (Albright & Wilson); (k) Crodafos SG (Croda Oleochemicals); (l) Glycerox HE (Croda Oleochemicals); (m) Empilan KB2 (Albright & Wilson); (n) Prostearyl 15 (Croda Oleochemicals); (o) Volpo N5 (Croda Oleochemicals); (p) Lanexol AWS (Croda Oleochemicals); (q) Croquat Soya (Croda Oleochemicals); (r) Crovol A70 (Croda Oleochemicals); (s) Crotein A (Croda Oleochemicals).

Procedures

Formulation I: [i] Charge the water and add the buffer. Initial charging of a portion of (24) will aid the dissolution of (3). The approximate level of salt addition required to achieve the desired viscosity should be determined prior to commencing large-scale production. [ii] Add (3) slowly with stirring until a homogeneous solution is obtained, increasing the temperature to about 40°C if necessary. [iii] Add coactive surfactant (5). [iv] After ensuring the temperature is less than 35°C, add (28). [v] If required, adjust pH to 6.5–7.0 with (26). [vi] Add (24) to adjust the viscosity.

Formulaton II: as *I* but ingredient (5) can be stirred in more rapidly, taking care to avoid excessive aeration.

Formulation III: as *I* but at stage (iii) add (10) and (13) and at stage (iv) add (21) and (28).

Formulation IV: as *I* but at stage (iii) add (6) and (17) and at stage (iv) add (21) and (28).

Formulations V and VI: Simple blend, adjust pH.

Formulation VII: [i] Mix surfactants. [ii] Dissolve (25) in cold water and add. [iii] Adjust pH to 4.8.

Formulation VIII: [i] Heat water plus detergents to 55–60°C. [ii] Add heated ingredient (22) with slow stirring to avoid aeration. [iii] Perfume at 35°C.

Comments

These formulations demonstrate the use of sodium lauryl ether sulfate, which has good flash foam properties, with stability in both hard and soft water. Small amounts of superfatting and skin-caring additives are included to alleviate drying of the skin. *Formulation VI*, which produces a moisturizing bubble bath, incorporates a quaternized soya protein derivative which exhibits high substantivity to skin at low concentrations and is compatible with anionic systems. Additional emollience is provided by ingredient (19), a water-soluble almond oil derivative. *Formulations VII* and *VIII*, based on lauryl sulfates, contain a number of emollient materials. *Formulation VII* is a crystal-clear liquid with an excellent, rich creamy lather on skin and *VIII*, which can be described as a mild, herbal foaming product, should be perfumed according to the nature of the herb. The formula produces a semi-solid gel suitable for packaging in tubes or squeeze-bottle packages.

4.2.2.2 Liquid, cream or gel bubble baths

	I [4]	*II* [8]	*III* [9]	*IV* [9]	*V* [5]	*VI* [5]	*VII* [4]
1. Sodium Laureth Sulfate, 28%	–	42.00[b]	50.00[c]	56.00[d]	42.00[d]	4.00[d]	–
1b. Sodium Laureth Sulfate, high active	30.0[a]	–	–	–	–	–	10.4[e]
2. Cocamidopropyl Betaine	–	–	–	–	–	27.00[f]	24.5[g]
3. Lauryl Betaine	–	–	5.00[h]	–	–	–	–
4. Sodium Lauroyl Sarcosinate	–	–	–	–	18.00[i]	–	–
5. Sodium Cocoyl Isethionate	–	–	–	–	–	7.00[j]	–
6. Disodium Cocoamphodiacetate	–	20.50[k]	–	–	–	–	–
7. Disodium Laureth Sulfosuccinate	–	–	–	–	–	–	25.0[l]
8. Sodium Laureth Sulfate (and) Glycol Stearate (and) Glycol Distearate (and) Cocamidopropyl Betaine	7.0[m]	–	–	–	–	–	5.5[m]
9. Sucrose Laurate	–	2.00[n]	–	–	–	–	–
10. Cocamide DEA	2.0[o]	–	5.00[o]	–	6.00[o]	–	2.1[o]
11. Lauramide MEA	–	–	–	5.00	–	–	–
12. Polyquaternium-39	–	1.00[p]	–	–	–	–	–
13. Polysorbate 20	–	–	–	8.00[q]	–	–	–

	I [4]	*II* [8]	*III* [9]	*IV* [9]	*V* [5]	*VI* [5]	*VII* [4]
14. PEG-75 Lanolin	–	–	10.00[r]	–	–	–	–
15. Laneth–20	–	–	–	5.00[s]	–	–	–
16. Acetylated Lanolin	–	–	1.50[t]	–	–	–	–
17. PPG-15 Stearyl Ether	–	–	–	–	10.00[u]	–	–
18. Propylene Glycol Dicaprylate/Dicaprate	–	–	–	–	–	0.50[v]	–
19. PEG-7 Glyceryl Cocoate	–	–	–	–	–	5.00[w]	–
20. Hydrolyzed Oats	–	–	–	–	–	1.00[x]	–
21. Isopropanol	–	–	–	7.00	–	–	–
22. Lactic Acid	–	1.10	–	–	–	–	–
23. Carbomer 1382 (2% aq. sol.)	–	–	–	–	–	15.00[y]	–
24. Styrene/Acrylamide Copolymer (and) Ammonium Nonoxynol-4 Sulfate	–	–	–	–	–	1.00[z]	–
25. Parfum/Fragrance	q.s.	1.20[aa]	q.s.	12.00	q.s.	q.s.	q.s.
26. CI 14700/FD&C Red No. 4	–	0.80[bb]	–	–	–	–	–
26a. Colour	q.s.	–	q.s.	q.s.	q.s.	–	q.s.
27. Quaternium 22	–	–	–	3.00	–	–	–
28. Imidazolidinyl Urea	–	0.15[cc]	–	–	–	–	–
29. Benzl Alcohol (and) Methylchloro-isothiazolinone (and) Methylisothiazolinone	–	–	–	0.10[dd]	–	–	–
30. Preservative	q.s.	–	q.s.	–	q.s.	q.s.	q.s.
31. Citric Acid/Sodium Hydroxide, to pH	6.5–7.0	–	–	–	–	–	see below
32. Sodium Chloride	q.s.	–	–	–	–	–	q.s.
33. Aqua/Water (deionized)	to 100	to 100	to 100	–	to 100	to 100	to 100

Sources (generic except for the following)

(a) Empicol ESB 30 (Albright & Wilson); (b) Rewopol NL3 (Witco Surfactants); (c) Empicol ESB 3 (Albright & Wilson); (d) Akyposal E 020 CP (Chem–Y); (e) Empicol ESC 70 (Albright & Wilson); (f) Incronam 30 (Croda Oleochemicals); (g) Empigen BS/P (Albright & Wilson); (h) Empigen BB (Albright & Wilson); (i) Crodasinic LS35 (Croda Oleochemicals); (j) Jordapon CI Powder (PPG Specialty Chemicals); (k) Rewoteric AM2C/NM (Witco Surfactants); (l) Empicol SDD (Albright & Wilson); (m) Empicol XP40 (Albright & Wilson); (n) Sisterna L70–C (Sisterna); (o) Empilan CDE (Albright & Wilson); (p) Merquat Plus 3330 [10% solution] (Calgon); (q) Mulsifan RT 141 (Zschimmer & Schwarz); (r) Aqualose L75 (Westbrook); (s) Aqualose W20 (Westbrook); (t) Acetadeps (Westbrook); (u) Prostearyl 15 (Croda Oleochemicals); (v) Crodamol PC (Croda Oleochemicals); (w) Glycerox HE (Croda Oleochemicals); (x) Cromoist O25 (Croda Oleochemicals); (y) Carbopol 1382 (B.F. Goodrich); (z) Opacifier E308 (Warner Jenkinson); (aa) Comp. SBS 35424 (Ribero); (bb) Ponceau SX [0.1% solution] (Williams); (cc) Germall 115 (Sutton); (dd) Euxyl K 100 (Shulke & Mayr).

Procedures

Formulation I: [i] Charge (33) and add the buffer. Initial charging of a portion of (32) will aid the dissolution of (1b). The approximate level of salt addition required to achieve the desired viscosity should be determined prior to commencing large-scale production. [ii] Add (1b) slowly with stirring until a homogeneous solution is obtained, increasing the temperature to about 40°C if necessary. [iii] Add coactive surfactant (10). [iv] After cooling to less than 35°C, add (8) with adequate stirring to ensure uniformity of the pearl effect. [v] Add perfume, dye and preservative. [vi] If required, adjust pH to 6.5–7.0 with (31). [vii] Add (32) to adjust the viscosity.

Formulation II: [i] Heat (33) to 70°C and add (1), (6), (9), (12), (22), and (28). [ii] Cool to room temperature and add (25) and (26) while stirring. Physical characteristics: viscosity 6000–7000 mPa.s (Brookfield RVT, G5 at 5 rpm); pH 5.5–6.5.

Formulation III: [i] Mix together (1), all but 5 parts of (33), (10) and (3) in this order. [ii] Mix together (14), (16), the remaining 5 parts of (33) and (30) in this order. [iii] Mix well together phases (i) and (ii). [iv] Add [25] and [26a].

Formulation IV: [i] Melt ingredients (11) and (15) and mix together. [ii] Mix together (1), (13), (21), and (27). [iii] Mix together phases (i) and (ii). [iv] Add (25), (26a) and (29).

Formulation V: [i] Preblend (1), (4) and (10). [ii] Add (33) followed by (17). [iii] Warm gently to blend together.

Formulation VI: [i] Combine (33) and (1) and heat to 60°C. [ii] With gentle agitation add (5) slowly, taking care not to aerate. [iii] When completely dissolved, remove from heat; adjust for evaporation. [iv] Add (19), (20) and (23) and stir until homogeneous. [v] Add (2) followed by (18). [vi] Stir until cool, adding (12) and (24) below 40°C. Fill off.

Formulation VII: [i] Charge (33) and add the buffer. [ii] Add (1b) slowly with stirring until a homogeneous solution is obtained; the rate of dissolution of (1b) can be increased if the water temperature is raised to approximately 40°C. [iii] Add (7). [iv] Add coactive surfactants (2) and (10). [v] After cooling to less than 35°C add (8) with adequate stirring to ensure uniformity of the pearl effect. [vi] Add (25), (26a) and (30). [vii] If required adjust pH to 6.3–6.8 with (31). When adjusting with sodium hydroxide a 10% solution should be used: this will prevent the possibility of local hydrolysis of (7). [viii] Add (32) to adjust viscosity.

Comments

These formulations all contain sodium laureth sulfate in combination: with either a sarcosinate, an isethionate, a betaine, a sulfosuccinate or an amphoacetate, all of which are used to improve the skin-friendliness and skin-feel of each preparation. Various types of secondary surfactants and superfatting agents have also been used (alkanolamides, esters, nonionics and lanolin derivatives).

Formulation I is intended for general use by the family. It exhibits good flash foam characteristics with stability in both hard and soft water. *Formulation III* produces a viscous cream bubble bath with good lathering properties and emolliency, and *Formulation IV* an elegant bubble bath with gentle emollient effect. In *Formulation V* the sarcosinate is used because it is milder than ether sulfate and foams in the presence of the emollient materials included to improve skin-feel. *Formulation VI* produces an opaque cream suitable for both bath and shower. It achieves superior superfatting effects from the combination of PEG-7 Glyceryl Cocoate and Propylene Glycol Dicaprylate/Dicaprate.

The Hydrolysed Oats ingredient functions as a moisturizing agent. Finally, *Formulation VII* is included to demonstrate the use of a sulfosuccinate to improve product mildness.

With strong colouring and suitable perfuming, e.g. 'fruity', any of these formulations could be marketed as a children's bubble bath.

4.2.2.3 Novelty bubble baths

	I [5] *Novelty gel bubble bath*	*II* [5] *Colour-change bubble bath*
1. Sodium Laureth Sulfate	20.00[a]	40.000[a]
2. Cocamidopropyl Betaine	10.00[b]	10.000[b]
3. Cocamidopropylamine Oxide	3.00[c]	3.000[c]
4. PEG-60 Almond Glycerides	2.00[d]	–
5. PEG-150 Pentaerythrityl Tetrastearate	3.00[e]	–
6. Styrene/Acrylamide Copolymer (and) Ammonium Nonoxynol-4 Sulfate	q.s.[f]	–
7. Bromothymol Blue (or Bromocresol Green)	–	0.003
8. Lactic Acid	–	to pH 5.0–5.5
9. Sodium Chloride	–	q.s.
10. Parfum/Fragrance, dye, preservative	q.s.	q.s.
11. Aqua/Water (deionized)	to 100	to 100

Sources (generic except for the following)
(a) Empicol ESB3/M (Albright & Wilson); (b) Incronam 30 (Croda Oleochemicals); (c) Incromine Oxide C (Croda Oleochemicals); (d) Crovol A70 (Croda Oleochemicals); (e) Crothix (Croda Oleochemicals); (f) Opacifier E308 (Warner Jenkinson).

Procedures
Formulation I: [i] Premix perfume and (4). [ii] Combine remaining ingredients and heat to 70–75°C with gentle agitation; mix until homogenous. [iii] Stir to cool and add [i] at 40–45°C.

Formulation II: [i] Cold mix all components. [ii] Check pH and adjust to 5.0–5.5 with (8). [iii] Add (9) to thicken.

Comments
Formulation I is a highly viscous mild detergent system, thickened by ingredient (5), to create a gel-like product with novel rheological properties. With bright and vibrant package graphics and coloured with fluorescent dyes, this simple formulation can be imaginatively marketed to either children or adults. *Formulation II* is a simple blend of detergents containing a pH indicator dye which dramatically changes colour on dilution. Additional moisturizing agents can be added to this visually impressive formulation to improve skin-feel.

These formulations are suggested where extremely mild products are required. Both sulfosuccinates and lauroamphoacetate are very skin-friendly materials that can also reduce the irritant effects of other surfactants.

4.2.2.4 Powdered bubble baths

Powdered bubble bath is no longer as popular as it once was. It does, however, have one advantage – it can be packed into a cheap paper envelope or sachet. The following is a simple formulation for what is really a bath salt with foaming action.

Sodium Carbonate (dried)	90.0
Sodium Lauryl Sulfate (powder)	10.0
Colour, Parfum/Fragrance, herbal extract, etc.	q.s.

By replacing the sodium carbonate in the above formulation with more emollient materials, much more elegant products can be formulated.

4.2.3 Foam testing

The bubbles of a bubble bath are usually generated by allowing the taps to pour hot water onto the product already added to some of the bath water. Some hand agitation is probably also employed. Since foaming is the main property required of a bubble bath, formulations are compared by evaluating them in a foaming apparatus.

The Ross-Miles foaming apparatus does not reproduce the conditions of use in a bath exactly but it is a well-known and reproducible test [10] used for comparing foaming agents, and many laboratories have the equipment already set up. The apparatus consists of two concentric vertical tubes, the outer forming a warm-water jacket for the inner. A specially designed 200 ml pipette, having a 2 mm orifice and a bottom stopcock, is filled with the test solution. The walls of the inner cylinder of the apparatus are wetted by pipetting another 50 ml of the test solution in a swirling motion down the side of the cylinder. Immediately, the 200 ml test solution is allowed to fall down the centre of the inner cylinder on to the 50 ml of test solution so that foam is generated.

Typical concentrations for the test solution range from 0.05% to 0.1% active matter. The test is performed at bath temperatures and with tap water of varying degrees of hardness. The initial amount of foam formed (the flash foam) is recorded, and also the foam remaining after 1 min and 5 min.

A simpler method is to place a solution of the product, calculated to approximate the bath dilution (which might be about 10 ml/50 l) in a calibrated cylinder, invert this a number of times and measure the amount of foam generated. Controlled shaking can also be used, but this technique is more difficult to standardize and most bubble baths produce too much foam in these circumstances.

4.2.3.1 Defoaming

Mention has been made of the defoaming effect of soap on some surfactants, particularly alkyl sulfates, in contrast to sulfosuccinates and sarcosinates which are usually unaffected, and this has been presented as if it were a disadvantage. However, the effect of allowing the foam to persist until the bather has finished, so that the bath does not drain cleanly may also be considered a disadvantage, and the bather may prefer the foam to collapse with the introduction of the soap bar after an initial period of relaxation and luxuriation in the aroma and bubbles.

4.3 BATH OILS AND ESSENCES

Bath 'oils' and bath essences are emollient, highly fragrant products which do not foam, or if they do so, foam only slightly. [None of the products are true oils, nor do many of the ingredients used conform to the technical definition of an oil as a liquid triglyceride, but we will follow the trade practice of referring to them in this way.] There are several types: floating, or spreading, oils which float on the surface of the bath water; dispersible oils (essences); and soluble oils (soluble fragrances).

To prepare effective bath oils and essences that are either non-foaming or only slightly foaming, it is conventional to use highly ethoxylated nonionic surfactants as emollients and solubilizers. Cationic surfactants are usually irritant, poor solubilizers and can make the bath surface too slippery, whilst anionic and amphoteric surfactants are not always effective solubilizers and usually foam too much (for which reason they are employed in bubble baths). Nonionic surfactants exhibit minimum foam, are not harsh on the skin and are good perfume solubilizers and dispersing agents, unaffected by hard water. Many nonionic surfactants are available and the choice is usually affected by whether solubilization, dispersion or solution of the oil phase is required, the feel of the skin after bathing and their effectiveness in solubilizing the perfume.

Since it is possible to prepare many of these products in an anhydrous condition, it is possible to pack them in spherical gelatin capsules or in some other shape. Spherical gelatin capsules coated with a pearling agent such as is used in nail varnish, for example, are sometimed marketed as 'pearls'. When gelatin capsules are added to the hot bath the gelatin dissolves in the hot water and the contents disperse or dissolve.

The high level of water-insoluble mineral oils in bath oil preparations allows for other unusual presentations, and products containing two or more separate layers are marketed on occasion. By the use of both water-soluble and oil-soluble dyes, each phase can be coloured differently (see Section 4.3.5).

4.3.1 Ingredients

Mineral oil is a liquid mixture of hydrocarbons obtained from petroleum. It is also called liquid paraffin or paraffin oil and in the EU must be described on

cosmetic labels as *Paraffinum Liquidum*. In this chapter we will continue to call it mineral oil except in formulations where both the EU and US names are provided. It is a water-white, colourless, odourless, natural and inexpensive emollient hydrocarbon used in almost all cosmetic creams and lotions as the major component of the oil phase, so it is not surprising that it is employed in bath oils to lubricate the skin. It forms an occlusive layer on skin and hair, so preventing moisture loss and, therefore, acting as a moisturizing agent, which is why some products can be described as moisturizing oils. The main disadvantage of mineral oil is that it is 'heavy' and greasy, and for many people it does not produce an elegant feeling on the body. There are many grades of mineral oil, usually distinguished by their viscosity and specific gravity. Most grades conform to the specifications of the *British Pharmacopoeia*.

To overcome the disadvantages of mineral oil while retaining many of its advantages, many synthetic emollients have been developed. These are often lighter in application than mineral oil and give a more pleasant feel to the skin. They can usually be recognized in formulations because they are hydrophobic esters – materials that do not contain any water-attracting groups. Isopropyl myristate, isopropyl palmitate and other isopropyl esters, and polypropylene glycol ethers (such as PPG-15 Stearyl Ether) are just a few examples of many such materials that are often used as a partial or whole replacement for mineral oil to reduce the 'greasiness' of the formulation.

The natural emollients frequently used include lanolin, which is even heavier than mineral oil but has good skin compatibility, and many different types of vegetable oils. Hydrophilic esters, recognizable because they contain ethylene oxide chains (often PEG-*x* Y in INCI nomenclature), are employed because they are emollient and also solubilizers for perfume oils. There are many examples, including the polysorbates, discussed under bubble baths, other ethoxylated sorbitan esters (such as PEG-40 Sorbitan Peroleate, a mixture of oleic acid esters of sorbitol condensed with an average of 40 moles of ethylene oxide) and such materials as ethoxylated glycerides, represented by PEG-15 Glyceryl Laurate (glyceryl monolaurate condensed with 15 moles of ethylene oxide).

The component parts of some esters, i.e. fatty acids and fatty alcohols, can be individually ethoxylated. The resulting materials are also emollient and (if enough ethylene oxide groups have been added) are solubilizers. As examples, consider PEG-12 Laurate, which is lauric acid condensed with 12 moles of ethylene oxide, and Laureth-3 (lauryl alcohol with 3 moles of ethylene oxide). This latter material is not an effective solubilizer for many materials but it is a useful emulsifying agent and is used in dispersible and floating oils. Soluble bath oils require 12-, 15-, or even 20-mole ethoxylates (Polysorbate 20 or Ceteth-20, for example).

4.3.2 Floating or spreading oils

Floating oils are prepared from an insoluble oily substance, often mineral oil, containing a surfactant to allow the film of oil to spread across the surface of the

bath water. This is more aesthetically pleasing than the effect that would be obtained if, say, pure mineral oil were poured in the bath, when the oil would move around in a large patch or 'slick'. Also, it maximizes the surface of the film, allowing for better evaporation of the perfume and adherence to the skin when the bather leaves the bath, coating him or her in a pleasant-smelling and emollient product. Mineral oil is the cheapest raw material to use although many people prefer the feel of other emollients, particularly in this application.

A recent trend has been the development of 'aromatherapy' products. These rely on the incorporation of reasonably high levels of fragrance or essential oil to obtain the real or imagined benefit of luxuriating in an exotic aroma. It cannot be too strongly emphasized that although cosmetic fragrances are tested for safety by the manufacturers, this is not necessarily the case with essential oils, which are sold without knowledge of their intended use. Many of these materials, whether natural or synthetic, can have a seriously adverse effect on skin, and the formulator must be satisfied of the safety of the intended product.

The level of surfactant should be kept low so as not to solubilize the oils in the bath water. The choice of surfactant is important and depends on the spreading coefficient and hydrophilic–lipophilic balance (HLB) of the oils to be spread. The HLB system is a method of ranking materials according to their ease (or otherwise) of emulsification. It can be calculated, for example, by the method of its inventor, Griffin [11], or determined empirically, and values are published [12]. The correct nonionic surfactant to use for a spreading bath oil is one with the highest HLB consistent with compatibility in the oil phase, since high HLB indicates a high spreading coefficient [13–15].

The main disadvantages of this type of product are that an oily ring can form around the edge of the bath and it is difficult to get the soap to lather in this environment, since mineral oil, lanolin and many other of the emollients likely to be present are excellent defoaming agents.

4.3.2.1 Formulations

Some suggested formulations for spreading oils are as follows:

	I [16]	*II* [17]	*III* [17]	*IV* [5]	*V* [5]	*VI* [9]
1. Paraffinum Liquidum/ Mineral Oil	45.0	40.0	–	to 100	to 100	to 100
2. Isopropyl Myristate	–	25.0[a]	–	47.50[b]	26.00[b]	–
3. Cetearyl Octanoate (and) Isopropyl Myristate	–	–	–	–	10.00[c]	–
4. Cetearyl Octanoate	–	5.0[d]	5.00[d]	–	–	–
5. PPG-15 Stearyl Ether	49.0[e]	–	–	–	–	–
6. PEG-40 Sorbitan Peroleate	1.0[f]	3.0[g]	3.00[g]	–	–	–

	I [16]	*II* [17]	*III* [17]	*IV* [5]	*V* [5]	*VI* [9]
7. C12-13 Pareth-3	–	–	–	–	2.00[h]	–
8. PPG-3-PEG-6 Oleyl Ether	–	–	–	1.00[i]	–	–
9. Isostearyl Alcohol	–	5.0[j]	5.0[j]	–	–	–
10. Lanolin Oil	–	–	–	–	–	10.00[k]
11. Lanolin Oil (and) Isopropyl Palmitate (and) Oleyl Alcohol	–	–	–	–	–	10.00[l]
12. Oysternut (Telfairia Pedata) Oil	–	2.0[m]	–	–	–	–
13. Grape Seed (Vitis Vinifera) Oil	–	19.0[m]	76.00[m]	–	–	–
14. Sweet Cherry (Prunus Avium) Pit Oil	–	–	10.00[m]	–	–	–
15. Parfum/Fragrance	5.0	1.0[m]	1.00[m]	–	q.s.	q.s.
16. Colour	–	–	–	q.s.	q.s.	–
17. Preservative	–	–	–	q.s.	q.s.	–

Sources (generic except for the following):
(a) Isopropyl Myristate (A&E Connock); (b) Crodamol IPM (Croda Oleochemicals) (c) Crodamol CAP (Croda Oleochemicals); (d) Cetearyl Octanoate (A&E Connock); (e) Arlamol E (ICI Specialty Chemicals); (f) Arlatone T (ICI Specialty Chemicals); (g) AEC PEG-40 Sorbitone Peroleate (A&E Connock); (h) Volpo L3 Special (Croda Oleochemicals); (i) Spreading Agent ET0672 (Croda Oleochemicals); (j) AEC Isostearyl Alcohol (A&E Connock); (k) Argonol 50 (Westbrook); (l) Argonol ISO (Westbrook); (m) (A&E Connock).

Procedures
Formulation I: Mix well, filter if necessary.
Formulation II: *N.B. All equipment must be absolutely dry when weighing, mixing and filling this product.* Weigh out (2) into a suitable, clean, dry vessel and add each item in turn with mixing.
Formulation III: *N.B. If to be coloured, dyestuffs must be approved oil-soluble colours for cosmetic use. See also note for Formulation I.* [i] Weigh each item in order and mix well with each addition. [ii] Mix items (9), (6) and (15). [iii] Mix items (14), (4) and (13). [iv] Add part [iii] to [ii] with stirring. A suitable oil-soluble preservative should be incorporated.
Formulations IV and V: Simple blend.
Formulation VI: [i] Mix together (1), (10) and (11). [ii] Add (15), stir until clear.

Comments
Vegetable oils may be used in some of these formations in place of mineral oil. An antioxidant should be added when vegetable oils are used. The mineral oil may also be completely replaced by isopropyl myristate, which reduces the oily feel on the skin and provides better solvent action for the perfume. *Formulation I*: Ingredient (5) is a spreading agent. *Formulation IV*: Ingredient (8) is a highly effective spreading agent, requiring the use of as little as 1% to achieve the desired effect. Low levels of (7) (as in *Formulation V*) and Oleth-3 are also useful in this application. *Formulation VI*: This is an elegant floating bath oil with emollience and good 'rub-in' characteristics.

4.3.3 Dispersible or blooming bath oils

Dispersible oils contain high levels of fragrance, emollient oils and surfactants which are capable of dispersing these oils in the bath water to produce an emulsion. The emulsion, formed instantly when the product is poured into the water, gives a bloom or white cloud.

The choice of emulsifying agent depends on the oil phase (usually mineral oil) and the fragrance. Because the surfactant level is higher in this type of product than in floating oils, less of an oily ring should be formed around the edge of the bath.

4.3.3.1 Formulations

Suitable formulations for dispersible bath oils are as follows:

	I [18]	*II* [19]	*III* [17]	*IV* [17]	*V* [9]	*VI* [5]	*VII* [5]
1. Mineral (Paraffinum Liquidum) Oil	–	65.00	–	–	to 100	to 100[a]	to 100[a]
2. Polyglyceryl-3 Diisostearate	–	12.50[b]	–	–	–	–	–
3. Diisostearoyl Trimethylolpropane Siloxy Silicate	–	–	–	2.00[c]	–	–	–
4. Cetearyl Octanoate	–	–	5.00[c]	5.00[c]	–	–	–
5. Octyl Palmitate	–	–	–	–	–	–	8.00[d]
6. Hybrid Sunflower (Helianthus Annuus) Oil	80.00[e]	–	–	–	–	–	–
7. Borage Seed (Borago Officinalis) Oil or Evening Primrose (Oenoethera (Biennis) Oil	–	–	–	–	–	–	3.00[f]
8. PEG-40 Sorbitan Peroleate	–	–	3.00[c]	3.00[c]	–	–	–
9. Laneth-4	–	–	–	–	30.00[g]	–	–
10. PPG-10 Cetyl Ether	–	–	–	–	–	16.00[h]	–
11. Polysorbate 85	20.00[i]	–	–	–	–	–	–
12. PEG-8 Caprylic/ Capric Glycerides	–	12.50[j]	–	–	–	–	–
13. PEG-12 Palm Kernel Glycerides	–	–	–	–	–	9.00[k]	–
14. PEG-20 Evening Primrose Glycerides	–	–	–	–	–	–	15.00[l]
15. Oleyl Alcohol	–	–	–	–	–	–	17.50[m]

	I [18]	*II* [19]	*III* [17]	*IV* [17]	*V* [9]	*VI* [5]	*VII* [5]
16. Isostearyl Alcohol	–	–	5.00[c]	5.00[c]	–	–	
17. Lanolin Oil	–	–	–	–	10.00[n]	–	–
18. Lanolin Oil (and) Isopropyl Palmitate (and) Oleyl Alcohol	–	–	–	–	10.00[o]	–	–
19. Grape Seed (Vitis Vinifera) Oil	–	–	86.18[c]	61.90[c]	–	–	–
20. Sweet Cherry (Prunus Avium) Pit Oil	–	–	–	5.00[c]	–	–	–
21. Tea Tree (Melaleuca Alternifolia) Oil	–	–	0.50[c]	–	–	–	–
22. Peppermint (Mentha Piperita) Oil	–	–	0.12[c]	–	–	–	–
23. Vegetable (Olus) Oil	–	–	–	–	5.00	–	–
24. Jojoba (Buxus Chinensis) Oil	–	–	–	2.00[c]	–	–	–
25. Apricot Kernel (Prunus Armeniaca) Oil	–	–	–	5.00[c]	–	–	–
26. Sweet Almond (Prunus Amygdalus Dulcis) Oil	–	–	–	5.00[c]	–	–	–
27. Peach Kernel (Prunus Persica) Oil	–	–	–	5.00[c]	–	–	–
28. Ethanol DEB100	–	–	–	–	–	10.00	–
29. Tocopherol	–	–	0.20[p]	0.10[p]	–	–	–
30. BHT	–	–	–	–	–	–	q.s.
31. Parfum/Fragrance	–	–	–	1.00[c]	q.s.	q.s.	q.s.
32. Colour	–	–	–	q.s.	–	–	q.s.
33. Phenoxyethanol (and) Methylparaben (and) Butylparaben (and) Ethylparaben (and) Propylparaben	–	0.20[q]	–	–	–	–	–
33a.Preservative	–	–	–	q.s.	–	–	q.s.
34. Aqua/Water	–	9.80	–	–	–	–	–

Sources (generic except for the following)
(a) 25 cS at 25°C; (b) Plurol Diisostearique (Gattefossé); (c) (A&E Connock); (d) Crodamol OP (Croda Oleochemicals); (e) Florasun 90 (Floratech); (f) Cropure Borage or Cropure Evening Primrose (Croda Oleochemicals); (g) Brij 30 (ICI Specialty Chemicals); (h) Procetyl 10 (Croda Oleochemicals); (i) Tween 85 (ICI Specialty Chemicals); (j) L.A.S. (Gattefossé); (k) Crovol PK40 (Croda Oleochemicals); (l) Crovol EP40 (Croda Oleochemicals); (m) Novol (Croda Oleochemicals); (n) Argonol 50 (Westbrook); (o) Argonol ISO (Westbrook); (p) Vitamin E Oil (A&E Connock); (q) Phenonip (Nipa).

Procedures

Formulation I: Blend ingredients with stirring.

Formulation II: At room temperature mix all components in the order (12), (2), (1), (34) and (33).

Formulation III: *N.B. It is essential that all weighing, mixing and filling equipment be absolutely dry – warn filling department.* Mix in order (19), (8), (16), (4), (29), (21) and (22) in a clean, DRY vessel. Final s.g. 0.913 approx.

Formulation IV: Mix in the order (19), (16), (8), (31), (24), (20), (4), (29), (25), (26), (27) and (3) in a clean, dry vessel. The finished product should be clear. It may be coloured using suitable oil-soluble colours and the addition of an oil-soluble preservative is advised.

Formulation V: [i] Mix together (17), (18), (1), (9) and (23). [ii] Add (31), stir until clear.

Formulation VI: Simple blend. Warm if necessary, stir until clear.

Formulation VII: Simple blend.

Comments

Formulation V: This produces a blooming bath oil leaving emollience on the skin, with vegetable oil (e.g. olive, sesame, peach) for added elegance. *Formulation VI* produces a dense white dispersion when added to water. PEG-12 Palm Kernel Glycerides is the surfactant which causes this dispersion. It is very mild and provides excellent emollience of skin. PPG-10 Cetyl Ether is used to reduce the greasy feel of the mineral oil and as a coupler for the alcohol. *Formulation VII* is an emollient dispersible bath oil with either borage or evening primrose oil.

4.3.4 Soluble bath oils

Soluble bath oils are solutions of nonionic surfactants in water, with small amounts of emollient materials added. Because the level of hydrophobic material is low, these materials can produce some foam, but since the main surfactants are nonionic, their foaming power is rather feeble. There are many nonionic surfactants that are capable of solubilizing fragrance oils and emollients in the bath. The choice is usually made after considering the cost and after-feel on the skin of the alternatives.

4.3.4.1 Formulations

	I [16]	*II* [16]	*III* [16]	*IV* [7]	*V* [7]
1. Polysorbate 20	5–25[a]	15.0[a]	–	–	–
2. PEG-12 Laurate	–	–	–	30.0	–
3. PEG-15 Glyceryl Laurate	–	–	–	–	25.0[b]
4. Ceteth-20	–	–	19[c]	–	–
5. Isopropyl Myristate	–	–	5	–	–
6. Lauramide DEA	–	–	5[d]	–	–

	I [16]	*II* [16]	*III* [16]	*IV* [7]	*V* [7]
7. Alcohol denat./ SD Alcohol 40	–	20.00	–	–	5.0
8. Propylene Glycol	–	61.97	–	–	–
9. Water/Aqua (deionized)	to 100	–	66	65.0	65.0
10. Parfum/Fragrance	5	3.00	5	5.0	5.0
11. Preservative	q.s.	–	q.s.	q.s.	q.s.
12. Bromcresol purple	–	0.03	–	–	–
13. Colour	–	–	–	q.s.	q.s.

Sources (generic except for the following)
(a) Tween 20 (ICI Specialty Chemicals); (b) Glycerox L15 (Croda Oleochemicals); (c) Brij 58 (ICI Specialty Chemicals); (d) Monamid 716 modified lauric diethanolamide (Mona Industries).

Procedures
Formulation I: [i] Mix (1), (10) and (11) well. [ii] Add (9) slowly to this mixture with agitation. [iii] Filter, if necessary.
Formulation II: [i] Mix all ingredients with agitation, until all of the dye has dissolved. [ii] Filter, if necessary.
Formulation III: [i] Heat (4), (5) and (6) to 90°C. [ii] Heat also (9) and (11) to the same temperature and then add to [i] with gentle agitation. [iii] Cool with stirring to 70°C, add perfume and mix completely. Fill hot.
Formulation IV and V: [i] Combine (10) and solubilizer, (2) or (3). [ii] Stir slowly and add to (9), and (7) when applicable, with constant stirring. [iii] The viscosity can be reduced by the inclusion of glycerol or propylene glycol.

Comments
Polysorbates and ethoxylated fatty alcohols in the HLB range of 12–18 are widely used in perfume oil solubilization, as also is PEG-25 Propylene Glycol Stearate. Two to five parts of surfactant will solubilize one part of many perfume oils in water. *Formulation I* demonstrates this application using Polysorbate 20. *Formulation II* is anhydrous. It is a clear solution which changes from golden yellow to purple on dilution in the bath water. The alcohol at this concentration gives lift to the perfume and acts as a preservative. *Formulation III* is a clear, ringing gel which is completely water-soluble and produces some foam. The gel softens at body temperature and can be applied directly to the skin.

In the above formulations, note the preference of adding the water slowly to the nonionic surfactant. Many nonionic surfactants produce stiff gels when added to water and to avoid this they can be either added to hot water or dissolved first in any solubilizers present in the formulation or mixed with the perfume. The presence of alcohol in some of the examples, as well as giving lift to the perfume, reduces the gelling tendencies of the nonionics. The presence of propylene glycol and, frequently, the perfume itself, will also have this effect.

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4.3.5 Novelty bath oils

Because bath oils can contain large amounts of both water-soluble and water-insoluble materials, it is possible to produce novelty effects from this incompatibility. The following formulation [5] produces a three-layer bath oil:

1. PEG-7 Glyceryl Cocoate	30.00[a]
2. Glycerin	35.00[b]
3. Mineral (Paraffinum Liquidum) Oil	33.00[c]
4. Aqua/Water (deionized)	3.00
5. Perfume, preservative	q.s.
6. Colour (see below)	q.s.[d]

N.B. The ingredients listed here are shown in parts only and not percentage weight/weight as elsewhere in this chapter.

Sources (generic except for the following)
(a) Glycerox HE (Croda Oleochemicals); (b) Croderol GV7000 (Croda Oleochemicals); (c) 25 cS at 25°C; (d) (Warner Jenkinson).

Procedures
[i] Add all the materials in the order stated above. [ii] Mix well until essentially clear. [iii] Some of the colours suggested below may be added to impart a greater visual impact of the three-layer system.

Middle phase: CI 47005/D&C Yellow No. 10*; CI 26100/D&C Red No. 17

Middle and lower phase: CI 15510/D&C Orange No. 4; 14700/FD & C Red No. 4; CI 47005/D&C Yellow No. 10; CI 45380:2 (Ariabel Cerise)/D&C Red No. 21; CI 26100/D&C Red No. 17

Lower phase: CI 42090/FD & C Blue No. 1; CI 15985/FD & C Yellow No. 6; CI 17200/D & C Red No. 33; CI 16185 (Amaranth)/Acid Red 27; CI 14720 (Carmoisine)/Acid Red 14; CI 16255 (Ponceau 4R)/Acid Red 18; CI 42053/FD & C Green No. 3.

Using these dyes, a wide variety of colours may be generated within the lower and middle phase. Suitable oil-soluble dyes may be introduced into the upper phase if desired. Oil-soluble colours available from Croda Novarom may be used, such as those from chlorophyll, nut and paprika. Light-fastness of any dyestuff should be evaluated prior to marketing.

4.4 BATH SALTS, CUBES AND POWDERS

Bath salts and bath cubes, although regarded by some as slightly old-fashioned, are still purchased, particularly at Christmas time, perhaps because they make

*The names for EU-approved colouring agents are listed in Annex IV of the EU Cosmetics Directive and are identified, with a few exceptions, by their Colour Index (CI) numbers. In the US the names of FDA-approved colourants are listed in Title 21, *US Code of Federal Regulations*, Parts 73, 74 and 82. In the formulations in this chapter both EU and US names are provided for each colourant.

4.3.5 Novelty bath oils

Because bath oils can contain large amounts of both water-soluble and water-insoluble materials, it is possible to produce novelty effects from this incompatibility. The following formulation [5] produces a three-layer bath oil:

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2. Glycerin	35.00[b]
3. Mineral (Paraffinum Liquidum) Oil	33.00[c]
4. Aqua/Water (deionized)	3.00
5. Perfume, preservative	q.s.
6. Colour (see below)	q.s.[d]

N.B. The ingredients listed here are shown in parts only and not percentage weight/weight as elsewhere in this chapter.

Sources (generic except for the following)
(a) Glycerox HE (Croda Oleochemicals); (b) Croderol GV7000 (Croda Oleochemicals); (c) 25 cS at 25°C; (d) (Warner Jenkinson).

Procedures
[i] Add all the materials in the order stated above. [ii] Mix well until essentially clear. [iii] Some of the colours suggested below may be added to impart a greater visual impact of the three-layer system.

Middle phase: CI 47005/D&C Yellow No. 10*; CI 26100/D&C Red No. 17

Middle and lower phase: CI 15510/D&C Orange No. 4; 14700/FD & C Red No. 4; CI 47005/D&C Yellow No. 10; CI 45380:2 (Ariabel Cerise)/D&C Red No. 21; CI 26100/D&C Red No. 17

Lower phase: CI 42090/FD & C Blue No. 1; CI 15985/FD & C Yellow No. 6; CI 17200/D & C Red No. 33; CI 16185 (Amaranth)/Acid Red 27; CI 14720 (Carmoisine)/Acid Red 14; CI 16255 (Ponceau 4R)/Acid Red 18; CI 42053/FD & C Green No. 3.

Using these dyes, a wide variety of colours may be generated within the lower and middle phase. Suitable oil-soluble dyes may be introduced into the upper phase if desired. Oil-soluble colours available from Croda Novarom may be used, such as those from chlorophyll, nut and paprika. Light-fastness of any dyestuff should be evaluated prior to marketing.

4.4 BATH SALTS, CUBES AND POWDERS

Bath salts and bath cubes, although regarded by some as slightly old-fashioned, are still purchased, particularly at Christmas time, perhaps because they make

*The names for EU-approved colouring agents are listed in Annex IV of the EU Cosmetics Directive and are identified, with a few exceptions, by their Colour Index (CI) numbers. In the US the names of FDA-approved colourants are listed in Title 21, *US Code of Federal Regulations*, Parts 73, 74 and 82. In the formulations in this chapter both EU and US names are provided for each colourant.

an inexpensive gift that everyone can use. Originally, they were intended to simulate the salt content of natural spas. They have recently been given a modern, 'natural' image by greater emphasis being placed on their mineral content and by the addition of herbal extracts and natural oils. Most bath crystals are sodium salts of weak acids and, consequently, alkaline. In great dilution, in the bath, they are normally considered harmless but it is advisable to make sure that any formulation disperses quickly and does not concentrate in the centre of the bath.

4.4.1 Ingredients

In order to appreciate the significance of the different formulations, the materials used and their properties are discussed briefly below.

Sodium Carbonate crystals, also known simply as soda or washing soda, are sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$. They occur as colourless, transparent crystals of various sizes and are readily soluble, one part dissolving in two parts of cold water or 0.25 parts of boiling water. *Sodium Carbonate monohydrate*, $Na_2CO_3 \cdot H_2O$, occurs as a white, small crystal or in the form of a crystalline powder. It is less soluble than the decahydrate.

Sodium Bicarbonate, $NaHCO_3$, occurs in the form of white, crystalline powder or granules. It is readily soluble in 10 parts of water, giving a slightly alkaline pH value of 8.3. It is mainly used, together with an acid (usually citric acid or tartaric acid), to prepare effervescent bath salts, but can also be used as an ingredient of bath crystals.

Sodium Sesquicarbonate, $Na_2CO_3NaHCO_3 \cdot 2H_2O$, is prepared from sodium carbonate and sodium bicarbonate. It occurs in the form of fine, needle-shaped crystals and remains stable when exposed to air. It is readily soluble in water and is easily coloured and perfumed. Owing to its stability it does not require any special precautions in packaging, so that it has become one of the most popular raw materials used in the preparation of bath salts. In solution it is only mildly alkaline due to the content of bicarbonate, and although it readily softens hard water, it does not have a harsh effect on the skin.

Sodium Phosphate (disodium phosphate) is the dodecahydrate $Na_2HPO_4 \cdot 12H_2O$. It occurs as colourless, translucent crystals or white granules. It is readily soluble in three parts of water, the solution being mildly alkaline with a pH value of about 9. When exposed to air at ordinary temperatures it effloresces, forming the less soluble heptahydrate. Sodium phosphate also occurs as *Trisodium Phosphate*, $Na_3PO_4 \cdot 12H_2O$. This material occurs as colourless or white crystals and is more stable than the dibasic salt. In solution, however, it is very strongly

alkaline, giving a pH value of about 11, and for reasons of safety it is not advisable to use this material on its own. Its high pH also makes it difficult to colour, but it is easily compressed and is therefore sometimes included as a constituent of bath cubes.

Sodium Chloride, NaCl, or common table salt, occurs as colourless, cubic crystals, granules or powder, and is soluble one part in three parts of water, the aqueous solution being neutral. It is anhydrous and only slightly hygroscopic and can readily be tinted and perfumed to present an attractive bath salt. In the bath, sodium chloride has a mild toning and stimulating effect. It does, however, have the disadvantages that it depresses the lathering effect of soap, tends to form a scum ring around the bath and has no water-softening properties. Bay salt, otherwise known as rock salt or sea salt, is produced either by mining or by the evaporation of sea water. It occurs as large, irregular, pale amber crystals.

Sodium Borate, sodium tetraborate or borax, $Na_2B_4O_7 \cdot 10H_2O$, occurs as hard, colourless and odourless crystals, as white granules or as a crystalline powder. It is obtainable in well-graded and regular crystals, and although it effloresces in dry air, it shows good stability in the presence of moisture. The insolubility of borax is, however, a disadvantage since one part of borax is only soluble in about 20 parts of water. Although alkaline, solutions having a pH value of 9.5, it does not have a harsh or drying effect on the skin; in fact, it has a mild, bacteriostatic action and is very slightly astringent when applied externally. Sodium borate is poorly absorbed through intact skin; however, it is absorbed through abraded, denuded or burned skin. The CTFA Cosmetic Ingredient Review Expert Panel concluded that in concentrations equal to, or less than 5 percent, it is safe to use as a cosmetic ingredient, but should not be used on infant skin or injured skin [20].

Sodium Perborate, $NaBO_3 \cdot 4H_2O$, occurs as white, odourless crystals which are stable in cool and dry air but decompose with the liberation of oxygen when exposed to warm and moist conditions. In water it is sometimes used with sodium sesquicarbonate to give an oxygenated preparation. Although the sesquicarbonate helps to maintain the perborate in a stable condition, it is necessary to pack bath preparations containing the perborate in well-closed containers.

4.4.2 Bath salts, crystals and beads

Bath salts or crystals are probably one of the earliest products used to perfume the bath water and give it a pleasant odour. The basic constituents of such preparations are similar and their final selling price is governed not by the raw material cost, which is usually low, but by the cost of the package, presentation and, above all, the cost of the perfume. From the manufacturer's point of view, it is necessary to pay particular attention to the keeping properties, stability, melting point and solubility of the final product.

4.4.2.1 Formulations

	I	*II*	*III*	*IV*	*V*	*VI*
Sodium Carbonate, crystals	100	–	–	–	–	–
Sodium Carbonate, monohydrate	–	80	–	–	–	–
Sodium Sesqui-carbonate	–	–	100	95	–	50
Disodium Phosphate	–	20	–	–	50	50
Sodium Chloride	–	–	–	–	50	–
Sodium Borate	–	–	–	5	–	–
Sodium Lauryl Sulfate, powder	←		q.s.			→
Herbal extract	←		q.s.			→
Parfum/Fragrance, colour	←		q.s.			→

Some suggested formulations are given above. Addition of small amounts of the surfactant sodium lauryl sulfate helps dispersion.

4.4.2.2 Preparation, colouring and perfuming

Any dyestuff used to colour bath salts or crystals must be resistant to alkaline conditions and also compatible with perfume. (The perfume itself must also be stable under alkaline conditions, and, usually, colour and fragrance suitable for soap are suitable for bath salts.) Bath salts are generally tinted by spraying an aqueous solution of dyestuff on to the crystals, followed by a mixing process to distribute the colour evenly. This method can also be modified by first placing the crystals in a tumbler-type mixer and spraying the colour on whilst the crystals are rotating. This process is simple to operate and gives evenly coloured crystals after only a few minutes' mixing time. Another method, which is sometimes preferred when larger quantities of crystals are being treated, is to immerse the crystals in a tank containing the solution of dyestuff. Here, drying becomes an important factor, and special arrangements for removing the excess water must be considered.

The colour solution used with either process can be prepared using either water or alcohol, or a mixture of both as the solvent. Ethanol is the preferred solvent because it evaporates quickly and does not damage the crystals. Used on its own, however, it is more suitable for the dipping process when losses will be proportionately small. Aqueous solutions are, however, equally effective in giving even dispersion of colour, provided the quantity is carefully controlled to

avoid the crystals becoming too damp. The ideal vehicle to use for tinting is probably a mixture of about 90 parts of water with 10 parts of alcohol. After the colouring process, the salts are spread evenly on trays and allowed to dry before packing. An alternative method of tinting is to add a dispersed pigment to the crystals during the mixing process. Dispersed pigments are often stable to perfume but may cause a coloured ring around the bath.

Normally, about 0.5–1.0% of perfume is added to the crystals, but all perfumes should be diluted before they are added. A rapid mix in a tumbler-type mixer ensures even distribution of the perfume, and the crystals should then be collected and spread over trays and given a short period of time to allow the perfume solvent to evaporate. The crystals should then be packed immediately to avoid loss of perfume. It should be borne in mind that the solvent is ultimately lost by evaporation, and this adds to the cost of the product. Denatured ethanol or isopropyl alcohol are suitable alcohols to use, but a water-soluble type of perfume can also be employed.

When using a water-soluble perfume, the solution of colouring material can be prepared together with the perfume, and the colouring and the perfuming of the bath salts can be carried out in one operation. The quantity of water should be kept at a minimum for obvious reasons, and the end-product should be packed immediately after the salts have dried. Herbal or other extracts added for sales appeal can be added with the perfume.

4.4.3 Bath cubes

Bath cubes owe their continued existence to the fact that they are inexpensive and can be elegantly yet cheaply packaged. In the main, they are prepared by compressing either sodium carbonate monohydrate or sodium sesquicarbonate. Sometimes these two materials are used together and a small amount of borax can also be added. When cubes are prepared mainly from sodium sesquicarbonate, they can be fed directly into the compression machine and do not necessarily require the addition of a lubricant. In addition, cubes made from sesquicarbonate disintegrate rapidly in bath water.

Cubes made from sodium carbonate are much firmer, and if the degree of compression is not carefully controlled they remain undissolved in the bath water for some considerable time. To help disintegration of cubes prepared from the carbonate, a small proportion of starch powder of the order of 2–5% should be mixed with the basic raw material before compression. The addition of talc to the product helps release from the mould.

4.4.3.1 Formulations

An example of a formulation for a bath cube mixture is as follows:

Sodium Sesquicarbonate	93
Talc	5

Sodium Borate	2
Colour	q.s.
Parfum/Fragrance	q.s.

4.4.4 Bath powders

Bath powders at one time were quite popular but have now been largely replaced by crystal or liquid preparations. Each package should contain enough powder for one bath. The powders can be prepared either from dry sodium carbonate or sodium sesquicarbonate crystals. A small proportion of borax can also be added. They are manufactured in a similar manner to bath crystals, the perfume and colour being sprayed on, and mixed until uniform. If they are based on sequicarbonate they can be mixed in a rotary-type mixer, but if true powders they are best prepared by using a machine of the sifter/mixer type. Powders are suitably perfumed and coloured using a trituration process. To do this, the perfume and colour are separately mixed with a small portion of the powder to prepare a concentrated mix. This is then added to the bulk of the material and mixed until both the perfume and colour are uniformly distributed.

Foaming bath powders are discussed under bubble bath preparations.

4.4.4.1 Formulations

An example of a powdered salts formulation is as follows:

Sodium Sesquicarbonate	95
Sodium Borate (powdered)	5
Colour	q.s.
Parfum/Fragrance	q.s.
Herbal extract, etc.	q.s.

4.4.5 Special bath crystals and powders

The idea of spray-drying actual spa water, so that it can be diluted at home, has been patented [21,22]. Mixtures which do not exactly replicate any particular spa water but include many of the minerals found at spas can be prepared using magnesium sulfate (Epsom salts, $MgSO_4 \cdot 7H_2O$), sodium sulfate (Glauber's salt, $Na_2SO_4 \cdot 10H_2O$), sodium thiosulfate, magnesium chloride and various potassium halides.

Effervescent bath crystals contain an organic acid and bicarbonate so that carbon dioxide is released when the product is placed in water. The intention is to simulate the effect of natural carbonated spas. Such products must be carefully manufactured and packaged to avoid moisture starting the carbonation reaction. They should either not be coloured or should be dyed with an alcoholic solution of colour.

4.4.5.1 Formulations

One formulation is suggested below:

Sodium Sesquicarbonate	70
Sodium Bicarbonate	5
Tartaric Acid	20
Sodium Lauryl Sulfate, powder	5
Herbal extracts, etc.	q.s.
Parfum/Fragrance	q.s.

Oxygenated salts are used either in the bath or for bathing the feet. In the bath they are considered to be of therapeutic value by helping to clean the skin and dissolve impurities. Typical formulae are given:

	I	*II*
Sodium Sesquicarbonate	5	90
Sodium Chloride	1.5	5
Sodium Perborate	5	5
Sodium Bicarbonate	30	–
Sodium Carbonate, monohydrate	58.5	–
Parfum/Fragrance, colour	q.s.	q.s.

The preparation of medicated bath products that include pharmaceutical substances to treat disease is outside the scope of this book. This subject is balneology or balneotherapy, or, more familiarly, hydrotherapy. It can be mentioned, however, that many substances have traditionally been added to bath water to effect 'cures', including sodium bicarbonate to relieve itching, such as is present in urticaria and eczema, magnesium sulfate for the treatment of sprains, bruises or other inflamed conditions and rheumatism, and also various herbal preparations (which is a separate subject – phytobalneology [23]). The simple addition of herbal extracts to bath preparations, without making specific medical claims, but relying upon the image that certain natural materials evoke, is acceptable in a toiletry product and commonly employed.

4.5 SHOWER PRODUCTS AND BODY SHAMPOOS

The comparatively recent introduction into homes of the douche, or shower, created the need for a new type of toiletry preparation. Shower products are now a fast-growing sector of bathroom toiletries, since aromatherapy, herbal or natural, medicated and body scrub products have become very popular. These products are usually packaged in special bottles with hooks or handles to enable them to be hung in the shower-stall. In contrast to bubble baths, they are frequently opaque or pearly.

Body shampoos, sometimes called hair and body shampoos, body gels or body cremes (or creams), do not need to foam as much as bubble bath products but they should have better cleaning properties. Since these products are also used on the hair, modified shampoo formulations are employed: the products should, however, be more viscous than conventional shampoos so that they are not washed off the body before the applicant has had a chance to rub them all over the skin. They should leave the hair clean and the body with a soft, smooth feeling. Since hair is more difficult to clean and leave in good condition than the skin, these products should be formulated with the requirements for a good hair product uppermost in mind.

The reader interested in formulating body shampoos is advised to study also Chapter 9 on Hair Shampoos.

4.5.1 Ingredients

Because shower products are generally packed in bottles which hang upside-down in the shower-stall, they are usually thickened to a gel-like consistency to avoid leakage from the cap. A high viscosity is also necessary to enable application to the body by the bather. Preferably they exhibit plastic or pseudoplastic flow so that their viscosity shows a drop in response as soon as a shearing force is applied, such as when the bottle is squeezed. As soon as the shear force is removed the viscosity should, ideally, revert to its original high value.

Although soap is commonly used to wash the body, and probably the hair of some, it has the disadvantage of poor performance in hard water and is a slippery object to hold in the shower. However, specially produced soap (e.g. on a hanging rope) is available, which reduces this problem.

Most of the ingredients used in shower products are the same as those employed in bubble baths (and hair shampoos). However, since the 2-mole version of sodium lauryl ether sulfate is a better cleansing agent than the 3-mole version, it is preferred in body shampoos. Both have the same INCI name of *Sodium Laureth Sulfate*. Sodium Laureth Sulfate is used for economy, good washing performance and ability to form the necessary high viscosity gel-like structures.

Alkyl sulfates, particularly when used in combination with sulfosuccinates, amphoacetates, amphopropionates, sarcosinates or betaines, for example, give products which wash hair well and leave the body feeling clean. *Sodium Lauryl Sulfate* or triethanolamine lauryl sulfate (*TEA-Lauryl Sulfate*) are the preferred materials, but ammonium, magnesium or monoisopropanolamine lauryl sulfates are sometimes employed.

Sodium Cocoyl Isethionate, $RCOOCH_2CH_2SO_3^-\ Na^+$, is also a very mild foaming agent which has excellent emolliency and gives a pleasant feel to the skin. It also has excellent lime-soap dispersing power. It is sold as a creamy white paste containing 30% solids, and is also available at much higher concentrations in powder or granule form.

A variety of emollients are used in these formulations, ranging from lanolin and protein derivatives to nonionics and certain surfactants, such as betaines, phosphates and taurates. Many natural and natural-derived materials are also likely to be found in shower products.

4.5.2 Formulations

4.5.2.1 Shower gels

	I [17]	*II* [17]	*III* [4]	*IV* [24]	*V* [5]	*VI* [9]
1. Sodium Laureth Sulfate	35.00	37.00	12.8[a]	–	40.00[b]	40.00[c]
2. Ammonium Lauryl Sulfate	–	–	17.5[d]	–	–	–
3. Magnesium Laureth Sulfate	–	–	–	28.5[e]	–	–
4. Sodium Cocoamphoacetate	–	–	10.7[f]	–	–	–
5. Sodium Cocoyl Isethionate	–	–	–	3.0[g]	–	–
6. Disodium Laureth Sulfosuccinate, 40%	–	–	–	7.0[h]	–	–
7. Sodium Laureth-6 Carboxylate	–	–	–	–	–	20.00
8. Cocamide DEA	3.00	2.00	–	1.0[i]	–	–
9. Lauramide MEA	–	–	–	–	–	2.00
10. Cocamidopropyl Betaine	–	–	–	–	15.00[j]	–
11. Lauryl Betaine	–	1.00	–	–	–	–
12. Sodium C14–16 Olefin Sulfonate (and) Glycol Distearate (and) Cocamidopropyl Betaine (and) Sorbitan Laurate	–	3.00[k]	–	–	–	–
13. Sodium Laureth Sulfate (and) Glycol Stearate (and) Glycol Distearate (and) Cocamidopropyl Betaine	–	–	5.0[l]	–	–	–
14. Cocamidopropylamine Oxide	–	–	–	–	4.00[m]	–
15. PEG-7 Glyceryl Cocoate	–	–	–	–	2.00[n]	–
16. Laneth-20	–	–	–	–	–	2.00[o]

	I [17]	*II* [17]	*III* [4]	*IV* [24]	*V* [5]	*VI* [9]
17. Polyquaternium-11	–	0.20[p]	–	–	–	–
18. Panthenol	–	0.20[q]	–	–	–	0.50[r]
19. Kukui Nut (Aleurites Molueeana) Oil	–	0.10[s]	–	–	–	
20. Herbal extract	–	–	–	–	–	1.00[t]
21. Disodium EDTA	0.05	0.20	–	–	–	–
22. Citric Acid	0.05	0.045	q.s.[u]	–	–	–
23. Lactic Acid	–	–	–	–	q.s.[u]	–
24. Sodium Hydroxide	–	–	q.s.[u]	–	–	–
25. Sodium Chloride	2.50	2.75	q.s.	–	q.s.	1.00
26. Magnesium Chloride ($MgCl_2 \cdot 6H_2O$)	–	–	–	7.0	–	–
27. PEG 400, etc (to reduce viscosity)	–	–	q.s.	–	–	–
28. Parfum/Fragrance	0.20[s]	0.30	q.s.	q.s.	q.s.	q.s.
29. Quaternium-22	–	–	–	–	–	3.00
30. Benzyl Alcohol (and) Methylchloriso-thiazolinone (and) Methyliso-thiazolinone	–	–	–	–	–	0.10[v]
31. Preservative	0.50	0.50	q.s.	q.s.	q.s.	–
32. Colour	q.s.	–	q.s.	q.s.	q.s.	q.s.
33. Water/Aqua (deionized)	58.70	52.705	to 100	53.5	to 100	to 100

Sources (generic except for the following)
(a) Empicol ESB 70 (Albright & Wilson) [alternatively use 32.0 parts Empicol ESB 3/M]; (b) Empicol ESB 3/M (Albright & Wilson); (c) Akyposal E 020 CP (Chem-Y); (d) Empicol AL 30/T (Albright & Wilson); (e) Elfan NS 243 S Mg (Akzo); (f) Empigen CDR 60 (Albright & Wilson); (g) Elfan ATG (Akzo); (h) Elfanol 616 (Akzo); (i) Lauridit KDG (Akzo); (j) Incronam 30 (Croda Oleochemicals); (k) Tego-Pearl S33 (Th. Goldschmidt); (l) Empicol XP40 (Albright & Wilson); (m) Incromine Oxide C (Croda Oleochemicals); (n) Glycerox HE (Croda Oleochemicals); (o) Aqualose W20 (Westbrook); (p) Gafquat 734 (ISP); (q) D-Panthenol, 75% (Roche); (r) D-Panthenol (BASF); (s) (A&E Connock); (t) Herbaliquid [unspecified herbal extract] (Novarom); (u) to pH 6.0–6.5; (v) Euxyl K 100 (Shulke & Mayr).

Procedures

Formulation I: [i] Dissolve (21) in (33) and stir in (1). [ii] Mix together (28) and (8) and add to [i]. [iii] Adjust pH and viscosity and add preservatives and colour to suit.

Formulation II: [i] Measure out (33) and add (21), (1), (17), (19), (28), (18), (8), (11), (12) and (31) in turn, mixing well with each addition. [ii] Adjust the pH with (22) and colour match before finally adjusting the viscosity by adding (25).

Formulation III: [i] Charge (33) and add a buffer. [When using Empicol ESB 3/M a calculated portion of (25) can be added at this point. Initial charging of a portion of (25) will aid the dissolution of Empicol ESB 70. The approximate level of (25) addition required to achieve the desired viscosity should be determined prior to commencing large-scale

production.] [ii] Add (1) slowly with stirring until a homogeneous solution is obtained. [Raising temperature to 40°C will help. Empicol ESB 3/M can be stirred in more rapidly than ESB70 , but take care to avoid aeration.] [iii] Add (2), keeping pH below 7 to avoid release of ammonia. [iv] Add (4). [v] After cooling to less than 35°C add (13) with adequate stirring to ensure uniformity of the pearl effect. Ingredients (28), (31) and (32) should be added at this point. [vi] If required, adjust pH to 6.0–6.5 with (22) or (24). When using (4) the formulator should determine the optimum pH, within the above range, with respect to the final viscosity of the formulation. [vii] Add (25) or (27) to adjust viscosity.

Formulation IV: [i] Heat (33) to 50°C. [ii] Add (5) with agitation until completely dissolved. [iii] Add (3), (6), (8) and (26).

Formulation V: [i] Blend the ingredients with slight warming and stir until homogeneous. [ii] Adjust pH to 6.0–6.5 with (23). [iii] Add (25) to thicken.

Formulation VI: [i] Melt (9) and (16) and mix together. [ii] Mix together (1), (7), (29), (20), (33) and (25). [iii] Mix [i] and [ii] together. [iv] Add (32), (30), (28) and (18) to [iii].

Comments

Formulation I is a simple and economical product. *Formulation III*, which produces a luxury shower gel, incorporates a cocoamphoacetate which enhances the mildness of the product by replacing a proportion of the primary anionic component, thus exerting a detoxifying effect, without compromising the cleansing effect of the formulation. *Formulation IV* gives a product with a viscosity of approximately 3000 mPa.s and cloud point of less than 5°C. The shower gel produced by *Formulation V* is suggested as a simple traditional base formulation to which a variety of conditioning agents may be added. Ingredient (15) has good solubility in surfactant systems and an excellent refatting effect on the skin, with the additional benefit of not impairing foam volume. *Formulation VI* produces a mild, gentle preparation ideal for use on sensitive skin.

4.5.2.2 Conditioning shower products and body shampoos

Although the formulations in this section can be claimed to have some conditioning or moisturizing properties, so too can some of those in Section 4.5.2.1, and the formulations chemist is recommended to consider the recipes in both sections.

	I [4]	*II* [4]	*III* [5]	*IV* [5]	*V* [5]
1. Sodium Laureth Sulfate	30.0[a]	–	55.00[b]	35.00[b]	45.00[b]
2. Sodium Lauryl Sulfate	–	15.5[c]	–	–	–
3. TEA-Lauryl Sulfate	–	27.5[d]	–	–	–
4. Sodium Cocoamphoacetate	20.0[e]	–	–	–	–
5. Sodium Lauroyl Sarcosinate	–	–	7.00[f]	–	–

	I [4]	*II* [4]	*III* [5]	*IV* [5]	*V* [5]
6. Cocamidopropyl Betaine	–	–	–	8.00[g]	14.00[g]
7. Lauryl Betaine	5.0[h]	–	–	–	–
8. Cocamidopropyl Hydroxysultaine	–	–	–	–	10.00[i]
9. Cocamidopropylamine Oxide	–	–	–	2.00[j]	–
10. Cocamide DEA	2.0[k]	4.00[k]	4.00[k]	3.00[k]	3.00[k]
11. Sodium Laureth Sulfate (and) Glycol Stearate (and) Glycol Distearate (and) Cocamidopropyl Betaine	5.0[l]	–	–	–	–
12. Cetearyl Alcohol (and) Sodium Lauryl Sulfate	–	4.00[m]	–	–	–
13. PEG-75 Lanolin	–	–	3.00[n]	–	–
14. PEG-7 Glyceryl Cocoate	–	–	–	–	3.00[o]
15. PEG-12 Palm Kernel Glycerides	–	–	–	0.80[p]	–
16. Caprylic/Capric Triglyceride	–	–	–	–	2.00[q]
17. Coconut (Cocos Nucifera) Oil	–	–	–	–	1.00[r]
18. Hydrolyzed Soy Protein	–	–	3.00[s]	–	–
19. Guar Hydroxy-propyltri-monium Chloride	–	0.45[t]	–	–	0.10[u]
20. Lauryldimonium Hydroxypropyl Hydrolyzed Soy Protein	–	–	–	0.50[v]	–
21. Hydroxypropyltrimonium Hydrolyzed Wheat Protein	–	–	–	–	0.50[w]
22. Glycol Stearate	–	9.25[x]	1.50[y]	0.80[z]	–
23. Glycol Distearate	–	–	–	–	2.00[aa]
24. Myristic Acid, 90%	–	–	–	–	3.70
25. Glycerin	–	–	–	–	3.00[bb]
26. Sodium PCA	–	0.20[cc]	–	–	–
27. Styrene/Acrylates Copolymer (and) Sodium Lauryl Sulfate (and) Octoxynol-9	–	0.75[dd]	–	–	–
28. Carbomer 980 (2% aq.sol.)	–	–	–	–	5.00[ee]

	I [4]	*II* [4]	*III* [5]	*IV* [5]	*V* [5]
29. Sodium Chloride	q.s.	2.30	0.50	–	–
30. Citric Acid	q.s.*	0.75†	–	–	–
31. Lactic Acid	–	–	q.s.‡	q.s.‡	–
32. Sodium Hydroxide	q.s.*	–	–	–	–
33. Parfum/Fragrance, preservative, colour	q.s.	q.s.	q.s.	q.s.	q.s.
34. Water/Aqua (deionized)	to 100	to 100	to 100	to 100	to 100

* To pH 6.5–7.5; † to pH 6.4; ‡ to pH 6.5–7.0

Sources (generic except for the following)
(a) Empicol ESC 3 [alternatively use 12.0 parts Empicol ESC 70]; (b) Empicol ESB 3/M; (c) Empicol LX 100; (d) Empicol TL 40/T; (e) Empigen CDR 60 (all Albright & Wilson); (f) Crodasinic LS 30 (Croda Oleochemicals); (g) Incronam 30 (Croda Oleochemicals); (h) Empigen BB (Albright & Wilson); (i) Crosultaine C50 (Croda, Inc.); (j) Incromine Oxide C (Croda Oleochemicals); (k) Empilan CDE (Albright & Wilson); (l) Empicol XP 40 (Albright & Wilson); (m) Empiwax SK (Albright & Wilson); (n) Solan E (Croda Oleochemicals); (o) Glycerox HE (Croda Oleochemicals); (p) Crovol PK40 (Croda Oleochemicals); (q) Crodamol GTCC (Croda Oleochemicals); (r) Cropure Coconut (Croda Oleochemicals); (s) Hydrosoy 2000 (Croda Oleochemicals); (t) Jaguar C-17 (Rhône-Poulenc); (u) Jaguar C-135 (Rhône-Poulenc); (v) Croquat Soya (Croda Oleochemicals); (w) Hydrotriticum WQ (Croda Oleochemicals); (x) Empilan EGMS (Albright & Wilson); (y) Cithrol EGMS N/E (Croda Oleochemicals); (z) Cithrol EGMS PE3127 (Croda Oleochemicals); (aa) Cithrol EGDS (Croda Oleochemicals); (bb) Croderol GV7000 (Croda Oleochemicals); (cc) Ajidew NL-40 (Ajinomoto); (dd) Lytron 621 (Morton International); (ee) Carbopol 980 (B.F. Goodrich).

Procedures
Formulation I: [i] Charge (34) and add a buffer. [Initial charging of a portion of (29) will aid the dissolution of (1). The approximate level of (29) addition required to achieve the desired viscosity should be determined prior to commencing large-scale production.] [ii] Add (1) slowly with stirring until a homogeneous solution is obtained. [In the case of Empicol ESC 70, raising the temperature to 40°C will help. Empicol ESC 3 can be stirred in more rapidly, but take care to avoid aeration.] [iii] Add the coactive surfactants (4), (7) and (10). [iv] After cooling to less than 35°C add (11) with adequate stirring to ensure uniformity of the pearl effect. [v] Add (33). [vi] If required adjust pH to 6.5–7.5 with (30) or (32). When using cocoamphoacetates (4) the formulator should determine the optimum pH, within the above range, with respect to the final viscosity of the formulation. [vii] Add (29) to adjust viscosity.

Formulation II: [i] Charge 19.0 parts of (34) and add (2) with stirring until a homogeneous solution is obtained. [ii] Heat to 70–75°C and add (12) and (22) with stirring until a homogeneous emulsion is obtained. [iii] Cool the emulsion to 30–35°C. [iv] In a separate vessel charge the balance of (34) and add (19) with stirring. After homogenization is complete add (3) and (10). [v] Blend [iii] with [iv] and add (30), (27) and (26). [vi] After ensuring the temperature is below 35°C add (33) and adjust the pH if necessary. [vii] Add (29) to adjust the viscosity (e.g. to 8900 cS at 20°C).

Formulation III: [i] Blend all components with warming. [ii] Stir to cool, perfuming at 40°C. [iii] Adjust pH.

Formulation IV: [i] Preblend (1), (6), (10) and (15). [ii] Add (34) and (22) and heat to 65–70°C. [iii] Stir to cool, adding the remaining ingredients at 35°C. [iv] Adjust the pH.

Formulation V: [i] Blend (10), (14), (16), (17), (23) and (24) together. [ii] Disperse (19) in a blend of (6) and (8) and add (34), (28), (21), (25) and (1) in that order, taking care not to aerate. [iii] Heat [i] and [ii] separately to 50–60°C. [iv] Add [i] to [ii] whilst stirring gently. [v] Stir to cool, adding (33) at 40–50°C. [vi] Fill off at room temperature.

Comments

Formulation I is intended to clean both the hair and body equally effectively. The inclusion of the cocoamphoacetate enhances the mildness of the product by replacing a proportion of the primary anionic component, thus exerting a detoxifying effect, without compromising the cleansing properties of the formulation. *Formulation II* is a combined 2-in-1 shower gel and body milk formulation. The shower gel gently cleanses the skin while the moisturizing body lotion is absorbed and not rinsed away, leaving the skin clean and soft. *Formulation III* produces a pearly shower shampoo and *IV* a pearly conditioning shower shampoo. *Formulation V* functions as a skin cleanser and moisturizer in one. The formulation uses a carefully selected blend of mild detergents and moisturizing agents, eliminating the need to apply a separate body lotion after showering. The excellent after-feel of this preparation is achieved by the combination of glycerin, modified wheat protein and ethoxylated coconut glyceride. The caprylic/capric triglyceride provides emollience.

4.5.2.3 Miscellaneous shower gels

These formulations are provided to illustrate the possibilities of designing a product to suit a particular market segment. Examples include shower gels suitable for use after sporting activities, products containing natural aromatic oils and skin-protecting products.

	I [4] Dermoprotector gel	*II* [5] Peppermint shower shampoo	*III* [5] Anti-chlorine hair and body wash	*IV* [25] Baby shower gel	*V* [26] Silicone 2-in-1 shower gel/body milk
1. Sodium Laureth Sulfate, 70%	8.0[a]	40.00[b]	40.00[b]	–	–
2. TEA-Lauryl Sulfate	10.0[c]	–	–	–	–
3. Ammonium Lauryl Sulfate	–	–	–	–	35.0
4. Ammonium Laureth Sulfate	–	–	–	–	26.0

	I [4]	*II* [5]	*III* [5]	*IV* [25]	*V* [26]
5. Cocamidopropyl Betaine	6.0[d] or 6.0[e]	5.00[f]	10.00[f]	–	10.0[g]
6. TEA-Cocoyl Glutamate, 30%	–	–	–	36.0[h]	–
7. Sodium Cocoamphoacetate, 30%	–	–	–	36.0[i]	–
8. Cocamidopropyl-amine Oxide	–	4.00[j]	–	–	–
9. Cocamide DEA	1.5[k]	–	2.00[k]	2.3[l]	–
10. Lauramide DEA	–	–	–	–	2.0
11. Glycol Stearate	0.5[m]	–	–	–	–
12. PEG-45 Palm Kernel Glycerides	–	4.00[n]	–	–	–
13. PEG-7 Glyceryl Cocoate	–	–	2.00[o]	–	–
14. Lauryldimonium Hydroxypropyl Hydrolysed Soy Protein	–	1.00[p]	–	–	–
15. Distearyl Phthalic Acid Amide	–	–	–	–	5.0[q]
16. Dimethicone	–	–	–	–	2.5[r]
17. Triclosan	0.15[s]	–	–	–	–
18. Sodium PCA, 50%	–	–	–	0.5[t]	–
19. Glycerin	–	–	–	3.6	–
20. Witch Hazel (Hamamelis Virginiana) Distillate	–	5.00[u]	–	–	–
21. Peppermint (Mentha Piperita) Oil	–	0.10	–	–	–
22. Lactic Acid	q.s.*	to pH 6.0	to pH 6.5–7.0	–	–
23. Citric Acid, monohydrate	–	–	–	1.1	q..s
24. Sodium Thiosulfate	–	–	2.00[v]	–	–
25. Sodium Hydroxide	to pH 6.0–7.0	–	–	–	–

	I [4]	*II* [5]	*III* [5]	*IV* [24]	*V* [25]
26. Sodium Chloride	q.s.	q.s.	–	q.s.	–
27. Ammonium Chloride	–	–	–	–	q.s.
28. Parfum/Fragrance, dye, buffer	q.s.	q.s.	q.s.	q.s.	–
29. DMDM Hydantoin	–	–	–	–	q.s.
30. Preservative	q.s.	q.s.	q.s.	0.2	–
31. Water/Aqua (deionized)	to 100	to 100	to 100	to 100	to 100

Sources (generic except for the following)
(a) Empicol ESB 70 [alternatively use 20.0 parts of Empicol ESB 3/M]; (b) Empicol ESB 3/M; (c) Empicol TL40/T; (d) Empigen BS/C; (e) Empigen BS/P (all Albright and Wilson); (f) Incronam 30 (Croda Oleochemicals); (g) Amphosol CB 3 (Stepan); (h) Amisoft CT-12 (Ajinomoto); (i) Softazoline CH (Kawaken); (j) Incromine Oxide C (Croda Oleochemicals); (k) Empilan CDE (Albright & Wilson); (l) Amisole CDE (Kawaken); (m) Empilan EGMS (Albright & Wilson); (n) Crovol PK70 (Croda Oleochemicals); (o) Glycerox HE (Croda Oleochemicals); (p) Croquat Soya (Croda Oleochemicals); (q) Stepan SAB-2 (Stepan); (r) DC 200 Fluid [350 cps] (Dow Corning); (s) Irgasan DP300 (Ciba-Geigy); (t) Ajidew N-50 (Ajinomoto); (u) (Croda Novarom); (v) Sodium thiosulfate-5 hydrate.

Procedures

Formulation I: [i] Charge (31) and the buffer. [Initial charging of a portion of (26) will aid the dissolution of (1). The approximate level of (26) addition required to achieve the desired viscosity should be determined prior to commencing large-scale production.] [ii] Add (1) slowly with stirring until a homogeneous solution is obtained. [Raising temperature to 40°C will help. Empicol ESB 3/M can be stirred in more rapidly than ESB70, but take care to avoid aeration]. [iii] Add (2). [iv] Dissolve (17) in (9) and add to the main mix together with (5) and heat the solution to 70–75°C before adding (11) with adequate stirring to ensure uniformity of the pearl effect. [The use of Empicol XP 40 will allow the flexibility of a cold process.] [v] After ensuring the temperature is less than 35°C add (28) and (30). [vi] If required, adjust pH to 6.0–7.0 with (22) or (25). [vii] Add (26) to adjust the viscosity.

Formulation II: [i] Preblend (21) and (12). [ii] Combine the remaining ingredients with slight warming and stir until homogeneous. [iii] Add [i]. [iv] Add (26) to the required viscosity. [v] Adjust the pH.

Formulation III: [i] Simple cold mix. [ii] Adjust pH to 6.5–7.0 with (22). *N.B.* In the US this system is covered by US Patent no. 4,295,985.

Formulation IV: [i] Melt all ingredients together at 70–80°C and cool to room temperature. [ii] Adjust pH to 5.3. Viscosity should be 590 mPa.s (B type, rotor no. 3, 30 rpm, 30 s, 25°C).

Formulation V: [i] Add (3), (4) and (10) to (31). [ii] Heat to 70–75°C, add (15) and mix for 15–20 min. [iii] Begin cooling to 25°C. At 45°C add (5), at 35°C add (16). Mix well. [iv] At 25°C add (29). [v] Adjust pH to 5.0–6.2 with (23). [vi] Adjust to desired viscosity with (27).

Comments

Formulation I (in two versions) incorporates Triclosan, an effective bactericide. The formulation has the effect of both cleansing and protecting the skin. The invigorating peppermint *Formulation II* contains witch hazel distillate for its stimulating properties and a quaternized soya derivative as a conditioning additive. This latter material is particularly

recommended in rinse-off products due to its inverse solubility which can provide an alternative means of depositing protein onto the skin and hair, conferring a more pronounced conditioning effect. *Formulation III* is suggested for use after swimming, when the effect of chlorine may leave both hair and skin feeling dry and unconditioned. This formulation contains an active chlorine-removing agent and provides all-over cleansing. *Formulation IV* is an extra-mild shower gel, suitable for use by very young children. *Formulation V* produces a viscous gel. It is a liquid soap/shower gel formulation which leaves a velvety after-feel on the skin.

4.5.2.4 Shower creams

Shower creams are offered as an alternative to clear or pearlized gels. They have a milk- or cream-like appearance and are usually either an oil-in-water emulsion or contain a suspended polymer. They may be marketed as dermoprotective, 2-in-1 (moisturizing/conditioning plus cleansing), soap-free, pH-balanced, hypoallergenic or with any or all of the usual rather vague marketing terms. They are used by applying to the body and then, because they contain an excess of surfactants, can easily be rinsed off in the shower.

	I [8]	*II* [8]	*III* [8]	*IV* [8]
1. Sucrose Distearate	3.50[a]	1.50[a]	3.00[a]	3.00[a]
2. Isostearyl Alcohol	2.00[b]	3.00[b]	2.00[b]	2.00[b]
3. Isostearic Acid	2.00[c]	2.50[c]	2.00[c]	2.00[c]
4. Phenoxyethanol	0.60[d]	0.60[d]	0.60[d]	0.60[d]
5. BHT	0.10[e]	0.10[e]	0.10[e]	0.10[e]
6. Laureth-2 Benzoate	–	0.25[f]	–	–
7. Sodium Cocoyl Isethionate	7.00[g]	–	15.00[g]	10.00[g]
8. Sodium Laureth Sulfate (and) Disodium Laureth Sulfosuccinate	27.00[h]	35.00[h]	–	17.00[h]
9. Disodium Cocoamphodiacetate	18.00[i]	10.00[i]	18.00[i]	18.00[i]
10. Panthenol	0.50[j]	–	0.50[j]	0.50[j]
11. Guar Hydroxypropyltrimonium Chloride	–	–	0.02[k]	–
12. Water/Aqua (deionized)	to 100	to 100	to 100	to 100
13. Cocamide DEA	2.00[l]	–	2.00[l]	2.00[l]
14. Imidazolidinyl Urea	0.20[m]	0.25[m]	0.25[m]	0.20[m]
15. Parfum/Fragrance	0.90[n]	0.70[o]	0.60[p]	0.70[n]
16. Polyquaternium-39	1.50[q]	1.00[q]	–	–

Sources (generic except for the following)
(a) Sisterna SP30-C (Sisterna); (b) Adol 66 (Witco); (c) (Henkel); (d) Rewopal MPG 10 (Witco Surfactants); (e) Merck; (f) Dermol 126 (Bernel); (g) Arlaton SCI (ICI Surfactants); (h) Texapon SBN (Henkel); (i) Rewoteric AM-2C/NM (Witco Surfactants); (j) (R.I.T.A.); (k) Jaguar C-13-S (Rhône-Poulenc); (l) Purton CFD (Zschimmer & Schwarz); (m) Germall 115 (Sutton); (n) BSB 35447 (Ribero); (o) Amie 0/256908 (Dragoco); (p) BSB 35433 (Ribero); (q) Merquat Plus 3330 (Calgon).

Procedures

All formulations: [i] Separately heat the oil phase (1 to 5 inclusive and 6 where prescribed) and the water phase (7 to 12 where prescribed, but keeping back 5 parts of water) to 72°C while stirring. [ii] Slowly add the oil phase to the water phase while stirring. [iii] Keep on stirring for 20 min, then add (13) where prescribed. [iv] Cool to room temperature then add (14) previously mixed with 5 parts of (12), followed by (15), and (16) where prescribed.

Comments

Formulation I has a pH of 6.8–7.3 and viscosity (Brookfield RVT, G5 at 5 rpm) of 18 000 to 23 000 mPa.s. For *Formulation II* the ranges are 6.4–6.9 and 15 000 to 20 000 mPa.s respectively; for *Formulation III* 6.8–7.3 and 8 000 to 15 000 mPa.s; and for *Formulation IV* 6.8–7.3 and 15 000 to 20 000 mPa.s.

4.5.2.5 Body scrubs and exfoliating shower gels

Body scrubs and exfoliating shower gels have only recently been developed. They are shower gels specially formulated to have the correct density and, especially, viscosity so that they will suspend, usually by use of a cross-polymer, small beads or particles which act as the exfoliating agent. Various solids are used, some natural, e.g. oat bran, molasses extract, aloe leaf powder, apricot seed powder, and powdered loofah (*Luffa cylindrica*), and some are synthetic, e.g. polyethylene and oxidized polyethylene. To enhance the presentation of the product, the beads, or prills, are available in various colours. The formulating chemist should experiment by adding different beads to the basic formulations given below.

	I [18] Body scrub	*II* [18] Body polishing shower gel	*III* [17] Shower gel with jojoba exfoliants	*IV* [17] Shower gel with avocado exfoliants
1. Sodium Laureth Sulfate	16.00[a]	8.00[a]	–	–
2. Ammonium Lauryl Sulfate, 30%	–	10.00	15.00	–
3. Disodium Laureth Sulfosuccinate, 40%	–	–	12.00	10.00
4. Disodium Dimethicone Copolyol Sulfosuccinate	15.00[b]	25.00[b]	–	–
5. Cocamidopropyl Betaine	3.00[c]	2.00[c]	5.00	3.00
6. Polysorbate 20	–	1.50[d]	–	–
7. PEG-10 Sunflower Glycerides	1.00[e]	–	–	–

	I [18] Body scrub	*II* [18] Body polishing shower gel	*III* [17] Shower gel with jojoba exfoliants	*IV* [17] Shower gel with avocado exfoliants
8. Hydrogenated Jojoba Oil	1.00[f]	5.00[g]	–	–
9. Jojoba Wax [prills]	–	–	2.00[h]	–
10. Avocado (Persea Gratissima) Oil [prills]	–	–	–	2.00[h]
11. Propylene Glycol	1.00	1.00	–	–
12. Butylene Glycol	–	2.00	–	–
13. Glycerin	2.00	–	2.00	2.00
14. Acrylates/ C10-30 Alkyl Acrylate Crosspolymer	1.00[j]	1.10[j]	1.00[j]	1.00[j]
15. Triethanolamine, 99%	1.10[j]	1.00[j]	0.80	0.80
16. Disodium EDTA	0.05	0.05	0.10	0.10
17. Phenoxyethanol (and) Methylparaben (and) Ethylparaben (and) Propylparaben (and) Butylparaben	q.s.[k]	–	–	–
18. Methylparaben, Propylparaben	–	q.s.	–	–
19. Phenoxyethanol	–	q.s.[l]	–	–
20. Preservative, colour	–	–	0.50	0.50
21. Parfum/Fragrance	q.s.	q.s.	–	–
22. Water/Aqua (deionized)	to 100	to 100	66.60	65.60

Sources (generic, except for the following)
(a) Standapol ES-2 (Henkel); (b) Mackanate DC-30 (McIntyre); (c) Lexaine C (Inolex); (d) Tween 20 (ICI Surfactants); (e) Florasun PEG-10 (Floratech); (f) Jojoba-White-28/60 Florabeads [0.45%], Jojoba-Oasis Verde-28/60 Florabeads [0.45%], Jojoba-Jade-28/60 Florabeads [0.10%] (all Floratech); (g) Jojoba-40/60 Florabeads (Floratech); (h) (A&E Connock); (i) Carbopol ETD 2020 (B.F. Goodrich); (j) Triethanolamine [to pH 5.0–5.5] (Dow); (k) Phenonip (Nipa); (l) Emeressence 1160 (Henkel).

Procedures
Formulation I: [i] Meter (22) into a stainless-steel mixing tank and add (16) with moderate propeller agitation. [ii] When dissolved, slowly sift (14) into the water with rapid propeller agitation and stir for 20 min. [iii] Combine (11), (13) and (17) and slowly add to [ii]. Heat to 50°C. [iv] Combine (1), (4) and (5) and heat to 50°C. [v] Slowly add [iv] to [iii] with slow to moderate propeller agitation and stir slowly for 10–15 mins. [vi] Heat (7) to 55°C and add to [v]. [vii] Neutralize [vi] using (15) with slow to moderate sweep agitation. [viii] Add (21) and (8) with slow sweep agitation and cool to room temperature.

Formulation II: [i] Meter (22) into a stainless-steel mixing tank. Slowly sift (14) into the water with rapid propeller agitation. [ii] Stir for 20 min. with moderate propeller agitation then heat to 50°C and add (16) with moderate propeller agitation. [iii] Combine (11), (12), (18) and (19) and warm to 45°C with moderate propeller agitation until parabens dissolve. [iv] Slowly add [iii] to [ii] and cool to 35°C. [v] Combine (1), (4), (5) and (6) at room temperature with slow propeller agitation. [vi] Slowly add [v] to [iv] with slow to moderate propeller agitation and stir slowly for 10–15 min. [vii] Neutralize [vi] using (15) with slow to moderate sweep agitation. [viii] Add (8) with slow sweep agitation and cool to room temperature.

Formulations III and IV: [i] Measure out (22) and disperse (14) in this with moderate agitation until homogeneous. [ii] Add (16), (13), (2), (3), (5) in turn to [i] with careful mixing. [iii] Add (20) to suit. [iv] Adjust pH to 6.0–6.5 by careful addition of (15) and then slowly mix in (9) [Formulation III] or (10) [Formulation IV].

Comments

Formulations I and II: Ingredient (7) [*I* only] moisturizes and refats the skin. The smooth, spherical hydrogenated jojoba oil beads provide gentle exfoliation and a residual emolliency in these exfoliating, clear cleansing gels. These natural-derived, mild, scrubbing beads are complemented by what is claimed to be the mildest sulfosuccinate available. *Note:* A similar formulation to *I*, described as an exfoliating, clear shower gel, is prepared by replacing (7) by Jojoba Wax PEG-120 Esters [Jojoba PEG-120 Florasolvs (Floratech)]. *Formulations III and IV:* Jojoba wax prills and Avocado prills are smooth, wax-like beads available in various colours and which act as a gentle exfoliant. They are suspended in the shower gel by the high yield strength of (14).

4.5.2.6 After-shower body moisturizers

This type of after-bath, or after-shower, preparation contains emollients and is designed to moisturize dry, flaky skin without depositing an unduly oily or sticky film. Since such products are intended to be showered off they are given here, rather than in the After-Bath Products section (Section 4.6). The dispersible or blooming formulations given in Section 4.3.3 can also be used in this way.

	I [5]	*II* [16]
1. Cetearyl Alcohol (and) Behentrimonium Methosulfate	1.90[a]	–
2. Steapyrium Chloride	1.00[b]	–
3. Lauryldimonium Hydroxypropyl Hydrolyzed Soy Protein	2.00[c]	–
4. Glyceryl Stearate (and) PEG-100 Stearate	2.80[d]	–
5. Mineral (Paraffinum Liquidum) Oil (and) Lanolin Alcohol	4.60[e]	–
6. Cetyl Acetate (and) Stearyl Acetate (and) Oleyl Acetate (and) Acetylated Lanolin Alcohol	1.30[f]	–
7. Lanolin Oil	2.50[g]	5.0[h]

	I[5]	*II*[16]
8. Petrolatum	1.90[i]	–
9. PEG-40 Stearate	1.00[j]	–
10. PEG-40 Sorbitan Peroleate	–	5–10[k]
11. Isopropyl Myristate	–	43–48
12. Propylene Glycol	2.80	–
13. Hydroxyethyl Cellulose	0.10[l]	–
14. Parfum/Fragrance	q.s.	2.0
15. Preservative, colour	q.s.	q.s.
16. Water/Aqua (deionized)	to 100	–

Sources
(a) Incroquat Behenyl TMS (Croda Oleochemicals); (b) Emcol E-607S (Witco); (c) Croquat Soya (Croda Oleochemicals); (d) Cithrol GMS A/S ES0743 (Croda Oleochemicals); (e) Liquid Base CB1145 (Croda Oleochemicals); (f) Crodalan LA (Croda Oleochemicals); (g) Fluilan (Croda Oleochemicals); (h) Lantrol (Henkel); (i) White Petroleum Jelly Continental Grade No. 3 (Meade, King, Robinson); (j) Crodet S40 (Croda Oleochemicals); (k) Arlatone T (ICI Surfactants); (l) Cellosize HEC5000A (Union Carbide).

Procedures
Formulation I: [i] Hydrate (13) in warm water (65°C). [ii] Add the rest of the water phase components (3) and (12) and reheat to 60–65°C. [iii] Heat oil phase components (1), (2), (4), (5), (6), (7), (8) and (9) to 65°C. [iv] Add [ii] to [iii] whilst stirring. [v] Stir to cool, perfuming at 40–45°C. Fill off at 30°C.

Formulation II: Mix ingredients at room temperature. Filter if necessary.

4.6 AFTER-BATH PRODUCTS

After-bath products form a miscellaneous group about which it is impossible to generalize except to say that they are frequently used after bathing or showering. The characteristics of each type of product will be discussed individually to elucidate the suggested formulations. Some products, for example massage oils, hydrotherapy preparations, exfoliating creams, moisturizing and various other skin creams, although obviously intended for use after bathing, cannot be dealt with adequately here and so are not described.

4.6.1 Bath, dusting or talcum powder

Talcum powder, frequently called talc, although talc is often only one of its ingredients, continues to enjoy a very wide sale. When marketed for use after bathing it is called body talc, bath powder, or dusting powder, when a powder puff is usually included in the package. It is used to absorb moisture after bathing, and, especially in warmer countries, to absorb perspiration and help cool the body. It acts as an efficient lubricant, allowing clothes to be more easily donned, and tends to allay any irritation of the skin due to chafing. It is also another means of perfuming the body.

4.6.1.1 Ingredients

Talc is employed as the major ingredient in talcum powders because it has a slippery feel and is the softest known mineral. Other materials are added to the product to improve absorbency, adhesion and water-repellency.

Talc is a finely powdered, native, hydrous magnesium silicate. Its primary physical characteristic is that of colour. Best-quality materials are white, second-quality materials are greyish-white, and others, which should be avoided, are distinctly grey. The next important point to notice is that of 'slip', which facilitates spreading without dragging on the skin, leaving a smooth feeling. This peculiar characteristic is best illustrated in talc of good quality; inferior qualities do not exhibit the requisite amount of slip. The last physical characteristic worthy of mention is that of lustre. A good sample should be lustrous without exhibiting any undue amount of glitter when examined in a fine film. Unusual radiance or glitter is often due to insufficient grinding or sifting of the powdered material. A particle size of smaller than 200 mesh is required for good-quality talc.

The physical characteristics of talc vary according to the country of origin, and it is generally acknowledged that the finest talc of good white colour, high lustre and adequate slip properties is of Italian origin. Indian talc of good quality is also available and other sources include France, the USA and Canada. The absence of a large quantity of impurity is desirable, largely because of its deleterious effect on the perfume, and to some extent because of the irritation it may cause to the skin. In the former case it will not only tend to alter the odour, but may also affect the colour of certain perfume ingredients. Contamination by bacteria is, of course, completely unacceptable, and talc is sterilized before sale.

Zinc stearate is often added to talcum powders to provide additional lubricating properties. It is considered to have beneficial dermatological properties, being soothing and mildly antiseptic, and is preferred to magnesium stearate. Zinc oxide is also used in talcum powder. It is a mild astringent on the skin and is also smoothing and has some healing effect on skin chafing or minor abrasions. It also relieves the prickling and irritation that occurs in prickly heat. Light magnesium carbonate and light calcium carbonate are included to increase fluffiness and also for their value as absorbing materials to aid the addition of perfume. Other materials sometimes added include fumed silica and, for their absorbency, kaolin and starch.

4.6.1.1 Formulations

The following formulae are typical for talcum powders:

	I	*II*
1. Zinc Stearate	5	5
2. Zinc Oxide	–	5
3. Calcium Carbonate, light	25	–

	I	*II*
4. Magnesium Carbonate, light	–	15
5. Talc	70	75
6. Perfume/parfum	q.s.	q.s.

Procedure

Mix (6) with (3) or (4) and allow to stand, preferably overnight, before mixing with the other ingredients. A concentration of 0.5% of perfume is generally adequate. Concentrations higher than this are often overpowering in their effect.

4.6.2 After-bath body lotions and gels

These preparations are intended for use after showering or bathing. There are various types, such as body silks, which are creams which leave the skin feeling soft and silky; moisturizers which are lotions with this same purpose; toning lotions, which are products employed to freshen the skin; fragrant body gels, the main purpose of which is the delivery of fragrance; and liquid talcs which enable talc to be applied in an alternative way.

	I [5]	*II* [5]	*III* [9]	*IV* [5]	*V* [27]
1. Mineral (Paraffinum Liquidum) Oil	–	–	–	8.00[a]	–
2. PEG-60 Almond Glycerides *or*	–	0.50[b]	–	–	–
2a. PEG-60 Evening Primrose Glycerides					
3. PEG-20 Stearate	–	–	–	0.40[c]	–
4. PEG-20 Stearate (and) Cetearyl Alcohol	–	–	5.00[d]	–	–
5. Cetearyl Octanoate (and) Isopropyl Myristate	–	–	–	3.50[e]	–
6. Laneth-20	–	–	4.00[f]	–	–
7. Evening Primrose (Oenothera Biennis) Oil	5.00[g]	–	–	–	–
8. Grape Seed (Vitis Vinifera) Oil	20.00[h]	–	–	–	–
9. Cetearyl Stearate	–	–	–	0.50[i]	–
10. Sorbitan Stearate	–	–	–	1.50[j]	–
11. Octyl Palmitate	–	–	12.00[k]	–	–
12. Decyl Oleate	–	–	5.00[l]	–	–
13. Isodecyl Laurate	–	–	10.00	–	–
14. Caprylic/Capric Triglyceride	to 100[m]	–	–	–	–

	I [5]	*II* [5]	*III* [9]	*IV* [5]	*V* [27]
15. Polysorbate 60	–	–	–	1.50[n]	–
16. Polysorbate 80	–	–	–	–	0.5[o]
17. Cyclomethicone	–	–	–	0.80[p]	–
18. Dimethicone Copolyol	–	–	–	–	1.0[q]
19. Tocopheryl Acetate	2.00[r]	–	–	–	–
20. Glycerin	–	2.50[s]	–	–	–
21. Propylene Glycol	–	–	4.00	–	–
22. Potassium Hydroxide, 10%	–	–	q.s.	–	–
23. Triethanolamine	–	0.50	–	–	0.22
24. Carbomer 980	–	0.50[t]	–	–	–
25. Carbomer 940	–	–	–	–	0.33[u]
26. Alcohol Denat.	–	–	–	–	33.0
27. Benzyl Alcohol (and) Methylchloro-isothiazolinone (and) Methylisothiazolinone	–	–	0.10[v]	–	–
28. Parfum/Fragrance, preservative, colour	q.s.	q.s.	–	q.s.	q.s.
29. Water/Aqua (deionized)	–	to 100	59.90	to 100	64.95

Sources

(a) 25 cS at 25°C; (b) Crovol A70 [2] or Crovol EP70 [2a] (Croda Oleochemicals); (c) Cithrol 10MS (Croda Oleochemicals); (d) Aquabase (Westbrook); (e) Crodamol CAP (Croda Oleochemicals); (f) Aqualose W20 (Westbrook); (g) Cropure Evening Primrose (Croda Oleochemicals); (h) Cropure Grapeseed (Croda Oleochemicals); (i) Crodamol CSS (Croda Oleochemicals); (j) Crill 3 (Croda Oleochemicals); (k) Ceraphyl 368 (ISP Van Dyk); (l) Ceraphyl 140A (ISP Van Dyk); (m) Crodamol GTCC (Croda Oleochemicals); (n) Crillet 3 (Croda Oleochemicals); (o) Tween 80 (ICI Surfactants); (p) Dow Corning 344 Fluid (Dow Corning); (q) Dow Corning 190 Surfactant (Dow Corning); (r) (Hoffmann–La Roche); (s) Croderol GV7000 (Croda Oleochemicals); (t) Carbopol 980 (B.F. Goodrich); (u) Carbopol 940 (B.F. Goodrich); (v) Euxyl K 100 (Schulke & Mayr).

Procedures

Formulation I: [i] Combine preservatives and (14) with gentle heating. Stir to cool. [ii] Add remaining ingredients whilst stirring.

Formulation II: [i] Hydrate (24) in warm water (60–65°C). [ii] Add oil phase [(2) or (2a), (23) and (20)] whilst stirring. [iv] Stir to cool, adding (23) at 60°C and perfuming at 40°C.

Formulation III: [i] Heat together (4), (6), (11), (12) and (13) to 75°C. [ii] Heat (21), (22), (27) and (29) to 80°C. [iii] Mix [ii] well with [i]. [iv] Cool to 40°C and homogenize.

Formulation IV: [i] Heat oil phase [(1), (5), (9) and (10)] and water phase [(3), (15), (17) and (29)] separately to 65–70°C. [ii] Add water phase to oil phase with stirring. [iii] Stir to cool, perfuming at 40°C.

Formulation V: [i] Disperse (25) in (29) and heat to 75°C. [ii] Add (16) and (18) and mix for 5 min. [iii] Cool to 50°C, add (26) [FLAMEPROOFING REQUIRED] and mix for 5 min. [iv] Add (23) and mix for 20 min. before packing.

Comments

Formulation I is described as a moisturizing body cocktail. *Formulation II* is a light, easily absorbed moisturizing gel. It is a useful vehicle for additional skin conditioning agents and for applying perfume all over the body. Depending on the perfume used, it may be necessary to pre-blend with (2) [or (2a)] or increase the amount, to produce effective solubilization. *Formulation III* is a lightweight, low-viscosity lotion, ideal as an after-bath preparation, nourishing the skin with valuable emollients. *Formulation IV* is a highly emollient body spritz based on a carefully selected blend of emulsifiers, giving a very fine particle size and stable emulsion. Ingredient (5), a branched-chain ester, improves the spreading of this very low-viscosity emulsion over the skin. *Formulation V* produces a clear, thick gel. The viscosity may be reduced by using lower levels of (23)/(25) or by diluting with water. Ingredient (18) may be used at 1–5% depending upon the degree of emolliency required.

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5

Colouring materials used in decorative cosmetics and colour matching

Pauline Riley

The colouring agents used in the development and manufacture of decorative cosmetics are vital for them to perform their primary function, colouring the skin of the user. Many of the colours used in these products are not used elsewhere in the cosmetics and toiletries field although they are often derivatives of those colours.

The chemistry of the colours used in decorative cosmetics has a large bearing on the type of products in which they are used. Some are not suitable for aqueous media but are widely used in anhydrous systems such as lipsticks and powder products. However, these two largely anhydrous systems are very different from each other. It was decided therefore that the properties of the colours themselves should be considered separately from the formulation of the products. In this chapter therefore the types of colouring matter, with their unique properties, and also some of the ways the colours themselves can be modified to improve the performance and effects achieved by the finished formulation, will be considered.

The formulator must check carefully the regulations for the markets for which the products are being developed to ensure that the materials they are using are legal in those markets. Colours are heavily regulated in all areas of the world, and unfortunately the regulations vary from country, or regional area, to country. Those within the EU are quite different from those in force in the USA and different again from those in force in Japan. Specifications for the individual colours may be needed in some places and also batch certification may be required.

5.1 DYES

A dye is defined as a colourant which is soluble in a solvent or range of solvents (this includes water). For obvious reasons, dyes themselves are rarely used in

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 151–165

decorative cosmetics, because the beautifying effect required is temporary, and stain ('dye') on the skin is not needed; but derivatives of the most common dyes are widely used in toiletries.

There is however one area where dyes are used. This is in some lipsticks where a claim of 'long-lasting' is required and a particular group of them is used called the 'Eosin' dyes. Other names for these dyes are:

D&C Red No. 21 – C I 453802
D&C Red No. 27 – C I 454101
D&C Orange No 5 – C I 453701

One drawback of these colourants is that the colour that 'lasts' on the lips often bears no relationship to the initial colour of the lipstick. Another drawback is that they are potential allergens.

5.2 COLOUR INDEX

The reference 'C I' given above and at various places through the main chapter is an abbreviation for 'Colour Index'. This is an international system of naming colours, related to their chemical structure. Each colour has its own basic five-digit number, and derivatives use the same base number with a suffix after a colon.

5.3 NATURAL COLOURS

This group of colours have come to the forefront of consumer awareness recently, mostly because of their increasing use in food products. They are fully permitted (in the EU anyway) for use in cosmetics provided that the materials used meet the required purity. They are not particularly stable, however, especially with regard to heat, light and pH.

Only one natural colour, or rather its aluminium lake, is widely used and this is carmine.

Carmine has a long history of use in the food industry. It is obtained from the 'Coccus cacti' insect (a type of beetle), by aqueous alkaline extraction. The pigment is achieved by forming the aluminium lake of carminic acid. Carmine provides a bright strawberry red shade. Chemically it is very stable and is unaffected by oxygen, light, sulphur dioxide, heat and water. Carmine is one of the few organic colours permitted for use around the eye area in the USA. Its major disadvantage however is its price, several hundred pounds per kilo.

5.4 PIGMENTS

Pigments can be defined as coloured or white chemical compounds insoluble in the liquids in which they are used. Chemically they can be divided into two main groups: the very bright, organic pigments and the relatively dull inorganic pigments.

5.4.1 Organic pigments

These colourants are all conjugated cyclic compounds mostly based on benzene, although some heterocyclic compounds exist. This conjugation produces a chromophoric system, which, with additional chemical groups known as auxochromes, gives colour. These auxochromic groups such as –OH or $-NH_2$ (hydroxyl or amino) are electron-donating groups, whereas halogens (chlorine, iodine, bromine), carbonyl or nitro ($-NO_2$) groups are electron-accepting. The overall effect is to produce an extensive population of delocalized electrons, which are easily excited by visible light and so appear coloured.

There are three main types of organic pigments: *(i)* lakes *(ii)* toners *(iii)* true pigments. Definitions of these follow, but as organic pigments are seldom used without diluents all three types are usually classified as 'lakes'. The purpose of the diluent or substrate is to maintain consistent strengths of the organic pigments which can vary from batch to batch. In terms of stability true aluminium lakes can be affected by extremes of pH resulting in the soluble dye reforming, a condition known as 'bleeding'. Also, they are relatively transparent and have poor light-stability. Toners are more resistant to heat, light and pH, although extremes of pH can result in shade changes. True pigments are the most stable but unfortunately only a few exist. Various definitions exist to describe the word 'lake', which depends on the industrial usage and country. The definition used in the cosmetics industry is that a lake is essentially an insoluble colourant produced by precipitating a permitted soluble dye onto an insoluble permitted substrate.

True lakes, made from the aluminium salts of water-soluble FD&C dyes deposited onto aluminium hydroxide, are widely used in many decorative cosmetics. For example:

FD&C Yellow No. 5 Al Lake	C I 19140 : 1
FD&C Yellow No. 6 Al Lake	C I 15985 : 1
FD&C Red No. 3 Al Lake	C I 45430 : 1
FD&C Blue No. 1 Al Lake	C I 42090 : 2
FD&C Red No. 40 Al Lake	C I 16035
D&C Red No. 21 Al Lake	C I 45380 : 3
D&C Red No. 27 Al Lake	C I 45410 : 2
D&C Yellow No.10 Al Lake	C I 47005 : 1
D&C Orange No. 5 Al Lake	C I 45370 : 2

Insoluble salts can also be made using other cosmetic-approved metals apart from aluminium. These colourants are called toners, i.e. the calcium or barium salts of compounds whose sodium salt is too soluble to be used as a pigment. The most common toners used in cosmetics are:

D&C Red No. 6 Ba Lake	C I 15850 : 2*
D&C Red No. 7 Ca Lake	C I 15850 : 1*
D&C Red No. 34 Ca Lake	C I 15880 : 1

* NB these are two different salts of the same dye, C I 15850.

True organic pigments are insoluble compounds which contain no metal ions.

D&C Red No. 36 C I 12085

5.4.2 Inorganic pigments

The range of inorganic pigments used in cosmetics is made up of several chemical types; generally they are all dull compared to the organic colours.

In terms of heat- and light-stability inorganic pigments are far superior to organic pigments. Their only drawback is that they can react under certain extremes of pH. For example iron oxides are discoloured by low pH; ultramarines react with acids to produce hydrogen sulphide; and iron blue and manganese violet react in alkaline pH to produce shade changes or colourless salts.

Most inorganic pigments can be used in all types of cosmetic products. Subject to purity levels of elemental heavy metals, their greatest use is probably in face and eye make-up.

5.4.2.1 Iron oxides

Iron oxides are the main class of inorganic pigments. There are three main colours: black, red and yellow. By blending these three in the required proportions brown, tans, umbers and siennas can be produced. Iron oxides are invaluable in liquid foundations and face powders as an almost infinite range of natural-looking flesh tones can be produced by careful blending.

(a) Yellow Iron Oxide (C I 77492) is hydrated iron III oxide (ferric oxide), $Fe_2O_3 \cdot H_2O$ or $FeO \cdot OH$. It is produced by the controlled oxidation of iron II (ferrous) sulfate. Depending on the conditions of manufacture used, the shade can vary from light lemon to orange yellow.

(b) Red Iron Oxide (C I 77491) is the familiar 'rust' red coloured pigment and is obtained by the controlled heating or calcining of yellow iron oxide. Chemically it is Fe_2O_3, iron III (ferric) oxide.

(c) Black Iron Oxide (C I 77499) is a ferroso-ferric (iron II–iron III) mixed oxide, chemically Fe_3O_4 or $FeO \cdot Fe_2O_3$. It is prepared by the controlled oxidation of ferrous sulfate in alkaline conditions.

5.4.2.2 Other iron compounds

Two forms of Iron Blue exist (C I 77510 and C I 77520); both are very intense dark blue pigments, and can be difficult to use as they are physically very hard, very light and 'fly-away' and very strong. Both are unstable in alkaline conditions. Chemically they are ferric ferrocyanide and ferric ammonium ferrocyanide – $Fe(NH_4)Fe(CN)_6nH_2O$.

5.4.2.3 Chromium oxide

Another major group of inorganic pigments are those based on chromium oxide, and two are used.

Cr_2O_3, Chrome Oxide (C I 77288), is a dull olive green and
$Cr_2O_3 \cdot 9H_2O$, Hydrated Chrome Oxide (C I 77289), which is a blue-green.

5.4.2.4 Ultramarines

Ultramarines are classified, regardless of shade, under the same number, (C I 77007). They are chemically polysulphide sodium aluminium sulfosilicates, and the colour produced can range in shade from blue to violet, pink or even green. The main form encountered in cosmetics is the traditional **Ultramarine Blue.** It has a complex structure, that can be written as $Na_7Al_6Si_6O_{24}S_2$. All are unstable in acidic conditions; although some manufacturers do sell 'acid-stable' ultramarines, which are usually coated to prevent the acid attacking the chemical.

5.4.2.5 Manganese Violet

Manganese Violet (C I 77742) which chemically is MnIII $NH_4P_2O_7$ is quite a bright purple or violet pigment; it is unstable in alkaline conditions.

5.4.2.6 Titanium Dioxide

Titanium Dioxide, (C I 77891) is probably the most commonly used white pigment. It has good covering power, or opacity, it is almost chemically inert, heat-stable, light-stable, and is easily incorporated into all types of cosmetic products.

5.4.2.7 Zinc Oxide

Zinc Oxide (C I 77947) is less opaque than titanium dioxide so that it can give more translucent products. It also has mild antiseptic properties when applied to the skin, which can be beneficial in some products. In its superfine state it has sunscreen properties.

5.4.2.8 Alumina, Aluminium Hydrate

Alumina, Aluminium Hydrate (C I 77002) chemically is $Al(OH)_3$ or $Al_2(OH)_6$. It is quite translucent and consequently gives very little opacity to any formulation in which it is used. It can be used in products such as lipsticks and mascaras to give structure without contributing to the colour.

5.4.2.9 Barium Sulfate

Barium Sulfate (C I 77120) is sometimes referred to as 'blanc-fixe'. It is relatively translucent and is often used as a pigment extender.

5.4.3 Speciality pigments

Although these novel pigments can give very interesting effects and very attractive products their legal status must be checked thoroughly. Although the dyes cannot themselves come into contact with the skin, and remain in the plastic coating, they are still covered by the cosmetic colour regulations and most of the dyes used are not approved for cosmetics either within the EU or in the USA. Only those glitter particles or fluorescence pigments that contain colourants whose C I numbers are listed in the regulations can be used.

5.4.3.1 Fluorescent pigments

These are also available; they are transparent organic resin particles containing fluorescent dyes in solid solution. They are usually used in non-aqueous products such as lip salves for skiers.

5.4.3.2 Glitters

A number of products are on the market that can be used for novelty or special effects. Glitters are precision-cut shapes of brilliant glittering polyester foil, epoxy coated with light-fast dyes 'captured' in the coating. These can have sharp edges and are therefore not recommended for use around the eye area.

5.4.4 Pearlescent pigments (often referred to as pearls)

Gloss or lustre are not always the same thing. Our eyes can detect fine differences between glimmer, sparkle or glitter. People have been fascinated for many years by the deep-down apparently three-dimensional lustre of pearls. Real pearls grow in oysters when a foreign body such as a grain of sand gets inside the oyster. The foreign body is encapsulated as the oyster covers it with alternating layers of protein and calcium carbonate. The layers act as thin transparent mirrors for rays of light; most pass through but some are reflected. This process happens at each of the calcium carbonate layers, and causes the effect of the pearly lustre; i.e. simultaneous reflection, refraction and transmission of light as it meets translucent or transparent substances of high refractive index.

Chemicals that give this effect are now widely used in decorative cosmetic products.

5.4.4.1 Natural pearl lustre pigments

Pearl lustre pigments were first mentioned towards the end of the 18th century. In 1781 Johann Christian Wiegleb described the 'manufacture of false pearls' in a book entitled *Handbook of General Chemistry*. From this an industry grew up around the Paris area manufacturing pearl essences. They were concentrated suspensions of guanine/hypoxanthine mixed crystals from fish scales. Natural pearls are still used today, principally in high-quality nail enamels. However this

usage is declining as the effects that can be achieved with synthetic pearls improve.

The crystals used in the natural pearl essences have a density of 1.6 g/cm^3; this means that they hardly settle in the nail enamel and is their one big advantage over the synthetic pearls. However, the refractive index is relatively low at only about 1.8 and the crystals are only about 20–50 microns long by 1–10 microns wide and 0.025–0.075 microns thick.

The main sources of natural pearl essence are herrings and sardines. Only about 1% of usable guanine/hypoxanthine can be obtained even from these fish scales as the extraction process is very complicated. All this leads to high prices for these pearls, and is another reason for their declining use.

5.4.4.2 Synthetic pearl lustre pigments

The first synthetically manufactured pearl lustre pigments were monocrystalline compounds of mercury chloride and lead arsenate, but their toxicity was obviously a problem and they are not used now.

In the 1930s lead carbonate compounds were developed; these had the general formula $2PbCO_3 \cdot Pb(OH)_2$, and are still used today, but of course not in cosmetics. Their main use now is in the production of buttons and artificial pearls for the jewellery industry although even in these fields their usage is declining owing to concerns about the toxicity of the lead.

Monocrystalline **bismuth oxychloride** pearls with the formula BiOCl have been on the market since the 1960s. They are only slightly soluble, therefore there are no worries on toxicity. Production of the lamellar monocrystals is carried out with a controlled precipitation reaction from aqueous bismuth salt solutions. Size, thickness and crystal form are controlled by the exact precipitation conditions. The process of growing the crystals is very sensitive and depends mainly on experience and a very exact procedure. Temperature, concentration and pH must be carefully controlled; even the smallest deviation in the shape of the vessel can significantly affect the product formed.

The powders that are formed are dense and white and have a fine particle size; larger more regular crystals are available only in dispersion form, because the crystals are so fragile. These dispersions, in castor oil for lipsticks, aqueous media for powder systems and nitrocellulose solutions for nail enamel, give high lustre and low opacity.

Bismuth oxychloride pearls are still widely used in decorative cosmetics, particularly in eyeshadows and lipstick where they can also improve the pressability or moulding characteristics. As well as their lustrous effect they give smooth, even application and good skin adhesion. They are hydrophobic and have good affinity for the skin. Owing to this the inclusion of bismuth oxychloride pearls improves the wear properties of a formulation. Their one major drawback is their poor light-stability although newer grades now show improvement in this

characteristic. Nevertheless the products used are, at present, protected from the light by using opaque packaging to prevent degradation.

A **matt bismuth oxychloride powder** can be used in formulations as a filler. It confers the traditional benefits of bismuth oxychloride – even application, pressability, skin adhesion – but without the lustre. It is also now possible to coat a platelet form of talc with bismuth oxychloride; this gives a product that has the skin adhesion and skin feel of the bismuth oxychloride but with a lower bulk density and less opacity.

5.4.4.3 An ideal pearl lustre pigment using titanium salts

An ideal pearl lustre pigment would be monocrystalline, lamellar titanium dioxide. Titanium dioxide has a high refractive index, 2.7 in its rutile form and 2.5 in the anatase form. It has excellent light-stability, is non-toxic and is both chemically and thermally resistant. Unfortunately all attempts to grow lamellar TiO_2 crystals have failed. It is however possible to attach a thin layer of TiO_2 to a lamellar substrate. To give the required effect, of course, it is vital that the substrate used is transparent, chemically inert, temperature-resistant and, if possible, cheap and readily available.

Mica fits these requirements almost completely, and it is found all over the world, although there are only a few areas where mining is commercially viable. It is mainly used as a cheap filling and insulation material in the electrical industry. Mica is classified as hydrous silicate in monoclinic crystalline form and can be easily ground to give thin flexible lamellae. The titanated mica pigments were a breakthrough and represented a new generation of pigments for a wide number of industries including cosmetics.

Before the mica can be coated with the titanium dioxide it has to be prepared. Rough mica blocks are ground and then classified and divided into different particle size distributions. This is a vital step as it affects the final quality of the pearl, and is used to give a range of different effects. The coating of the mica with the titanium dioxide is usually carried out by the hydrolysis of titanium salt solutions in a mica suspension. There are two main methods, which are detailed below.

In the first a calculated amount of titanium sulphate (*titanyl sulphate,* or *titanox sulphate),* $TiOSO_4$, is added to an aqueous mica suspension. By slowly heating the mixture the titanium salt is hydrolysed to insoluble titanyl hydroxide which increasingly coats the mica particles. Once all the titanium salt has been hydrolysed the pigments are filtered, dried and calcined. During the calcining water is eliminated, forming titanium dioxide which completely coats the mica.

Alternatively the pearls can be produced by a titration method, which is easier to control. In this process an aqueous, strong acid $TiOCl_2$ solution is continuously dosed into a mica suspension. Titanyl hydroxide is precipitated at a specific pH and this is kept constant by the addition of NaOH. The pigments are then dried and calcined as before.

Titanium dioxide has two main forms, rutile and anatase; the former has the higher refractive index and would therefore be the preferred form.

Unfortunately when depositing on mica the anatase form is always formed. It seems as if the mica forces the modification of the titanium dioxide. Rutile titanium dioxide can be formed, however, if the mica is precoated with a very small amount of tin oxide. Tin oxide is permitted in the EU and USA *but* it is not a listed cosmetic colour in Japan, consequently pearls containing tin oxide are not permitted in products to be sold on the Japanese market.

The first types of titanated pearls formed were silver-white pearls of varying particle sizes, and in these the thickness of the TiO_2 coating is 40–60 nm. Their shine is dependent upon the particle size, and ranges from silky-matt for the smallest particles to glittering for the largest.

If further titanium dioxide is added to the reaction mixture the particles first appear to gleam gold-yellow then with more TiO_2 this colour disappears and is replaced by a copper-red and then a lilac gleam, followed by blue and then finally green. This effect occurs because the titanium dioxide layers have reached a thickness where they behave according to the principle of colours from thin platelets and interference of the incident light occurs. This effect has been used effectively to produce another range of pearls, the 'Interference Pearls'.

5.4.4.4 Mica coated with iron oxide and other inorganic pigments

It is now possible to coat the mica with the other inorganic pigments mentioned above. To get similar effects with other colours they have to have some of the same properties as TiO_2. Most importantly they must have a high enough refractive index and exist in a form suitable to coat the mica.

Iron oxide in the haematite form has a refractive index of 2.9 and is therefore ideal. In a similar way to the hydrolysis process used with titanium dioxide an iron salt solution is hydrolysed in a mica suspension and the iron oxide hydrate is dehydrated at high temperatures. The effect and colour of the pigments are dependent on two properties, absorption and interference.

(a) Colours: yellow, copper and red to red-violet and red-green. By carefully controlling the thickness of the iron oxide layer during manufacture so that the red-brown absorption colour of haematite (rust) is covered by an interference colour, bronze, copper and various shades of red can be achieved. In these shades the red-brown colour of the iron oxide pigment is amplified by practically identical interference colours – yellow, copper and red. With relatively thick layers it is possible to manufacture red-violet or even red-green colours.

(b) Black pearl pigment. It is also possible to produce a black pearl using the magnetite form of iron oxide to coat the mica rather than the haematite form. This pigment has one minor problem associated with it. Its

magnetism can lead to some problems in the factory when processing products containing it.

(c) Gold-tinted colours using titanium salts and iron oxide. If the mica is coated first with titanium dioxide and then with another absorption colour another range of coloured pearls can be produced. The main pigment used is again the haematite form of iron oxide. The most important colours obtained by coating the mica with a nanometre-thickness layer of titanium dioxide and then further coating it with haematite are a range of gold shades. The spectrum ranges from pale yellow-gold and brilliant red-gold to greenish gold which looks quite like real gold. To produce the redder shades the iron oxide is precipitated onto mica titanium dioxide pigment in layers of different thickness. To produce the green shade a titanium and an iron hydroxide are precipitated onto the mica at the same time. In the calcining step a highly refractive iron titanium mixed oxide is formed.

This process can be used to produce shades other than gold. Variations in the layer thickness of titanium dioxide and/or iron oxide give a wide spectrum of colours and interference effects, ranging from yellow to red, red-brown, violet-blue and finally green. In theory the range of colours that could be produced is infinite.

5.4.5 Other mica-based pigments

Other materials can also be used as the second colour component to titanium to coat the mica; however these must have a high enough refractive index.

(a) Iron Blue. Blue-green to moss-green shades can be produced using a combination of titanium dioxide and chromium oxide and Iron Blue.

(b) Carmine. To produce bright red pearls is more difficult; it would seem logical to expand the processes above to include the **bright organic colours** (see Section 5.3.1) to give these shades. However, the use of these pigments or lakes around the eyes in the US market is in the most part prohibited, and this ban includes these colours when they are deposited on to mica. As the main use of pearls is in eye products other ways had to be found. Carmine is allowed around the eyes in the US, so pearls have been formed by depositing this along with titanium dioxide. The manufacturing process of these pigments is very complex because of the high purity requirements.

5.4.6 Coated pigments with properties which enhance the skin appearance

(a) The non-pearlescent effect is useful for ethnic cosmetics, among other excellent properties. The technology of pearl production can be used to form other pigments to give different effects in the finished formulations. Depositing

individual iron oxide crystals onto the mica surface produces pigments that combine the optical properties of the conventional iron oxide with the physical properties of the mica substrate. These pigments do not show any pearlescent effect, are transparent and diffuse light. They can be dispersed in both wet and dry formulations easily and give full colour development, unlike conventional pigments. They can be used to give even skin coverage without creating a mask-like effect, and are therefore particularly useful in products for darker skin as they avoid the chalkiness associated with conventional pigments.

(b) Improved skin feel, application and wear properties. Other speciality pigments can also be produced using this theory. These are incorporated into formulations not to impart colour but to improve skin feel, application characteristics and wear properties. If mica is coated with sub-micron particles of spherical **silica** the resulting pigment has exceptional slip, because the spherical particles of silica act like ballbearings. This filler can be used in a variety of formulation types to improve the skin feel.

(c) Pigments to minimize the appearance of wrinkles. Coating the mica with a mixture of barium sulfate and titanium dioxide or colloidal titanium dioxide and ultrafine particle-size titanium dioxide gives pigments that have a light-diffusing effect. These pigments scatter the light and can be incorporated into formulations to minimize the appearance of wrinkles.

(d) Coated pigment with excellent slip and skin adhesion with a soft skin feel. It is also possible to coat the mica with bismuth oxychloride, which results in a pigment that combines the properties of both of the components. It has excellent slip and skin adhesion with a soft skin feel; it is also much easier to press than mica or other mica-based pigments.

5.5 TREATED PIGMENTS

It is now possible to treat both organic and inorganic pigments and pearls with various chemicals to give them different properties.

5.5.1 Improvement in pigment properties other than colour

(a) Hydrophobicity. Hydrophobicity is desirable as it gives cosmetic products that are much longer-wearing than those produced with traditional pigments. This property, in combination with the improved skin feel of the treated pigments, results in finished formulations with greater skin adhesion. Products produced with these pigments crease and smudge less, as well as being longer-wearing.

Most treatments used in the surface coating of pigments and substrates impart a very soft, smooth, silky feel, which can be carried forward to the finished

formulations. The surface treatment also modifies the surface characteristics of the pigments. In nail enamels this means it is possible to eliminate the problem of some heavy pigments settling.

The chemicals used in treating the pigments can add moisturizing properties to the pigments and any substrates that might also be treated. This results in finished products that can provide skin-care-type benefits as well as colour. Included in this is smoothness of application and spreadability of the finished products containing the treated products.

(b) Processing benefits. Processing benefits can also be gained from using treated pigments. Many treated colours are easier to disperse than their untreated counterparts. The treatment imparts more uniform surface properties to the pigments and keeps them from agglomerating in both processing and storage. These properties result in both shorter processing times and reduced energy usage. These improved mixing properties aid in the pressability of powder formulations as the pigments and substrates used are more easily blended with the binder ingredients.

(c) Effect of oil absorption. The modification of the surface characteristics of the pigments also changes the oil absorption characteristics of the pigment. This allows the formulation of products with higher pigment loads but without the normal associated increase in viscosity. When used in wax-based products the equalizing of the oil absorption characteristics of the pigments leads to less wax ratio adjustments in the production of a complete range of lipstick colours.

(d) Less moisture absorption. The hydrophobic nature of the surface-treated pigments means they absorb less moisture. This property is particularly important in the production of pencils as it means there is less water to be released after manufacture, resulting in less shrinking of the pencil core.

(e) Treatment. A silicone (methicone) was the first treatment and it provides the greatest degree of hydrophobicity. It is very beneficial in nail enamels as it is very good at preventing the pigments from settling. On its own this type of treatment can produce a rather draggy skin feel, which can be overcome by combining it with a treatment of mineral oil. Treatment with polyethylene gives good skin adhesion and good miscibility with oils, but its primary function is to prevent settling of pigments in nail enamels.

If the silicone treatment is combined with a treatment of hydrogenated egg oil, the hydrophobicity of the silicone treatment is maintained but is complemented by a smooth creamy skin feel. In pressed powders, pigments and substrates treated in this way, improved pressing characteristics are also exhibited.

Using dimethicone rather than methicone to produce an absorbed silicone treatment eliminates the possibility of hydrogen liberation in emulsion-based products, whilst giving a creamy feel on the skin.

The best treatment for use in liquid make-ups is to use amino acids; they impart hydrophobicity, thus leading to improved skin adhesion and wear. This treatment results in a slightly acid coating which means ingredients treated in this way are more compatible with the skin and can impart skin-care-type benefits to the formulations in which they are used. An ester of lysine, Lauryl Lysine confers similar properties to that of a simple amino acid treatment but is mainly applied to substrates and pearls rather than pigments.

Hydrogenated lecithin used as a treatment provides the smoothest, softest, creamiest feel of any treatment. By combining the lecithin with a polyacrylate treatment it is possible to impart both hydrophobic and hydroscopic properties to the pigments and substrates, such that materials treated in this way absorb 30 times more moisture than those treated with silicone. This allows the formulation of long-wearing cosmetics with added moisturizing properties.

Collagen-treated colours and substrates exhibit both hydrophobic and hydroscopic properties along with excellent skin adhesion.

Treatment with metal soaps provides hydrophobicity and a smooth soft feel in powder cosmetics and also helps with pressing by acting as a binder.

Pigments treated with Teflon™ when used in liquid foundations provide more slip and a smoother skin feel. This treatment is also good when used in nail enamels for preventing sedimentation of pigments.

Hydrophilic treatments, such as dimethicone copolyol, are also possible. They are beneficial in water-based systems where they impart improved product stability and decreased colour separation. Pigments treated in this way are also easier to disperse than the untreated pigments, and aid in processing.

The use of metal alkoxides produces materials with excellent skin feel that can be used in both wet and dry products. Treatment with fluorocarbons imparts both hydrophobic and lipophobic properties to the materials, resulting in pigments that are affected by neither oil nor water in the formulation, producing less shade drift than in other systems.

When using pigments treated in any of the above ways it is important for the formulator to check that they are not contravening patents taken out by other cosmetic companies or the companies that produce the treated pigments. Many companies have discovered the benefits that can be incorporated into their finished formulations. They buy the *use* of treated pigments and patent their use in an effort to prevent competitors copying their finished products.

5.6 COLOUR MATCHING

It is not advisable to add large quantities of pigment to any type of finished formulation to correct the colour as this will unbalance the formulation, possibly

leading to separation or thickening over time if it is an emulsion, or a heavier, dry draggy effect if a lip product. Neat pigment is very difficult to disperse once the formulation has been completed.

5.6.1 Foundation make-up

When colour matching emulsion products such as foundation make-up a very small amount of additional pigments is added to a small amount of base removed from the batch and the pigments dispersed in this using high shear mixing. Once homogeneous this is returned to the bulk and stirred with a paddle until the batch is homogeneous again.

If a lot of colour corrections are required, or a number of shades of the same formulation are being produced at the same time, the preferred way is to produce separately, prior to production of the marketed shades, a white, black, yellow and red foundation make-up. In these all the pigment in the base formulation is either Titanium Dioxide (for white), Black, Yellow or Red Iron Oxides. When colour matching of the final shade is carried out small aliquots of the appropriate primary coloured base (PCB) can be added as required. In this way the balance and percentage ratio of the product is not disturbed so no long-term stability problems are likely to arise.

5.6.2 Lip products

With lip products additional pigment pastes can be added, but the total dry pigment level should be carefully controlled within well-defined limits. If colour matching within these limits is not possible, extra base ingredients must also be added.

5.6.3 Powder products

Colour adjustment in powder products such as eyeshadows and face powders is usually accomplished by milling the additional required pigments into a small amount of the finished product and then blending this into the bulk, after ensuring full dispersion has been obtained.

5.6.4 Comparison with standard

Whichever way the adjustments are made it is important that the colour of the batch is compared to a previously approved standard. For foundation make-up the comparison is best done on the skin, the forearm being the preferred site. Two strips of the standard are applied, one in line with the base of the thumb, the other higher up the arm on the inside. Two further strips of the production batch are then also applied, one higher up the arm in line with the base of the

thumb, the other near the wrist under the second strip of standard. The products are then allowed to dry fully before being compared for colour. By applying the strips in this way on the forearm, any skin tone variation can be cancelled out and a true comparison of the colour achieved. Other products can be compared on the back of the hand or by using the pale skin at the base of the thumb on the palm using the same four-grid pattern.

5.6.5 The correct lighting for comparing shades

The light used for colour matching is also vital. Many artificial sources of light can distort the colours seen, a phenomenon known as metamerism. This is why a skirt and jumper that appeared to match when seen together in the shop look different from each other when taken home. Northern daylight is recommended for all colour matching as this light causes no distortion. If it is not possible to have a north-facing window in the laboratory then a light box should be used with artificial bulbs that produce light of the same wavelength as northern daylight. The inside walls of the light box are painted with a special grey paint so that they do not contribute to the light.

BIBLIOGRAPHY

Further reading on the subject can be found in the following general references. The companies mentioned are suppliers of specific materials and usually offer information and formulations as examples of their use.

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6

Decorative cosmetics

Pauline Riley

6.1 INTRODUCTION

Decorative cosmetics, for skin, hair and other appendages, e.g. lips and nails, on sale today, can be divided into those which aim to improve and/or protect and maintain good health, and a vast range of preparations to enhance and change appearances and at the same time cover up defects. This chapter describes the latter type which have added colours. Chapter 5 gives a technical description of the different colour compounds that can be used safely and legally in cosmetic products. In three parts this chapter will describe (A) facial make-up, (B) eye products and (C) lip products.

The formulation of the finished products starts with a clear understanding of the target consumer requirements and any product claims that the marketing department wish to make. These considerations could be performance, user type, usage instructions, method of application and the type of packaging that will hold the product. With the more sophisticated materials now available claims are being made about specific ingredients contained in products which increase the necessity of accurate planning of the development of new or changed finished products. The development brief must be clear with detailed tests for stability, safety, compliance with the legislation in force in the countries where the product is to be marketed and challenge tests for microbiological status, during the development stage, and manufacture, with positive results for the finished product and final in-use consumer panel trials. Reports must be kept at every stage and results recorded in the PIP. Chapters 18 and 20–23 give general methods for regulatory quality control, many of which apply to the development of products described in this chapter.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 167–216

A. FACIAL MAKE-UP

6.2 INGREDIENTS

Many of the following raw materials are found in Sections A, B and C. Note: The INCI names used for them in formulations can be used as identification and suppliers obtained from the author. Where specialist materials are used they will be described in the relevant text.

To attain the necessary properties outlined above modern face powders are a blend of several ingredients. No one material possesses all the desired characteristics though some possess more than one attribute. The choice of these basic ingredients used in the formulation of face powders is limited, each playing a significant role in the final powder formulation. The quality of each material used in these relatively simple formulations is therefore all the more important.

6.2.1 Talc

Talc is the main component of face powders; in some products it could comprise up to 70% or 75% of the formulation. Chemically it is a hydrated magnesium silicate with the assigned formula $3MgO_2 \cdot 4SiO_2 \cdot H_2O$, and is found in Italy, France, Norway, India, Spain, the USA, Australia, China, Egypt and Japan. Of these the Italian, French, American, Australian and some Indian and Chinese grades can be used for cosmetic powders. Grades of talc should be judged on slip, smoothness, fineness, grit, density, colour and odour. In addition a check should be made for impurities such as carbonates and water-soluble iron and the talc must be free from asbestos. Care must be taken to ensure that the talc has been adequately treated to overcome any possible microbial contamination, the major concern being tetanus spores.

Talc is used mainly because of outstanding spreadability (slip) and low covering power (translucency). It and the metallic soaps are the most widely used ingredients that impart slip. Also its inclusion in a face powder increases its adhesiveness to the skin and avoids the powder dissipating in a short period of time. Whichever talc is used it should be white – some cheap grades can be rather grey – free from asbestos, and sterilized (talc from an open mine has been known to contain tetanus spores). It should also be free from gritty particles and be the foliated variety (thin plates) to give maximum slip.

The particle size of the talc can significantly affect the appearance and feel of the finished formulation; the smaller the particle size the smoother it will feel. However, very fine talc can start to feel gritty. It is also important to note that the finer the talc the more opaque it becomes, and it therefore becomes a question of balance to give the desired feel and opacity.

6.2.2 Kaolin

Kaolin, also known as 'China clay', a naturally occurring compound, is a hydrated aluminium silicate. It was first mined in China from a mountain called

Kaoling, hence its name. There are three different groups of clays (**kaolinite**, **nacrite** and **dickite**) having essentially the same formula ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) that are classified as kaolin. It is almost white in colour. It has less slip than talc, and the product can end up with a harsh feel. Not more than 25% should be used in a face powder, for the following reasons. Owing to its hygroscopic nature excessive use is not recommended since it will tend to streak in damp weather. Also it is very matt and with high levels the dreaded 'clown' effect can occur.

However, a low level does help to negate the slight shine that talc can leave on the skin. It is dense and can be used to reduce unacceptably low bulk densities in loose powders. In addition to its high moisture-absorption properties kaolin has good covering power and excellent grease-resisting properties, and imparts some degree of skin adhesion to the finished product.

Note: Talc and kaolin are also colour extenders. This operation is described in Section 6.4.1(a).

6.2.3 Zinc oxide

Zinc oxide is occasionally used at moderately low levels in face powders because it has quite good covering power, is slightly astringent and a recognized skin protectorant; it therefore imparts soothing properties to the skin. Only the finest grades should be used and preferably a BP (British Pharmacopoeia), or equivalent, grade, as lower grades can be rather gritty. Zinc oxide has a tendency to form balled particles; it is therefore often sieved prior to mixing with any other ingredients in a formulation.

6.2.4 Calcium carbonate

Calcium carbonate (precipitated chalk) is a mildly alkaline, white, odourless microcrystalline powder available in special grades with differing particle sizes and densities. It is mainly used because of its excellent absorption characteristics. It is matt and can give a 'bloom' effect to the coating on the face. As a material it has good absorption characteristics and, like kaolin, it may also be used to remove some of the inherent shine of talc. Excessive use is not recommended (greater than 15%) because of its undesirable dry powdery feel and adverse effect on the slip of the product.

6.2.5 Magnesium carbonate

Magnesium carbonate is often used to absorb fragrance prior to mixing it into the face powder. It can also be used to give more 'bulk' to the powder. However, in the same way calcium carbonate does, it can affect the feel if used at too high a level.

6.2.6 Metallic soaps

Metallic soaps such as **zinc** and **magnesium stearates** are very important ingredients for all types of powder products. They help the finished products

adhere to the skin and in pressed powders can help the cake stick together in the godet. In addition to increasing the adhesion of the final powder the metal soaps also impart a degree of water repellency and render the ultimate product soft and fluffy. The levels of usage range between 3% and 10%; higher levels than this can result in a blotchy effect on the skin, as they will reduce the slip properties of the other ingredients. In pressed powder products too high a usage level can lead to flow problems which affect the pressing mechanism and can also lead to 'greasing' of the cake in use, as sebum is transferred from the puff or brush to the product and absorbed. Again the purity of the grade used is important; the presence of residual unsaturated fatty acids should be avoided as they can cause rancidity in the finished product. Of the two, zinc stearate is preferred as it is also considered to have soothing properties.

6.2.7 Other materials

Additional materials can be incorporated to improve the adhesion of powders to the skin; e.g. emollients such as **cetyl** or **stearyl alcohols** and **glyceryl monostearate;** other materials such as **magnesium myristate, petroleum jelly** or **mineral oil** are normally added at low levels of between 0.5% and 2%. When trying to formulate a very light fluffy powder, and still achieve good adhesion, materials such as **encapsulated mineral oil** may be used.

6.2.8 Starches

These are often used in face powders. In particular **rice starch** was very common as a basic ingredient in formulations. It was considered to give a 'peach-like' bloom to the face. Because the particles are spherical it gives a very smooth feel when applied to the skin. It has excellent absorptive properties and in addition has good covering power. In the presence of water it tends to cake, and cling to facial hair, giving an unpleasant appearance. It can also become sticky. **Corn starch** is also widely used and has similar properties to rice starch. **Tapioca starch** is particularly useful as it gives a very smooth feel to the product.

6.2.9 Modified starches

Modified starches are now available which can be very beneficial in powder products. These treated starches do not swell or agglutinate in the presence of moisture but retain the high absorptive power for both oils and water. They can be used as talc replacements in some products. They also improve the aesthetics of the formulation and can act to absorb excess oil from the skin. Because they are free-flowing powders they can prevent caking. They are virtually transparent on the skin and therefore lessen the opacity of the formulation. An added benefit is, of course, their natural derivation.

Unfortunately both starches and modified starches are ideal media for microbiological growth; it is therefore important that the grades used are sterilized prior to use, that the manufacturing environment is as clean as possible to prevent contamination and that sufficient preservatives are used in the formulation.

6.2.10 Walnut flour

Another naturally occurring material, **walnut flour,** in combination with non-pearly titanium dioxide/barium sulfate-coated **mica,** is recommended as having good oil absorption characteristics. Silicates such as **magnesium trisilicate** have high water- and oil-absorption properties and they may also be used as perfume carriers. The **silicas,** in addition to the silicates, are useful in maintaining the free-flowing properties of powders in high humidity.

6.2.11 Micronized plastics

Micronized plastics such as **polythene, polystyrene** and **nylon** can impart a very smooth feel to formulas. These particles are usually spherical and the ball-bearing effect comes into play. Typically these can be used at between 5% and 10% but they are expensive so their use is somewhat limited.

6.2.12 Mica

Mica is translucent and gives a fine shine. This is one of the effects to be overcome so mica itself and the other pearls are rarely used in face powders. Some other mica-based ingredients are widely used. Those coated with spherical barium sulfate for example [1], will diffuse the incident light giving a soft focus effect, and will thereby minimize the appearance of fine lines and wrinkles.

6.2.13 Fumed silica

Fumed silica can be used to decrease the bulk density of the system. It has a very dry unpleasant feel on the skin, and the usage level is consequently kept very low; less than 1% would be typical.

6.2.14 Powdered silk, etc.

Many ingredients can be added to powder products such as **powdered silk, silk protein** or **'goodies'** to meet specific marketing department requirements. Levels of these are usually low and care must be taken to ensure that they do not adversely affect the skin feel, flow and pressing characteristics, and do not oxidize. **Silk powder** is the pulverized fibroin, crystallite material extracted from natural silk by degumming, followed by partial hydrolysis. This process

removes most of the sericin and other impurities. Its chief constituents are the following amino acids: glycine, tyrosine, serine, glutamic acid, proline, alanine, leucine, aspartic acid and phenylalanine. Cosmetic grades are light and bulky and of a good colour. Silk has good absorption characteristics for both water and aromatic compounds. **Silica** may also be used to prepare powders of a light transparent type. It is also used because of its good adhesive property and to increase the bulk, since it is very finely divided and very fluffy.

6.2.15 Colour

Inorganic pigments widely used in face powder include: iron oxides, of which there are three basic colours, yellow, red and black; ultramarine which gives blue; and chrome hydrate and chrome oxide which give green. These inorganic pigments are dull in hue. The quantity or colour required in a given formula will vary and is dependent upon the base formulation. The strength of the colours and the transparency of the talc used will have a considerable influence on the quantity of colour needed. Wherever practicable, the blend of colours used should be kept as simple as possible. This facilitates subsequent colour matching with new batches of raw materials.

The colour effect when the powder is applied to the skin is dependent upon the opacity of the white and tinted pigments used, their particle size, the degree of dispersion, the thickness of the applied film and the skin's colour. The performance of coloured products is always assessed when it is applied to the skin. The inner forearm is an area often used by formulators. The reason for this assessment of colour is that the colour of a thin film of pigment may be different from the effect given by the powder when viewed in bulk. The thin film colour effect is known as the 'undertone' and the bulk effect as the 'mass' tone.

Colour dispersion within a base formula, and colour grinding to bring out maximum shade development, are both important stages of make-up preparation, both in the laboratory at the development stage and in final manufacture. If these stages are not followed rigorously, batch-to-batch colour variation will arise from poor pulverization of pigments resulting in under-development of shade intensities.

6.2.16 Treated pigments

In addition to the materials mentioned above, treated or coated pigments are now available. One important advantage of these pigments, highlighted by Driscoll [2], is easier dispersion. They are cosmetic pigments that have been coated with a variety of cosmetic materials such as dimethicone, methicone, silicone copolyol, lecithin, collagen, metal soaps, and Teflon™, metal alkoxides and amino acids. Each coating imparts its own characteristics and advantages such

as water repellency, improved 'pay-off' and skin adhesion, and improved feel and texture. More details of these treatments can be found in Chapter 5, p. 161. These materials are worth considering for their ability to impart improved performance. They also allow for additional marketing claims to be made about the product.

6.2.17 Preservation

The Regulations governing the sale of cosmetics mean that results of microbiological challenge tests carried out at the development stage during manufacture and routinely on the finished product must be recorded in the Product Information Package (PIP) for the authorities to see when asked for, confirming that the product is safe in use (see Chapter 21).

The aim is to prevent contamination of the product during manufacture and also during use by the consumer, who may introduce microorganisms into the product every time she uses it, either from her fingers or from the puff, brush or applicator. Raw material specifications should show that they are free from microorganisms. The type of products used in powder systems usually means that they are hard to contaminate microbiologically but the use of water-based additives, such as plant extracts, can dramatically alter this, and these ingredients should be avoided if possible (oil-based extracts should be used in preference). Care should also be taken in controlling the ingredients used in powder products that go around the eye area; in particular, there are stricter microbiological limits for materials to be used in these products.

6.2.18 Antioxidants

The use of antioxidants may be required to protect some ingredients from degradation and consequent rancidity. Low levels of butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT) or vitamin E should be used when necessary.

6.2.19 Fragrance

This is an important constituent of most face powders. The fragrance level of face powders should be kept low and a subtle type of fragrance note used. Because of the large surface area of the powder, product oxidation of the fragrance can occur very easily. It is therefore important to use a specially designed fragrance that contains ingredients that are not oxidized easily. The addition of an antioxidant can help, but may cause irritation. Normally a soft floral fragrance is used.

6.3 FOUNDATION MAKE-UP

The most popular facial products are found in foundation make-up. Simple foundation creams and lotions which rub in easily, so that applied coloured make-up can be applied smoothly and adhere well, are covered in Chapter 14. In the present chapter the decorative pigmented type will be discussed. These are

used to unify the colour of the skin, to cover blemishes and skin defects and to provide a basis for further enhancement by the application of lip and eye colour cosmetics. Many of these modern types are also used for their skin-care benefits, with additions such as sunscreens, natural extracts and vitamins, so that with pigmented products the consumer applies colour whilst looking after her skin. This is the one area of decorative cosmetics not affected by the extremes of fashion. Many shades are popular for many years. All shades rely on the products giving a uniform skin colouration. The 'natural' look, so popular now, relies on the consumer using tones close to those of her own skin, changing the colour she chooses only as her own skin tones change, either with the seasons or with age. The more 'painted' look uses more adventurous shades, with perhaps one of the most extreme being the almost-white, pale 'china-doll' look of the geisha girls.

The products are marketed in several different ways: the traditional 'foundation pan cake' and different forms of foundation liquids which are opaque creams or lotions. The consumer uses one appropriate to her individual skin type. All these forms consist of a dispersion of pigments in an emulsion or wax base.

6.3.1 Cake foundation make-up

Cake foundation make-up was modified and developed from that used in the theatre and film industries. The professionals used stick make-up which became Max Factor's Pan Sticks, the first products to become commercially available. They were a mixture of talc, kaolin, magnesium carbonate, titanium dioxide and iron oxides added to molten waxes and oils. In Max Factor's Pancake make-up, a development of the stick, the powders were first dispersed in water before being added to the oils and waxes [3], and the resultant mixture was dried, ground and pressed into cakes in godets or small pans (hence the name 'pancake make-up'). Application to the face was by using a damp sponge. No further application of face powder is considered necessary but the overall effect in the early days was mask-like and often character lines were lost, copying the film-star beauties of the day.

6.3.2 Liquid foundation make-up

The liquid products are a suspension of pigments in an emulsion base, the same types as those used for facial moisturizers. Either oil-in-water or water-in-oil emulsions can be used, although the latter can be rather heavy in texture. Traditionally they were based on either anionic or cationic emulsification systems. Many modern products are water-in-silicone emulsions which have superior skin feel and better wear characteristics. Originally liquid foundations darkened when applied to the skin, but with today's formulations there is minimal colour change when the product is on the skin, resulting in the consumer finding it easier to choose the colour most suited to her skin tone.

The major requirements of all the different systems are: good skin feel, ease of spreading, even coverage, quick-drying, all-day lasting, colour staying

constant during wear, and combating shiny skin, so that it has a matte appearance throughout the day.

The major components of this type of system are: emollient oils; emulsifiers; humectants; pigment wetting agents; pigment suspending agents; pigments; pigment extenders, e.g. talc, kaolin; water; preservatives; fragrance; additives if required, e.g. vitamins, sunscreens, etc.

6.3.3 Anionic foundation make-up

Anionic oil-in-water emulsions were the most popular because these systems were cheap and easy to produce.

6.3.4 A typical oil-in-water foundation make-up formulation

Formula I

	% w/w	
Oil phase		
Stearic acid	2.60	
Propylene Glycol Monostearate	1.90	
Lanolin Alcohols (and) Mineral Oil	9.50	A
Cetyl Palmitate	1.00	
Isopropyl Myristate	4.00	
Pigments		
Kaolin	4.25	
Titanium Dioxide	6.75	B
Yellow Iron Oxide	0.50	
Brown Iron Oxide	0.80	
Water phase		
Deionized Water, Water; Aqua (INCI)	64.00	
Triethanolamine 99%	1.00	
Carboxymethyl Cellulose	0.20	C
Magnesium Aluminium Silicate	0.50	
Lecithin	2.00	
Propylene Glycol	1.00	D
Preservative	q.s.	
Fragrance	q.s.	E

Method of manufacture

1. Blend and mill the pigments with the extender of B. Check with a standard sample that colour dispersion is complete.
2. Add the lecithin to the water of C using a high shear mixer (a Silverson or equivalent). Add the triethanolamine, carboxymethyl cellulose and magnesium aluminium silicate, and continue mixing until homogeneous.
3. Add the dispersed pigments from (1).

4. Heat to 75°C with stirring.
5. Mix together the oil phase ingredients of A and heat, with stirring, to 75°C.
6. When both phases are homogeneous and both at 75°C add the oil phase to the water phase with high shear mixing.
7. Continue with high shear mixing until the product is smooth and homogeneous, and emulsification is complete.
8. Change to paddle stirring while cooling.
9. Dissolve the previously determined amount of preservatives in the propylene glycol of D with minimum heat and add to the batch with stirring. The preservatives will dissolve in the oil and water phases according to their partition coefficients in those phases.
10. When the temperature has cooled to 35°C add the fragrance, E.
11. Mix until homogeneous.
12. Match colour with standard (see Chapter 5, p. 163). When the colour is approved cool to 25°C and transfer to storage containers prior to filling.

As already said, **water-in-oil emulsions** are rarely used in foundation products owing to their greasy skin feel, and they are more expensive and more difficult to stabilize.

6.3.5 Water-in-silicone foundations

Water-in-silicone systems are also difficult to manufacture and stabilize but their in-use advantages make them the preferred choice for the future. The major one is that the colour seen in the bottle is the colour of the product on the skin. They also have an exceptionally good skin feel, but can be quite expensive. Standard pigments do not perform well in water-in-silicone emulsions as they tend to aggregate and float to the surface. The pigments in this type of product are incorporated into the oil or silicone phase rather than the water phase so it is better to use silicone-treated pigments.

6.3.6 A water-in-silicone foundation cream formulation

Formula II

Ingredients	*Function*	*% w/w*	
Silicone phase			
Cyclomethicone (and) Dimethicone Copolyol	Combined silicone and emulsifier	10.00	
Cyclomethicone	Volatile silicone	10.00	
Beeswax	Co-emulsifier	3.00	A
Polyglyceryl-4 Oleate	Co-emulsifier	2.00	
Absorbed Silicone-Treated Pigments		10.00	

Ingredients	*Function*	*% w/w*	
Water phase			
Water; Aqua (INCI)		63.00	
Sodium Chloride	Stabilizer	2.00	B
Preservative		q.s.	
		100.00	

Method of manufacture

1. Disperse the pigments in the cyclomethicone and dimethicone copolyol, the cyclomethicone, the beeswax and the polyglyceryl-4 oleate then heat the mixture to 50°C.
2. Dissolve the sodium chloride in the water with the preservative. Warm to 50°C.
3. Add the water phase to the silicone phase *drop-wise* and mix with a paddle stirrer.
4. When about one-third of the water phase has been incorporated speed up the rate of addition.
5. Transfer to high shear mixing when all the water phase has been incorporated. This will thicken the system. Continue mixing until maximum viscosity is obtained.

6.3.7 Cationic liquid foundation make-up

Cationic liquid foundations can give a very pleasant feel to the skin. Having a pH closer to that of the skin, they are better than anionic systems for it. Taking the pH too low, however, can cause problems as iron oxides are not stable at low pH and will decompose, resulting in loss of colour and emulsion breakdown.

6.3.8 Cationic liquid foundation make-up formulation

Formula III

Ingredients	*Function*	*% w/w*
Oil phase		
Cholesterol/Lanesterol Ester	Emollient	0.50
Cetyl Alcohol	Viscosity modifier	2.00
PPG-Myristyl Propionate	Emollient	1.50
Dimethicone	Emollient	0.20
Quaternium-7 Steapyorium Chloride (INCI)	Cationic emulsifier	1.50
Water phase		
Water (Deionized); Aqua		80.30
Glycerin	Humectant	4.00
Titanium Dioxide	Pigment	6.00

Ingredients	*Function*	*% w/w*
Talc	Filler	1.00
Iron Oxides	Pigments	3.00
Preservatives		q.s.
Fragrance		q.s.

Method of manufacture

1. Disperse the blended and milled Titanium Dioxide, Iron Oxides and Talc in the Water and Glycerine, heat to 75°C and maintain.
2. Blend together the oil phase ingredients and heat to 75°C and maintain.
3. Add the preservatives to the respective phases in which they will be soluble.
4. Add the water phase to the oil phase using high shear mixing; when emulsification is complete change to slow speed stirring and cool.
5. Add the fragrance when the temperature is below 35°C. Match batch colour with standard sample.

6.4 FACE POWDERS

Face powders are used to cover minor imperfections and reduce the shine that appears on the skin due to sebum or perspiration. They are required to give a matt, smooth finish to the skin and remain this way for as long as possible. This means that all the ingredients used must adhere well to the skin. In recent times the fashion has changed from a 'painted clown' look to one that appears to be as natural as if the skin had no product applied, but without the imperfections. Modern products are also required to be 'long-lasting', preferably all day, and consequently avoid repeated application; they should not rub off onto clothing (either that of the wearer or of anybody else).

There are two main forms of face powder. Loose face powder comes in a sealed tambourine inside a decorative plastic container. It is either applied directly from this by a puff or large brush, or is transferred to a special compact in which it can be carried in a handbag and is applied with a sponge or small puff that also fits in the compact. To prevent leakage a nylon mesh covers the surface of the powder. In its second form the powder is compacted or compressed and a binding agent is used in its manufacture.

Whatever the format, the face powder must have the following characteristics:

1. The powder should have the required covering power to mask minor visible skin imperfections.
2. It should adhere to the skin and must not be completely dissipated in a short time, so avoiding frequent re-powdering.
3. The finish given to the skin must complement the skin colour, imparting a velvet or peach-like character.

4. Shine on or around the nose must be completely eliminated. The powder must be absorbent without changing its appearance on the skin.
5. There must be sufficient slip to enable the powder to be applied to the skin with a suitable applicator, such as a puff or brush, without dragging or producing a blotchy effect.
6. The constituents of the powder should be such that a clown-like effect is impossible. The preference should be towards transparency.

The popularity of loose face powders waned with the advent of compact (compressed) powders and developments in foundation and liquid make-up. However, it is still considered by some that loose powder gives a more 'professional' finish and there is a resurgence in popularity from time to time.

New uses for 'face powders' have been established, such as the correction of heightened colour where there is too much red colouration or too much yellow in the case of sallow complexions. The borderline between what constitutes a face powder and a foundation has become very blurred with the development of dual-function products.

(a) Colour of the finished face powder

The colour of the finished face powder is a matter of taste and fashion. It is normally necessary to produce a range of shades that will blend with and enhance the natural complexion. Today's natural skin colour tends more towards a cream colour with only a few complexions tending towards blue for which the 'clear pink' shades are suitable. The range of colours offered should be based on shades suitable for the main complexion types such as blond and fair-skinned or brunette and dark-skinned.

The colour effect when the powder is applied to the skin is dependent upon the opacity of the white and tinted pigments used, their particle size, the degree of dispersion, the thickness of the applied film and the skin's colour. The performance of coloured products is always assessed when it is applied to the skin. The inner forearm is an area often used by formulators. The reason for this assessment of colour on the skin is that the colour of a thin film of pigment may be different from the effect given by the powder when viewed in bulk. The thin film colour effect is known as the 'undertone' and the bulk effect as the 'mass' tone.

Colour dispersion within the base formula, and colour grinding to bring out maximum shade development, are both important stages of face powder preparation, both in the laboratory at the development stage and in final manufacture. If these stages are not followed rigorously, batch-to-batch colour variation will arise from poor pulverization of pigments resulting in under-development of shade intensities.

6.4.1 General manufacturing process

The initial stages of the manufacturing process are the same for both loose and pressed powders, but the latter requires the addition of a binder, either prior to or with the perfume.

(a) Colour extension

A key stage in the processing of pigmented powder products is the homogeneous dispersion of the pigments in the white base. Dispersion is dependent upon the efficiency of the mixing equipment and the physical characteristics of the materials included in the powder mixture. Homogeneous dispersion of the pigments is achieved by adequate extension of the pigments by passing the pigment and talc through a hammer mill. This breaks up the pigment agglomerates, which then stabilize by becoming coated onto the talc particles. There are now several types of equipment available to replace, wholly or partially, the hammer mill. One, a vertical vortex mixer, employs a fluidized vortex motion, reducing particle size by particle–particle collision. Another, a high-speed mixer, is known as a plough-shear device. This equipment uses a high-speed chopper in addition to mixing paddles rotating on an axial shaft. The chopper is mainly responsible for the powder extension.

(b) Base powder preparation

The white base ingredients are first mixed in a stainless-steel ribbon-type blender. The initial mixing time could be from 20 minutes to 3 hours, depending on the mixer type, capacity and the batch size. Next, the extended colours are added to the blended white base. This mixture is blended until a homogeneous mixture is achieved. With a loose face powder the perfume is the final addition. Spraying the perfume into the blender assists even distribution. For pressed powders the binder system will also be sprayed in at this stage. Finally the colour is checked against the standard and any corrections made. If mica-based materials are used in the formulation, great care is taken to ensure the fragile platelets are not damaged by processing. Colour correction is generally done by removing a small quantity of the bulk and mixing in the appropriate extended colours. This is then added back to the main vessel and the bulk is re-mixed and checked again for colour. The effect of the pearlescent pigments on the final colour of the powder is taken into account during the colour correction work.

The checked bulk is then emptied into double polyethylene bags for storage or, to achieve a fine powder, pulverized and screened prior to bagging. The powder is ready for the next stage in the process: filling in the case of a loose face powder, or pressing in the case of a compact powder.

(c) Compacting process

Three different procedures can be employed to obtain a compact powder: wet moulding, damp compressing and dry compressing. The latter is the most widely used method.

For the dry compacting process there is a choice of machinery available, each working on a different principal: pneumatics used in the Air-Mite press; hydraulics used by Alite, the ram type with the punch coming down onto the powder as seen in the Kemwall press; and the Ve-Tra-Co press where the punch remains fixed and the godets are pushed from beneath.

Providing the bulk powder has been carefully manufactured and is allowed to stand to enable the release of any trapped air, pre-pressing should not be necessary. Pre-pressing occurs when a lower pressure is slowly applied to the powder to assist the removal of trapped air, prior to the compacting pressure being applied. The amount of pressure required to produce an acceptable cake is influenced by several factors, such as the base formulation, the type and quantity of binder, the moisture content of the powder and the godet size. Trial pressings need to be carried out to determine the correct machinery settings.

6.4.2 Formulation of loose face powder

Formula IV

Ingredients	*Function*	*% w/w*
Talc	To impart slip on the skin	74.80
Zinc Stearate	To give skin adhesion	7.50
Magnesium Carbonate	Absorbent base for fragrance	1.00
Black Iron Oxide	Pigment	0.30
Red Iron Oxide	Pigment	3.00
Yellow Iron Oxide	Pigment	3.00
Mica, Barium Sulphate, Titanium Dioxide*	To disguise the 'wrinkles'	10.00
Fragrance		0.15
Preservative		q.s.

*Low Lustre Pigment – Merck KGaA [1]

Method of manufacture

1. Disperse the fragrance on the Magnesium Carbonate to form a free-flowing powder.
2. Place the Talc, Zinc Stearate, Magnesium Carbonate/Fragrance, Preservatives and Pigments into the ribbon blender and mix for 20–30 minutes.
3. Pass the mixture through the hammer mill until the pigments are fully dispersed.
4. Return the mixture to the ribbon mixer and add the Low Lustre Pigment, mix for 15–25 minutes.
5. Sieve if necessary and place in lined storage bins, until required for filling. Match colour with standard (see Chapter 5, p. 163).

6.4.3 Compact face powder

As the name suggests, this is a powder that has been compacted or compressed. Such powders were first developed and marketed in America in the 1930s. This form of face powder was very successful owing to the ease of application and convenient storage. The important characteristics of a pressed powder are identical to those for a loose face powder. However there is an additional requirement when the powder is presented in a pressed form; this is easy removal from the cake with an applicator, a puff in most cases, without the cake crumbling or breaking. Also the bulk powder should be free-flowing in nature to enable easy filling of the pans or godets and prevent adherence to the punches. This can be a critical time in the manufacturing stage because any air trapped in the powder will result in uneven compression and will cause the cakes to break.

The raw materials used for a pressed powder base are identical to those in loose powders. The difference is the addition of binding agents. These materials are necessary to ensure the powder will compress easily and remain in a pressed cake without crumbling or chipping under normal conditions of usage and shipment. Ease of 'pay-off' is also considered. 'Pay-off' is a term used to describe the removal of *powder* from the surface of a pressed cake. To achieve a pressed cake that will remain intact and 'pay-off' easily the correct balance must be achieved between the binder system type, quantity of binder and the pressure applied. When this balance is not achieved a variety of problems occur. These problems range from poor flow of powder, cakes breaking and poor 'pay-off', to cakes that are too hard and glaze easily in use.

6.4.4 Binding agents

The materials used as binding agents provide greater cohesion. There are a large number of suitable materials to choose from, such as: dry (powder), oil, silicone and emulsion.

The materials suitable as dry binders such as the metallic stearates (zinc and magnesium stearate) are described in Section 6.2.6. The level of the metallic stearates incorporated into a pressed powder will be higher than in a loose face powder. In addition the level of kaolin and zinc oxide will also tend to be higher. Starch is considered by some to act as a good binding agent, but some care is needed to ensure too hard a cake is not produced.

Oil binders can be used on their own in a variety of compressed powder formulas. These are materials such as mineral oil, isopropyl myristate, and lanolin derivatives.

The water-repellent or insoluble materials such as lanolin and its derivatives, mineral oil, fatty esters, cetyl or stearyl alcohols, paraffin wax and microcrystalline waxes, and more recently the high molecular weight silicones, can be used in combination to produce a binder system. Even distribution of these

materials throughout the bulk powder can be a problem. The method of addition and subsequent mixing needs careful consideration when deciding the manufacturing procedure.

Oil-in-water emulsion binder systems have been developed to overcome the distribution problems encountered with the water-insoluble materials used on their own. In addition to facilitating dispersion the emulsion-type binders also tend to reduce the tendency for lumping that can occur with the oils alone. Emulsifiers such as triethanolamine stearate, nonionic emulsifiers and glyceryl monostearate will be needed in this type of binder system. Emulsion systems can use a wide variety of materials that otherwise have been problematic. The incorporation of water into an otherwise anhydrous system highlights the need to add preservatives to the emulsion as the water present in the binder could encourage microbiological growth in other ingredients in the formulation. Examples of binder systems are given below:

	% w/w of finished formulation
Octyldodecyl stearyl stearate	8.0
Calcium acid stearate (B-122)	3.0

Source: B-122 (United Guardian)

This system could be modified to improve the feel of the finished product by the addition of a high molecular weight silicone gum dispersed in cyclomethicone or dimethicone*. A drier, more powdery feel can be achieved by replacing part, or all, of the octyldodecyl stearyl stearate with cetyl octanoate or glyceryl octanoate.

*Such as DC 1501 or DC 1503

	% w/w
Isopropyl myristate	45.0
Sorbitan oleate	9.9
Mineral (Paraffinum Liquidum) Oil	45.0
BHA	0.1
	100.0

6.4.5 Pressed face powder formulation

Formula V

Ingredients	*Function*	*% w/w*
Talc	To give slip on the skin	65.00–65.35
Zinc Stearate	Powder binder, also gives adherence to the skin	7.50
Liquid Ester	Liquid binder	5.00

Ingredients	*Function*	*% w/w*
Modified Starch	Absorbent	3.00
Magnesium Carbonate	Absorbent for fragrance	1.00
Titanium Dioxide	Pigment	3.00
Black Iron Oxide	Pigment	0.15
Red Iron Oxide	Pigment	3.00
Yellow Iron Oxide	Pigment	2.00
Mica, Barium Sulphate, Titanium Dioxide*	To disguise 'wrinkles' [1]	10.00
Preservative		q.s.
Fragrance		q.s.
		100.00

*Low Lustre Pigment, Merck KGaA [1]

Method of manufacture

1. Disperse the fragrance on the magnesium carbonate to form a free-flowing powder.
2. Place the talc, zinc stearate, modified starch, magnesium carbonate/fragrance, preservatives and pigments into the ribbon blender and mix for 20–30 minutes.
3. Pass the mixture through a hammer mill until the pigments are fully dispersed.
4. Return the mixture to the ribbon blender and spray in the liquid ester, mix for 15–20 minutes.
5. Pass the mix through the hammer mill again, until the oil has been fully dispersed.
6. Return to the ribbon blender and mix in the low lustre pigment by tumbling for 15–20 minutes.
7. Sieve if required and place into lined storage bins.
8. Match colour with standard (see Chapter 5, p. 163).

Note: The variation of the talc content allows for the minimum amount of preservatives required as a result of challenge testing and the desired amount of fragrance.

6.5 TWO-WAY FOUNDATION MAKE-UP

Two-way foundations are a form of compact powder foundation that can be applied to the skin by use of either a wet or dry sponge. The overall function is to provide a natural-looking smooth finish. In many ways they combine the properties of a foundation with that of a face powder, with extended wear and the potential to minimize the appearance of wrinkles, blemishes and skin pores.

6.5.1 Base ingredients

(a) The most important criteria of substrates and extenders for two-way foundations are their platelet shape and flexibility of structure; this is because they

are applied in a similar way to face powders rather than to pancake or liquid foundations. The use of platelet-type substrates and extenders also enhances the feel of the formulation. Sericite and mica minerals are ideal substrates for these types of formulae. Chemically sericite is almost identical to mica but is preferred in two-way foundations owing to its appearance and feel. It has a silkier, creamier feel than mica and has better skin adhesion. It also confers less shine to the skin – an important consideration in this type of product. The amount incorporated in a typical formulation varies from 10% to 40%, optimally between 15% and 20%. Mica is also used in two-way foundations at between 5% and 10% because it adds transparency. The total content of the mica group of minerals is usually 20–35%.

(b) In general the use of talc in two-way foundations is limited to no more than 10%, otherwise the benefits of the sericite can be lost. Talc also gives a much whiter, less transparent look on the skin because after pulverization the particle size is significantly reduced, resulting in higher diffuse reflection of the incident light. The particle size of the substrates and extenders in two-way foundations typically falls between 6 and 10 microns. Products with high amounts of smaller particulates tend to become whiter and give an opaque finish on the skin.

(c) Spherical powders such as nylon, silica or polymethyl methacrylate contribute to two-way foundations by giving a silky smooth feel, enhanced pay-off, and smoother skin application. Some, such as silica, act to absorb sebum and perspiration, therefore giving a uniform finish throughout the day. They can also act as light diffusers, minimizing the appearance of pores.

The ideal level of spherical powders in two-way foundations generally ranges from 10% to 13%. However if the formulation also contains microfine titanium dioxide or zinc oxide, for their sunscreen properties, the level of the spherical powders is usually increased to between 16% and 18%, to compensate for the coarse feel of the microfine pigments. Increasing the level of spherical powders used results in greater slip, but at the expense of creaminess. Excessive amounts of spherical powders can lead to unstable pressed cakes and to break-up of the cake during use.

(d) It is common to include in two-way foundations composite materials such as those based on mica previously discussed. Aluminium hydroxide has a refractive index of 1.56 which is almost identical to that of the skin (1.55); when thin layers of aluminium hydroxide are deposited onto mica in a honeycomb structure the light-diffusing properties of the skin are simulated. This gives a composite material [4], that can be used in a two-way foundation to minimize the appearance of unevenness of the skin, such as wrinkles and blemishes, in a natural way.

Iridescence is not exhibited by titanium dioxide-coated mica where the layer of titanium dioxide is 25–50 nanometres so it can be used in two-way foundations for its light-diffusing properties [5].

(e) Spherical composites can also be beneficial in two-way foundations as they both improve the skin adhesion and minimize shine. One such material is a three-layer structure which has silica as the base material and then a layer of titanium dioxide and a further layer of silica on the top [6]. This material and others like it are particularly effective in hiding pores and reducing shine.

6.5.2 Colours to use

As in foundations and face powders, pigments such as titanium dioxide, zinc oxide and the iron oxides are the primary colours used in two-way foundations to give skin tone and coverage. These pigments have varying refractive indices and absorption characteristics and these can significantly affect the performance of the formulation. Yellow iron oxide has the lowest refractive index of the pigments and because of this has a tendency to become more transparent in colour than red or black iron oxide when wetted out with sebum or perspiration. This leads to a drift of the shade on the skin towards the red or black as the yellow loses its intensity. As the red and black iron oxides have much higher refractive indices the finish over time has a tendency to become dull. One way to overcome this is to use a very yellow shade of red oxide; another is to replace the black oxide with ultramarine blue. The colour drift towards dull red has been attributed to the intensity of the black iron oxide (refractive index 2.43), so the use of ultramarine blue (refractive index 1.54) tends to produce less colour drift because of the lower refractive index. To give satisfactory transfer of the powders to the skin the powder components should be treated to make them hydrophobic. Treating the powder ingredients also improves the wear, coverage, slip, moisturizing characteristics and overall aesthetics of the formulation. The most common treatments used are silicone, amino acid or metal soap.

6.5.3 Binders and oil components

The oily components of a two-way foundation help with the skin adhesion of the powder ingredients and act as binders to hold them together. Because of the oiliness of the skin, oils with a greasy feel should be avoided; silicone oils such as low-viscosity dimethicones, cyclomethicones and phenyl trimethicone are the best type of oils because they are odourless, and have a light feel and better water repellency than conventional hydrocarbons and esters. However they do not have the optimum skin adhesion properties so it is usual to use a mixture of esters and silicones. Popular esters for two-way foundation binder systems are cetyl octanoate, octyldodecyl myristate and octyldodecyl oleate. The skin adhesion of the formulation can be further enhanced by adding a small amount of a relatively high-viscosity oil such as lanolin oil or octyldodecyl myristate/glyceryl rosinate.

6.5.4 Two-way powder foundation

Formula VI [7]

Ingredients	*% w/w*
Dimethicone Treated Sericite	44.3
Dimethicone Treated Talc	37.2
Dimethicone Treated Titanium Dioxide, Alumina	3.5
Dimethicone Treated Yellow Iron Oxide	2.4
Dimethicone Treated Red Iron Oxide	0.9
Dimethicone Treated Black Iron Oxide	0.3
Dimethicone (20 cc)	4.4
Octyldodecyl Oleate	3.5
Squalane	3.5
Preservative	q.s.

The minimum amount of preservative, assessed as a result of challenge testing, is added to the batch and the amount of *dimethicone treated sericite* is reduced to compensate for the addition.

Method of manufacture

1. Blend together all dry ingredients and pulverize to disperse pigments into white powders.
2. Separately blend together the liquid ingredients.
3. Spray liquid ingredients onto powders, pulverize to disperse oils.
4. Colour match (see Chapter 5, pp. 163–4); see also Section 6.6, below.
5. Press into godets.
6. Test for quality.

There are a wide variety of single and combinations of pressed powder materials with which to formulate. The above suggestions for the different types of powders give a starting point for the formulator.

6.6 QUALITY CONTROL TESTING

The finished product must meet all the requirements of the original development brief and match the standards. The standards will be either laboratory or pilot plant standards in the case of new or changed formulations, and manufacturing standards in the case of an established formula. This final phase of testing is carried out on every batch that is made. Large batches should be sampled morning and evening. A complete record of results of tests which all products must undergo from the development stage, throughout production and during panel trials must be made and kept for the PIP to show that they will be safe during consumer use, as described in Chapters 18, 20–23. In addition the different forms of the coloured facial products need to be tested for shade control, colour

dispersion, 'pay-off', and pressure and breakage testing for compressed powders.

6.6.1 Shade control

Batch-to-batch variation of colour is the most frequent problem in quality control of face powders. The powder is normally checked for colour in three ways: firstly when the bulk of the powder is spread out and flattened on a white background; secondly when the powder is applied to the skin, using the correct applicator; thirdly the colour of the pressed powder surface (or in the case of a loose powder the bulk colour in the correct container) is assessed. In each case the sample being assessed is compared for shade to the standard.

When evaluating powders for colour, north light or a good artificial light duplicating natural daylight, should be used.

6.6.2 Dispersion of colour

Colour dispersion is checked by spreading the powder onto a white surface and examining under magnification. There should be no evidence of colour streaks, inadequate dispersion due to poor or inadequate pulverization or incompatibility due to bleeding of colour. Any such evidence must mean further processing of the bulk to ensure full colour development.

6.6.3 Pay-off

Pay-off should be assessed on the skin using the correct applicator. Incorrect compaction adversely affects this parameter. With too much pressure, insufficient powder will come off the cake surface and there will be insufficient adhesion of the powder to the puff. Too low a pressure will result in excess powder on the puff and a tendency for the cake to crumble and break.

6.6.4 Pressure testing

Face powders in general are pressed into godets larger than those used for eyeshadows and blushers. The pressing must be uniform, otherwise uneven pay-off can result. In addition, entrapment of air will result in an easily broken cake or under some conditions the cake erupting on the surface. The uniformity of pressing can be checked using a penetrometer. As the name implies this is an instrument which measures the penetration of a sharp metal point into the pressed powder. Readings should be taken at various positions across the cake surface.

6.6.5 Breakage testing

This test assesses the ability of the pressed product to undergo normal handling in use, and highlights any possible problems with shipment. In the case of a new

formulation it may be necessary to carry out further testing which simulates shipping conditions more closely. The breakage test is one in which the filled godet is dropped onto a wooden surface from a height of 8–10 inches. This is the best method for assessing the tendency of the pressed powder to chip or break.

6.7 BLUSHERS

Blushers, often also called rouges, are applied to the cheeks, usually over a foundation make-up, to emphasize and highlight the cheek bones. They also give structure to the face. Most are now compressed powders or emulsions, but previously they have been available as aqueous gels that contained water-soluble dyes which actually stained the skin. Since the mid-1980s powder blushers and rouges have become the preferred format. These are supplied as pressed powders in godets which are applied with a brush to the appropriate part of the face.

6.7.1 Base ingredients

The base ingredients used in blushers are the same as those used in pressed powders, as are the binder ingredients.

6.7.2 Blusher pigments

The three iron oxides and titanium dioxide are used plus several of the organic lakes:

D&C Red No. 6 Ba Lake	C I 15850:2
D&C Red No. 7 Ca Lake	C I 15850:1
D&C Red No. 30 Al Lake	C I 73360
D&C Red No. 33 Al Lake	C I 17200
D&C Red No. 34 Ca Lake	C I 15880:1
D&C Red No. 36 Al Lake	C I 12085
D&C Yellow No. 10 Al Lake	C I 47005:1
FD&C Yellow No. 5 Al Lake	C I 19140:1
FD&C Yellow No. 6 Al Lake	C I 15985:1
FD&C Red No. 3 Al Lake	C I 45430:2
FD&C Red No. 40 Al Lake	C I 16035

All the pearls can be used in blushers, although in practice the main ones used are the white and the interference ones, with limited use of the metallic and pinks. Treated pigments and base ingredients are widely used in blushers to give improved application, skin adhesion and long-wearing characteristics.

6.7.3 Pressed powder blusher formulation

Formula VII

Ingredients	*Function*	*% w/w*
Talc	To give slip	78.20
Zinc Stearate	Powder binder and gives skin adhesion	5.00
Liquid Ester	Liquid binder	5.00
Titanium Dioxide	Pigment	2.00
D&C Red No. 6 Ba Lake	Pigment	0.05
D&C Red No. 7 Ca Lake	Pigment	0.40
Yellow Iron Oxide	Pigment	1.00
Black Iron Oxide	Pigment	0.05
Methylparaben	Preservative	0.10
Propylparaben	Preservative	0.05
Imidazolidinyl Urea	Preservative	0.10
Titinated Mica Pearl		8.00
Fragrance		0.10
		100.00

Method of manufacture
As for pressed face powder.

6.7.4 Liquid blushers

Liquid blushers would use similar bases to those used for liquid foundations. They are usually sold in small tubes and are gently smoothed over the skin with the fingers to blend with the foundation make-up already applied.

6.7.5 Wax-based blushers

Wax-based blushers are available in a wind-up stick format, similar to a small deodorant stick mechanism. These are softer than a lipstick, to avoid pulling at the skin during application, but similar in formulation. Face powders and blushers are now available as mixtures of different or similar coloured balls of lightly compressed powders. The consumer blends the powder together using a large brush before applying it to the skin. A type of granulation process is used to produce these.

6.7.6 Clear blusher/emollient stick

Formula VIII

Ingredients (INCI names)	*% w/w*
PPG-3 Myristyl Ether*	73.00
Propylene Glycol	10.00
Water; Aqua	3.00
Sodium Stearate†	8.00

Ingredients (INCI names)	*% w/w*
Fragrance	q.s.
Colour	q.s.

Supplier:
*Witconol APM [Witco Organics] [8].
†Sodium Stearate C-1 [Witco Organics] [8].

One company is well known for a special type of powder product that it markets. These are baked powders which are usually seen as domed blushers or eyeshadows. The powders are formed into a thick paste which is then poured into moulds and then baked in an oven at very high temperatures. The base of the mould is often ceramic and this base is then used to stick the finished product into the compact.

6.7.7 Bronzing powders

Bronzing powders are a favourite summer product. They give a sheen and healthy glow to the skin making the consumer appear to have a suntan. These products are very similar to loose face powders, with much higher levels of pigment. One feature is that if the colour develops on the skin of the consumer this means that the pigment in the powder itself is often not fully dispersed.

6.7.8 Bronzing powder formula

Formula IX [9]

Ingredients	*Function*	*% w/w*
Polymethyl Methacrylate*	Translucent on skin, spreads easily	62.00
Mica (seracite)	Translucent on skin, spreads easily	15.00
Nylon-12†		20.00
Lithium Stearate	Adheres well to skin	3.00
Iron Oxides§		0.30
Preservatives		q.s.
		100.00

Note: The minimum amount of preservative required as a result of challenge testing is deducted from the polymethacrylate.

*BPA-500, Kobo.
†SP 500, Kobo.
§C33-115, Sun Chemicals.

Procedure
Mix well in blender. Pass through a pulverizer. Sieve, match with standard and pack.

This powder does not contain talc so does not whiten skin; it therefore eliminates a chalky appearance and suits ethnic coloured skins as well as lighter-skinned consumers for summer use.

B. EYE PRODUCTS

Eyes are the dominant features of the face, especially during conversation. They reflect emotional states as well as being indicative of our state of health. Large eyes are seen as a sign of beauty, and this has been the case for thousands of years. Inspection of ancient Egyptian statues and other artefacts clearly shows this. However, Egyptology based on scientific research has shown that the colours used in the past were based on, among others, lead compounds which we now know to be poisonous; kohl, a black colourant, was based on lead sulphide and occasionally carbon has been found. Antimony trisulphide was used in the corner of the eye to cause the eyes to shine. Eye cosmetics have been a major part of facial make-up for many centuries. It has developed from the use of black kohl around the eyes through more subtle browns, blues and greens to the modern-day products in which virtually any colour can be used and the most extraordinary effects generated. Modern eye make-up products include eye liners and pencils for the eyebrows and to contour the eyes, eyeshadows of different forms and mascara for the eyelashes.

6.8 EYESHADOW

Eyeshadow is used to give colour and gloss to the eyelids. The whole range of colours is available from pure white through pinks, blues, yellows, violets and purples to green and even black. This is the most fashion-conscious area of decorative cosmetics, the popular shades varying with the season and clothes that are in fashion at the time.

There are certain requirements for the finished formulation for any form of eyeshadow. They must all be easily applied without dragging at the sensitive skin in the eye area and, as with all decorative cosmetics, longevity of wear is a modern requirement. Greasing was an undesirable characteristic of many eyeshadows which, with careful choice of ingredients, can now be avoided. One area of particular concern in products used in the eye area is the microbiological purity of the ingredients used.

Whilst this aspect of raw material control is important in all cosmetic and toiletry products it is even more important for ingredients that are to be used around the eyes. A contaminated product, if it enters the eye, can cause blindness, so great care must be taken in the choice of the ingredients used, and their handling.

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6.8.1 Pressed powder eyeshadow

The commonest form of eyeshadows now are pressed powders. These are sold as single colours in a small compact with or without an applicator, or as collections of colours that tone together in larger compacts or tins with a number of applicators. The base ingredients used in pressed powder eyeshadows are very similar to those used in face powder. Talc is the main constituent with zinc stearate to act as a powder binder and also give skin adhesions. Liquid binders are widely used and can also impart additional properties to the formulation. Moisturizing agents can be included to give added benefits. Ingredients such as silicates and carbonates are not as widely used in eye powder products due to their drying effect on the skin and harsh gritty feel. Fragrances should never be used in eyeshadows.

Almost all colourants are available for use in the eye area in the EU, but the regulations in the USA prohibit the use of most organic colours around the eye area. The exceptions are the lakes of FD&C Yellow No. 5, FD&C Blue No. 1 and FD&C Red No. 40. As a consequence of this the main red pigment used in eyeshadows in the US market is Carmine.

Pearlescent ingredients find one of their main uses in eyeshadows, where shine is one of the requirements. The same restriction on the use of organic pigments around the eye area applies to pearls, so any pearl containing an organic colourant, apart from those mentioned above, would also be prohibited in eye cosmetics in the US market. Some novel effects can be achieved by using a mixture of pearls. Applying an interference pearl on a black or very dark background accentuates the interference colour. Incorporating these pearls in an eyeshadow already containing a black interference pearl [10] results in stunning dramatic effects.

The use of bismuth oxychloride pearls in pressed eyeshadows has reduced over recent years, but they can significantly improve the pressing characteristics of the formulation. Using instead very high levels of mica-based ingredients reduces the pressability of the system, leading to a higher level of binder being required. This in turn can lead to further development of the pigments and in hard cakes which give little pay-off and grease up during use.

6.8.2 Pressed-powder eyeshadow formulation

Formula X

Ingredients	*Function*	*% w/w*
Talc	Imparts slip/base	57.75
Zinc Stearate	Powder binder and gives adherence to the skin	5.00
Liquid Ester	Liquid binder	7.50
Ultramarine Blue	Pigment	4.00

Ingredients	*Function*	*% w/w*
Chrome Oxide Green	Pigment	3.00
FD&C Yellow No. 5 Al Lake	Pigment	0.50
Colorona Dark Blue*	Coloured Pearl	12.00
Timiron MP 115*	White Pearl	10.00
Methylparaben	Preservative	0.10
Propylparaben	Preservative	0.05
Imidazolidinyl Urea	Preservative	0.10

*Merck KGaA.

Method of manufacture

1. Place the talc, zinc stearate, pigments and preservatives in the ribbon blender and mix for 20–30 minutes.
2. Pass the mixture through the hammer mill until the pigments are fully dispersed.
3. Return the mix to the ribbon blender and spray on the liquid ester, mix for 15–20 minutes.
4. Pass through the hammer mill again until the oil is fully dispersed.
5. Return to the ribbon blender again and tumble in the Colorona Dark Blue* and Timiron MP 115*, mix for 15–20 minutes.
6. Sieve if required and place into lined storage bins.

With the fashion for very high pearl products some companies sell pearl alone in small pots and this can be applied with the fingers or an applicator to the eyes or cheeks.

6.8.3 The properties and quality control of finished pressed-powder products

(a) Dispersion of pigments

The methods of manufacture used to produce pressed-powder eyeshadows and blushers are the same as those used for similar face products (see Section 6.6). Dispersion of the pigments is critical; they are often used at higher levels in powder eyeshadows and blushers than they are in face powders, so undispersed pigment would show up as streaks on the skin of the consumer.

Pearlescent pigments are also used at higher levels in these products, leading to a requirement for higher binder levels. This can lead to reduced flow characteristics and difficulties when pressing the powders.

(b) Matching of shade

It is also important to check that every batch of a specific shade is the same as previous batches of the same shade. This is done at all stages of production by

comparing the product produced with a batch previously accepted as a standard for the particular shade being produced. This is another reason for ensuring full pigment and oil dispersion, as the shade will darken with further processing, therefore affecting the final shade. Usually a small portion of the product is taken after the oil and pigments have been dispersed, but before adding any pearls; a proportional amount of the pearls to be added is then mixed with the sample and the resulting mixture compared to the standard. Any additional pigments required can then be milled in without damaging the pearls in the finished product.

When comparing the colours of the manufactured batch and the standard it is vital to check that the colours are comparable both in mass tone and on the skin. There should also be no metamerism, so they should be checked under different light sources.

(c) Powder-cake stability

Another aspect of the product that can be adjusted at the time of manufacture is the stability of the pressed cake. By pressing the product to a predetermined pressure and then dropping the pressed godet from a set height on to a standard surface (usually a bench top), the stability of the finished cake can be determined and more oil or powder binder added if required.

If too much binder has been added this becomes apparent by testing the pressed cake with an applicator or finger to see if the pay-off is correct and no greasing-up occurs. If necessary more base can be added to compensate for the excess oil and the powder colour re-matched.

(d) Bulk density

The bulk density of any powder is also important. It can significantly affect the fill of the final pack or godet and should always be checked once the product has been completed.

(e) Microbiological check

One final check must always be carried out on the completed powder before it can be allowed to progress to the filling or pressing stage; this is a microbiological test to ensure that no contamination has occurred during manufacture.

6.8.4 The mechanics of compressing the powder

Pressed powders are produced by compacting the loose powder into a shallow metal pan or dish (godet). This is achieved by either forcing the powder down into the godet by a punch exerting pressure from the top or lifting the filled godet up towards a fixed plate and exerting pressure from below. The first type

of technique is best demonstrated by a Kemwall press. This consists of a circular table with holes, into which the godets are neatly fitted, so that a separate plate is required for each different shape of godet used. The godets are fed either by hand or mechanically into the plate. The plate can rotate and the godet comes under the hopper that contains the powder. This hopper is fitted either with a wire-type stirrer similar to that used in the loose powder filling machine or with a vibrator that shakes the powder down into the godet. The stirrer or vibrator is linked to the movement of the base plate so that when the empty godet comes underneath the hopper the required amount of powder is transferred. The godet then passes under the punch where the powder is compressed by an appropriately shaped punch (separate punches are required for each godet shape used). The pressed powder then moves to the next station and is subsequently ejected. If the metal punch were to come into direct contact with the powder it would soon become clogged, also no air would be able to escape from the powder, so a thin nylon mesh is stretched beneath the punch. This ribbon must be of a suitable weight and mesh size so as not to interfere with the pressing process by becoming stuck between the punch, godet and plate, or stopping the air escaping. It is this ribbon that gives the 'pattern' that we see on pressed powders. The ribbon could also easily become clogged so a fresh piece is used for each pressing by attaching rolls of ribbon to the machine in such a way that it is automatically rolled on after each pressing.

The second type of pressing mechanism is best demonstrated by the Ve-Tra-Co, an Italian powder press that presses many godets at once. This machine consists of two plates and a punch. The first plate holds the godets, the second has holes the exact shape of the godets to be pressed and this holds the powder; the head/punch then covers the powder and the godets are pushed up from below, compressing the powder against the punch. The powder is stored in a hopper but is scraped over the empty godets in their wells in the base plate by the operator so no stirring mechanism is required. Again thin sheets, or a large roll of nylon mesh, are used between the powder and the head to allow the air to escape and the pattern on the surface would be identical to that produced by the Kemwall. Once pressing has been completed the filled godets are pushed to one side where a second operator stacks them into trays for storage. Ve-Tra-Co are much better for pressing highly pearlized shades as the reduced flow characteristics of these products are not relevant to the pressing process.

The Kemwall and the Ve-Tra-Co are not the only pressing machines available but they are the most widely used. New processing equipment is now available, from Japan, that enables 'pressed powders' to be formed from a slurry. No actual pressure is applied to the powders, which are mixed with a volatile solvent, such as isopropyl alcohol, to form a slurry. This is then filled under vacuum by injecting the slurry into the base of a plastic vacuum-pack instead of godets. The solvent is then drawn off and the powders remain. Totally different types of formulations are required with these systems, but their one

big advantage is that many shades can be filled at one time, the shapes that can be achieved are infinite, and the presentation is no longer bound by the restrictions of metal godets. It has also been found that lower levels of pearls can be used to achieve comparable effects with this equipment because the use of other materials that detract from the performance of the pearls can be eliminated.

It was fashionable at one time to produce pressed powders that contained several different colours in the same godet. These products require careful formulating to ensure that the colours used together have the same pressing characteristics. These products can be produced on either Kemwalls, by using a divided hopper with one shade in each segment, or on specially modified Ve-Tra-Cos; the new Japanese method of production using slurried powders enables many colours to be filled into the specially designed vacuum pack giving the same overall appearance. The major problem was that the shades chosen to go together were usually a matt and a pearly shade to enable the consumer to blend them on her skin, which had different flow and pressing characteristics and needed careful adjustment to achieve cakes that were not too hard on one side and too soft on the other. Cross-contamination of the colours was also a problem, which is reduced by use of the slurried method of manufacture.

Using the Ve-Tra-Co it is possible to produce domed rather than flat cakes. This requires the use of a specially designed top plate and is best done on small godets. The powders need to be adjusted slightly to ensure that they can withstand the extra stresses placed on them by this shape. Very highly pearlized shades are not recommended as they tend to shear across the top of the dome.

By engraving the punches of a Kemwall or the top plate of a Ve-Tra-Co patterns can be embossed or indented on the surface of the powder. The designs must be carefully chosen, however, and sharp geometric patterns avoided. The edges of the design should be as smooth as possible to prevent sharp corners as this can lead to the pattern shearing away from the rest of the powder. Again very high pearl shapes are not recommended as the platelet structure of the pearls can cause the pattern to break up.

6.8.5 Cream eyeshadow

This has to be of the correct consistency, such that it can spread easily on the skin, but not be greasy or crease during wear, and the pigments or pearls in the pot or tube in which they are sold remain suspended. This means that the thixotropy of the system is critical. The word 'cream' is somewhat of a misnomer as these products are rarely emulsions, being anhydrous systems, mixtures of oils thickened with either waxes or clay gelling agents. The products have high viscosity, so the pigments and pearls do not sink or float, but the products are thixotropic when squeezed from the tube, so allowing easy application.

6.8.6 Cream eyeshadow formulation (no. 1)

Formula XI

Ingredients	*% w/w*
Pigments	approx. 20.0
Petroleum Jelly, Petrolatum	to 100.0
Isopropyl Myristate	36.0
Liquid Lanolin	4.0
Microcrystalline Wax	8.0
Beeswax	4.0

Method of manufacture

1. Disperse the pigments in the petroleum jelly and isopropyl myristate.
2. Heat and mill.
3. Add remaining ingredients.
4. Heat mixture to 70–75°C and mix until homogeneous.

6.8.7 Cream eyeshadow formulation (no. 2)

Formula XII

Ingredients		*% w/w*
A	Magnesium Aluminium Silicate	4.3
	Water; Aqua	63.7
B	Propylene Glycol	1.7
	Acetylated Lanolin	1.7
	Mineral Oil (and) Lanolin Alcohol	5.1
	Petrolatum	8.5
C	Pigments/Pearls	15.0
	Preservatives	q.s.

Method of manufacture

A. Add the magnesium aluminium silicate to the water slowly, agitating continually until smooth.

B. Mix the propylene glycol, acetylated lanolin, mineral oil and lanolin alcohol, and petrolatum. Add B to A and heat the mixture to 70°C. Mix until uniform.

C. Add the pigments, pearls and preservatives and mix until they are fully dispersed.

6.8.8 Eyeshadow sticks

These are manufactured using similar ingredients and methods of production to lipsticks (see below p. 213) and other stick products.

6.8.9 Stick eyeshadow formulation

Formula XIII

Ingredients	*% w/w*
Candelilla (Euphorbia Cerifera) Wax	7.7
Beeswax (Cera Alba)	5.4
Ozokerite wax	3.0
Isopropyl Myristate	5.0
Isopropyl Lanolate	10.0
Castor (Ricinus Communis) Oil	40.0
Glyceryl Oleate	8.0
Antioxidant, e.g. BHA or BHT	0.2
Liquid Lanolin	3.4
Pearlescent pigments	17.3
	100.0

Method of manufacture

1. Mix all the materials together with the exception of the pearlescent pigments.
2. Heat with stirring to 80–85°C.
3. When clear add the pearlescent pigments.
4. Mix thoroughly and mould.

The base can be modified to make it softer and less greasy. The castor oil is often replaced with another oil that has a nicer skin feel. The addition of 'dry feel' esters such as Cetyl Octanoate can significantly reduce the greasy feel of these products.

6.9 MASCARA

Coloured pigments mixed with fats and waxes have been used since ancient times to enhance the appearance of the eyelashes. Nowadays the colour, thickness and length of eyelashes are enhanced by using suspensions of coloured pigments in a film-forming medium to which lengthening ingredients such as nylon flock can be added.

Colourless mascaras were popular at one time; these were just a transparent film-forming resin in a suitable base, often a gel based on Carbomer, without any pigments. This dried on the lashes to give a transparent film.

Various types of mascara exist, all having the same requirements: safe, non-irritating, smooth and lump-free to give good application, quick-drying, should not smudge during wear, should not flake, should not run when wetted ('Love Story' proof), give even coverage on the lashes, be easy to remove without hurting the delicate skin round the eye. Most formulations are compromises between these requirements.

6.9.1 Cake mascara

Cake mascaras were the first type of product to appear on the market in the 1920s and are still available today. Application is by wetting the brush and rubbing it onto the cake to pick up product, and then using the brush to transfer the product to the lashes. Most formulations of this type tend to have little water resistance and will smudge if the wearer cries or rubs her eyes. This is because they are based on a soap/wax/pigment blend which is emulsified when the wet brush is applied to the surface.

6.9.2 Cake mascara formulation

Formula XIV

Ingredients	*% w/w*
Triethanolamine Stearate	40.00
Paraffin Wax	30.00
Beeswax (Cera Alba)	12.00
Anhydrous Lanolin	5.00
Black Iron Oxide	13.00
Preservative	q.s.

Method of manufacture
Melt all the waxes together, add the other ingredients and mix until homogeneous. The product can then be extruded or cast straight into the godets. Alternatively it can be milled to form a powder and pressed into a godet.

6.9.3 Cream mascaras

The most common type of mascara used today is the cream-type. This type is packaged in small thin plastic bottles with an integral applicator (or wand) incorporated into the cap. The formulations are either oil-in-water emulsions with a film-former incorporated, to give water and smudge resistance, or totally anhydrous, to give totally waterproof products.

Many of the film-formers used come from hair spray or polish technology. Commonly used film-formers are: PVP, PVP/VA copolymer, PVP/hexadecene copolymer, PVP/dimethylaminomethacrylate copolymer, PVA, ammonium acrylates copolymer, carboxy methyl chitosan.

When including film-formers the formulation and manufacturing procedure must be adjusted to take account of the requirements of the film-formers for heat stability, neutralization and solubility. The benefit of any film-former can be negated if care is not taken with the other ingredients. There is no point adding them if the other ingredients are going to promote smudging by either disrupting the film or being in such a state on the lashes that the mascara can be

rubbed off. The use of ingredients such as cyclomethicone will help with evaporation and drying of the product once applied, but incorporating a silicone gum, which would aid application because of its exceptional slip, may increase the risk of smudging because this type of silicone never completely dries out. Other ingredients can have a similar effect on the characteristics of the finished product so all additions must be carefully monitored.

Many colours can be used in mascaras; most products however are black, brown, brown/black or blue. To give these shades the iron oxides are widely used – predominantly black iron oxide. Blue mascara can be produced using either ferric blue to give a navy shade or ultramarine blue to give a brighter, lighter shade. The incompatibilities of the latter two pigments must be considered when formulating with them. Ferric blue is unstable in alkali media and ultramarine blue will give off hydrogen sulfide if exposed to acid pH.

6.9.4 Formulation for a basic cream mascara

Formula XV

Ingredient	*INCI names*	*% w/w*
Oil phase		
Stearic Acid		8.00
Cetyl Alcohol		2.50
Beeswax	Cera Alba	7.50
Microcrystalline Wax		15.00
Cyclomethicone		6.00
Water phase		
Demineralized Water	Water, Aqua	to 100
Triethanolamine 99%	Triethanolamine	4.40
Lecithin		0.50
Disodium EDTA		0.10
Film-former		8.00
Panthenol		1.50
Hydroxyethyl cellulose		0.50
Ultramarine Blue	C I 77007	8.00
Black Iron Oxide	C I 77499	2.00
Preservatives		q.s.

Method of manufacture

1. Place the water into the main vessel and add the lecithin and, using high shear, disperse the pigments.
2. Add the hydroxyethyl cellulose and disperse.
3. Add the disodium EDTA and the film-former. With stirring heat this phase to 75°C.
4. Place the stearic acid, cetyl alcohol, beeswax and microcrystalline wax into a side vessel and heat to 85°C; mix until homogeneous, cool to 75°C.

5. Pump the oil phase into the water phase and mix together using high shear. When smooth and homogeneous add the triethanolamine; continue mixing until emulsification is complete.
6. Commence cooling and change to paddle stirring.
7. When the temperature has fallen to 40°C add the preservatives. Continue cooling to 30°C; Quality Control, and when approved pump into storage drums.

6.9.5 Waterproof mascaras

The best way to make something waterproof is to exclude water from it totally and use ingredients that are insoluble in water. Waterproof mascaras are therefore usually solvent-based systems. The basic solvent has to be volatile to give a quick-drying formulation.

A branched chain or isoparaffin is often used as the main solvent. The film-forming ingredients tend to be high-melting-point waxes that result in a stiff but sometimes brittle film. Incorporating low-melting-point waxes such as beeswax can lead to smudging as the resultant film can become soft and therefore is easily disturbed. It is still possible to incorporate more traditional film-formers to increase the smudge resistance, but these must be compatible with the solvent system.

This system can be thickened in two ways. Aluminium Stearate is well known for its oil-thickening properties and the incorporation of a low level of this will give the required viscosity. Alternatively the use of pre-gelled solvent, where an organically modified clay has been incorporated into the solvent, can give viscosity to the whole product.

Silica is a useful low refractive index filler often used in waterproof mascaras; it aids the transparency of the product, allowing the pigments to impart maximum colour to the lashes. It will also thicken the system.

6.9.6 Formulation for a waterproof mascara

Formula XVI

Ingredients	*Function*	*% w/w*
$C_{10\text{-}11}$ Isoparaffin	Solvent	52–52.50
Microcrystalline Wax	Film-forming wax	12.00
Hydrogenated Castor Oil	Film-former	5.00
Candelilla Wax	Film-forming wax	5.00
PVP/Hexadecene Copolymer	Film-forming polymer	5.00
Petroleum Distillate (and) Stearalkonium Hectorite	Pre-gelled solvent	8.00
Preservative		q.s.
Black Iron Oxide	Pigment	5.00

Ingredients	*Function*	*% w/w*
Mica and Black Iron Oxide (Black Mica – Merck KGaA)	Pearl	5.00
Silica	Filler	2.00

Method of manufacture

1. Melt the waxes in a stainless-steel jacketed vessel, heat to 85°C.
2. In a separate jacketed vessel warm the solvent to 50°C, disperse the pigment, pearl and silica using high shear. Also disperse the polymeric film-former and add the preservatives.
3. When both 'phases' are homogeneous add the molten waxes to the solvents and mix using high shear.
4. When product is homogeneous change to anchor or gate stirring and commence cooling.
5. Cool to 40°C, sample and test for quality.

Waterproof mascaras are applied in the same way as cream mascaras, using a slim bottle with a brush attached to a wand that forms part of the cap. However the solvents used in waterproof mascaras can attack the plastic usually used to make the wands. This manifests itself by the wand lengthening, and due to the restricted space available, bending as it absorbs the solvent. Consequently special wands must be used for these products.

When developing any mascara it is also important to consider the brush that will be used to apply it, and the wiper unit in the top of the bottle. These must work together so that excess mascara is removed from the stem and brush; however, if too much is removed there will be poor application. The shape of the wiper can also affect the product during use. If the excess mascara it removes from the brush and stem accumulates in the wiper, rather than falling back into the bottle, it will eventually spill out over the top, resulting in product collecting around the thread and outside of the bottle. The shape of the brush also contributes greatly to the ease of application and final appearance of the product on the lashes.

6.10 EYELINERS

Eyeliners are applied to the rims of the eyelids following the eyeshadow to accentuate the shape of the eyes. There are two main types. Liquid eyeliners are marketed in slim bottles, similar to those used to apply mascaras, with the mascara brush replaced by a thin pointed brush, or in a pen-type format, in which the product is incorporated in a rigid bottle to which is attached a nib. Eyeliners are also available as pencils, which can be sharpened to allow a line to be drawn, the traditional Kohl pencil being the best known of these.

All eyeliners must be easy to apply without dragging on the delicate tissue around the eye. Smudge-proof or water-resistant, they should not flake or contract too tightly as the film dries, causing pulling of the tissue, and should be easy to remove.

6.10.1 Liquid eyeliners

Liquid eyeliners are suspensions of pigments usually, or though not exclusively, in an aqueous base which also contains film-forming agents similar to those used in mascaras.

6.10.2 Formulation for a liquid eyeliner

Formula XVII

Ingredients	*Function*	*% w/w*
Demineralized Water		75.70
Lecithin	Pigment wetter	0.30
Propylene Glycol	Humectant	2.50
Acrylic/Acrylate Copolymer	Film-former/thickener	5.00
Triethanolamine	Neutralizing agent	1.00
Ammonium Acrylate Copolymer	Film-former	5.00
Preservative		q.s.
Black Iron Oxide	Pigment	5.00
Mica and Black Iron Oxide*	Pearl	5.00

*Black Mica – Merck KGaA.

Method of Manufacture

1. Place the water into the mixing vessel, add the lecithin, preservative and propylene glycol.
2. Disperse the pigment and pearl using high shear.
3. Add the ammonium acrylate copolymer and the acrylic/acrylate copolymer, change to slow speed stirring.
4. Slowly add the triethanolamine to neutralize the acrylic/acrylate copolymer and thicken the product.

6.11 EYE PENCILS

Pencils can be used for the application of eyeshadow or eyeliner. Long thin pencils with a hard 'lead' would be used for eyeliners, and shorter fatter pencils with a softer 'lead' that would not pull at the eyelid for eyeshadows. Whichever type the leads are blends of waxes, hardened fats, fats, oils, pigments and pearls along with antioxidants and preservatives, with the pigments and pearls being evenly dispersed throughout. The texture of the lead can be modified by the waxes used, higher levels of hard, high-melting-point waxes resulting in harder leads. The leads are produced by extrusion or moulding. The wood cases are precut with grooves lengthways; after moulding or extrusion the lead is placed in the groove of one piece of wood and a second, with glue already applied to the edges, is positioned on top and the two are pressed together. The lengths are then cut and finished by sharpening one end and applying a colour-coded cap to

the other. This requires specialist equipment so the production of pencils is restricted to a few specialist companies who often produce pencils and nothing else.

Similar characteristics are required for pencils. They should be smudge-resistant, non-flaking, easy to remove and in the case of eyeshadow pencils should not crease during wear. The latter is difficult to achieve as the level of oils in these softer products is higher, which increases the tendency to crease. This can be overcome to some extent by basing the pencil lead on silicones rather than traditional oils, so that, once applied, the silicone will evaporate, leaving behind a powdery product on the eyelid which will have less tendency to crease.

6.11.1 Formulation for wooded eye pencil, moulded wax type

Formula XVIII

Ingredients	*INCI name*	*% w/w*
Beeswax	Cera Alba	24.0
Ozokerite Wax	Ozokerite	24.0
Propyl Stearate		9.0
Lanolin		3.0
Castor Oil	Castor (Ricinus Communis) Oil	25.0
Mineral Oil	Mineral (Paraffinum Liquidum) Oil	15.0
Antioxidant – e.g. BHT		q.s.

C. LIP PRODUCTS

Lip products have been used since ancient times to enhance the appearance of the lips by imparting colour and gloss, and by re-defining the outline of the lips. The three most common products used to achieve this are lipsticks, lipglosses and lipliners, of which lipsticks are the most common. Many women will wear lipstick even if they use no other make-up. If applied skilfully lip products can significantly alter the apparent facial characteristics of the wearer. They can enable the user to adjust the outline of her lips and modify the external perception and visual impact of the mouth form and texture. Lipliners can accentuate the outline and lipglosses increase the glamorous effect.

A modern range of lipsticks will include many shades to suit all skin types and colourings, from true reds through rose, pink and coral to taupe and browns. Shades vary with the fashion trends that are popular at any one time, but a lot of women choose one colour and stick to it for many years.

6.12 TECHNICAL REQUIREMENT AND RAW MATERIALS

6.12.1 Technical requirement

During application the product must be smooth, but not greasy; it should adhere well to the skin of the lips and, during wear, the colour should remain the same

and not smear or run. It should remain on the lips as long as possible and not transfer from the lips to other surfaces such as cups (or shirt collars). With lipsticks it is important that the stick should be strong enough so that it does not break when force is applied; for example during application. However, too rigid a stick will be difficult to apply and would pull at the skin. The stick should be free of blemishes and airholes or pinholes. The properties of the stick should remain consistent during its life and it is important that with time the formulation remains consistent and that particles of wax or oil should not form on the surface, a property called 'sweating'. These products are regularly carried around by the user and, as such, can be subjected to a variety of temperatures. The stick should not be affected by these changes of temperature and should retain its applications characteristics at all times.

6.12.2 Raw materials

As we are always licking our lips, a large proportion of the product we place on them we actually eat; therefore the finished formulation has to be made from ingredients that are edible or suitable for ingestion and which have an acceptable taste and smell.

There are three main types of raw materials used in lip products: oils, waxes and colours, the ratios varying between the different product types.

(a) Oils

Any **oils** used in lip products must have a smooth feel and not drag when applied to the lips. They should impart gloss and act as a suspending medium for the pigments and pearls. They should also have a pleasant, or preferably no, taste or odour and not be subject to rancidity.

Castor oil is the main oil used in lipsticks. It is very thick and maintains this viscosity when hot, making it ideal as a suspending medium for the colouring agents. It has a reasonable taste provided a good quality is used. Unlike most other oils castor oil is soluble in alcohol and its associated surface activity. This and its high viscosity means it is well suited to the wetting and dispersion of pigments, a function as we will see that is vital during the production of lipsticks, lipglosses and pencils. Beeswax, one of the commonly used waxes, is partially soluble in castor oil producing an even more viscous but tacky system, which confers drag to the finished formulation and helps prevent the product from 'creeping' or 'bleeding' into the small fine lines around the lips.

The main disadvantage in the use of castor oil is its inherent instability. This can be overcome, however, with the inclusion of a small amount of antioxidant such as butylated hydroxy toluene or anisol (BHT and BHA). Without these the odour and taste becomes offensive as the material oxidizes and finally becomes rancid.

Oleyl alcohol is a widely used co-solvent in lipsticks. It aids pigment dispersion and has a pleasant skin feel and virtually no taste or odour.

Many liquid esters can be used in lipsticks and other lip products, including **isopropyl palmitate** and **isopropyl myristate**, although use of these two is limited as many holders are made of polystyrene, which they both attack. Many of the long-chained esters available today have useful properties in lipsticks. They are often quite thick and maintain this viscosity to a certain degree with increasing temperature, therefore aiding in pigment dispersion. The use of liquid esters in lip products contributes greatly to the overall feel of the final product. Many of the newer esters have soft silky application characteristics and can reduce the greasy feel of the castor oil.

The use of **mineral oil** in lip products is not recommended without a co-solvent, such as **isocetyl alcohol**, as it is insoluble in castor oil, and without the co-solvent an unstable system results with the mineral oil tending to sweat out.

Petroleum jelly is a blend of mineral oil and paraffin wax; its use in lipsticks is limited but it is widely used in lipglosses.

Polybutene is also one of the major constituents of lipglosses as it is extremely sticky, very thick and almost tasteless.

Many other oils can be added to lip products to give specific effects, for example sunscreens and fragrances or flavours. The stability of any ingredients must be fully tested, particularly their resistance to repeated heating, sometimes to quite high temperatures. This is especially important for the fragrance or flavour.

(b) Waxes

Waxes are considered as unctuous solids with different levels of lustre and plasticity. In lip products they are used to give structure to lipsticks and lipliners; they also help them to keep their form in high temperatures. All the waxes used must be flexible but not brittle and have the ability to retain oils in their crystal structure. A combination of hard and soft waxes is used to give the balance of application and rigidity required by the consumer.

Waxes can be divided into two main groups, **natural** and **synthetic**. Natural waxes are further subdivided into hydrocarbon waxes such as paraffin wax, microcrystalline waxes, mineral waxes such as ozokerite, ceresine and montana, vegetable waxes, candelilla, sugar cane, carnauba, Japan and rice, and animal waxes such as beeswax and lanolin.

Paraffin waxes are mainly linear hydrocarbon blends with a molecular weight of between 300 and 400 g/mole, melting points between 45°C and 70°C and a microcrystalline structure. They are translucent, odourless, tasteless and inflexible but have an oily feel. They are obtained through the distillation of crude oil and represent the higher boiling fractions. Following distillation they are hydrogenated. Being hydrocarbon they have poor solubility in castor oil and high levels of usage can result in an unstable crystalline system.

Microcrystalline waxes are long-chained saturated hydrocarbons (mainly linear) with a molecular weight between 500 and 700 g/mole. Their melting points lie in the range of 60°C to 120°C; this allows for a variety of levels of hardness, plasticity, adhesiveness, brilliance and oil absorption. Microcrystalline waxes cannot be distilled without decomposition; they therefore come from the heavy ends of the distillation of crude oils through different separation phases with a solvent. They have small crystal size and absorb oil very well thus helping to maintain the crystal structure of the lipstick and prevent sweating. Their main disadvantage is that they have only limited solubility in castor oil.

Mineral waxes such as **ozokerite** and **ceresine** were originally obtained from bituminous products. They are brown when crude and must be bleached to give a cosmetically acceptable grade, but they have been replaced by blends of microcrystalline waxes and other oil products which still go by the names of ozokerite and ceresine waxes.

Vegetable waxes are present in the plants for protection, their main function being to reduce evaporation of water from the surface of the leaves.

Candelilla wax is extracted from *Euphorbia cerifera* and *Euphorbia antisiphilitica* plants which are found in the rocky deserts of Mexico. Candelilla wax consists mostly of hydrocarbons and esters and has a melting point of approximately 70°C. It is a very hard, brittle brown wax with a characteristic odour and is used to confer some strength to the bullet.

Carnauba wax which is extracted from the leaves of the Brazilian palm tree, *Copernica prunifera* (Tree of Life), is obtained by cutting, then drying and beating the leaves. There are three colours, yellow, grey and brown. It is a hard, brittle wax comprising mostly esters (84–85%), with a high melting point of about 85°C, and is used to give rigidity to the stick. As it cools it contracts and therefore aids in moulding, by shrinking the stick away from the mould's surface allowing easy removal.

Japan wax is obtained by squeezing the berries of the Sumac tree. It is a brittle glyceride wax with a high molecular weight and a melting point of between 50°C and 56°C, an oily feel and a fatty odour. Its main cosmetic use is in pencils.

Rice wax results from the hydrogenation of crude rice oil. It is purified by washing in methanol and chloroform. It consists mostly of esters and has a melting point of about 75°C. It is a hard yellow wax with an unpleasant odour.

Sugar cane wax is a by-product of sugar production. It is very hard and has excellent crystallization. It is primarily esters (78–82%).

Animal waxes. Beeswax is probably the best known animal wax. It is secreted by the abdominal glands of the bee and then chewed by the worker bees in order to build the cells in the hives. The colour of crude beeswax varies according to the plants which the bees feed upon, the quantity of residual bee glues and the age of the cell. Yellow and white beeswax are obtained by precipitation of impurities on a water layer, filtration with activated carbon and sun or chemical bleaching. The activated carbon also partially eliminates the odour and

pesticides. Beeswax feels oily and flexible, it has good plasticity, a very fine crystal structure and pleasant honey-like odour. It comprises approximately 70% fatty esters with 10–13% hydrocarbons. Beeswax is one of the softer waxes used in lipsticks, with a melting point around 50–55°C; it does not confer much rigidity to the system but is widely used to help the harder waxes in application. Too much beeswax in a formulation can lead to poor crystallization and poor stability of the system, and a pronounced dragging effect on application.

Lanolin or wool wax is classified as a wax although it is really a fat. It is extracted from wool with a water–detergent blend via centrifugation and then treated with an alkali to eliminate free acids and other matters. It is then bleached, deodorized and dried. Lanolin consists mainly of aliphatic alcohol esters, stearols and triterpenic alcohols.

(c) Colours

The colour of the lipstick is the main reason for its purchase. The most popular shades are variations on types of red, from pinks through to true reds. Many lipsticks also contain pearls to give a high degree of gloss to the lips. The lips can either be coloured by covering them with a suspension of pigment or by staining them with a dye dissolved in the lipstick.

The main pigments and lakes used in lipsticks are:

D&C Red No. 6 Ba Lake	C I 15850:2
D&C Red No. 7 Ca Lake	C I 15850:1
D&C Red No. 6 (Sodium salt)	C I 15850
FD&C Red No. 3 Al Lake	C I 45430:1
FD&C Yellow No. 5 Al Lake	C I 19140:1
FD&C Yellow No. 6 Al Lake	C I 15985:1
FD&C Blue No. 1 Al Lake	C I 42090:2
D&C Yellow No. 10 Al Lake	C I 47005:1
D&C Red No. 33 Al Lake	C I 17200
D&C Red No. 21 Al Lake	C I 45380:2
D&C Red No. 27 Al Lake	C I 45410:2
D&C Red No. 28 Al Lake	C I 45410:1
D&C Red No. 30 Al Lake	C I 73360
D&C Red No. 36	C I 12085
D&C Orange No. 5 Al Lake	C I 45370:1
Black Iron Oxide	C I 77499
Red Iron Oxide	C I 77491
Yellow Iron Oxide	C I 77492
Titanium Dioxide	C I 77891

The use of Chrome Oxide (C I 77288), Chrome Hydroxide (C I 77289), Ferric Ferrocyanide Blue (C I 77510), Ultramarine Blue (C I 77007) and D&C Red

No. 34 Ca Lake (C I 15880:1) is permitted for products to be sold within the EU but they are banned in lip products in the USA.

In some lip products, dyes, known as eosin dyes, are used to impart a stain to the lip. In the past this was the only way to achieve a 'long-lasting' effect. However the resulting stain was often a very different colour from that of the lipstick when originally applied. Usage of dyes in this way has declined in recent years owing to the known sensitizing potential of the dyes used. The main staining dyes used in lipsticks are:

D&C Red No. 21	C I 45380:2
D&C Red No. 27	C I 45410:1
D&C Orange No. 5	C I 45370:1

The mica-based and bismuth oxychloride pearls are widely used in lip products to impart lustre to the lips. Bismuth oxychloride pearls also improve moulding of the bullets.

(d) Other additives

1. **Antioxidants** are required, as already seen, to protect the castor oil from oxidation. Other unsaturated materials, vegetable oils or ingredients prone to oxidation will also require their addition to the formulation. Only a very low level is needed, typically 0.01–0.05%. BHT, BHA and vitamin E are the most common, but oil-based blends are now commercially available which contain mixtures of these with propyl gallate, ascorbyl palmitate (vitamin C palmitate) or citric acid.
2. **Preservatives.** The likelihood of bacteria or moulds actually growing within the lipstick is low as it is usually totally anhydrous; however if the product were applied to the lips after drinking a sweet drink there is a possibility that the surface could become contaminated, leading to microbiological growth. It is therefore recommended that a small amount of preservative be included in the formulation. The preservative used must be suitable for ingestion. Consequently the most commonly used are methyl and propylparaben at levels ranging from 0.05% to 0.20%.
3. **Moisturizer addition.** Many recent products claim additional benefits for the lipstick. 'Moisturizing' lipstick is a popular description; the fact of applying an oily film to the lips which should prevent them drying out should be sufficient to justify a moisturizing claim, although some lip products can actually dry out the lips if the wrong blend of waxes and esters or oils is used.

   It is now possible to incorporate into this totally anhydrous system traditional **moisturizing agents.** It should be realized that the majority of these are usually incorporated into the water phases of creams and lotions so special technology is required to incorporate them into a lip product. This is

usually achieved by forming a water-in-oil emulsion, where the external oil phase takes up 99% of the product. Using special emulsifiers, known moisturizing agents such as hyaluronic acid can be incorporated.

4. **UV protection** claims are also popular; the mere fact of covering the lips with a pigment film will offer some protection from UV light, but increasingly high levels of traditional UV absorbents are now being included. The use of both microfine **titanium dioxide** and **zinc oxide**, sometimes in conjunction with organic sunscreens, has led to very high SPF claims for lip products in some markets. These products have particular uses as 'beach' products or products for use when skiing.
5. Modern lipsticks make the claim of 'long-lasting'. Advertisements for them show no lipstick transferring to the glass or coffee cup, or more importantly perhaps clothes. The traditional way, as previously mentioned, of achieving a 'long-lasting' claim is to incorporate one of the eosin dyes. It is now becoming possible to incorporate **film-forming agents** into the base to achieve the long-lasting effect. Most of these are water-based so use is made of the technology used to incorporate the moisturizers.
6. The use of **treated pigments** in the formulation can also improve the wear characteristics, by increasing the affinity of the pigments for the skin. **Encapsulated pigments** can have a similar effect.
7. **Silicone waxes**. It is rare to incorporate silicone oils into traditional lipsticks. In castor oil-based lipsticks, silicones can have a very detrimental effect on the formulation. Low-viscosity silicone oils are used as mould release agents in automatic moulding processes, but the incorporation of too much contaminated bulk or too many recycled bullets causes some very strange surface effects on the bullets, particularly in highly pearlized shades. It is however possible to incorporate small amounts of silicone waxes into traditional systems.
8. Most of the new lipsticks launched recently are based on **volatile silicones**. The volatile component is used to deliver to the lips a film incorporating the pigments; this results in a very long-wearing product. Unfortunately the traditional lipstick mechanism is not suitable for a product of this type as it allows the volatile silicone to evaporate very easily and hence the stick to dry out. Slim-line lipsticks can however accommodate this type of system, but special filling equipment is required for these components.

6.13 LIPSTICKS

A **lipstick,** which is by far the commonest form of lip product, consists of a wedge- or 'bullet'-shaped stick that is moulded hot and then cooled before being placed into a small plastic cup or godet, which is held in a plastic or metal case. The godet can be moved up and down inside the case by a screw or push action. When the stick is at the bottom of the case the whole is sealed by a cap.

Typically weighing 5–6 g, lipsticks are presented in this specialized type of container, which is cylindrical and specifically designed to aid application whilst protecting the stick. Modern systems require more sophisticated components that prevent evaporation of the volatile ingredients used.

The ingredients for lipsticks are included in Section 6.12.2, Raw materials.

6.13.1 Typical lipstick formulation

Formula XIX

Ingredients	*INCI name*	*% w/w*
Castor Oil	Castor (Ricinus Communis) Oil*	40.65
Carnauba Wax	Carnauba (Copernicia Cerifera) Wax*	5.00
Beeswax	Cera Alba	4.00
Candelilla Wax	Candelilla (Euphorbia Cerifera) Wax*	6.00
Paraffin Wax		2.00
Octyldodecyl Stearoyl Stearate		5.00
Lanolin Oil		1.00
Propylparaben		0.10
BHT		0.05
Titanium Dioxide 1 : 3 Paste		12.00
D&C Red No. 6 Ba Lake 1 : 3 Paste		8.00
D&C Red No. 7 Ca Lake 1 : 3 Paste		6.00
Timiron MP1001 (Merck KGaA)	Mica (and) Titanium Dioxide	10.00
Fragrance	Parfum, Fragrance	0.20

*INCI names with Latin names included for international recognition.

Method of Manufacture

Combine the waxes, propylparaben, ester and castor oil, melt and mix until homogeneous, stir in the pigment pastes and then stir in the pearl. When homogeneous again submit for colour matching and add colour as required; when colour has been approved, add the fragrance and mix. When homogeneous again run off into lined trays to set. When set wrap and label, place in storage until required for filling.

6.13.2 Silicone lipstick formulation (Dow Corning)

Formula XX

Ingredients	*INCI name*	*% w/w*
White Ozokerite Wax	Ozokerite*	4.00
Candelilla Wax	Candelilla (Euphorbia Cerifera) Wax*	11.00
Octyl Dodecanol		25.00
C30-45 Alkyl Methicone		5.00
Cyclomethicone		26.00
Petrolatum		4.00
Lanolin Oil		9.00

Ingredients	*INCI name*	*% w/w*
Avocado Oil	Avocado (Persea Gratissima) Oil	2.00
Oleyl Alcohol		8.00
Pigments		6.00

*INCI names for plant materials.

Method of manufacture

1. Heat all materials together to 80–90°C. Mix until homogeneous, avoiding aeration.
2. Mould and leave to set.

6.13.3 Manufacture of lipsticks

The first stage of manufacture is the formation of the wax base. This is a straightforward blending of the various waxes and oils, including the preservatives and any antioxidants, by heating and stirring in a jacketed stainless-steel vessel until clear and homogeneous. The actual temperature required to achieve this will depend upon the melting point of the waxes used, typically 80–90°C. The contents can then be run off into lined shallow trays to set, or be used immediately to manufacture the total formulation.

Dry powder pigments are never added into a lipstick as they are very difficult to disperse uniformly. Each pigment is first milled into a paste in some of the castor oil, typically in a ratio of 1 : 3. The pigment should be stirred into the castor oil and then left to stand, preferably for several hours or overnight, and then the whole mixture is passed through a triple roller mill, colloid mill or ball mill to grind the pigments into the castor oil fully. The milling process is repeated until the pigments are fully dispersed, the dispersion being checked after each pass on a Hegman gauge.

The wax base is first melted in a stainless-steel jacketed vessel. Any additional castor oil and the pigment pastes are then added then stirred using a paddle stirrer. High shear mixers should not be used as they introduce air into the product which is difficult to remove and can cause problems later when moulding and flaming the finished bullets. Any pearls in the formulation can be added when the lipstick pastes have been fully mixed in; again only light stirring should be used. Finally the perfume is added and the colour-matched lipstick run off into lined trays to set prior to moulding.

The traditional method of moulding lipsticks was to use a 'split mould'. This involved heating the mass to about 80°C (the actual temperature depending on the composition of the base), in a small jacketed vessel fitted with a small stirrer and a small tap at the bottom. The molten lipstick mass is then run out of the vessel via the tap into the pre-warmed and lubricated moulds which are filled to the top to allow for shrinkage of the mass on cooling. The filled moulds are then placed either on a cooling table or into a large fridge/freezer to set. When the mass has set completely the mould is removed from the cooling area, the surface lipstick is scraped away and can be recycled. The mould is then opened up and

the lipstick bullets carefully removed and either transferred straight into the lipstick cases or stored in trays until required for finishing.

Once filled into the holders the surface imperfections can be gently smoothed away and the lipsticks flamed to give them their final gloss. Flaming is an intricate procedure if carried out by hand and needs plenty of practice to achieve the required finish without melting the bullet. The moulded lipstick is passed through a flame whilst being rotated. On a larger scale the holders can be placed on a conveyor belt and are flamed whilst spinning past in front of a flame or hot-air jet.

Split moulding many lipsticks is a time-consuming, wasteful and labour-intensive method of manufacture; it also produces poor-quality sticks in general with many surface imperfections. Most modern lipsticks are produced on automatic lipstick machines of which there are several on the market.

One of the most common automatic machines consists of a table of moulds which rotates through various heating and cooling chambers. The warm moulds are first lubricated by spraying in a small amount of oil, usually a low-viscosity silicone fluid; they then pass under the filling head where the molten lipstick is injected into them. As they move round the table they are cooled by refrigerated compartments and finally ejected out of the moulds by a small jet of compressed air straight into the cases. The full holders are then placed onto a conveyor belt and passed through a tunnel; while spinning they pass in front of jets of hot air which 'flame' the surface to give the required glossy finish. The next stage of the belt then twists down the holder to allow operators to put the caps in place. The labels are then applied to the base, again automatically, and the completed lipsticks stored until required for dispatch, or shrink-sleeved and placed into display cases for the shops.

On other even larger automatic machines the lipstick base is filled through the bottom of the mechanical holder. This is delivered to the factory with a plastic sheath attached that is the shape of the bullet required, and this forms the mould for the lipstick. Specially designed cases are required for this type of machine and they are especially useful for long runs of the same shade. The basic procedure is the same. Molten lipstick mass is injected through the base into the warm moulds, which then pass through cooling chambers to set the product. The sheaths can then be removed and the lipsticks transferred to a finishing line to be flamed and labelled as before.

6.14 LIPGLOSSES

These products are usually far more liquid than a traditional lipstick and the use of waxes is limited.

They are usually dispensed from clear tubes to which is fitted either a roller-ball in a housing or a cap that incorporates a wand with an applicator attached to the bottom. Alternatively they can be packed in either a small jar, when it would

be applied by a finger, or a thin plastic bottle from which it could be applied to the lips as before by the use of an applicator on the end of a wand.

6.14.1 Formulation for a roll-on lipgloss

Formula XXI

Ingredients	*Function*	*% w/w*
Castor (Ricinus Communis) Oil	Base oil	57.13
Saccharin BP	Sweetener	0.02
Dioctyl Sebacate	Liquid ester to give feel	5.00
Propylparaben	Preservative	0.10
BHT or Vitamin E	Antioxidant	0.05
Titanium Dioxide 1 : 3 Paste	Colour	10.00
D&C Red No. 6 Ba Lake 1 : 3 Paste	Colour	7.50
FD&C Yellow No. 5 Al Lake 1 : 3 Paste	Colour	5.00
Timiron MP 1001*	Pearl	10.00
Bentone Gel CAO-V†	Thickening/suspending agent	5.00
Flavour/Fragrance		0.20
		100.00

INCI names for specialities
*Mica (and) Titanium Dioxide – Merck KGaA
†Castor (Ricinus Communis) Oil (and) Stearalkonium Hectorite (and) Propylene carbonate – Elementis

Method of manufacture
Blend together all the ingredients and mix until homogeneous, warm gently if necessary, match colour with standard. Check viscosity and taste. This type of product can be filled on more conventional equipment into the chosen pack.

The main problem associated with this type of product is separation with time. It is vital to get the rheology of the system correct. The product must have the right application characteristics, not be too greasy and not rub off too easily. However, the viscosity must be sufficiently high to hold up the pigments and pearls. The use of agents such as the Bentone Gels (Elementis) is the most efficient way of achieving this. Other agents that can also do this include silica powder, but this can dry out the lips if used at too high a level. Also the incorporation of a small amount of beeswax or other low-melting-point waxes can be effective.

6.14.2 Clear lipglosses

Clear lipglosses are also possible; however, the use of castor oil is rare in this type of product as it has such a dark colour. Using polybutene in this type of product, and carefully choosing the esters to blend in with it, can give water-white products that just impart shine to the lips.

6.15 LIPLINERS AND PENCILS

These are blends of waxes, the same as those used in lipsticks, but the finished formulation is much harder and the level of pigments slightly lower. Production is by the same process as for eye pencils.

6.15.1 Lipliners

These are most often slim pencils, or fluids encased in special 'pens' to which is attached a fine brush through which the product is dispensed, and with which the outline of the lips can be drawn.

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7

Dental hygiene

Stephen Mason

7.1 INTRODUCTION

An initial superficial examination of the consumer oral health industry might conclude that very little has changed over the previous two decades. Dental anatomy, the development of the dentition, the potential diseases and conditions which can be influenced by brushing or rinsing with oral products are constant (Cummings, 1997). Similarly, the basic ingredients, the product development strategies and the production technologies are also relatively unchanged (Prencipe *et al.*, 1995).

However, this is extremely misleading since today oral health care is an extremely dynamic and competitively aggressive, fast-moving consumer goods category of products.

Today, the oral care industry is a truly global concern, dominated essentially by perhaps six major multinational corporations with others following their lead. Their research, product development and formulations are often centrally developed and standardized to control costs with only relatively minor regional adaptations permitted. This provides the necessary flexibility to meet the ever-changing demands of the market where innovation and change in the category are generally driven by providing products which meet the consumers' perceived needs.

Products are all generally based on the use of fluoride to provide basic anti-cavity benefits (Mariotti, 1998). In addition to this, products can currently be broadly categorized into three different areas: speciality products for specific oral conditions, multi-benefit therapeutic products, and products for cosmetic attributes.

Within each product variant, a dynamic offering of visual product forms, e.g. colours, multi-stripe, gel and packaging executions, are offered. Thus, a single company may have to manufacture more than twenty different formulations for

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 217–253

a single marketplace, e.g. seven products with two or three formula variations (colour, flavour, etc.), for each product. Packaging choice only serves to increase further the manufacturing complexities.

Interestingly, the same marketing and development techniques which have led to an explosion of choice in the dentifrice category have also been applied to the toothbrush category. Despite the significant capital investment requirements for toothbrush moulds and manufacturing technologies, the speed of development and consumer choice now available is wider than ever before.

The end-result of all of this commercial activity makes the oral care section of any supermarket in the developed world extremely large and active with literally hundreds of potential choices available, and that change almost daily (Smith, 1996). However, it is important and worthwhile to emphasize that despite the wide choice of products, and significant investments in advertising made by the branded goods manufacturers, the overall per-capita consumption of oral care products generally falls far below the recommendations of health professionals. For example, generally it is recommended that teeth are brushed at least twice a day with approximately 1 gram of dentifrice per brushing, and that a toothbrush is replaced every 1–3 months. This would result in each adult using approximately 800 grams of dentifrice (eight 75 ml tubes) and using over six toothbrushes per year, a far cry from the actual mean consumption figures of most countries.

With this background this revised edition will review the current state of dental preparations, focusing on toothpastes, which are routinely available to the public.

7.2 EUROPEAN LEGISLATIVE FRAMEWORK

Excluding drug classified products, the sale of dental preparations within the European Union is subject to the national rules emanating from the EEC Cosmetics Directive 76/768/EC. In 1993 the European Community further expanded and harmonized the legislation concerning the sale of cosmetic products by passing the 6th Amendment (1993: 93/35/EEC).

This defines a cosmetic product as 'any substance or preparation intended to be placed in contact with the various external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membrane of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, or changing their appearance and/or correcting body odours, and/or protecting them or keeping them in good condition.'

This is clearly in keeping with the principal role of oral preparations. The *Oxford English Dictionary* gives the definition of a dentifrice as: 'A powder, or other preparation for the rubbing or cleansing of the teeth (1558)'; a toothpaste: 'A paste used for cleaning teeth'; and a mouthwash as: 'A therapeutic wash for the mouth'; and for years these preparations have been traditionally promoted for their ability (with the aid of a toothbrush) to clean and to remove stain and/or debris from the mouth in addition to providing cleaner, fresher breath.

However, by the very nature of the cleaning effect which toothpaste can deliver, secondary benefits upon oral health can also be achieved and demonstrated. This has grown to such an extent that a 'simple' cleaning preparation with no other therapeutic benefits is rarely found in the marketplace today. Thus, the formulation chemist has to consider not only the quality and consumer preferences of the product, but also the trends in dental research such that new active ingredients may be incorporated to give additional therapeutic benefits.

It is probably for this reason that the 1993 amendment requires manufacturers to be able to substantiate satisfactorily all advertising claims that are made. However, it has not as yet appeared to have an impact on a highly competitive market.

7.3 PHYSIOLOGY OF THE TEETH

Before the current state of commercially available dental preparations can be reviewed, it is first necessary to provide a brief overview of the teeth, their function, and the problems associated with poor oral hygiene. Following this, the role of oral care products in preventing or treating dental diseases may be more easily understood.

7.3.1 The teeth

In any individual's lifetime it is normal to have two sets of teeth, 20 deciduous and 32 permanent. The deciduous teeth (or baby, milk teeth) start to appear between the ages of five and nine months, and the complete dentition is usually in place by the age of two and a half years. The permanent teeth start to appear at about six years of age and slowly replace the initial deciduous set. There are normally 16 teeth in both the upper and lower jaws, which are intended to remain for the individual's entire life.

While teeth can have a variety of functions, such as defensive or offensive weapons, their primary role is for biting, tearing and grinding solid foods with their points, edges and relatively horizontal grinding surfaces. There are basically four different types of permanent teeth: incisors (for cutting), canines or cuspids (for tearing), premolars or bicuspids (for crushing), and molars (for grinding).

A tooth can be considered to consist of two parts: the crown that is visible above the gumline, and the root that anchors into the jawbone and remains invisible until recession of the gum exposes some of the root surface. In the 1990s the visual, cosmetic appearance of the teeth in the mouth (e.g. colour, alignment), became of crucial importance for many consumers.

7.3.2 Structure of the teeth (Jenkins, 1978; Manhold and Balbo, 1985)

Enamel

The teeth are able to last throughout an individual's lifespan, almost in continuous use, only because their exterior, exposed surface is 'enamel'. This white

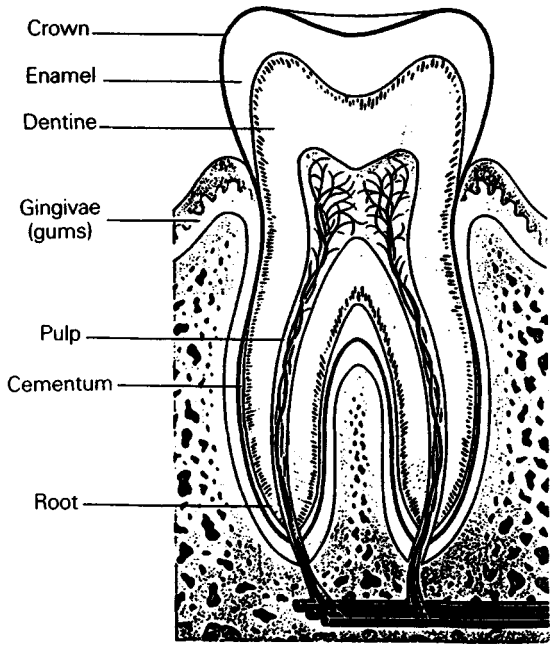

Fig. 7.1 Structure of a human tooth.

outer layer is an approximately 2–3 mm thick coating consisting predominantly (98%) of mineral which is based on $Ca_5(PO_4)_3OH$, hydroxyapatite with various impurities. It is the hardest material in the body and prevents the tooth from wearing away under the pressure of chewing.

Generally, enamel is the only portion of the tooth to be visible, but underlying this are the relatively complex structures of dentine and the pulp cavity (see Fig. 7.1).

Dentine

Dentine, which forms the bulk of the tooth, is a yellowish bone-like material, and lies immediately beneath the enamel. It is still predominantly a mineralized tissue (approximately 70%), but is less dense than enamel because of a greater content of protein and water. Thus it is more porous, softer, and more susceptible to decay and wear if exposed. An interesting structural feature of dentine is that it is perforated throughout by microscopic tubules or canals (over 10 000 per mm^2) which radiate from the pulp cavity to the exterior of the tooth. Unlike enamel, dentine is a vital tissue and gives rise to pain when stimulated.

Cementum

The root of the tooth is covered by the special connective tissue – cementum. This is a thin, highly mineralized bone-like tissue with associated proteins, similar to dentine, and is between 0.1 and 0.5 mm thick. Its primary function is to provide attachment for the fibres of the periodontal ligament and assist the retention of the teeth in the jawbone. It also serves to protect the dentine of the root of the teeth.

Pulp cavity

Underlying the dentine is the pulp cavity that contains the nerve fibres, blood and lymph vessels and is the living part of the tooth. Since it is rich in nerves it acts as a sensory signal of damage (i.e. toothache).

Gingiva

Once the tooth erupts through the gum tissue covering the jawbone, a portion of the gum surrounds and extends onto the enamel of each tooth and forms the gingiva. At the point at which the gingiva meets the teeth it becomes extremely thin, and this is described as the gingival margin. It is within the gingiva that the first signs of gum disease appear in the absence of good oral hygiene. Ultimately gingival recession can lead to periodontal disease and/or sensitivity to hot and cold stimuli.

Periodontal ligament

Finally the teeth are set in the sockets (alveoli) which occur in the jawbone, and are held in place and supported by the periodontal ligament.

7.3.3 Major oral health problems

The prevalence of dental problems amongst communities of the western world makes them the most common of diseases to afflict the human race (Moller, 1990) and they can be broadly generalized into two major categories: dental caries and periodontal disease.

Dental caries (tooth decay) (Bowen and Tabak, 1993)

Dental caries is an universal problem affecting all ages and all geographic locations around the globe. It can be defined as 'disease resulting in the breakdown and destruction of the hard tissue of the tooth structure via demineralization'. Demineralization describes the process by which the mineral structure of enamel and dentine is dissolved and removed as a result of continued attack of acids produced by the action of microorganisms on sugars and carbohydrates that are present in the mouth.

In order for caries (demineralization) to occur, three factors must be present simultaneously (Sognnaes, 1963):

(a) caries-producing bacteria,
(b) susceptible teeth,
(c) foods and drinks with caries-producing potential.

However, these conditions must prevail for weeks, months or years in order for the tooth substance to become sufficiently destroyed in order for caries to become visible to the dentist. Thus, the amount of decay is directly related to the frequency at which the above three parameters occur simultaneously. It is most often localized to the pits and fissures of the teeth since it is these areas which are the most difficult to clean and where the carbohydrates, etc., can be impacted and retained for a long period of time.

Periodontal disease (gum disease) (Rateitschak, 1989)

At its simplest, periodontal (or gum) disease can be described as a group of diseases that destroy the supporting tissues of the teeth and the retention of the teeth in the jaw. There are several defined stages to the disease starting with gingivitis. Gingivitis is an inflammation of the gums, and can occur very rapidly with poor oral hygiene. Plaque bacteria around the gum produce toxins and enzymes that irritate them. This may be sufficient to cause the gum to start to recede exposing the softer root of the tooth. (*Note*: this can then be susceptible to decay.) In its early stages gingivitis is reversible and resumption of good oral hygiene over a period of time will generally bring about a return to good oral health. If left untreated, tissue breakdown will begin and a pocket can form between the tooth and gum. The pocket serves as a reservoir for toxic bacteria, intensifying the breakdown processes and eventually the periodontal ligament can be destroyed, causing loss of the tooth. In adults, periodontal disease is a more common cause of tooth loss than dental caries.

7.3.4 Causes of oral health problems

Both dental caries and periodontal disease can be traced to the formation of bacterial plaque on the exterior surface of the teeth. The formation of this layer rapidly follows the formation of the pellicle.

Pellicle

The pellicle is rapidly formed on all freshly cleaned tooth surfaces by the deposition and absorption of some salivary proteins. It is less than 0.1 mm thick and is invisible to the naked eye.

Plaque

Following the deposition of pellicle on a freshly cleaned tooth surface, plaque forms rapidly. Plaque is an invisible sticky film of bacteria, salivary proteins,

and polysaccharides that accumulates on everyone's teeth. It is not washed away by the saliva, and the composition of bacteria depends upon the host, the site in the mouth and the age of the plaque layer. In the event of poor oral hygiene, plaque ages and there is a shift in bacterial population to more harmful organisms as the plaque ages (Kleinberg, 1970).

Since the structure and composition of plaque is complex, it is generally seen as the main culprit of poor oral health. It is widely accepted that certain bacteria produce the acid that cause dental caries while other bacteria cause redness, swelling and bleeding of the gums (gingivitis). If left untreated, plaque above the gumline (supragingival), may spread below the gumline (subgingival), resulting in the loss of bone and the supporting structure of the teeth and ultimately leading to the loss of the teeth (periodontal disease).

Dental calculus (tartar)

Dental plaque may itself become mineralized and this hard deposit is called calculus. It accumulates on the tooth surface mainly at the gingival margin opposite the salivary ducts. It is a hard mineral deposit, containing predominantly calcium and phosphate, very tightly bound to the tooth surface. Once it has formed, it is virtually impossible to remove it except by a dental hygienist (Mandel, 1987).

Calculus can become unsightly if growth is left unimpeded and elimination is desirable for various reasons. One of these is that the porous surface of the calculus is always covered by a thin layer of unmineralized plaque which can cause constant irritation of the gums, particularly if it extends below the gum.

7.4 TOOTHPASTE INGREDIENTS AND MANUFACTURE

7.4.1 Requirements of a toothpaste/dentifrice

The major requirements of oral preparations, especially toothpastes, have been summarized on many occasions in the past. For a toothpaste, these requirements were:

1. When used properly, with an efficient toothbrush, it should clean the teeth adequately, that is, remove food debris, plaque and stains.
2. It should leave the mouth with a fresh, clean sensation.
3. Its cost should be such as to encourage regular and frequent use by all.
4. It should be harmless, pleasant and convenient to use. (It should conform to the EC Cosmetics Directive in that it is 'not liable to cause damage to human health when applied under normal usage conditions'.)
5. It should be capable of being packed economically and should be stable in storage during its commercial shelf-life.
6. It should conform to accepted standards in terms of its abrasivity to enamel and dentine.
7. Claims should be substantiated by properly conducted clinical trials.

These requirements remain valid today, with perhaps only the priority and emphasis placed on any individual point being changed.

At their simplest, these requirements are analogous to cleaning hard surfaces in the home, and similar logic is used to provide teeth-cleaning preparations. However, consideration must be given to the important constraints of time of brushing (less than one minute), and temperature (body temperature).

Today, the desired cleaning effect can be achieved by taking a mildly abrasive powder, to buff and polish, in combination with a surface-active agent (surfactant), which aids in the penetration and removal of any adherent film. An additional property of the surfactant is to provide foam so that it both suspends any debris that is removed from the surface during cleaning and also provides a psychological cleaning effect. However, because both of these ingredients can have distinctive and possibly unacceptable tastes, flavour oils and sweetening agents are usually added in order both to mask the taste of the ingredients and provide a pleasant, fresh, clean sensation after use. Using this combination it is relatively easy to produce preparations which are suitable and effective in giving the desired cleaning effect.

Tooth powders were the original commercial products sold for cleaning teeth. Although efficacious and perhaps cost-effective, powders are certainly not easy to use since they are difficult to apply to the brush, and they have several drawbacks both from a consumer perspective and in terms of the incorporation/dosage of ingredients such as fluoride. Therefore, considerable efforts in improving the manner of presentation have occurred throughout the 20th century, culminating in the current consumer desire for paste that can be easily applied to a brush head (e.g. from a tube or dispenser).

To achieve this it is necessary to have a high solid suspension in a stable viscous form and therefore gelling agents or thickening polymers have to be incorporated. To prevent it from drying out it also becomes necessary to add humectants to the system. Finally, colours (if desired), and preservatives (if necessary), are also added, creating a complex matrix of ingredients which can be classified as a 'simple' cosmetic toothpaste, i.e.

1. Cleaning and polishing agents (abrasives).
2. Surfactant (cleaning and foaming).
3. Humectants.
4. Binding (gelling) agents.
5. Sweetener.
6. Flavouring agents.
7. Minor ingredients (colours, whitening agents, preservatives).

In such a complex system many interactions can take place depending upon internal and external factors. Even the 'simple' formulations require extensive stability testing, over a range of temperatures and time, in order to be confident that the product quality does not change upon storage. Only in this way can the manufacturer

have a high degree of confidence that the product seen by the consumer is of premium quality.

In addition, the important caveat that the cleaning action should not be harsh to either the soft tissue of the mouth, the enamel or the softer root surface dentine if exposed, has to be respected. 'A dentifrice should be no more abrasive than is necessary to keep the teeth clean – that is free of accessible plaque, debris and superficial stain'. (American Dental Association, 1970.) Thus, considerable performance testing on the final formulation is necessary.

Adding to the complexity of the situation are the recent technological advances that have resulted in the therapeutic benefits of the products becoming more dominant. Thus, in addition to the normal stability testing, it is also increasingly important that the formulation chemist understands and evaluates the modifications caused to the toothpastes by the incorporation of active ingredients. This adds the burden of both understanding clinical research requirements and generic equivalency tests. The latter become necessary because of the formulation changes required to produce improved cosmetic stability or acceptability.

All these needs have to be considered in the development of any toothpaste/dentifrice.

7.4.2 Ingredients used in toothpastes

The formulator's life is made somewhat easier because, other than introduction of new therapeutic ingredients, few other major ingredients have been introduced into dental preparations in recent decades. It is mainly the specifications of the raw materials that have been modified slightly in an attempt to differentiate products by providing the desired visual or tactile stimuli. Thus the vast amount of activity in the category has centred on formulators using the previously known chemistry and well-established ingredients in different combinations and concentrations with differing colours and flavours. In this section the main ingredients will be summarized in more detail. All ingredients generally have specifications approved for use in foodstuffs or are special grades available for dental preparations, especially abrasives.

1. Cleaning and polishing agents (abrasives)

Clearly the main purpose of the cleaning and polishing agent is to remove any adherent layer on the teeth, and the materials normally considered are given below.

1(a) Dental grade silicas $(SiO_2)_n$. The relatively recent introduction, during the 1970s, of precipitated or amorphous silica abrasive, has added a new dimension to formulation of dental creams. In a relatively short period of time silica has generally become the abrasive of choice because it offers great flexibility to the formulator. It can be produced to a high state of purity giving excellent

compatibility with therapeutic additives and flavours. Varying the particle size can alter the finished product abrasivity. Clear gels can be formulated by carefully matching the refractive indices of silica used with the liquid phase of the toothpaste. Silica can also give additional thickening properties to the dental cream if extremely fine particle sizes are used (silica thickeners). When used in toothpastes, silica is generally incorporated at levels between 10 and 30%.

1(b) Dicalcium phosphate dihydrate (DCPD) $CaHPO_4 \cdot 2H_2O$. DCPD is one of the most commonly used dental cream abrasives, perhaps because it gives good flavour stability. It is normally white in colour and gives toothpaste which generally does not require additional whitening agents. The main drawback is that it is only fully compatible with sodium monofluorophosphate as the fluoride source because of the presence of free calcium ions. Formulating with other therapeutic fluoride sources does not appear to have been successful. The abrasive is usually formulated at levels between 40% and 50% to give relatively dense toothpaste.

1(c) Calcium carbonate $CaCO_3$. Calcium carbonate is probably one of the most commonly used dental cream abrasives. Precipitated calcium carbonate (chalk) is available with a white or off-white colour and both particle size and crystalline form can be varied, depending upon its conditions of manufacture. As a result of its structure and calcium content, precipitated calcium carbonate is incompatible with sodium fluoride, but is stable with the less reactive sodium monofluorophosphate. Calcium carbonate is also used at levels between 30% and 50% to give a relatively dense paste.

1(d) Sodium bicarbonate (or baking soda $NaHCO_3$*).* Sodium bicarbonate is an ingredient that has seen a resurgence of use in the early 1990s. Although potentially soluble, it is used primarily as an abrasive ingredient. It has a unique 'salty' mouth-feel that tends to polarize consumers, many finding it attractive possibly due to its heritage as a cleaner/deodorizer. It is a very mild abrasive, usually used at a 5–30% level, in combination with other abrasives such as silica or calcium carbonate to achieve the required cleaning action. It is used as the sole abrasive agent in some products, but the high formula level needed to obtain cleaning (50–70%) does give rise to a negative taste which may be objectionable.

1(e) Hydrated alumina $Al_2O_3 \cdot 3H_2O$ *or* $Al(OH)_3$. Hydrated alumina has been a widely used abrasive in the past although its use declined significantly during the late 1980s. It is relatively inert, cost-effective, and available as a white amorphous solid. It has good compatibility with sodium monofluorophosphate and other ingredients added to give a therapeutic benefit. The abrasive is usually formulated at levels between 40% and 50% to give a relatively dense paste.

1(f) Other abrasives. Insoluble sodium metaphosphate (IMP) $(NaPO_3)_x$, is available as a free-flowing white powder, with moderate abrasivity and good compatibility with flavour oils, sodium monofluorophosphate and ionic fluoride sources (stannous and sodium fluorides). Although extensively used in the past, it is now only used in extremely limited amounts.

Calcium pyrophosphate (CPP), $Ca_2P_2O_7$, was the original abrasive purposely developed for its compatibility with stannous fluoride to give the first commercially available therapeutic dentifrice containing fluoride (American Dental Association, Council on Dental Therapeutics, 1960). Again, the history is similar to IMP in that it is no longer used, having been superseded by silica.

2. *Surfactants*

Surfactants are used in the toothpaste to aid in the penetration of the surface film on the tooth by lowering the surface tension. They also provide the secondary benefits of providing foam to suspend and remove the debris, and the subjective perception of toothpaste performance.

Surface-active agents tend to be intrinsically 'aggressive' materials, and it is therefore mandatory that those chosen for use in dentifrices are non-toxic and non-irritating to the oral mucosa under normal usage conditions. This very much limits the choice of materials available.

Originally, soap was the surfactant used, but it is strongly alkaline and, therefore, incompatible with some other components of the paste. It can also affect the taste of a product since it can have an unpleasant odour and a bitter taste. Therefore, synthetic materials are preferred. They often have better foaming properties, and are more compatible with other ingredients since their pH range is essentially neutral. They are also available with a higher degree of purity that can eliminate some of the bitter flavour components that affect taste.

In general, surfactants are used at a concentration of around 1–2% by weight in the dental cream.

2(a) Sodium lauryl sulphate (SLS) $ROSO_3Na$. R is an alkyl radical with an average chain length in the region of C12 to C14, since SLS is synthesized from a cut of naturally occurring alcohols. This has been the main surfactant of choice, used in nearly all toothpaste brands across the globe, throughout the past two decades.

It is useful to note that even this compound has been subject to some criticism within Europe in recent years, because of experimental results obtained when evaluated under exaggerated use conditions and extreme concentrations. However, while alternative surfactants have been considered, and will continue to be looked at and developed, none is in widespread use since all have some disadvantages compared to SLS.

3. Humectants

Humectants are used to prevent the paste from drying out and hardening to an unacceptable level. At the same time they give shine and some plasticity to the paste. Generally only two major humectants are considered for use in toothpaste, often in combination with small amounts of additional minor humectants.

3(a) Glycerin, $CH_2OHCHOHCH_2OH$. Glycerin is still the humectant used in greatest bulk quantity in toothpaste. It is one of the best humectants, producing a shiny, glossy product. It is stable, non-toxic, available from both synthetic and natural sources, and provides a useful sweetening function to the paste.

3(b) Sorbitol, $CH_2OH(CHOH)_4CH_2OH$. Sorbitol syrup (approximately 70%) is also extensively used throughout the industry and is sometimes considered superior to glycerin depending upon the formulation. It also imparts sweetness, and is a stable humectant.

3(c) Propylene Glycol, $CH_3CHOHCH_2OH$ and Polyethylene Glycol, $CH_2OH(CHOH)_nCH_2OH$. Propylene glycol and polyethylene glycol are not normally used as the sole humectant in a paste since they are more expensive and, in the case of propylene glycol, can impart a slightly bitter taste. They are more generally used in relatively small amounts in combination with either glycerin or sorbitol.

The amount of humectant in any formula obviously has to be adjusted depending upon the other constituents of the formula (especially abrasive nature), but generally the total humectant loading is in the range 10–30% by weight.

3(d) Xylitol ($CH_2OH(CHOH)_3CH_2OH$). Xylitol is a polyol equivalent of sorbitol, but with a five-carbon chain instead of six. Like sorbitol it is a naturally occurring material with a relative sweetness equal to sugar (Merck, 1996). However, its current use in toothpaste is to augment the anti-caries effect of fluoride. See Section 7.5.1, Anti-cavity (Fluoride). Currently its high cost and limited availability restrict its use.

4. Gelling agents

Gelling or binding agents are hydrophilic (water-loving) colloids which disperse and swell in the water phase of the toothpaste and are necessary to maintain the integral stability of the paste and prevent separation into component phases. They are probably the most widely variable components of toothpaste and the choice of gelling agent can greatly influence the dispersibility of the paste in the mouth, the generation of foam and, above all, the release of the flavour components. Some formulations have combinations of gelling agents in order to achieve the desired consumer preferences. As a result of the number of gelling agents available and used in toothpastes, only a few are detailed below.

4(a) Sodium Carboxymethyl Cellulose CMC. Carboxymethyl cellulose is one of the preferred gelling agents for use in toothpaste. It can be manufactured to a high state of purity, and tailor-made for an individual requirement by varying the degree of substitution on the cellulose chain. This can give flexibility in terms of solubility, elasticity and some increased stability in the presence of electrolytes.

4(b) Carrageenan. This is the generic name for gelling agents derived from the harvesting and extraction from seaweed, *Chrondrus crispus*. It is a purified colloid, consisting of a mixture of sulfated polysaccharides and, as with all natural products, it can be of variable quality, which could cause a problem for any formulator. Therefore, it is standardized either by repeated blending, or dilution with variable amounts of inert material. Some flexibility in the gelling properties of carrageenan can be achieved by controlling the cations present by ion exchange. However, although relatively common in the past, its use has declined in favour of cellulose derivatives, primarily for cost reasons.

4(c) Miscellaneous gelling agents

(a) *Xanthan* – this is a polysaccharide produced by fermentation technology. It offers excellent properties for use in toothpaste since it gives a highly structured gel, relatively easily broken down when sheared, but which recovers rapidly. It is relatively insensitive to electrolytes and heat, but unfortunately it is generally incompatible with cellulosic materials because of contaminating enzymes that degrade cellulose.
(b) *Hydroxy ethyl cellulose HEC* – this is occasionally used as an alternative to carboxymethyl cellulose (CMC), especially when a greater electrolyte tolerance is required.
(c) *Synthetic polymers* – crosslinked acrylic acid polymers have become more intensively used in the past decade because of their useful thickening and suspending properties combined with their inertness and their stability to heat and ageing.
(d) *Clays* – colloidal clays, either natural processed bentonites or synthetic clays, have been used as binding agents because of their thixotropic properties.

Depending upon the rest of the formula components (e.g. abrasive, amount of free water), the level of gelling agent added to a paste can vary from 0.5% to 2.0% by weight.

5. Sweetening agents

These are important for product acceptance, since the final product must be neither too sweet nor too bitter. These ingredients must always be considered in partnership with the flavour because of their combined impact.

5(a) Sodium saccharin. This is the sweetening agent in widest commercial use, and is generally used at a level between 0.05% and 0.5% by weight.

6. Flavours

Flavours are probably the most crucial part of toothpaste because of consumer preferences. They are also the most proprietary part of the formulation. Exotic flavours, although available, are generally not well liked under long-term usage conditions, since one of the primary consumer requirements of toothpaste is the perception of freshness and cleanliness after brushing. Conventionally, therefore, mint flavours tend to predominate.

The flavour is a blend of many suitable oils, with peppermint and spearmint being the major base components. These are nearly always fortified with other components such as thymol, anethole, menthol (to give a pleasant cooling effect), eugenol (clove oil), cinnamon, eucalyptol, aniseed, and wintergreen (to give a medicinal effect). Many others are used at various levels to achieve the right balance.

Thus, the flavour is an extremely complex part of the toothpaste and is also one of the most costly (up to 25% of the raw material cost). In addition, because the flavour is a mixture of sparingly soluble organic oils, its interactions with the other dentifrice components are often unpredictable and unexpected. Taste and stability can be influenced greatly by both the other components of the dental cream, e.g. free water content, or absorption by the abrasive (perhaps to the surface), and also by the physical properties of the dental cream, e.g. pH, viscosity etc., all of which can cause alterations or even complete changes in flavour perception. For this reason the contribution of expert flavourists is essential.

Depending upon the formulation, e.g. the abrasive nature and level, the gelling agent used and the presence of therapeutic ingredients which may impact taste perception, the flavour level may vary from around 0.5% to 1.5% by weight.

7. Minor ingredients

This section is intended to cover all additional ingredients added to the paste to form either a functional or cosmetic aspect, other than those ingredients which are added to give a documentable, clinically tested, therapeutic benefit, which will be dealt with in the final section of this chapter.

7(a) Titanium Dioxide TiO_2. Titanium dioxide may be added to give additional whiteness and brilliance to the paste.

7(b) Colours. Colours can be an integral part of the aspect of any toothpaste that may influence consumer preference and purchase intent. Examples of their use are given below.

A small amount of colour may be added to the paste as a whole to give it a pastel shade (often associated with products that claim therapeutic benefits). Equally if a translucent gel had been formulated then colour would be added to give it a different visual appearance.

Finally colour can be mixed with a portion of the cream. Then in combination with a portion of white cream and additional packaging components, coloured striped toothpaste on a white base (or vice-versa) can be produced.

The EEC Cosmetics Directive (Annex IV) lists the permitted colours and only a small amount is necessary to create a large impact, $<0.01\%$ by weight.

7(c) pH regulators. Occasionally buffering systems need to be added to the dental cream to adjust the pH of the final finished product.

7(d) Sparkles. A recent introduction in the marketplace is the addition of small reflective mica particles to coloured transparent gel products. This gives toothpaste the appearance of containing 'sparkles' and is especially aimed at younger children. Micro-granules have also been added in the 1990s that are primarily silica agglomerates of different particle size than normal abrasive or thickening silica. These ingredients were included in toothpaste to provide the consumer with tactile stimuli when brushing, differentiating it from other products in the category and supporting the consumer advertising.

8 and 9. Fluoride and other 'active' ingredients

The incorporation of these ingredients (e.g. fluorides, anti-microbial and desensitizing agents) into toothpastes is discussed separately in Section 7.5. Inclusion of this type of ingredient pushes the toothpaste industry into a borderline classification area somewhat beyond the simple definition of a 'cosmetic'. Thus the ingredient, level, formulation and claimed therapeutic benefit to the consumer need to be reviewed together.

7.4.3 General formulation of toothpastes

Specific examples of toothpaste formulae are detailed in Section 7.5. These are categorized according to their benefits to the consumer. In terms of a general formulation for toothpaste, specific examples are less relevant because of the great variety of raw materials and combinations available. The following example serves to give a general overview:

Example 1

Code used in 7.4.2–7.5.5	*Ingredient*	*Formula % (by weight)*	*Examples*
1(a–f)	Abrasive	10–50	SiO_2, $CaHPO_4 \cdot 2H_2O$, $Al_2O_3 \cdot 3H_2O$ $\{Al(OH)_3\}$, $CaCO_3$, $Ca_2P_2O_7$, $(NaPO_3)_x$

(*Continued*)

Code used in 7.4.2–7.5.5	*Ingredient*	*Formula % (by weight)*	*Examples*
2(a)	Surfactant	1.0–2.0	SLS
3(a–c)	Humectant	10–30	Glycerin, Sorbitol (70%), Propylene Glycol
4(a–f)	Gelling Agent	0.5–1.5	CMC, Carrageenan, HEC, Organic Polymers
5(a)	Sweetener	0.05–0.5	Sodium Saccharin
6(a)	Flavour	1.0–3.0	Spearmint, Menthol, Peppermint Anethole
7(a–d)	Colour etc.	<1.0	Titanium Dioxide, colours, pH adjusters, Sparkles, etc.
8(a–d)	Fluoride	<0.5	Sodium Fluoride, Sodium Monofluorophosphate
9(a–l)	Other 'active ingredients' added for therapeutic benefits or claims	<10.0	Triclosan, Pyrophosphate salts, Potassium Nitrate, Strontium Chloride, Hydrogen Peroxide (see Section 7.5)
10	Water	to 100	

7.4.4 Manufacture of toothpastes

Toothpaste can be manufactured via two separate distinct batch processes, both of which are, in principle, three-step methods. Continuous or semi-continuous variations of these methods can be found among the larger manufacturers. A brief outline of the fundamental batch processes are given below:

General method A
Stage 1 is to carefully blend all powder components of the toothpaste together, including the gelling agents, abrasives and thickening agents:

1(a–f) Abrasives
4(a–f) Gelling agents
8 and 9 Powdered Therapeutic Agents
5a Sweetener
7(a–f) Whitener/Colours

This blend is essential to avoid aggregation of the gelling agent.

Stage 2 is then to mix this blend with all the aqueous and liquid components of the paste (humectants, water) in a heavy-duty mixer:

3(a–d) Humectants
10 Purified Water

Following complete swelling of the gelling agent a homogeneous paste will be obtained.

General method B

In stage 1 of this process, the gelling agent is fully hydrated in the presence of sufficient water and heat if necessary. In addition all soluble salts may be added:

3(a–d) Humectants
4(a–f) Gelling Agents
8 and 9 Powdered Therapeutic Agents
10 Purified Water

Several processing variations may be used, especially in the hydration of the gel, but generally the manufacturer of the gelling agents recommend either (a) dispersion in the non-aqueous portion of the humectant system (glycerin or propylene glycol) before addition of the free water and the ingredients added in solution in order to ensure good hydration and prevent gel lump formation; or (b) continually hydrating the gelling agent by pulling small amounts of the powder into a stream of cold water.

Stage 2 of the process is to mix the fully dispersed gel and the powders together also in a duty mixer:

1(a–f) Abrasives
5(a) Sweetener
7(a–f) Whitener/Colours

Following complete mixing a homogeneous paste will be obtained.

Addition of flavour and surfactants

In stage 3 the homogeneous paste obtained from either process must then be mixed with both the surfactant and the flavour under vacuum. This is essential in order to de-aerate the product at the final stage, otherwise a cosmetically unacceptable 'mousse'-type consistency will be produced. These are often added as late as possible in the manufacture because mixing the surface-active agent will create foaming and air entrapment if caution is not taken. Equally mixing under vacuum with the flavour added could cause unnecessary loss of some flavour components that can be up to 25% of the total raw material cost of the toothpaste.

When manufactured, appropriate analytical tests must be carried out to verify that the concentration of therapeutic ingredients is within acceptable ranges. Finally, microbial testing is necessary to confirm the quality of the product, specifically that it is not contaminated and that it prevents the growth of microorganisms.

7.5 TOOTHPASTE FORMULATIONS

7.5.1 Anti-cavity (fluoride)

Early in the last century, epidemiological studies showed that people living in areas with naturally fluoridated water (optimal < 1 ppm), had significantly lower levels of dental caries compared to those living in a non-fluoridated region (Mellberg and Ripa, 1973). This led manufacturers in the 1950s to add 'fluoride' to a toothpaste in order to add the anti-cavity benefit of fluoride to the cleaning effect of toothbrushing. Extensive clinical trials have been carried out since then, testing various formulation options, in co-operation with both the dental profession and academic researchers. These typically show that correctly formulated toothpastes with 1000 ppm F^- can give caries reduction in the range of 10–30% after three years. This can be increased by a further 10–15% when the content of F^- is increased to 1500 ppm (Hodge *et al.*, 1980; Fogels *et al.*, 1988). (*Note*: The maximum level permitted by the EEC Cosmetics Directive is 1500 ppm F^-.) These studies have resulted in various professional bodies, such as the Council of Dental Therapeutics of the American Dental Association, and the British Dental Association, giving a formal qualification and acceptance of toothpastes once the data showing their clinical effectiveness have been reviewed and accepted. Such accreditation was first given in the US to a stannous fluoride–calcium pyrophosphate toothpaste in 1960 (American Dental Association, Council on Dental Therapeutics, 1960).

Ultimately in the early 1990s the World Health Organization recognized that use of an appropriately fluoridated dental cream was one of the major reasons for a dramatic decline in caries in the developed world (WHO, 1994). They concluded that the additive results of long-term usage far surpassed the initial reductions measured in the 3-year clinical trials. Today, anti-cavity toothpastes containing fluoride salts at either 1000 or 1500 ppm have almost become generic and are the 'cost of entry' into the category. Significantly less than 5% of the dentifrice volume sold in developed world countries is non-fluoridated.

Various fluoride sources have been used throughout the past thirty years, depending upon the formulator's objectives:

8(a) Sodium Monofluorophosphate (Na_2PO_3F)
8(b) Sodium Fluoride (NaF)
8(c) Organo (amine) Fluorides
8(d) Stannous Fluoride (SnF_2)

Examples of anti-caries toothpastes are shown below:

Example 2 (Weyn *et al.*, 1982)

Ingredient	*% by wt*
Glycerin	22.0
CMC	1.1
Na Saccharin	0.2
$Na_4P_2O_7$	0.5
MFP	0.76
NaF	0.1
Dicalcium Phosphate	48.0
SLS	1.5
Flavour	0.8
Water	to 100.0

Example 3 (Denny and Wetzel, 1982)

Ingredient	*% by wt*
Sorbitol (70%)	58.8
Glycerin	15.0
$NaH_2PO_4 \cdot 2H_2O$	0.03
$Na_2HPO_4 \cdot 2H_2O$	0.2
Na Saccharin	0.3
Silica (Thickener)	3.0
Silica (Abrasive)	13.0
SLS1.2	
Flavour	0.9
NaF	0.243
Carbopol 940	0.3
Xanthan Gum	0.2
Colour Water	to 100.0

Example 4 (Forward, 1978)

Ingredient	*% by wt*
Glycerin	25.0
CMC	1.0
Saccharin	0.2
NaMFP	0.76
Ammonium Dihydrogen Phosphate	1.9
Calcium Carbonate	45.0
SLS	2.0
Preservative	0.2
Flavour	1.0
Water	to 100.0

Although the precise reasons for the clinical effectiveness of fluoride-containing dentifrice can still be debated it is generally accepted that, for optimal effects, the fluoride must be in a soluble state. It is not effective if it is bound to the abrasive. This gives the formulator some important constraints. For example if free flouride ions are present in a calcium carbonate formula, then insoluble calcium fluoride will be quickly precipitated and the anti-caries activity lost. For this abrasive, sodium monofluorophosphate would be chosen as the fluoride source since the fluoride is present in a protected form (PO_3F^{2-} instead of F^-).

However, this understanding of the basic science has led to the growth of generic, 'own-label' products since a whole battery of laboratory tests are now available to demonstrate equivalency between clinically and non-clinically tested products. This helps the formulator and the manufacturer avoid a long and expensive clinical testing programme (American Dental Association, 1985).

In turn this has provoked the major multinational dentifrice manufacturers that invest heavily in clinical research to support their products, to utilize significant research dollars and academic resources to debate which fluoride source and which basic dentifrice formulation could provide the best protection against cavities. This discussion centres primarily around a comparison between the reactive sodium fluoride (NaF) in a highly compatible silica abrasive [Formula 3], or the more stable sodium monofluorophosphate (MFP) in a variety of abrasives [Formulae 2 and 4].

In laboratory studies the evidence would favour the reactive NaF/Silica system, simply because of the chemical steps and processes involved in the 'test tube'. However, in large-scale clinical studies any difference is insignificant. Thus, despite the use of meta-analysis techniques to investigate the large body of human clinical data available, no absolute consensus and conclusion was achieved (Various, 1993a,b, 1994) and in the mid-1990s dental researchers essentially divided into two groups with opposing opinions (Various, 1994; Volpe *et al.*, 1995a). Clearly the discussions and conclusions of these initiatives were closely tied to major international marketing efforts, which perhaps also devalued or influenced the potential conclusions.

The discussion was also less relevant to the emerging markets where the relative cost to the average consumer of the international dental cream formulations can be a significant barrier to purchase and usage. In these markets a more appropriate discussion is how to deliver an effective anti-caries dentifrice formulation to the mass of the population at the lowest cost possible. This drives the formulators to make compromises on absolute purity of the raw materials and in general necessitates the use of sodium monofluorophosphate (MFP) as the fluoride source.

Thus, in the mid-1990s, with fluoride toothpaste being perceived by most consumers and dental professionals as being generic, and with the maximum concentration being limited by the EC Cosmetics Directive, the major manufacturers began investing in technologies which might improve the 'basic' efficacy of the fluoride. One such approach has been to add xylitol, a non-fermentable polyol, as a 'booster' technology. This formulation with NaF/silica/10.0% xylitol was shown in a 3-year human clinical study to provide a statistically significant reduction in dental caries (12.0%), when compared to a positive control product containing NaF/Silica alone (Sintes *et al.*, 1995). Lower concentrations of xylitol have not yet been proven to provide a clinical benefit. Although most major dentifrice manufacturers have marketed products based on these results, they have had little success in the marketplace, probably due to

Example 5 (Gaffar *et al.*, 1992)

Ingredient	*% by wt*
Sorbitol (70%)	54.1
Silica (Abrasive)	18.0
Xylitol	10.0
Silica (Thickener)	5.5
Polyethylene Glycol 600	3.0
SLS	1.2
Flavour	0.9
Tetrasodium Pyrophosphate	0.5
Titanium Dioxide	0.5
Sodium Benzoate	0.5
Carboxymethyl Cellulose	0.35
NaF	0.243
Sodium Saccharin	0.2
Colour Water	to 100.0

consumer indifference and cost. (These formulae have high costs, due to the use of 10% xylitol.) However, as a future direction for the category, improved anti-caries efficacy over currently marketed products is a potential opportunity.

This is further confirmed by initiatives by an American entrepreneurial company to introduce dual-chamber tubes into the marketplace. This technology utilizes laboratory research that shows that the efficacy of fluoride (F^-) may be enhanced if it is combined with the calcium ion (Ca^{2+}) at the moment of brushing. Using conventional technologies this is not possible, since the fluoride and calcium ion react in the dentifrice. Previous attempts with analogous technologies have utilized the less reactive and protected form of fluoride – sodium monofluorophosphate and calcium. However, this requires the monofluorophosphate to be hydrolysed in the mouth – an extra step perhaps providing less than optimum reactivity of the fluoride. In the new technology, dual-chamber packaging is utilized and the basic dentifrice ingredients are separated until the moment of brushing, thus minimizing any potential reactions.

This technology has not yet been proven to provide superior anti-caries performance in humans over existing products available in the market (despite the initially promising laboratory studies). It is however no doubt under far more rigorous and extensive testing by the major multinational corporations. Clearly, if it were to provide a clinically greater caries reduction over current technologies low-cost dual-chambers could probably revolutionize the category, far beyond its potential current impact in the field of anti-caries toothpaste.

During the early 1990s there was continual debate and concern over the overall amount of fluoride ingested by very young children (less than seven years

Example 6 (Usen and Winston, 1997)

Ingredient	*Part 1* *% by wt*	*Part 2* *% by wt*	*Combined product* *% by wt*
Sorbitol (70%)	30.0	30.0	30.00
Dicalcium Phosphate	40.0	0	20.00
Sodium Metaphosphate	0	40.0	20.00
Glycerin	5.0	4.0	4.50
Monosodium Phosphate	0	6.5	3.25
Cacium Nitrate	3.5	0	1.75
SLS	1.2	1.8	1.50
CMC	1.2	1.5	1.35
Flavour	0.9	0.7	0.80
Sodium Saccharin	0.3	0.2	0.25
NaF	0	0.48	0.24
Colour, Water	to 100.0	to 100.0	to 100.00

old), and its relation to a reported increase in the prevalence of dental fluorosis. (Cutress and Suckling, 1990; Fejerskov and Richards, 1996). Fluorosis is a side-effect of chronic fluoride overdose during the pre-eruptive stages of tooth development resulting in a continuum of signs varying from fine white opaque lines to chalky white teeth (Cutress and Suckling, 1990). Clearly although young children are only at risk of fluorosis in the years when the permanent teeth are forming, (0–6 years of age), their inability in the first years of life to expectorate dentifrice after brushing is a risk factor for fluorosis. Thus, while the greatest risk factor is the inappropriate use of additional fluoride supplements, e.g. tablets, drops, etc. for a variety of reasons (e.g. marketing, academic pressure, PR, etc.), the industry as a whole has responded by introducing low-fluoride toothpastes in some countries. These contain between 400 and 600 ppm fluoride, are often formulated for low abrasivity and have low foaming characteristics. They also carry clear dosage instructions for young children under 7 years old and are generally marketed towards young mothers.

7.5.2 Anti-tartar toothpastes

The second half of the 1980s saw an extensive promotion of anti-tartar (anti-calculus) toothpastes.

Good oral hygiene can prevent the build-up of tartar. Once formed, however, it is not removed by brushing. It should not be dissolved by sequestering agents, because of its chemical similarity to the tooth mineral. Recent advances in technology therefore have concentrated upon adding crystal growth inhibitors as a means of slowing down or preventing the build up of tartar and its adhesion to

the teeth (Mandel, 1987). A prerequisite is therefore that the teeth should be thoroughly and professionally cleaned in order to obtain maximum benefit from the product, a point which should help encourage regular dental visits.

Although high concentrations of zinc salts have been shown to inhibit crystal growth the most common method for inhibiting the mineralization processes is to add pyrophosphate ions. These have been introduced in various forms:

9(a) Tetrasodium pyrophosphate (TSPP)
9(b) Tetrapotassium pyrophosphate (TKPP)
9(c) Disodium dihydrogen pyrophosphate

because of the solubility constraints.

Clinical studies have shown that, starting from a clean mouth, toothpastes containing 3.3% pyrophosphate ion can inhibit the growth of tartar by approximately 30% after three months of regular use (Mallat, 1985).

An interesting patented technology is the addition of 1.5% of an organic copolymer (Gantrez®, GAF Corporation) to the 1.3% pyrophosphate ion. This is said both to protect the pyrophosphate in the mouth and enhance its effectiveness, and to give a better-tasting product without compromising clinical activity (Schiff *et al.*, 1990). Examples of anti-tartar toothpastes are shown below:

Example 7 (Parran and Sakkab, 1986)

Ingredient	*% by wt*
Sorbitol	50.7
Silica	20.0
$Na_4P_2O_7$	3.4
$Na_2H_2P_2O_2$	1.4
SLS	1.4
Flavour	1.3
Xanthan Gum	0.6
Dye Solution	0.4
Sodium Saccharin	0.3
NaF	0.243
Carbopol 940	0.2
Water	to 100.0

Example 8 (Gaffar and Polefka, 1986)

Ingredient	*% by wt*
Sorbitol (70%)	30.0
Glycerin	10.0
Iota Carrageenan	0.8
Silica Abrasive	20.0
Silica Thickener	3.0
Flavour	1.0
PEG 600	3.0
$Na_4P_2O_7$	2.0
Gantrez	1.5
SLS	1.2
NaOH (50%)	1.0
Titanium Dioxide	0.5
Sodium Saccharin	0.3
Sodium Fluoride	0.243
Water	to 100.0

However, since the latter half of the 1980s this area of the toothpaste industry has seen a considerable decline in activity. Most manufacturers continue to offer anti-tartar formula variants from within their portfolio, but they have not made this an area of competitive point of difference. Thus, no significant new formulations have been introduced in recent years.

7.5.3 Toothpaste for the control of plaque and gingivitis

A major oral health problem is periodontal or gum disease which is caused by plaque. It is obvious that plaque control beyond normal brushing and toothpaste usage is a desirable objective. Thus, compounds with anti-microbial properties have been tested in toothpastes in order to develop products that can retard plaque formation and perhaps prevent gingivitis. However, it is important to use an ingredient that is retained in the oral environment after the short brushing period (substantive), so that it can exert its anti-microbial properties over a long period of time. This is because of the rate at which the plaque bacteria reproduce and regrow (Cummings, 1997).

Perhaps the most extensively investigated compound in this section is chlorhexidene (Gjermo, 1989). This is a broad-spectrum anti-bacterial agent that has been shown to be highly effective at reducing plaque and gingivitis when delivered in simple forms to the oral environment. This is because it is positively charged, a feature which enables it to be bound and retained in the mouth for several hours. Unfortunately, the property which makes it effective creates considerable problems for the toothpaste formulator, since it reacts with many of the ingredients used in a normal toothpaste (Cummings, 1997). This, combined with important side-effects such as staining of the teeth, increased calculus formation, and alteration in taste perception, has resulted in the commercialization of this material primarily in mouthrinses which are prescribed for specialist uses or sold under the supervision of the pharmacist.

In recent years a non-cationic anti-microbial, triclosan **(9d)**, 2,4,4′-trichloro-2′-hydroxydiphenyl ether, has been introduced and is now in widespread use in toothpastes. However, triclosan does not have a high affinity for the oral tissues and several approaches have been utilized to improve its efficacy. In some formulations it has been combined with such ingredients as zinc citrate **(9e)**, which has anti-bacterial properties. Alternatively, adding the organic co-polymer Gantrez® has increased the retention of triclosan in the oral environment for long periods of time.

Clearly this has been one of the areas of greatest activity in the industry in the 1990s. This has led to the continual refinement of the formulations to produce clinically proven products which not only prevent and control plaque and gingivitis but which are also pleasant to use and suitable for mass market applications.

Many long-term (six months or greater) human clinical trials have been carried out by the major manufacturers. These have nearly all followed the American Dental Association guidelines for testing chemotherapeutic anti-plaque and anti-gingivitis agents (American Dental Association, 1986). These clearly confirm that the correctly optimized versions of these formulations are beyond doubt effective and help to prevent and control plaque and gingivitis (Jackson, 1997). The degree of activity is such that it has prompted a full-scale review of the area in one of the major dental professional review journals (Various, 1997). The two

most successful formulations that ultimately resulted from the testing and iterative development processes are shown below:

Example 9 (Lane *et al.*, 1988)

Ingredient	*% by wt*
Sorbitol (70%)	45.5
Silica Abrasive	10.0
Silica Thickener	8.0
SLS	2.4
SDBS	0.8
CMC	0.8
Zinc Citrate Trihydrate	1.0
Triclosan	0.3
Flavour	1.2
Sodium Chloride	1.0
NaMFP	1.12
Sodium Saccharin	0.3
Water	to 100.0

Example 10 (Nabi and Gaffar, 1990)

Ingredient	*% by wt*
Sorbitol (70%)	25.0
Silica Abrasive	20.0
Glycerin	10.0
Silica Thickener	5.5
SLS	2.5
Gantrez	2.0
NaOH (50%)	2.0
Flavour	1.1
Ethyl Alcohol	1.0
Iota Carrageenan	0.6
Titanium Dioxide	0.5
Sodium Saccharin	0.4
Triclosan	0.3
Sodium Fluoride	0.243
Water	to 100.0

The efficacy of both of these have been clinically substantiated (e.g. Formula 9, Svatun *et al.*, 1993a,b), but, of these, the technology based on the triclosan/copolymer has probably been the most extensively studied oral care product/formulation ever developed. Over 9000 subjects in 25 different clinical studies have been investigated to document the formula's safety and effectiveness, against caries, plaque, gingivitis and tartar (Volpe *et al.*, 1995b). Despite the above formulations being sold in Europe and approved by the UK Medicines Control Agency in the early 1990s, the US Food and Drug Administration classified triclosan in toothpaste as a 'new drug' ingredient. However, in June 1997 the FDA finally approved the triclosan/copolymer system for sale in the US, the only dentifrice that has so far received this approval.

The long-term impact of this technology on the overall public health of long-term users (>5 years) is obviously something which remains to be proven, but initial results show a most promising impact on the status of periodontal health of susceptible individuals (Rosling *et al.*, 1997). If this result is repeated and conclusively documented, then mass market toothpaste as a true therapeutic adjunct for the maintenance of general oral health can become commonplace, and probably constitutes the greatest advance in therapeutic dentifrice technology since the introduction of fluoride in the 1960s.

7.5.4 Toothpaste offering whitening or sensory signals

Perhaps the most commercially active segment of the category in the 1990s has been the offer of 'look good and feel good' attributes to the consumer. Given the major research effort in the therapeutic control of plaque and gingivitis, the growth in this sector is not surprising both for the smaller companies less inclined to invest heavily in the clinical research required to compete and as the next logical step for the multi-national corporations.

Initial formulations based on baking soda were markedly different. Although in reality only anti-caries toothpastes their commercial positioning enabled them to grow and segment the category. This is possibly because of the heritage of the ingredient as a general cleanser/deodorizer and the final formulation's taste which is generally salty, gritty in texture and polarizing. Examples of baking soda toothpastes are shown below:

	Example 11 (Winston *et al.*, 1988)	**Example 12 (Winston and Miskewicz, 1990)**
Ingredient	*% by wt.*	*% by wt.*
Baking Soda	62.0	30.0
Glycerin	17.0	27.6
CMC	0.75	0.3
Silica Abrasive	0	14.0
Silica Thickener	0	4.5
SLS	0.3	0.15
Sodium Lauroylsarcosinate	0.3	0.15
Saccharin	0.5	0.9
Flavour	0.7	0.76
NaF	0.22	0.22
Water	to 100.0	to 100.0

Perhaps one of the most innovative developments in the category in recent years has been the introduction of dual-chamber packaging (Pettengill, 1991). Initially pioneered in a dispenser form it was developed to enable a baking soda and hydrogen peroxide dentifrice to be commercialized. One side contained a classical dentifrice formulation, while the other side contained a stabilized peroxide gel. This obviously avoided potential chemical inconsistencies between the ingredients and allowed them to be kept separate until they were delivered to the brush head. Depending upon the legal jurisdiction (EU and US differ on this ingredient), the peroxide has been added at a low level, 0.1–0.5 % active oxygen either from hydrogen peroxide (H_2O_2) or as calcium peroxide (CaO_2). The main purpose of its introduction into toothpaste has been to impart a credibility to products positioned as 'whitening' products.

Example 13 (Williams and Ryles, 1991)

Ingredient	*Part 1* % by wt	*Part 2* % by wt	*Combined product* % by wt
Glycerin	0	40.0	20.00
Sorbitol (70%)	48.7	0	24.35
Pluoronic F127	0	20.0	10.00
Silica Abrasive	15.0	0	7.50
Sodium Bicarbonate	10.0	0	5.00
PEG 32	5.0	0	2.50
Hydrogen Peroxide (35%)	0	4.285	2.143
Silica Thickener	4.6	0	2.30
SLS	2.98	0	1.49
Ethyl Alcohol	2.85	0	1.425
CMC	0.80	0	0.40
Menthol	0.50	0	0.25
Methyl Salicylate	0	0.50	0.25
Na Saccharin	0.50	0	0.25
NaF	0.46	0	0.23
Titanium Dioxide	0.30	0	0.15
Phosphoric Acid (85%)	0	0.15	0.075
Colour, Water	to 100.0	to 100.0	to 100.00

Positioned at the borderline of the therapeutic segment and meeting a growing consumer demand for cleaner, whiter teeth, this unique packaging/formula combination was a major commercial success in the North American marketplace, possibly also because it delivered clear, sensorial different attributes (i.e. bubbles/effervescence).

This was relatively rapidly followed by the second-generation 'baking soda and peroxide' products that could deliver similar benefits but from a single tube. These avoided the cost of the complex dispenser packaging, but used complex, almost anhydrous dentifrice chemistry to avoid interactions.

Example 14 (Hsu *et al.*, 1997)

Ingredient	*Part 1* % by wt	*Part 2* % by wt	*Combined product* % by wt
Glycerin	25.0	25.0	25.00
Silica Abrasive	20.0	22.0	21.00
Propylene Glycol	17.6	17.6	17.64
Sodium Bicarbonate	12.0	12.0	12.00
Water	6.0	5.5	5.78
PEG 600	3.0	3.0	3.00
Sodium Carbonate	2.0	2.0	2.00

(*Continued*)

Ingredient	*Part 1* *% by wt*	*Part 2* *% by wt*	*Combined product* *% by wt*
Silica Thickener	2.0	2.0	2.00
Tetrasodium Pyrophosphate	2.0	2.0	2.00
Sodium Tripolyphosphate	3.0	3.0	3.00
Titanium Dioxide	2.0	0	1.00
SLS	1.7	1.7	1.70
Calcium Peroxide	1.0	0	0.50
Flavour	1.0	1.0	1.00
Na Monofluorophosphate	0.76	0.76	0.76
Na Saccharin	0.5	0.5	0.50
CMC	0.2	0.2	0.20
Xanthan Gum	0.2	0.2	0.20
Colour	to 100.0	to 100.0	to 100.00

These products, combined with heavy advertising, continued to drive this segment of the category towards offering the consumer 'perceived' improvements in the colour of their teeth (whitening). Other products were also developed to fuel the growth of this segment, utilizing slightly more abrasive ingredients. A culmination of the intense commercial activity is perhaps the combination of the previous anti-tartar technology (Examples 6–8) with these newer approaches, to give a multi-benefit – 'whitening and anti-tartar' product. An example of this is given below:

Example 15 (Ibrahim and Sodano, 1991)

Ingredient	*% by wt*
Sorbitol (70%)	29.6
Silica Abrasive	14.0
Glycerin	10.0
Silica Thickener	8.0
Sodium Tripolyphosphate	5.0
PEG-8	3.0
Sodium Hydroxide (25%)	1.8
SLS	1.15
Titanium Dioxide	1.0
Xanthan	0.7
Flavour	0.8
NaF	0.243
Sodium Saccharin	0.2
Colour, Water	to 100.0

7.5.5 Toothpastes for sensitivity

Sensitivity of the dentine is associated with the exposure of the dentine tubules, particularly around the gumline once the gingiva has receded to expose the root dentine.

Dentifrices are available which specifically claim to have a beneficial effect on sensitive teeth (painful responses to hot and cold stimulation of the teeth). The most commonly used ingredients which are incorporated into a toothpaste to provide relief from sensitivity are those which are believed to block the open dentine tubules, either by deposition of mineral salts or precipitation of proteins in the tubules. These are:

9(f) Strontium Chloride
9(g) Strontium Acetate
9(h) Formaldehyde
9(i) Hydroxyapatite

However, in the 1980s the use of soluble potassium ions as a desensitizing preparation became more prevalent. The proposed mechanism of action for these dental creams is that the soluble potassium ion can penetrate the open dentine tubules to reach the nerve fibres at the base, where it can exert a depolarizing and thus desensitizing effect. Ingredients used in these type of dental creams typically are:

9(j) Potassium Nitrate
9(k) Potassium Chloride
9(l) Potassium Citrate

However, sensitivity is perhaps one of the most disappointing therapeutic areas for the industry. Many manufacturers market products in the category within their variant range, but the formulations and ingredients used tend to be similar, with small variations on the established technologies. These clearly only provide limited relief from the condition of dentinal hypersensitivity and are not necessarily pleasant to use. In reality a breakthrough product offering true, long-lasting relief while still tasting good remains elusive. Examples of desensitizing toothpastes are shown below:

Example 16 (Hodash, 1975)

Ingredient	*% by wt*
Potassium Nitrate	10.0
Glycerin	25.0
HEC	1.6
Polyoxyethylene Sorbitan Monolaurate	2.0
Silica	24.0

Example 17 (Jackson *et al.*, 1995)

Ingredient	*% by wt*
Sorbitol (70%)	33.1
Saccharin (30%)	1.0
Strontium Acetate	8.0
Potassium Acetate	4.9
Sodium N-methyl-N Cocyl Laurate	2.0

(*Continued*)

Ingredient	*% by wt*
Flavour	1.0
Na Saccharin	0.2
Water	to 100.0

(*Continued*)

Ingredient	*% by wt*
Xanthan	1.0
Glycerin	11.0
TiO_2	1.0
Silica (Thickening)	6.5
Silica (Abrasive)	14.0
Preservative	0.1
Flavour	1.0
Water	to 100.0

7.6 MOUTHRINSE INGREDIENTS AND MANUFACTURE

7.6.1 Requirements of a mouthrinse

The primary function of a mouthrinse, like that of a dentifrice, is to freshen the mouth and breath by swishing/swilling the product around the mouth, followed by expectoration (spitting out). It achieves this by a combination of three factors:

1. the mechanical effect of rinsing debris from the mouth,
2. the effect of the flavour,
3. the effect of any agent specifically added to deliver the required end benefit (e.g. anti-bacterial).

Mouthrinses remain one of the most enigmatic and elusive aspects of a category driven by marketing underpinned by a solid technical foundation. Mouthrinses are the simplest dosage form, and most therapeutic agents are compatible with this vehicle. Thus they should be easily formulated to give documentable therapeutic benefits. However, use of a mouthwash is often perceived to be more of a social function, since the neutralization of bad breath and the feeling of a clean refreshing mouth is most often achieved in between periods of toothbrushing, and is not a substitute for brushing. Thus, the essential feature of a good mouthwash is its flavour so that it tastes good and encourages usage (Cummings, 1997).

7.6.2 Ingredients used in mouthrinses

Most mouthrinses contain five basic ingredients: alcohol, flavours, humectants, surfactants, fluoride and other active ingredients, with water and minor ingredients making up the remainder of the product.

Alcohol

Most mouthrinses contain ethyl alcohol. This serves a variety of functions, acting as a preservative, and enhancing the flavour impact of the product. It also

helps in the stability of the solubilized flavour oils and lowers the freezing point considerably, giving the rinse greater cosmetic stability.

Alcohol can be used at levels varying between 5% and 25% by weight of the product, depending upon the consumer target (i.e. children's rinse products may contain minimal quantities).

Flavour

As in toothpastes, taste is one of the key reasons for consumer preference. Thus the assistance of expert flavourists is also essential in this area in order to produce the right balance of flavour and sweetness. Flavour blends of a similar style to toothpastes are often chosen, and saccharin is the most widely used sweetening agent.

Humectant

Although using the same humectants as dental creams (glycerin and sorbitol), their function and rationale for usage in mouthrinses is totally different. With a mouthrinse they increase the viscosity of the liquid, and result in a good mouth-feel after product usage. Products without humectants have a harsh chemical-like taste/feel. Obviously humectants also impart some sweetness to the product.

Levels of humectant in mouthrinses can vary between 5% and 20%.

Surfactant

Surfactants also have a slightly different role in a mouthrinse in that they are necessary to solubilize the flavour oils and give stability to the mouthrinse. They also provide some foaming for the product. Unlike dentifrice, a greater variety of surfactants are often used in mouthrinse. These include poloxamers 407 and 338 (trade names Pluoronic F127, F108) which are polyoxyethylenated polyoxypropylene nonionic block polymers, and Polysorbate 80 which is a copolymer of ethylene oxide and a mixture of partial oleic acid esters of sorbitol. Sodium methyl cocyl taurate is often used for compatibility with ionic ingredients. Sodium lauryl sulfate has a reduced usage in mouthrinse formulations.

Levels of surfactant in a mouthrinse can vary between 0% and 1%.

Fluoride and other active ingredients

Obviously nearly all therapeutic ingredients used in toothpastes have been used in mouthrinses if they are water soluble. This includes Fluoride, Pyrophosphate ions, Triclosan, Chlorhexidene, Cetyl Pyridinium Chloride, Hydrogen Peroxide, Potassium ions and others (Cummings, 1997; Mariotti, 1998).

Minor ingredients

Minor ingredients include colours and sweeteners. It is also advisable to add a small amount of preservative to prevent or inhibit bacterial growth since a

mouthrinse is predominantly a water/humectant system. The presence of alcohol obviously gives a major preserving action, but this is often supplemented with sodium benzoate or some other preservative.

7.6.3 Manufacture of mouthrinses

Mouthrinse manufacture is extremely simple and in principle only requires one or more stainless-steel tanks, efficient mixers and a storage tank. This is because all ingredients are soluble and the finished product has a viscosity of a similar order of magnitude to water. Stringent safety precautions are, however, mandatory both from a manufacturing perspective and from a customs and excise point of view, because of the large volume of food-grade alcohol used in this type of product. This requires explosion-proof equipment (pumps and mixers) and a bonded storage area.

7.7 MOUTHRINSE FORMULATIONS

Examples of several different types of mouthrinse formulations are shown below:

7.7.1 Anti-cavity mouthrinses

Sodium fluoride, normally at 0.05% for daily use, provides an anti-caries benefit. Studies conducted on school children (10–11 years of age) typically show that after 3 years of regular daily use, fluoride mouthrinses can produce a significant, additive anti-caries benefit in the region of 20–40% on top of that provided by a fluoridated toothpaste (Ripa, 1992; Mariotti, 1998). An example of this type of formulation is shown below:

Example 18

Ingredient	*% by wt*
Alcohol	5.0
Glycerin	7.5
Sorbitol (75%)	7.5
Pluronic F-127	1.0
Pluronic F-108	1.0
Na Saccharin	0.02
NaF	0.05
Flavour	0.08
Colour, Water	to 100.0

7.7.2 Anti-tartar mouthrinses

In the 1980s the application of the patented pyrophosphate/copolymer anti-tartar technology was applied to mouthrinses. This has resulted in products which can

reduce tartar formation by up to 35% after 3 months' regular usage (Singh, 1988). An example of this type of formulation is shown below:

Example 19 (Gaffar and Polefka, 1986)

Ingredient	*% by wt*
Ethyl Alcohol	15.0
Glycerin	10.0
Tetrasodium Pyrophosphate	1.6
Poloxamer	2.0
Flavour	0.4
NaF	0.05
Gantrez	1.0
Sodium Saccharin	0.03
Water	to 100.0

7.7.3 Plaque and gingivitis mouthrinses

In the 1990s branded goods manufacturers made a consistent and heavy commercial investment behind the segment. A historical mouthrinse containing a mixture of essential oils became the first non-prescription mouthrinse to receive the Seal of Acceptance of the Council on Dental Therapeutics (American Dental Association). This was based on its effect on plaque and gingivitis measured in 6-month human clinical studies (Lamster *et al.*, 1983; Gordon *et al.*, 1985). New formulations were produced, initially by the smaller manufacturers, some of which were essentially marketing-driven in the early stages (e.g. plaque removal pre-brushing rinse). These formulae were often based on laboratory investigations, but with the commitment of the major manufacturers to the segment these were gradually upgraded to formulae whose efficacy could be documented in well-conducted human clinical trials. One formula was produced which was pleasant to use, suitable for mass market applications, and had two 6-month clinical trials documenting its long-term effect on both plaque and gingivitis reduction (compared to a placebo) when used as a pre-brushing rinse in combination with a basic anti-cavity toothpaste (Worthington *et al.*, 1993).

Example 20 (Gaffar *et al.*, 1993)

Ingredient	*% by wt*
Ethanol	12.5
Glycerin	10.0
PVM/MA Copolymer	0.2
PEG	5.0

(*Continued*)

Ingredient	*% by wt*
SLS	0.2
Flavour	0.4
Triclosan	0.03
Sodium Saccharin	0.2
Colour, Fluoride, Water	to 100.0

7.7 CONCLUSION

Trying to predict future trends for the next 5 years in a category which has experienced such tremendous innovation and growth in the last 10 years is difficult. The speed of development appears to be ever increasing and global. Previously multi-national manufacturers might try a particular approach in a country and region for an extended period of time. Today, at the first sign of success the product can be marketed and distributed in over 200 countries in less than 6 months. It is because of this that major manufacturers pay ever-increasing attention to the consumer benefits and positioning of the products prior to launch.

For the formulator of toothpaste the advent of low-cost dual-chamber packaging clearly opens up a plethora of previously impossible options that can go in many different directions. New or modified materials are continually being developed, as are other packaging options that will continue to deliver much-needed differentiation in the marketplace. Product forms, e.g. multi-stripes, gels, speckles, etc., will help the marketers drive the category (white pastes are becoming less and less frequent, unless linked to therapeutic benefits), and more complex patterns or forms are clearly under development. In the cosmetic area improvement in products which truly deliver brighter whiter teeth and thus a better appearance is an obvious route to follow.

Clinical research continues to drive part of the dentifrice category in the direction of providing ever more meaningful therapeutic benefits and ever closer to the pharmaceutical/drug category. However, this domain is probably restricted to the large multi-national corporations who can afford the extensive testing programmes. If the dual-chamber fluoride technology delivers the promise of superior anti-cavity performance, this could truly revolutionize the category. Clearly the long-term health benefits of the triclosan/copolymer technology on oral health will be studied and could prove to be an enormously significant advance. Improved versions of the triclosan technologies, adding additional benefits, will undoubtedly be developed and could perhaps be combined with the dual-chamber technologies. Superior products offering long-lasting benefits against dental hypersensitivity should be developed.

Finally, the mouthrinse category does not appear to have been successful for the branded-goods manufacturers, probably due to the economics involved.

Many branded-goods manufacturers have either withdrawn from the category or at least withdrawn a number of formula options to focus on the most profitable. The explosion of media advertising observed at the beginning of the 1990s has dissipated. It is perhaps because of their high cost relative to toothpaste and brush, or simply that, in an era of highly therapeutic mass market toothpaste, the use of supplemental mouthrinses which are available to the mass market is relatively unnecessary except as a simple breath-freshening convenience. Currently mouthrinses are, in general, the domain of the 'own-label' manufacturers and are probably likely to remain so. If, however, a highly significant and clear therapeutic benefit of using a toothpaste and mouthrinse can be documented (better than brushing alone) this may change.

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8

Hair treatments

F.J. Mottram and C.E. Lees

8.1 HAIR PHYSIOLOGY, STRUCTURE AND GROWTH

8.1.1 Physiology

Ebling and Johnson [1,2] have shown how each hair follicle originates from an interaction between epidermal and dermal layers of the skin. The hair follicle is a sheath of epidermal cells and connective tissue that encloses the root of the hair (Fig. 8.1).

Specific cells from the superficial dermis increase in number and grow forward to form a 'peg'. Beneath this are specialized fibroblasts which will become the dermal papilla. Epidermal cells adjacent to the dermal papilla multiply and push a column of keratinizing cells towards the scalp surface, and these keratinizing cells become the hair shaft. The hair 'peg' migrates downwards to form the follicle with swellings appearing as the column elongates. These are the sites of the *erector pili muscle* and *sebaceous glands*. The hair follicle has one of the highest rates of cell division in the human body and makes considerable demands on energy to sustain such growth.

8.1.2 Structure

It is the nature of the hair shaft which is of primary interest. The outermost structure is the cuticle which surrounds the cortex. It is composed of flat cells which overlap in a roof-tile formation with an intercellular cement to bind them together. Each cell has an outer membrane and contained within the membrane are three distinct layers, the *A-layer*, the *exocuticle* and the *endocuticle* (Fig. 8.2(b)).

The cortex comprises the majority of the fibre mass, consisting of elongated keratinized cells bound together with intercellular material. The cells are

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 255–287

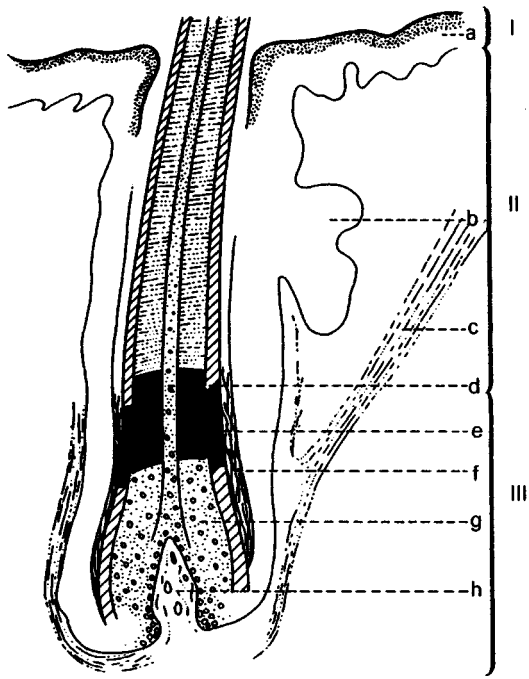


Fig. 8.1 Diagram to illustrate structure of hair follicle in relation to epidermis I, corium II and connective tissue III, showing epidermis (a), sebaceous gland (b), erector pili (c), medulla (d), internal root sheath (e), external root sheath (f), hair bulb (g) and papilla (h).

roughly 5 μm wide and 50 μm long. There are in fact two regions of cortex, the *paracortex*, which is predominant, and the *orthocortex*, which is the minority component. The paracortex cells are embedded in a sulfur-rich matrix (Fig. 8.2a) with chemical cross-linkages, but the orthocortex cells do not have this protection. Macrofibrils are found within the cortical cells. The variation in length is due to pigment granules and nuclear remnants. Within the macrofibril, subfilamentous structures called microfibrils can be found. The width of a macrofibril is 0.1 μm to 0.4 μm, whereas the microfibril is 0.007 μm approximately. A further sub-structure has been identified within the microfibril, which has an estimated width of 0.002 μm and is called a protofilament. These are thought to consist of three α-helix polypeptide chains forming the basic and fundamental structure of the hair.

Melanins (natural colour pigments) occur within the cortex. These are derived from an amino acid, tyrosine, and are of two types, *eumelanin* and *pheomelanin*. These pigments are formed by melanocytes situated in the pigmented part of the hair bulb and the outer sheath of the hair follicle. The eumelanin gives brown to black colouration and the pheomelanin gives an auburn tone.

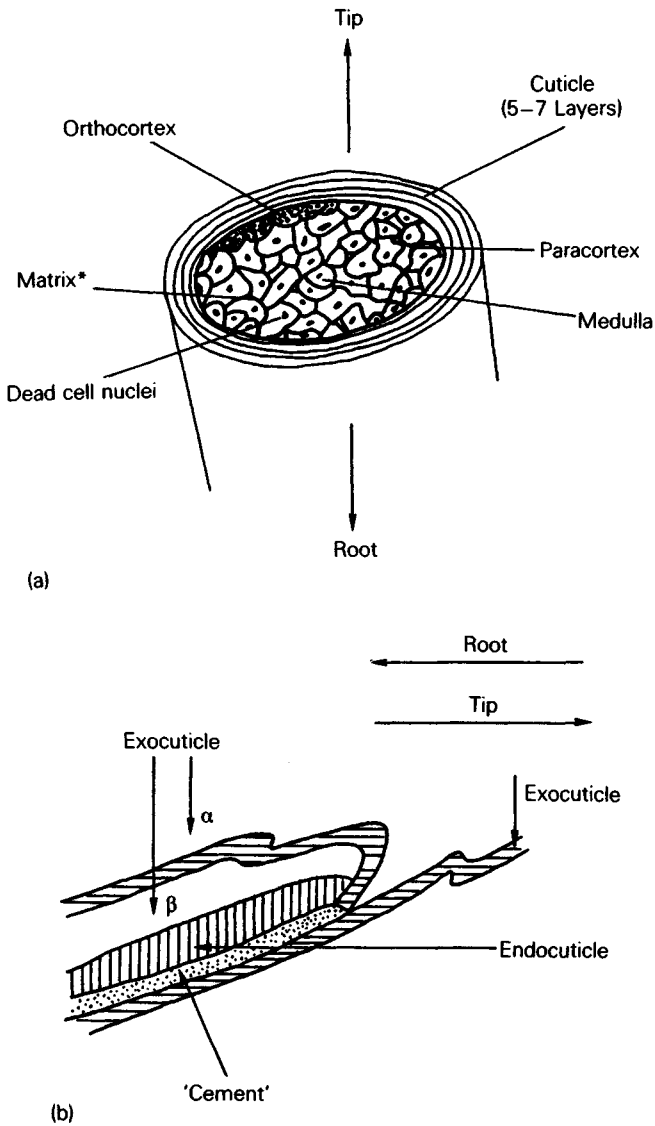


Fig. 8.2 The structure of hair fibres: (a) the hair fibre in cross-section, (b) details of the structure of the cuticle.

The *medulla* forms only a small proportion of the total fibre mass and contributes very little to the mechanical and chemical properties of the hair. It comprises a series of vacuoles or air spaces formed due to dehydration of the loosely packed cells during the keratinization process. Figure 8.2(a) is a diagrammatic cross-section of a typical hair fibre.

Ethnic hair structure

Afro-Caribbean hair is very tightly curled and has an elliptical transverse section when viewed under the microscope. Chemically, the amino acid content is similar to Caucasian hair but the distribution of the sulfur amino acids differs, giving rise to the curly appearance. The non-uniform distribution of the disulfide bridges on one side of the hair fibre causes the curliness. This gives rise to problems such as difficulty in combing, dryness and brittleness, which in turn can lead to hair breakage.

8.1.3 Growth

A typical growth rate for human hair is 0.3–0.5 mm per day. A healthy scalp (the top of the head extending from 2–3 cm above the ear), supports something of the order of 100 000 hair follicles, according to Szabo [3]; but Mottram [4] considers the number to be nearer 150 000. The tendency in such an experiment is to underestimate the count rather than to exaggerate it.

(a) The cyclic nature of hair growth

Kligman [5] offers a detailed account of this subject, of which the following is a summary. Practically all of the follicles participate in a cyclic activity. The active growth or **anagen** in which the hair is produced alternates with a resting period known as the **telogen** phase. In the latter period the fully formed or club hair remains fixed in the follicle by its expanded base and the dermal papilla is free from the epidermal matrix. The latter is reduced to a small secondary growth. Between the anagen and telogen stages there is a short transitional period, known as the **catagen**, in which the newly formed club hair moves towards the skin surface. All of the hair fibres reach a terminal length which is determined by the duration of the anagen phase. At any one time some 85% of the scalp hairs are said to be in the anagen phase, and 12% and 3% are in the telogen and catagen phases, respectively. These proportions are very similar to those found in a study of the mechanical properties of scalp hairs from one particular head [6]. A scalp anagen phase may be as long as three years.

Table 8.1 Amino acid composition of hair keratin

Amino acid	*mol %*	*Amino acid*	*mol %*
Alanine	5.6	Lysine	2.9
Arginine	7.0	Ornithine	0.2
Aspartic acid	7.0	Phenylalanine	2.0
Cystine*, cysteine*, methionine*	12.3	Proline	7.0
Glutamic acid	12.9	Serine	10.2
Glycine	6.0	Threonine	6.7
Histamine	0.8	Tyrosine	2.0
Isoleucine	3.2	Valine	6.2
Leucine	8.0		

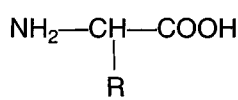
*Sulfur acids.

8.2 HAIR CHEMISTRY

Hair fibres are composed of approximately 85% of the complex protein *keratin*, with some 7% of associated water. The other principal constituents are lipids 3%, and pigment 2%. This last component is *melanin*, derived in biosynthesis from the amino acid tyrosine. Also present are trace amounts of many metals such as aluminium (Al), chromium (Cr), calcium (Ca), copper (Cu), iron (Fe), manganese (Mn), magnesium (Mg) and zinc (Zn), the last in a fairly high concentration of 22 mg per 100 g of hair. Phosphorus compounds are also abundant (80 mg per 100 g hair), mainly derived from degraded nuclei of the cortex cells. The most important material is keratin which has been formed biochemically from the condensation of some 18 types of amino acids (Table 8.1).

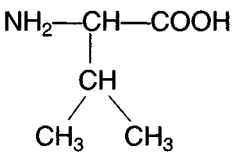
8.2.1 Amino acids

Amino acids may be represented by the generic structural formula below:

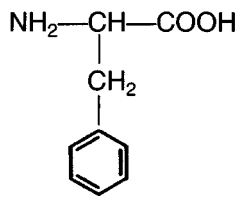


Amino acids may be classified according to the following convention. Other systems of classification are often used, none of which is entirely satisfactory.

Hydrophobic. Examples: valine and phenylalanine

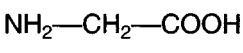


Valine

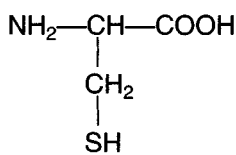


Phenylalanine

Polar. Examples: glycine and cysteine

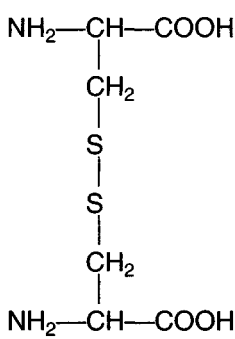


Glycine



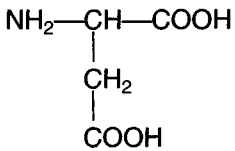
Cysteine

Cysteine is the fission product of cystine (below). Later these two amino acids will be shown to be technologically important in the context of hair-waving products.

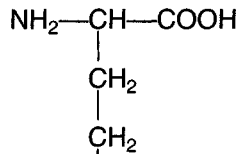


Cystine

Acidic. Examples: aspartic and glutamic acids

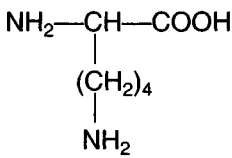


Aspartic acid

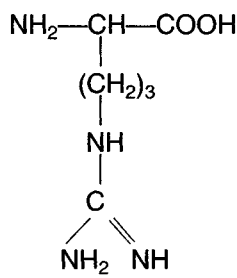


Glutamic acid

Basic. Examples: lysine and arginine



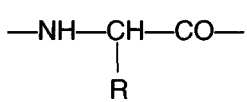
Lysine



Arginine

(a) Peptide linkage

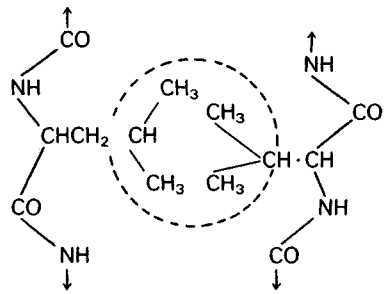
In the protein chain, individual amino acids are joined linearly by the group formed from the condensation of a carboxyl group with an amino group to form what is known as a peptide linkage; i.e. —CONH—. Thus the repeat unit in the keratin chain is



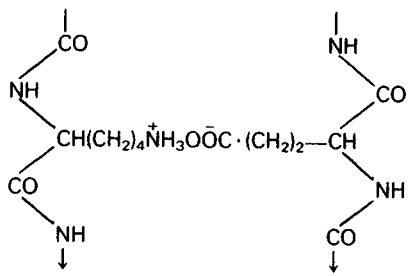
where R may represent the same or different amino acid characterizing groups, e.g. for glycine R = H, for lysine R = —$(CH_2)_4$—NH_2.

In the hair fibre, keratin chains run roughly parallel to each other and to the fibre axis. These chains are bonded to each other in a lateral sense through physicochemical interactions between the R groups of the amino acid 'residues'.

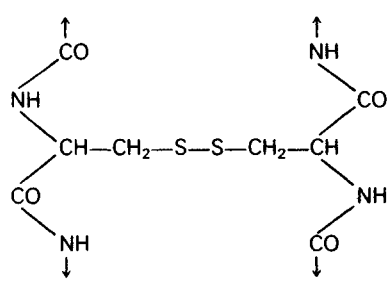
Thus where hydrophobic residues are adjacent, hydrophobic links form the bonds in that particular segment of the protein chain:



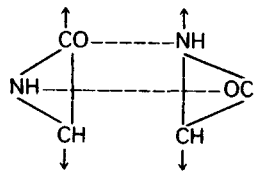
Similarly, where an acidic amino acid (e.g. glutamic acid) on one keratin chain is opposite a basic R group on an adjacent chain a salt linkage can be formed:



In hair keratin there is an abundance of sulfur amino acids (cysteine and cystine), and in the biosynthesis of keratin, cysteines in neighbouring chains can combine via a disulfide bond, and this provides a strong covalent bond between chains:



Quantitatively, hydrogen bonds may contribute considerably to the cohesion between keratin chains. These may arise in a number of ways; one of which is illustrated below:



Here the hydrogen bonding arises from the interaction between the peptide linkages of adjacent protein chains.

These several mechanisms by which keratin chains can be bonded laterally account for the unusually high values for hardness, density, optical refraction, etc., which characterize hair keratin.

(b) Limitations of amino acid analysis

Gillespie [7] believes that amino acid analysis alone is an inadequate basis for the correlation of chemical composition with the morphology, physical properties and functionality of the keratins. His approach could be termed 'chemical affinity' classification. It involves chemically separating the various protein types liberated after the disulfide bonds have been broken by bisulfite reduction (aided by urea acting as a swelling agent), followed by sequential precipitation into fractions. He recognizes the following fractions:

1. A low sulfur component which contains a high level of extensible α-helix protein. This is the component of hair keratin which is responsible for the phenomenon of 'set'. It is the main constituent of the protofibrils of the cortex cells.
2. A high sulfur component, which is present in the matrix, or cement, between the cortex cells.
3. A third fraction which is rich in the amino acid tyrosine.

Consider two contrasting forms of mammalian keratin, human scalp hair and porcupine quill. The hair is very rich in the high sulfur protein fraction, about 40%, and contains only a nominal amount of the high tyrosine fraction. At the other extreme, the porcupine quill is low in high sulfur protein (about 7%), but very rich in the tyrosine fraction. Other examples along these lines may be quoted.

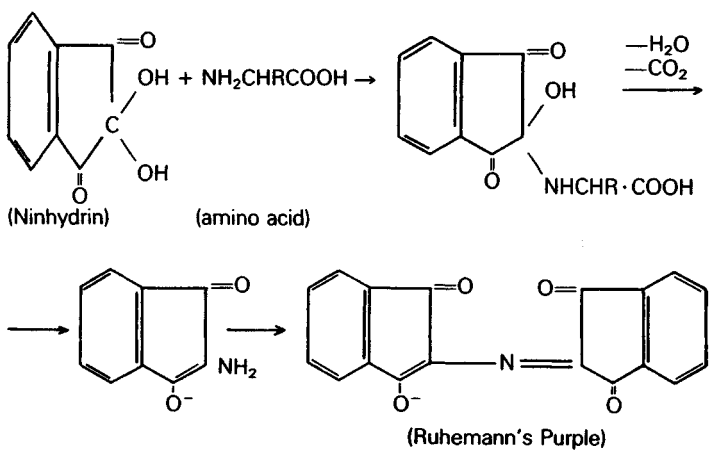
8.2.2 Chemical reactivity of hair keratin

(a) Alkali hydrolysis

Hydrolysis by strong alkalis is less complete than acid hydrolysis, in the sense that, as well as liberating individual amino acids, some of the keratin is broken down only so far as the peptide state. This is demonstrated by use of a colorimetric test, the biuret test, which works positively upon the alkali hydrolysate. This test applies only where peptide linkages, —CONH—, are present.

(b) Acid hydrolysis

The acid hydrolysis of keratin, e.g. with moderately strong hydrochloric acid, breaks down the protein into its constituent amino acids almost entirely. Thus, upon completion, virtually no material which incorporates the peptide unit is present. However, through the mechanism of deamination of the amino acids with the reagent ninhydrin a purple colour (Ruhemann's Purple) can be developed. This reaction can be used to detect and quantify proteins in their hydrolysates. It is useful in measuring the extent of the damage to hair cuticle and the alleviation of the damage by certain hair-care treatments.

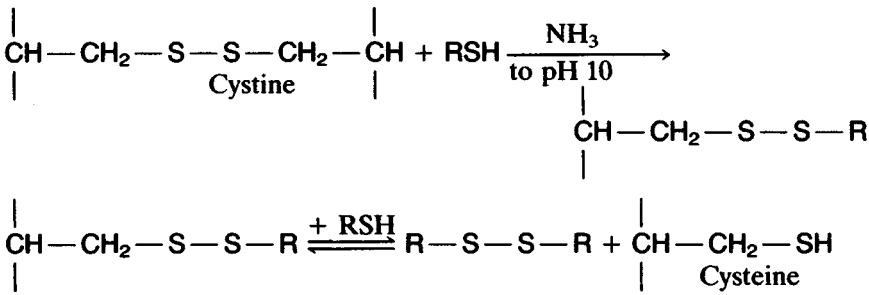


(c) Reactions of sulfur amino acids

The most interesting sulfur amino acid, cystine, may be reduced to general thiol groups (—SH) by a number of reducing agents. These agents include mercaptans such as thioglycollic acid, alkali bisulfite (e.g. $NaHSO_3$) and certain phosphorus derivatives [8] such as tertrakis (methylol) phosphonium chloride (TMPC).

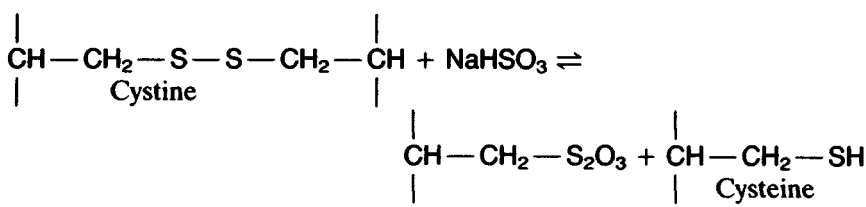
Commercially the mercaptan, ammonium thioglycollate, is the most important as it forms the basis of most permanent waving processes and also many hair-straightening products.

Mercaptan reduction

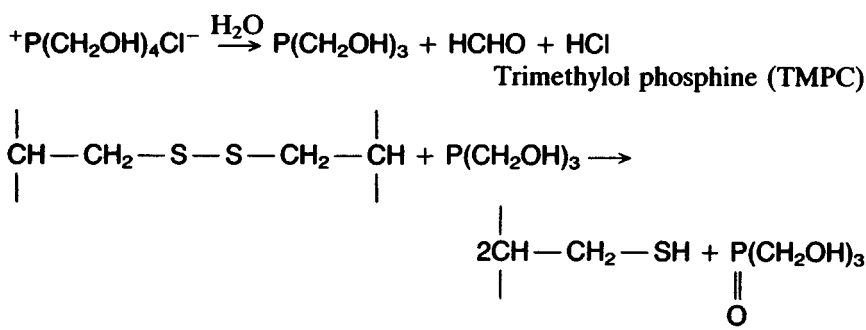


The equilibrium constants are of the order of unity. Hence an excess of the reducing agent is necessary to achieve an adequate degree of cystine reduction.

Alkaline bisulfite reduction



Reduction with phosphine derivatives

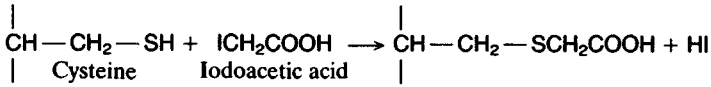


In all cases when the degree of reduction is sufficient for the hair to be made plastic enough to be 'set' it can then be fixed (neutralized) by application of an oxidizing agent. Alkali bromates and hydrogen peroxide are practical examples of oxidants.

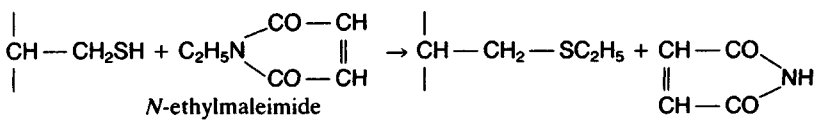
(d) Alkylation of thiol (SH) groups

Alkylation can be readily accomplished with a wide range of alkylating agents; some of the better known ones are described below:

Reaction of thiols with iodoacetic acid. This has an obvious application in the determination of the degree of reduction of hair which has been treated with reducing agents.



Reaction of thiol group with maleimides. This includes the difunctional compound phenylenedimalimide (PDMI). In theory the reagent should also work as a cross-linking agent, establishing a covalent bond between two keratin chains. Sterically, this would appear to be an unlikely linkage [9]. It has not been verified in terms of changes in the physical properties of hair which has been reacted with PDMI [10]. The reaction with the simpler *N*-ethylmaleimide proceeds as follows:



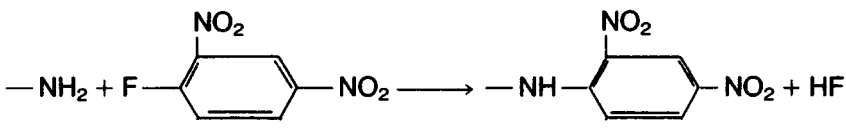
(c) Reactivity of 'free' amino groups

'Free' amino groups are those which do not participate in either the continuous protein chain, or in the cross-linking bonds formed between adjacent protein chains. The deamination of amino acids is an example of amino reactivity which has already been discussed. Amino groups can be made to enter into the formation of interprotein chain bonds by reaction with aldehydes, including formaldehyde.

$$\underset{\text{N-terminal amino acid}}{-NH_2} + \underset{\text{Formaldehyde}}{HCHO} + -NH_2 \rightarrow -NH-CH_2-NH- + H_2O$$

A physiologically safe way of producing such bonds is to employ a *N*-methylol compound as a formaldehyde donor. Examples of such compounds are the *N*-methylol ureas, thioureas and melamines. These are readily prepared by reacting the parent compound quantitatively with the aldehyde. The latter is released, ready for the reaction with amino groups by acidification.

Some useful alkylation reactions can be performed upon free amino groups of hair keratin. In particular, one such reagent in this connection is 1-fluoro-2,4,dinitrobenzene (FDNB).



FDNB

These derivatives are not decomposed in hydrolysis and as a consequence can be used to identify the individual amino acids in their hydrolysates.

8.3 PHYSICAL PROPERTIES OF HAIR KERATIN

Hair keratin is highly complex in respect of both chemical composition and molecular architecture. Much information on the structure can be gained from the study of its physical properties. Hair has an unusually large specific gravity for an organic substance, of the order of 1.32, and a very low thermal conductivity, comparable to that of asbestos.

(a) Mechanical properties

Human scalp hair fibres have diameters within the range 30–100 μm, depending upon age and racial group. They have a hardness similar to that of stainless steel (hair fibres pressed between the jaws of a stainless steel vice leave a score mark). The breaking load of a typical hair is of the order of 100 g, substantially lower than its root strength. Young's modulus for hair in the stretching mode is of the order of 2×10^{10} dynes/cm^2. The corresponding value for a typical polymer as used in hairspray formulation is typically 10^7 dynes/cm^2.

(b) Electrical properties

The resistivity of hair is of the order of 800 megohms, measured after equilibrium in an atmosphere of 50% relative humidity. It also has a particularly high dielectric constant of 8.3, similar to that of calcite, this measurement having been carried out at 25°C and 60% relative humidity. The iso-electric point (pH value at which the substance has no net electric charge) is approximately 5.

(c) Influence of water

The water content of hair varies according to the relative humidity of the surrounding atmosphere. Figure 8.3 represents the relationship between water content and relative humidity at constant temperature; this type of figure is generally described as the 'regain isotherm'. At humidity of 85–87% the water content, and consequently the physical properties of hair, undergo large changes. Water uptake at much less than 85% humidity occurs in the adsorption part of the 'regain isotherm'. The corresponding regime at humidities greater than 85% is termed the 'solution region'.

The thermal effects following the treatment of hair with water are surprisingly large. This observation applies to both the heat of surface wetting and to the heat of water absorption. The latter effect is easily detected by the senses. In water-saturated atmospheres hair fibres will swell to the following extent: radially, 16%; longitudinally, 1.2%; in volume, 37%.

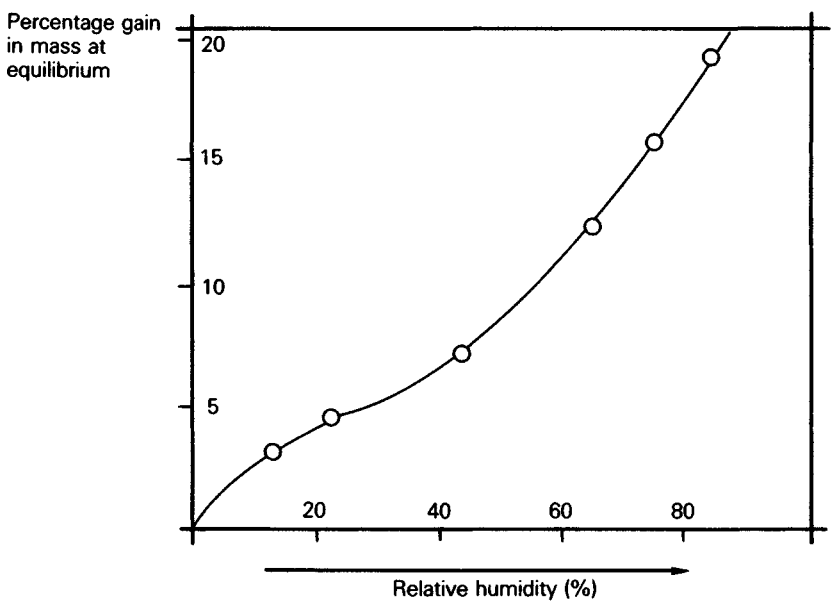


Fig. 8.3 Water content of human hair in relation to the ambient humidity at 23°C.

(d) Optical properties

The refractive indices of hair measured at a wavelength of 578 μm are respectively 1.557 and 1.540. These values are high and similar to those of flint and crown glasses.

8.3.1 Interpretation of the physical properties

1. The extreme anisotropy of the hair fibre is demonstrated by a number of its properties, e.g. the contrasting values for radial and longitudinal swelling.
2. Hardness measurements also give unexpectedly large values, indicating the closeness of packing and strength of the lateral bonding operative in the keratin molecule.
3. The equally large values for the mechanical moduli, e.g. Young's modulus and rigidity modulus can be attributed to the factors described in (2) above.
4. That strong thermal effects are met when hair is allowed to interact with water reflects the highly polar nature of the keratin chain segments and the generous surface area available for adsorption of water.
5. The magnitude of the volume swelling of hair in water is a consequence of the abundance of water-sensitive bonds between adjacent keratin chains.
6. Hair has a high electrical resistivity and a fairly low dielectric constant. In practical terms these properties relate well to the fact that it is easy to generate electrostatic charges by brushing and combing. These charges leak away only very slowly, giving rise to the hairdressing phenomenon of 'flyaway hair'.
7. The refractive index of hair is high, making it difficult to enhance its gloss by depositing films of organic polymers upon its surface.

8.4 'SET': A UNIQUE PHYSICAL PROPERTY OF KERATIN FIBRES

Keratin fibres (hair, wool) may be extended by a pulling action to exactly twice their initial length. X-ray diffraction studies by Astbury [9] provided a molecular explanation of this effect. The unstretched fibre gave rise to a spacing on the X-ray diagram corresponding to 5.2 angstroms (Å); The corresponding spacing for a fully extended fibre is $3.4 \times 3 = 10.2$ Å. The 3.4 Å spacing was deduced to be the length of a single amino acid residue. The above observations allowed a molecular model to be developed: unstretched keratin chains are folded (corrugated), whilst in the fully stretched condition keratin exists in a planar, sheet-like form. These states are known as alpha (half-length) and beta (1 in 1) keratin, respectively. Astbury viewed the keratin chains as molecular 'springs', which has always served as a good analogy.

In the stretched condition the fibre is said to have 'set'. Quantitatively, set may be defined as follows. If the original length of the fibre is L and the extended length is $L + \delta L$, then the set produced in the fibre is $\delta L/L$. This set,

like the beta state of keratin, is intrinsically unstable, thus the set fibre will try to revert to its original length, i.e. δL diminishes with time. This process is accelerated by exposure to liquid water or its vapour, thus after time t has elapsed the excess length will be δL_t, where δL_t is $<\delta L$.

The set retained at t, expressed in percentage terms will be given by the expression:

$$\text{Set retained} = \frac{100(\text{set at time } t)}{\text{Initial set}} = \frac{100(\delta L_t)}{(\delta L/L)} = \frac{100(\delta L_t)}{\delta L} \qquad (1)$$

This treatment can be applied directly to the set achieved in single fibres. However, in the testing of products for use on hair it is more useful to apply the method of Micchelli and Kohler [11] to tresses of hair made of many parallel hair fibres. These conveniently should weigh 1 g each and will approximate quite well to a portion of a head of hair. The tresses are wound into spiral curls after the setting treatment has been applied, and their lengths measured at various intervals. Usually, to speed up the process, they are exposed throughout the test to an atmosphere of high humidity. The set retained by the spiral tresses after a time t is calculated along the lines already explained for the case of the set of single fibres:

Let the length of the unwound tress $= L$

Initial length of spiral unwound form (t_o) $= L_o$

Initial set $= L - L_o$

Length of spiral at time t $= L_t$

The set at time t $= L - L_t$

The percentage set at time t

$$= \frac{100(\text{set at } t)}{(\text{Initial set})}$$

$$= \frac{100(L - L_t)}{(L - L_o)} \qquad (2)$$

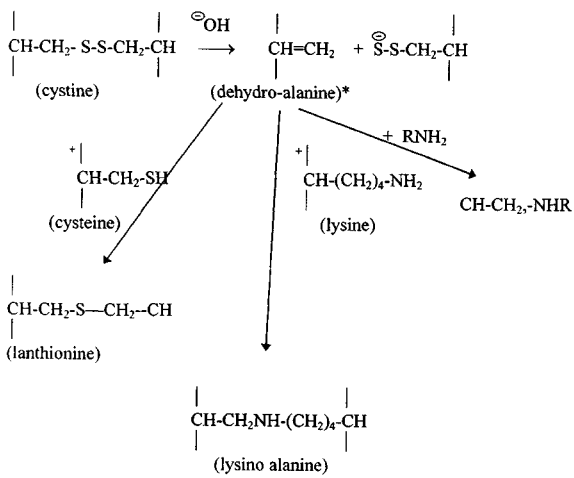
8.4.1 Permanent and temporary set

A temporary set is achieved by use of water waving techniques followed by treatment with wave sets, hairsprays, etc. These treatments work by physical as opposed to chemical mechanisms. From their nature the set will span days rather than weeks or months.

Permanent sets are obtained through the use of chemical treatments, such as thioglycollate-based hair-waving and -straightening products. Processes which make use of other keratin-reducing agents also fall into this category, as do caustic lye products, the latter being used almost exclusively in straightening

products for negroid hair. Basically those products giving rise to a permanent set introduce new chemical bonds into the hair structure, especially new disulfide bonds. This topic has already been discussed in the section of this chapter devoted to the chemical reactivity of hair.

Interestingly, the wool industry would regard the above chemical treatment as producing a temporary set! The explanation is that textile technologists realize that the set obtained by interchain disulfide bonding can be eroded by subjection to mechanical strain, particularly repeated strains. In structural chemistry, strains of sufficient size and persistence can rearrange the disulfide bonds responsible for the set. This effect is known as the sulfydryl-disulfide interchange [12,13]. When native hair keratin is sufficiently stressed, fission of the disulfide bonds occurs by means of the above interchange reaction. Eventually α-keratin becomes irreversibly denatured (effectively destroyed). A technically permanent set can be obtained by replacing disulfide bonds with other covalent cross-linkages which cannot participate in the interchange. Two examples of mechanically stable cross-linkages are (a) the lanthionine bond and (b) the lysino-alanine bond. Both of these can be developed in the keratin structure by a controlled treatment in alkaline conditions according to the scheme set out below:



*Alternative name: amino-acrylic acid.

8.5 HAIR-CARE PRODUCTS

During the 1990s there have been various constraints imposed on the formulator of hair-care products. These can be categorized as performance-related, environmental, and a growing concern for health hazards.

This has led to a far greater toxicological knowledge of the individual ingredients used in formulations. The environmental fate of those formulae will also be well documented so that there is a significant degree of confidence in products delivering the claimed performance without adverse effects to the environment or to human health.

8.5.1 Classification of hair-care products

Hair-care products may be classified into two groups:

1. Those working by physical mechanisms, e.g. shampoos, conditioners and hair sprays.
2. Those bringing about chemical changes in the hair, e.g. permanent waving, hair-straightening preparations, and permanent hair colourants.

Hair-care products are intended to deliver positive benefits to the hair and eliminate or reduce undesirable attributes. Hair is an extremely important factor in personal appearance, but despite its great strength, hair is prone to damage by weathering, chemical attack, heat and abrasion. Poor hair condition shows as roughness and dryness.

8.5.2 Hair-care products: relevant hair characteristics

Characteristic properties of hair can be measured objectively in the laboratory or in psychometric tests. The latter involve the use of human observers in a statistically designed experiment (see 'Evaluating Hair Products', p. 573). The data obtained in the objective tests must be able to be correlated with the consumer's perception. An attribute of hair is a characteristic which can be reliably assessed by the product user.

Omitted from Table 8.2 are such negative characteristics as dandruff (a scalp skin disorder) and the greying of hair. The favoured product form for alleviating the former is a shampoo containing an 'active ingredient', and for the latter a range of hair colourants.

8.6 CURRENT POST-SHAMPOO HAIR-CARE PRODUCTS

One strategy in developing new products is to relate the ability of existing hair products to produce the desirable properties listed in Table 8.2; deficiencies can be made up and negative characteristics can be reduced or eliminated. Products assigned an asterisk (*) in Table 8.3 utilize a good deal of technology of film-forming polymers. Similarly those marked with a dagger (†) involve a detailed knowledge of pressurized packaging technology. Instead of quoting highly detailed formulae, a building-block formula will initially be examined for each type of product. This will be followed by an investigation aimed at finding how

Table 8.2 Hair characteristics: descriptive terms

Original hair		*After treatment*	
Condition	*Set/control*	*Condition*	*Set/control*
Favourable			
Gloss	'Body'	Gloss	Curl strength
Shine	Springiness	Shine	Springiness
Lustre		Lustre	Body
Softness		Soft	Ease of styling
Ease of combing		Ease of combing (wet and dry)	Ease of setting
Absence of flyaway		Absence of flyaway	Set retention, 'hold'
Unfavourable			
Dry	Fine	Dry	Fine
Greasy	Limp	Greasy	Limp
Coarse	Unmanageable	Coarse	Unmanageable
Damaged	'Bushy'	Damaged	'Bushy'
Flyaway		Flyaway	

the simplified formula may be modified to achieve the properties required by the products listed in Table 8.3.

The formulae quoted in the following sections do not include detailed information and proportions of product 'builders' such as perfumes, preservatives and colours. These important ingredients must, however, be included early on in the development of a product so that they may be evaluated for long-term stability and physiological safety.

Some formulae contain special additives which are regarded as being effective in relatively low concentrations. The term 'effective' means bringing about significant changes in product performance or introducing novel properties, i.e. properties not formerly associated with that type of product. The range of silicone compounds now available includes examples of such additives, and the use of many of them in hair-care products has been reviewed by Alexander [14]. These raw materials are well defined chemically, unlike others proposed, such as protein derivatives.

8.6.1 Hair conditioners

Conditioners applied to the hair after shampooing are designed to confer the following properties on the hair:

1. Smooth, tangle-free wet and dry combing.
2. Reduction of static electricity generated by combing and brushing dry hair, otherwise known as 'flyaway' hair.

Table 8.3 Important post-shampoo hair products

Physical mechanisms	
Hair conditioners	Also available as aerosol for mousses*†
Cream rinse	
Clear rinse	
Leave-on types	
Wave sets	
Lotions*	
Aerosol lotions*†	
Aerosol foams (mousses)*†	
Hairsprays	
Aerosols*†	
Non-aerosol (pump) sprays*	
Hair dressings	
Brilliantine gels	
Brilliantine liquids	
Emulsion creams (O/W and W/O)	
Non-greasy gels	
Aerosol foams (mousses)	
'Tonics'	
Chemical mechanisms	
Permanent waving preparations	
Roller or pin curl types	
Hair straighteners	
Thioglycollate creams	
Caustic lye creams	
Press oils and gels	

*† See text.

3. Improved gloss or lustre.
4. Improved body or volume.
5. Improved texture of chemically or heat damaged hair.

The rinse conditioner is applied to the hair after shampooing and rinsing away the shampoo. The hair is towel-dried and then the conditioner uniformly distributed through the hair. A few minutes after application the treated hair is rinsed with clean water and styled as desired.

(a) Formulation of rinse conditioners

Formula I represents a traditional composition for this category of product. The cationic wetting agent, cetyl trimethyl ammonium chloride (CTAC) is the key

ingredient. The hair has an anionic (−ve) charge, and anything with a cationic charge (+ve) will be attracted to the hair and attach itself to the hair shaft. The result is a diminished comb to hair friction, leading to smooth tangle-free combing and a reduction in 'flyaway'.

CTAC also behaves as an emulsifier for the cetyl alcohol which is present to confer viscosity to the product, making it easier to apply and control on the head.

Substantivity is higher when the hair is damaged or more porous, therefore the conditioner will work harder where the need is greatest.

Formula I Hair conditioner

	% w/w
Cetrimonium chloride (CTAC) 30% active	3.00
Cetearyl alcohol	2.80
Perfume	q.s.
Preservative	q.s.
Citric acid	pH 3.0–5.0
Colour	q.s.
Water (deionized)	to 100.00

Manufacture

1. Add 90% of the water and the cetrimonium chloride to the main manufacturing vessel. Heat to 70–75°C.
2. Melt the cetearyl alcohol in a jacketed side vessel. Heat to 70–75°C.
3. When both phases are at 70–75°C, add the oil phase to the water phase with homogenization to form an emulsion.
4. When the emulsion has formed, commence cooling to 40°C with paddle stirring only.
5. Dissolve the preservative in a portion of the reserved water. Add to the main vessel with continuous mixing.
6. Add colour to the main vessel. Continue to cool.
7. Add fragrance to the main vessel. Mix until homogeneous.
8. Adjust pH with citric acid dissolved in water to pH 3.0–5.0.
9. Cool to 35°C.

There are other ingredients which can give added performance to basic hair conditioners:

Panthenol, a provitamin of pantothenic acid, can be shown to give an increase in volume to the hair.

Dimethicone copolyol improves wet combability, reduces flyaway and confers softness to the hair.

Hydrolysed proteins of vegetable origin act as humectants, providing body to damaged hair. More terminal amino and carboxylic acid groups are available if a lower molecular weight protein is selected, thus conferring greater substantivity to hair. Formula II represents a more intensive conditioner. This type of formula is of a high viscosity with a creamy appearance.

Formula II Intensive hair conditioner

	% w/w
Cetrimonium chloride CTAC (30% active)	4.00
Cetearyl Alcohol	5.00
Dimethicone Copolyol	1.00
Glycerin	1.00
Cocamide MEA	1.00
Benzalkonium Chloride	4.00
Perfume	q.s.
Preservative	q.s.
Colour	q.s.
Citric Acid	pH 3.0–5.0
Water (deionized)	to 100.00

Manufacture

1. Add 90% of the water, cetrimonium chloride, benzalkonium chloride, dimethicone copolyol and glycerine to the main manufacturing vessel. Heat to 70–75°C.
2. Melt cetearyl alcohol and cocamide MEA in a jacketed side vessel. Heat to 70–75°C.
3. When both phases are at 70–75°C, add the oil phase to the water phase with homogenization to form an emulsion.
4. When the emulsion has formed, commence cooling to 40°C, with paddle stirring.
5. Dissolve the preservative in a portion of reserved water. Add to the main vessel.
6. Add colour to main vessel.
7. Add perfume to main vessel.
8. Adjust pH with citric acid dissolved in water.
9. Continue cooling to 35°C.

Glycerin is included in its capacity as humectant. It attracts water to the hair, thus conferring moisturizing benefit for dry, permed or damaged hair.

Synthetic ceramides of the type shown to be present inside hair as acyl derivatives of fatty acids have the ability to improve cuticle cell cohesion, decrease UV damage, and limit the loss of water-soluble polypeptides. Consideration should be given to such an inclusion in more intensive hair-conditioning formulations to promote hair gloss and elasticity, and to protect against internal stress.

Formula III Hair-conditioning mousse

	% w/w
Polymer VC 713*	5.00
Mulgofen ON 870†	0.50
Cationic Emulsion‡	0.15
Alcohol (denatured)	12.00
Water (deionized); Aqua (INCI)	82.35

*Polymer VC 713 – terpolymer of vinyl pyrrolidone, vinyl caprolactam and an aminomethacrylate – 50% active (ISP).
†Mulgofen – ethoxylated fatty alcohol (Rhône-Poulenc).
‡Cationic emulsion 929 – emulsion of an amido-methicone silicone (Dow Corning).

Use 90% of the solution with 10% propane/butane mixture in an aerosol pack.

Formula III represents essentially a styling product. It is generally agreed that styling encompasses elements of both setting and conditioning. Specialist co-polymers have been developed to improve the condition of hair, and by varying the ratios of the constituent monomers, film-formers with either optimized conditioning or setting properties can be obtained; or, indeed, versatile materials with a balanced combination of both attributes.

The current popularity of mousse products may be due in part to the ease of application. The correct dosage can be selected merely by filling the palm of the hand to varying degrees; for example, the size of an egg, the size of a golf ball, etc., directly from the container. Owing to the opacity of the foam the distribution on the hair can be easily observed. The mousse foam breaks down fairly rapidly on wet hair, but not too quickly so as to prevent the user from being able to control distribution.

(b) Evaluation of conditioners

Conditioning products are well served by objective methods to establish their various properties. Test swatches of hair can be assessed *in-vitro* to determine their effect on combing. A comb with a spring gauge attached measures the resistance to combing. The method can easily be used *in-vivo* without modification for the whole head or half-head assessment. Similarly, the conditioner's effect on static electrification of dry hair can be assessed using a charge locator as used by factory engineers. This instrument is a valve voltmeter in which the grid is connected to a probe. The greater the bias of the grid, the larger the charges affecting the probe. Again, measurements can be *in-vitro* or *in-vivo*.

Gloss or lustre can be quantified by scientific instrument *in-vitro* [15,16]. Gloss measurements *in-vivo* are more difficult since perception of gloss takes account of both reflected and scattered light.

Texture and softness may also be evaluated *in-vitro* or *in-vivo*, but attributes such as control and manageability are best assessed *in-vivo.*

8.6.2 Styling products

The original liquid setting lotions were designed to prolong the life of a water wave. A variety of styles can be achieved without affecting the internal structure of the hair. Traditional setting lotions are ethanol/water mixtures in which polymeric materials have been dissolved. Application is to towel-dried hair with combing to distribute the product evenly through the hair. The hair is then set on curling rollers and dried. On removal of the curling rollers the hair should be combed gently into the desired style. Setting lotions do not work by sticking hair fibres together, but by coating each hair fibre, creating greater interfibre friction and reducing moisture uptake, thus conferring greater control to the hair.

Formula IV Setting lotion

	% w/w
Copolymer of vinyl pyrrolidone and vinyl actetate*	2.50
Ethoxylated fatty alcohol†	0.50
Alcohol (denatured)	50.00
Perfume	q.s.
Colour	q.s.
Water (deionized)	to 100%

*PVP/VA copolymer (INCI name).
†Undeceth 5 (INCI name).

The choice of polymer is important to ensure a flexible film is left on the hair which does not become sticky under conditions of high humidity. The vinyl acetate copolymers have better water resistance than polyvinyl pyrrolidone and give greater flexibility to hair.

Formula V Styling mousse

	% w/w
Copolymer of vinyl pyrrolidone and vinyl actetate*	2.00
Ethoxylated fatty alcohol†	0.50
Copolymer of vinyl pyrrolidone and amino methyacrylate	5.00
Alcohol (denatured)	10.00
Perfume	q.s.
Water (deionized)	to 100%
Propellant (Butane/propane)	5.00

*PVP/VA copolymer (INCI name).
†Undeceth 5 (INCI name).

The above formula can be used as an aid to producing roller curls or for blow-drying. Both processes involve applying the product to 'towel-dried' hair, but blow-drying involves simultaneous use of heat and styling with brush or comb.

Such products are very effective in improving body, texture and control of the hair mass.

A feature of this product is that it is discharged from its container by a mixture of butane and propane propellant which is dispersed in the product by shaking. On release from the container, the propellant droplets rapidly expand to form a characteristic foam. The physical properties of the mousse are important to the user. Oteri *et al.* [17] and Breuer and Tsai [18] have developed relatively simple methods for measuring the mechanical and rheological properties of mousses.

Formula VI Styling gel

	% w/w
Carbomer 940	0.60
Alcohol (denatured)	10.00
Sodium Hydroxide	0.27
Polyvinyl Pyrrolidone	0.40
Polysorbate 20	0.10
Preservative	q.s.
Perfume	q.s.
Colour	q.s.
Water (deionized)	to 100.00

Styling gel formulations are derived from setting lotions by adding structure. They can be formulated in a variety of strengths as well as other attributes such as 'wet look', conditioning/moisturizing or 'shine'.

Dispersion of the carbomer is critical in this type of formula. It should be added to the water/alchohol mix slowly and carefully with high-speed shear to allow lump-free dispersal. Sodium hydroxide is the last ingredient to be added. This neutralizes the carbomer, thus producing the desired viscosity. The rheology can be varied by controlling the ratio of carbomer to sodium hydroxide.

Packaging is usually in tubes or pots and such products have greater appeal for the male user. Used sparingly they give texture and shape, but used generously, stiff, spiky styles can be created.

Other ingredients which may be of benefit are: propylene glycol for a 'wet look', silicone for gloss and condition, panthenol for condition and moisturizing.

8.6.3 Hairsprays

The largest proportion of the styling market is taken by hairsprays. They may be in aerosol or non-aerosol packaging, the greater proportion of the market being the pressurized pack.

The aerosol hairspray is conventionally formulated to provide various strengths of hold from normal to maximum. The propellant provides the pressure which forces the product out of the container when the valve is opened by depressing the actuator. Profound changes in performance can be made by altering the dimensions of the chambers and orifices in the valve and the actuator chosen for the product. For example, a finer spray could be obtained if the actuator orifice was reduced, the expansion chamber enlarged and diameter of the swirl chamber in the valve increased. Changes to the ratio of propellant to product concentrate can also change the spray rate.

The aerosol hairspray should be held at a distance of approximately 20 cm from the hair to allow satisfactory even coverage. Particle size is an important factor in achieving satisfactory coverage without the potential for particle inhalation.

The manner in which hairspray droplets interact with fibres has been investigated in depth [19,20]. When the droplets arrive on the hair most of the propellant has been lost through evaporation. The droplets are therefore quite concentrated polymer solutions and will react with the hair fibre in one of two ways [19,20]. This is dependent on surface energy, volatility and viscosity. If they are not spread efficiently they will bind adjacent hair fibres by 'beads' of polymer. Conversely, if they are less concentrated and less viscous, efficient spreading occurs and the hair mass is bound by seams of dried polymer. The former effect is known as 'spot welding' and the latter as 'seam welding'.

Increasing the concentration of polymer does not always increase the holding power because the extra polymer can make the droplet too viscous to spread sufficiently to form seam welds.

The ideal hairspray has a relatively fine spray which is gentle enough not to disturb the configuration of the hair. It should give whole-head coverage quickly, thus the spray pattern should be wide-angled. Drying time should be relatively rapid. The dried spray should not be tacky on the hair, nor should it become tacky with exposure to high humidity. It should be easily removable by brushing or shampooing; if not, 'build-up' will occur and the hair becomes dull and coarse in texture.

Hydrocarbon-propelled aerosols have been reviewed by Alexander [21].

(a) Hairspray formulations

Formula VII Hairspray

	% w/w
Amphomer resin	2.00
2-amino-2-methyl-1-propanol*	0.33
Dimethicone Copolyol	0.10
Fragrance	q.s.
Alcohol (denatured)	to 100.00
Propellant (butane/propane)	60.00

*Aminomethyl Propanol (INCI name).

Formula VIII Hairspray (pump-driven)

	% w/w
Vinyl acetate/crotonic acid copolymer	3.00
2-amino-2-methyl-1-propanol*	0.24
Dimethicone Copolyol	0.10
Propylene Glycol	1.00
Fragrance	q.s.
Alcohol (denatured)	to 100.00

*Aminomethyl Propanol (INCI name).

Both formulae contain a hair-control polymer which is neutralized with an amino alcohol, AMP, to ensure that the spray residues can be removed more easily during shampooing. The formulations contain dimethicone copolyol, a surfactant of the silicone glycol type, which confers superior combing properties together with a softer, smoother texture to the hair.

The main disadvantage of the pump-driven product is that a coarser, wetter spray is produced.

Environmental considerations have led to the evaluation of alternative propellants allowing formulators flexibility to create products containing less volatile organic compounds (VOCs). DME (dimethyl ether) is a more polar propellant than the hydrocarbons, and can be used with aqueous-based formulae. If DME is to have consideration in a hairspray context, then the chosen resin must also be compatible with water.

(b) Manufacture

Manufacture of the liquid hairspray must be done in a flame-proof area with spark-proof manufacturing equipment. A top-entry mixing vessel with a variable-speed mixer is required.

1. The alcohol is added to the mixing vessel.
2. The resin is added to the alcohol and mixed until all the solid has dissolved.
3. The neutralizer is added to the mixing vessel and mixed for approximately ten minutes.
4. Dimethicone copolyol, perfume and any other additives are added and mixed until the product is homogeneous and clear.

8.6.4 Hairdressings

Hairdressings are a category of product which the male user tends to dominate. There is a wide variety, some products very traditional, and others quite modern. The list below covers the major categories:

1. Brilliantines:
   (a) Jelly
   (b) Pomade
   (c) Liquid
   (d) Wax

2. Emulsions.
3. Aerosol hair dressings.

Pomades are based on petrolatum, with mineral or vegetable oil, beeswax and silicones as possible additives. The newer formulae are lighter-textured due to the use of vegetable wax and oil. The major use is to add lustre, whilst giving style definition, and reducing frizziness.

Styling waxes are exactly that. They are composed of carnauba, ceresin or ozokerite combined with mineral oil or lanolin to make the formula pliable. Such a product can be used on specific areas of hair to produce spiky styles which require rigidity. They can confer a deep gloss to the hair.

Liquid brilliantines are based on vegetable or highly refined mineral oils. They induce gloss by coating the hair fibres in a very thin film of oil and help to lubricate the scalp, preventing dryness.

Emulsion hairdressings, of which Formula IX is representative, have some unique properties, although this is a very traditional water-in-oil emulsion type of formula. Such an emulsion is quite stable until rubbed briskly, when it breaks, giving rise to freed droplets of water. The water acts as a grooming aid and reduces greasiness of the product. The higher fatty acids in the beeswax are critical to the formula. The paraffin wax is also an important constituent, but it is possible to replace this with microcrystalline wax.

Formula IX Emulsion hairdressing

	% w/w
Beeswax	2.00
Mineral (Paraffinum Liquidum) Oil	30.80
Paraffin Wax	0.20
Petrolatum	6.00
Stearic Acid	0.50
Perfume	q.s.
Calcium Hydroxide	to 100.00

Aerosol hair dressings formulae designed for male use have lower polymer concentrations than their female counterpart. This prevents excessive rigidity, and the inclusion of materials such as PEG 400 and PEG laurate will allow some re-groomability. There has been further innovation in this area with the advent of gel sprays.

8.7 HAIR-CARE PRODUCTS WITH CHEMICAL MECHANISMS

8.7.1 Permanent waving

This is a two-stage process. Firstly, there is a reduction or breaking of the disulfide bonds, followed by a neutralization or oxidation process which re-forms the bonds in a different configuration.

Formula X Permanent waving relaxing (Part I)

	% w/w
Thioglycollic Acid*	8.00
Ammonia (0.88)	1.00
Polysorbate 40†	3.00
Lanolin	1.50
Sorbitan Oleate†	1.00
Mineral (Paraffinum Liquidum) Oil	0.50
Preservative	q.s.
Perfume	q.s.
Water (deionized)	to 100.00

*Thioglycollic acid $CH_2SH{\cdot}COOH$ is the reducing agent.

†Polysorbate 40 and sorbitan oleate are emulsifying agents.

A typical neutralizer formulation to be used in conjunction with Formula X is shown below:

Formula XI Neutralizer (Part II)

	% w/w
Cetrimonium chloride	0.30
Hydrogen peroxide (20 vols)	27.00
Water (deionized) at pH 4.0	to 100.00

The ammonium thioglycollate which is formed in the reaction between the first two ingredients of Part I is the active reducer of keratin at pH values near 10. Permanent waving products of this kind are generally used in an emulsion vehicle. There are two main advantages: (a) the viscous vehicle moderates the reaction rate of the thioglycollate with hair and (b) in the emulsion form the application of the product on to the hair is safer and more controllable. These properties are particularly useful to the home-user, but well appreciated also by professional salon operators.

The emulsions are of the oil-in-water type (o/w) and Formula X would normally require only one emulsifier which would be of a high HLB value. HLB measures the affinity of the emulsifying agent for water. This formulation uses two emulsifiers whose combined HLB values are additive and give the desired stability.

Thus the effective combined HLB is given by the expression:

$$\text{HLB (combined)} = H_M = wH_L + (1-w)H_H \tag{3}$$

where: H_L is the HLB of sorbitan oleate = 4.3
H_H is the HLB of polysorbate 40 = 15.6
Formula ratio percentage of each is 1 : 3

w is the weight fraction of sorbitan oleate = 0.25
$1 - w$ is the weight fraction of polysorbate 40 = 0.75

Evaluating equation (3)

$$\begin{aligned} H_M &= 0.25 \times 4.3 + 0.75 \times 15.6 \\ &= 1.0775 + 11.7 \\ &= 12.8 \end{aligned}$$

The HLB value of approximately 13 means that the combined effect of the two emulsifiers is equivalent to one of about 13. Tween 21, HLB 13.1, would in theory be just as effective. However, it has been discovered in practice that mixed emulsifiers have definite advantages in ease of preparation and the subsequent stability of the emulsion.

8.7.2 Hair straighteners

These products are almost exclusive to the ethnic hair-care market. Straightening changes the hair strands' physical shape through a chemical process. The breaking and re-forming of bonds permanently rearranges the internal protein structure. It is a two-stage process initiated by application of the relaxer, which has a high pH, causing the hair to swell and open the cuticle. The alkaline agent penetrates the hair fibre and, after gaining entry to the cortex, reacts to break the structural bonds. The breakage of disulfide bonds permits the fibre to be extended into a straight configuration. Optimum hair fibre extension is found by measuring the force needed to deform the fibre by 25%. Effective bond breakage with minimum damage can be achieved by manipulating this balance.

A neutralizing (acid) shampoo then initiates the formation of new bonds which lock in the new shape and close down the cuticle.

Hair type has a marked bearing on relaxer choice and this is why salon application predominates as professional guidance achieves best results.

(a) Caustic lye formulae

These are traditional hair-straightening products:

Formula XII	**Caustic lye hair straightener**
	% w/w
Stearic acid	15.00
Oleic acid	5.00
Glycerin	8.00
Sodium hydroxide	4.50
Perfume	q.s.
Water (deionized)	to 100.00

Polysorbate 40 can be used to increase the stability of the product if desired.

Method of use

1. Apply a regular shampoo followed by combing in a petroleum jelly preparation.
2. Apply the caustic lye preparation working quickly to keep processing time to a minimum.
3. Treat with neutralizing solution.
4. Treat the hair with a pomade if desired – shampoo as necessary with a regular shampoo.

(b) Thioglycollate hair straighteners

If a less aggressive treatment is required, a formula utilizing thioglycollates which disrupt the sulfur–sulfur bonds in the hair protein can be used.

Formula XIII Thioglycollate cream straightener

	% w/w
Glyceryl Stearate	15.00
Stearic Acid	8.00
Ceresin	1.50
Paraffin Wax	1.00
Thioglycollic Acid	6.50
Ammonia (0.88)	2.00
Detergent	1.00
Water (deionized)	to 100.00

This treatment must again be followed by the application of a neutralizer:

Formula XIV Thioglycollate cream neutralizer

	% w/w
Lanolin	2.00
Sorbitan Trioleate	2.00
Sodium Bromate	14.00
Propylene Glycol	2.00
Sorbitan Palmitate	1.00
Detergent	3.00
Water (deionized)	to 100.00

The ammonium thioglycollate products tend to be viscous creams or gels. Application time can be as much as one hour, before the straightened hair

is wrapped on curling rods. The neutralizer is then applied in emulsion form for extra safety. This process shows great similarity to permanent waving processes.

(c) Post-conditioning treatments

The hair relaxer treatment has a defatting action on the hair, therefore various post-conditioning treatments are available to lubricate the scalp, moisturize and add lustre to the hair.

The art of plaiting the hair close to the scalp in a variety of patterns is called 'canerow'. Once natural oils such as coconut oil or shea butter were used to maintain scalp suppleness during the teasing, stretching process as the hair is plaited. Now, more modern hair pomade formulae are used which are blends of waxes, oils and petroleum jelly.

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9

Hair shampoos

F.J. Mottram and C.E. Lees

9.1 INTRODUCTION

Washing the hair and scalp has become a near-universal practice. The method of doing so varies depending on both geographic and economic factors.

Shampoos assumed importance as a product category with the advent of synthetic detergents. These were developed in the 1930s, became widely used in laundry markets by the mid-1940s and appeared in a shampoo format during the 1950s. Shampoos are probably the most widely used hair products today; based on synthetic detergents they are relatively insensitive to water hardness, thus allowing for efficient rinsing since there are no scum residues. In the early days a shampoo could be defined as an effective cleansing agent for hair and scalp, but today the shampoo must do much more. It must leave the hair easy to comb, lustrous and controllable whilst being convenient and easy to use.

9.1.1 Requirements of a shampoo

1. To remove sebum (the secretion of the sebaceous glands) and atmospheric pollutants from the hair and scalp.
2. To remove the residues of previously applied hair treatments, e.g. polymeric constituents from styling lotions and hair sprays.
3. To deliver an optimum level of foam to satisfy the expectation of the user.
4. To leave the hair in a satisfactory condition after rinsing so that it can be combed easily both in the wet and dry state.
5. To perform as a vehicle for the deposition of beneficial materials onto the hair and scalp.
6. To be non-toxic and non-irritating to the hair and the scalp.
7. To be non-damaging to the tissues of the eye if inadvertently splashed.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 289–306

9.1.2 Classification of shampoos

Shampoos are usually classified according to function, e.g. anti-dandruff, medicated, 2-in-1 shampoo, mild baby shampoo, basic beauty shampoo, premium conditioning shampoo.

9.2 THE ACTION OF SHAMPOO ON THE HAIR

The original prime purpose of the shampoo is to cleanse the hair. The underlying science has been reported by Lawrence [1,2] and by Breuer [3], who recognized three basic components of hair soil:

1. Sebum, the oily secretion of the sebaceous glands.
2. Proteinaceous matter arising from the cell debris of the *stratum corneum* layers of the scalp, and the protein content of sweat.
3. Atmospheric pollutants and residues from other hair-care products.

There is an extensive literature on the subject of sebum, much of it summarized in a review by Gershbein and Barburoa [4]. They examine both the physicochemical and biological aspects of sebum. An example of the latter may be found in a paper by Kligman and Shelley [5] which deals with the physiology of the secretion. In order to gain an insight into the *in-situ* properties of sebum a number of studies were made, most noteworthy those of Curry and Golding [6]. In the course of their investigations they reached the conclusion that the free fatty acids of sebum may well be linked to the protein surface of hair through calcium atoms. The same concept also emerges from the work of Koch *et al.* [7] and from a consideration of the nature of detergency by Davies and Rideal [8].

Breuer [3] has studied the kinetics of the regreasing of freshly cleaned hair. He regards a representative composition of sebum to be as in Table 9.1. Squalene is a triterpene containing four unsaturated –C=C– bonds; its relative molecular mass is 410 and it is the biosynthetic precursor of lanesterol. Basically the above composition is not radically different from the artificial sebum used by Spangler [9] for his studies of the laundering of textiles.

Among the methods used by Breuer to monitor the spreading of sebum was a sophisticated optical technique which measured changes in hair-fibre spacing as

Table 9.1 Composition of sebum

Component	*% by weight*
Cholesterol	8.5
Fatty acids (free)	22.0
Triglycerides	35.0
Wax and wool–wax esters	18.6
Squalene	11.3
Sundry hydrocarbons	4.6

the sebum spread in a parallel assembly of hair fibres. He also established in other experiments that the rate of sebum spreading, when the hair had been dried in a current of hot air from an electric hair drier, was considerably greater than when the hair had been allowed to dry at room temperature.

9.2.1 The process of soil removal

There are three types of soil to be dealt with. These are oily soil or sebum, soluble soils, and insoluble particulate soils. All three types of soil require to be wetted, thus the surface tension of the water is reduced by the shampoo surfactant allowing full contact with the soil's surface. Any soluble soil is then removed in the aqueous medium.

Oily soil or sebum is removed by a process known as 'roll-up', i.e. the displacement of the soil by the detergent solution.

Insoluble particulate soils tend to be removed by electrostatic repulsion between the soil and the hair fibre assisted by repulsion between the surfactant molecules adsorbed onto the hair fibre and those dissolved onto the soil.

Breuer also considers the rheological properties of sebum to exert a strong influence upon soil removal, and it is conceivable that the phenomenon of myelenesis contributes to soil displacement, although less than in the case of textile laundering.

Myelenesis can be observed (through a microscope), when a layer of lipid material, even material of low polarity such as fatty alcohols, is immersed in water. The lipid layer develops peninsular-like processes which penetrate into the aqueous medium. These appear to function like pipes, transporting the lipid progressively into the bulk water phase. In that region the former surface lipid coexists within the micelles of the detergent solution as co-micelles of detergent and lipid. The effect is best seen when the lipid is highly polar, e.g. in the phospholipids, lecithin and cephalin. The rate at which the lipid migrates into the aqueous phase is very temperature-dependent. Chan [10] proposes a third mechansim which is illustrated by Fig. 9.1.

According to Chan the detergent micelles make contact with the lipid surface for a finite time during which they take up an increment of lipid. This is assimilated to form lipid–detergent co-micelles which detach and 'float away' into the bulk aqueous solution. It is felt that Chan may be expressing the process of myelenesis in different terms. In Fig. 9.1 the rectangular 'core' of diagrammatic micelles can be considered to represent the hydrocarbon domain created by the non-polar regions of the detergent molecules; the small circles represent the polar heads of these molecules.

9.2.3 Summary of cleansing

Although detergency plays an important role in the cleaning of hair with shampoo, other factors must be considered. For example, gaps exist in our knowledge

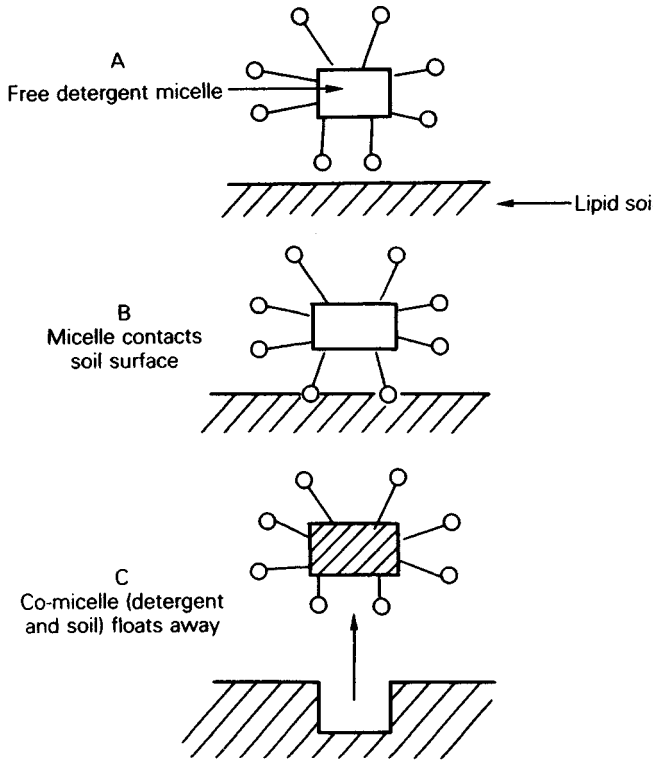


Fig. 9.1 The Chan 'float-away' cleaning mechanism.

of the physicochemical nature of the ageing of sebum and how this is related to its rheological properties. We would also wish to know the extent to which captured particles of soil from the atmosphere modify the fluidity of sebum. One of the few attempts to describe the physical properties of sebum extant is that of Boré *et al.* [11], who employed thermal analytical techniques (differential thermal analysis, DTA).

It is also important to be able to apportion the individual contributions of surface energy and surface rugosity to the rate at which hair is regreased. Another element of fundamental information which is not currently available to us attaches to the relative importance of tactile and visual factors in determining the perception of cleanliness of hair.

9.3 THE FOAMING OF SHAMPOOS

The 'signal' to which the user responds when applying a shampoo is how quickly it builds up lather and how copious that lather is. This tends to colour the user's later impressions of the other performance characteristics of the

shampoo. Three well-defined stages appear to be involved: the rapidity with which the foam is formed; the peak volume of the foam; and the consistency of the lather. A high-consistency foam is judged as being 'creamy'. It is not surprising, therefore, that the shampoo formulator needs to be able to measure the important foaming properties, even though the fundamental properties of a foam, e.g. interfacial tension and film modulus, do not form a reliable guide to the performance of the shampoo in practice. One version of a technique by Ross and Miles [12] to measure foaming properties is outlined below.

A standard volume of shampoo solution is transferred to a tap-funnel. The solution in the funnel is run in a standard time into a large measuring cylinder which already contains a set volume of the solution, or merely the dilution water. The result of the stream of solution from the funnel impacting on the liquid in the cylinder is to generate a foam, the volume of which can be read directly. The procedure can be modified; for example, the cylinder may contain a suitable quantity of sebum-treated hair, or the gravity feed from the tap-funnel can be replaced by a pump.

The Ross–Miles method, like some other methods for quantifying foam, usually ranks the foaming of shampoos in the same order as human judges do (users, panellists and hairdressers), but not invariably. Other methods of quantifying shampoo foaming capacity utilize propeller stirring or air injection to generate foam but are, in general, less reliable.

The quantification of the consistency of foam (creaminess) by *in-vitro* laboratory techniques is less well provided for than the measurement of foam volume. However, an innovation by Hart and Degeorge [13] offers some promise. The principle of the method is that a high-consistency foam will take considerably longer to flow out via the stem (broad) of a powder funnel than a foam which is thin and dubbed as non-creamy.

An *ideal* laboratory method for predicting the foaming power of shampoos would closely simulate the practical shampooing process. It would ensure that the foam was generated in a way similar to its formation on the head of the user. Similarly, the composition of the system in which the experimental foam is produced would be as similar as possible to that of the hairdressing situation in terms of materials present (hair, sebum, detergent, water). The temperature and humidity profile would also be modelled upon that met with in hairdressing practice. Perhaps the most important simulation would be that of the mechanics and dynamics of foam generation. Lather production in practical shampooing is not by cascading water, mechanical stirring or gas injection. It is in fact achieved by a process of compressing and shearing hair when it is saturated with shampoo solution. The foam produced by compression and shear is then modified by the practice of separating by finger action a particular mass of hair fibres and shampoo solution into smaller 'swatches' before recombining them. The engineering problems of designing a machine to meet the requirements described above are formidable, but not insurmountable.

9.4 SHAMPOO INGREDIENTS

A shampoo is basically a solution of a detergent modified by additives to render it easier to apply and to safeguard against deterioration of the hair condition after the shampoo has been rinsed away. The following list classifies the materials of shampoo formulation; the subdivisions are not, however, mutually exclusive, e.g. viscosity modifiers can sometimes be used to stabilize or boost the foam and some opacifying agents can also improve foam quality. Likewise, amphoteric wetting agents can be used as the main detergent for specialist shampoos. They are also valued as hair-conditioning agents.

- Main detergents
- Foam boosters and stabilizers
- Opacifiers
- Hydrotopes
- Viscosity modifiers, including hydrocolloids and electrolytes
- Special additives for hair condition
- Special additives for scalp health, including antidandruff additives
- Sequestering agents.

9.4.1 Main detergents

These are classified according to the way in which they ionize.

Class 1: Anionics

(a) Alkyl sulfates. Alkyl sulfates are produced by reacting a fatty alcohol with either chlorosulfonic acid or sulfur trioxide:

$$\underset{\text{Fatty alcohol}}{ROH} + \underset{\text{Chlorosulfonic acid}}{ClSO_3H} \rightarrow \underset{\text{Acid ester}}{ROSO_3H} + \underset{\text{Hydrochloric acid}}{HCl}$$

$$\underset{\text{Acid ester}}{ROSO_3H} + \underset{\text{Sodium hydroxide}}{NaOH} \rightarrow \underset{\text{Sodium alkyl sulfate}}{ROSO_3Na} + H_2O$$

R = Alkyl radical between C_6 and C_{18}

The acid ester formed requires neutralization to prevent it splitting to the original fatty alcohol and sulfuric acid. Sodium hydroxide, triethanolamine, monoethanolamine, ammonia and magnesium carbonate are commonly used bases.

The carbon chain length of the original fatty alcohol affects solubility, foaming, detergency, and irritation potential of the resulting alkyl sulfate.

(b) Alkyl ether sulfates. The manufacturing process for alkyl ether sulfates is similar to that for alkyl sulfates, but an ethoxylated fatty alcohol is used. The

choice of base for neutralization is the same. The number of molecules of ethylene oxide in the resulting alkyl ether sulfate will affect foam, viscosity and mildness:

$$R\text{–}(OCH_2CH_2)_n\text{–}OH + ClSO_3H \rightarrow R\text{–}(OCH_2CH_2)_n\text{–}SO_3H + HCl$$

Ethoxylated fatty alcohol + Chlorosulfonic acid → Acid ester + Hydrochloric acid

$$R\text{–}(OCH_2CH_2)_n\text{–}SO_3H + NaOH \rightarrow R\text{–}(OCH_2CH_2)_n\text{–}SO_3Na + H_2O$$

Acid ester + Sodium hydroxide → Sodium alkyl ether sulfate

$R = C_{12}$ to C_{18}

n = 1 to 6 molecules of ethylene oxide

(c) Sulfosuccinic acid mono and di-esters (sulfosuccinates). The mono-esters are very mild, with good foaming and detergent properties. The di-esters are superior for their wetting properties. Since they are sensitive to hydrolysis and are difficult to structure they tend to be used in conjunction with alkyl ether sulfates to produce mild shampoos.

(d) Isothionates, taurides and sarcosinates. These are materials that have other interesting properties for the shampoo formulator, other than foam potential and detergency. *Isothionates* are exceptionally mild to skin and eyes, and are particularly tolerant to hard water.

$$R\text{—}COOCH_2\text{—}CH_2\text{–}SO3^-M^+$$

Donaldson and Messenger [14] have reported on the shampoo performance of both alkyl sulfates and alkyl ether sulfates.

Class 2: Nonionics

Materials in this class are not usually the major ingredient of a shampoo. They are important, however, as co-surfactants, rheology modifiers and solubilizers for insoluble components such as fragrance oils.

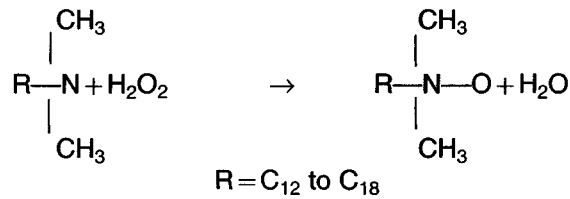
(a) Fatty acid alkanolamides. These are formed by reacting a fatty acid with an alkanolamine, usually monoethanolamine or diethanolamine, to produce the corresponding alkanolamide:

$$R.COOH + NH_2C_2H_4OH \rightarrow R.CONHC_2H_4OH + H_2O$$

$$R = C_{12} \text{ to } C_{18}$$

The major use is to modify rheology and to control foam consistency and quantity. They have largely been superceded by amphoterics in modern formulations.

(b) Fatty amine oxides. These are obtained by reacting a tertiary amine with hydrogen peroxide. They have similar uses to the fatty acid alkanolamides.



(c) Alkylpolyglucosides. These are formed by condensing fatty alcohols with starch. The ratio of starch to fatty alcohol can be varied such that foam properties and detergency can be controlled. It should be noted that when these materials are based on natural fatty acid the whole molecule is derived from natural, renewable sources. They have low toxicity, low irritation and are readily biodegradable.

Class 3: Amphoterics

These are defined as having both anionic and cationic charges in the hydrophilic head. The negative group is usually carboxylic and the positive group amino.

In alkaline solutions the anionic function predominates whilst in acidic solutions the cationic function predominates. The isoelectric point lies between the two extremes at a position where the two charges are equal. The molecule at this point is called a *zwitterion*, and does not behave as a surfactant. Raising or lowering the pH allows the molecule to regain its surfactant properties.

Amphoterics are compatible with all classes of surfactants. In combination with anionics, beneficial effects on foam and viscosity can be demonstrated and there is also a synergistic effect on mildness.

(a) Imidazoline derivatives. The more commonly used dimidazoline derivatives are cocoamphocarboxyglycinate and cocoamphoacetate. They have a very low irritation potential and are utilized in baby or other mild shampoo systems.

(b) Alkylamidobetaines and alkylbetaines. These materials are used as cosurfactants. They have the ability to modify rheology and foam character, whilst conferring mildness through their synergistic effects.

Class 4: Cationics

The surfactants in this group are normally incompatible with anionics, and, therefore, are unlikely to be used in shampoo systems.

9.4.2 Shampoo additives

(a) Thickeners

Sodium chloride is a suitable additive for a large number of formulae, achieving functionality by modifying the *micelle* structure. However, where a sulfosuccinate has been used as a primary detergent, polyethylene glycol diesters are much more effective.

Hydrocolloids such as polyvinyl alcohol or cellulose derivatives can also be utilized, although incorporation of a cellulosic derivative requires care.

Glucose esters can create difficulties with their rheological profile, but do enrich the foam characteristics and reduce irritation.

(b) Pearlizers and opacifiers

Opacifying materials give the shampoo a creamy appearance which appeals to consumers with dry or damaged hair. A pearlized effect can be created by *glycol distearate*, but this requires a hot process and inconsistencies are inevitable. It is more usual to use prepared pearl concentrates.

Latex opacifiers do not have the sparkle of the pearlizers, but are used to obtain a flat opaque appearance.

(c) Preservatives

A wide variety of preservatives exist. Liquid preservatives may be easier to incorporate, but choice is governed by challenge testing and stability of the formulation. Kumanova [15] has reviewed these test methods in relation to shampoos.

The *isothiazolinones* or *parabens* are frequently used, but it must be emphasized that reference should be made to the regulatory status for permitted concentrations.

(d) pH modifiers

The isoionoic point for the hair fibre lies between pH 5.6 and 6.2. It is advisable to balance the pH of the formulation to within this range. *Citric acid* is typically used to achieve this.

9.4.3 Functional additives

Functional additives are those which promote good condition of the hair. Hair in good condition is easy to comb both in wet and dry state. The dried hair should be free from 'flyaway', and be lustrous and manageable.

As specific hair needs are better understood, ingredients can be tailored to deliver specific attributes. It is however *incumbent* on the formulator to substantiate the desired product claims, and to ensure that patents are not infringed. Listed below are some of the newer materials found in shampoos:

- Polyquaterniums
- Silicone additives
- Proteins and amino acids
- Ceramides
- Panthenol
- Glutamic acid derivatives.

(a) Water-soluble polyquaterniums: mechanics of deposition from solution

This topic has been investigated by Goddard and co-workers [16,17], mainly for Polyquaternium 10. Surface tension versus surfactant concentration measurements were obtained in the presence and in the absence of 0.1% of the cationic Polyquaternium 10. This procedure was repeated for several surfactants. For some combinations of Polyquaternium 10 and surfactant there was a considerable lowering of the surface tension at the lower surfactant concentrations. For the rest there was no real change from the plot for the surfactant alone. Table 9.2 summarizes the results, which are illustrated in Fig. 9.2. It can be seen that a reduction in surface tension occurs only when an anionic surfactant is used in association with Polyquaternium 10. No change in surface tension is measured when an anionic detergent is tested with a nonionic, neutral polymer substituted for Polyquaternium 10.

'Change' infers a strong interaction between the anionic surfactant and the cationic polymer. Visual examination reveals a pattern of precipitation near the critical micelle concentration (the inflection point in curves shown in Fig. 9.2). It is reasonable to assume that the maximum precipitation occurs at ratios of polymer to surfactant at which the polymer charge is balanced by that of the surfactant, compliant with the expression:

$$(PS_i)^{n-1} + S - (PS_i + 1)^{n-1-1}$$

$$P^{n+1} + nS - PS^n$$

where: n = positive charges
S = surfactant
P = polymer

Finally, as the surfactant is increased the precipitate is redissolved. The technique is useful in screening additive–detergent systems for their propensity to deposit a complex which is potentially beneficial in a shampoo formulation. Having identified a case where a useful level of precipitation occurs, the next step is to determine how substantive (to hair) the precipitated material is. Goddard and Harris [18], using ESCA (electron spectroscopy for chemical analysis) determined the relative deposition of several cationic polymers. They also measured the substantivity of the deposits. It was established that certain cellulose-based cationics gave a high level of deposition but that it was fairly easily washed away by a dilute detergent solution. This would have the virtue for a product of avoiding the troublesome build-up of an active ingredient, i.e. one resisting removal by several shampooings.

(b) Silicone additives

The following are representative of silicone additives: *dimethicone copolyols*; block copolymers of *dimethyl siloxane* and *ethylene oxide*; and *amodimethicones* which contain an active amino group.

Table 9.2 Effect of the ionicity of surfactant and polymer upon surface tension reduction

Surfactant	*Polymer*	
	Polyquaternium 10	*Cellosize*
Sodium lauryl sulfate	✓	×
Sodium alkyl aryl sulfate	✓	Not tested
Sodium laurate	✓	Not tested
C_{14} betaine derivative	×	Not tested
Nonionic	×	Not tested

✓, Change; ×, no change.

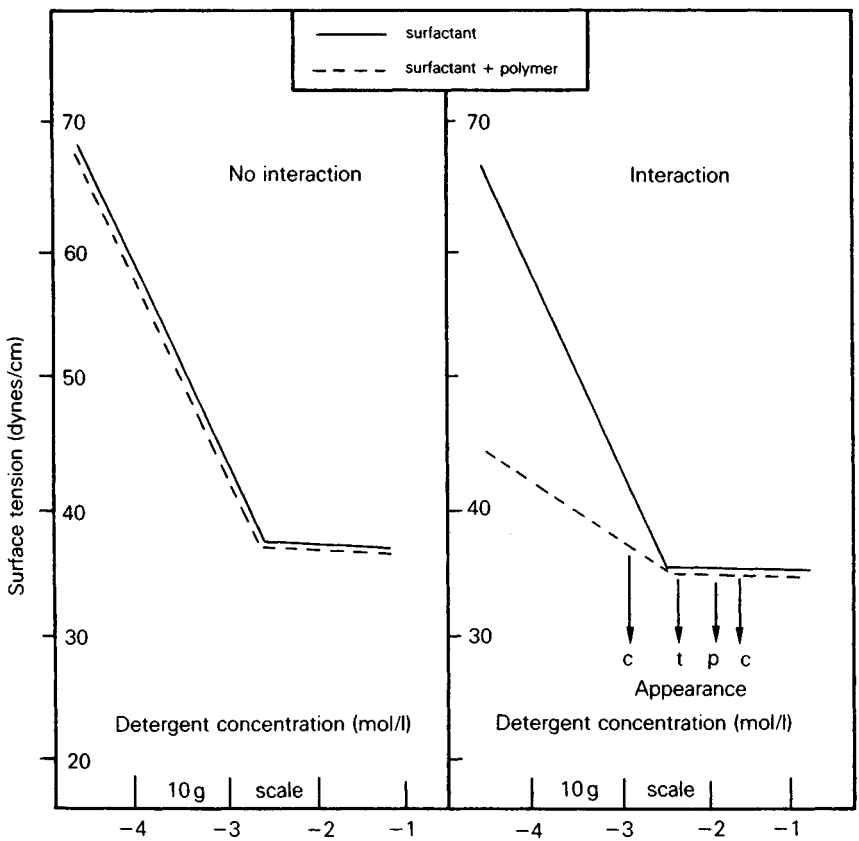


Fig. 9.2 Surface tension versus concentration plots can reveal association between surfactant (detergent) and polymer. Appearance: c, clear; t, turbid; p, precipitates.

Alexander [19] reports that silicone surfactants such as the *dimethicone copolyols*, when incorporated into shampoo formulations, greatly improve combing and antistatic properties at surprisingly low concentrations, 0.1–0.5%. Alexander also described another novel series of silicones, the amino-functional amodimethicones which, surprisingly, have good compatibility with anionic vehicles. Amodimethicones impart much the same benefits to hair as the dimethicone copolymers but have as an added feature a very good substantivity to its surface. This is not totally unexpected as the functional amino group is capable of forming an amine salt linkage with the free carboxyl groups of the hair surface; rather in the manner that the carboxyl groups of certain hairspray polymers are neutralized by treatment with amino alcohols. Starch [20] has described how the substantivity of the amodimethicones has been demonstrated using ESCA methods.

(c) Proteins and amino acids

In recent years the trend has been towards vegetable-derived materials such as those obtained from wheat, soya, maize or almond. All proteins are composed of amino acids, but the composition varies from protein to protein and this has a major bearing in performance on a substrate such as hair. It has been shown that protein derivatives can influence the mechanical properties of hair fibre, with beneficial effect. To do this there must be penetration into the cortex or some indirect effect on the cortex. The ability to do this will vary depending on size of molecule and charge. Gamez-Garcia [21] has reported on the use of hydrolysed wheat protein containing wheat oligosaccharides.

Quaternization of the protein or amino acid reduces the ability to penetrate into the hair fibre, but increases the substantivity to the cuticle.

(d) Ceramides

Hussler *et al.* [22] have determined that the *ceramide* fractions present in a free form in human hair constitute about 0.01% of total hair weight. Their purpose is to bind the cuticle cells to the cortex and perform a 'barrier' function as a cell membrane complex in association with a proteinaceous matrix. The ceramide or lipid fraction is sensitive to chemical and physical attack such that extreme damage can lead to the cell membrane complex vanishing from the cuticle.

Natural ceramides have a specific stereochemical configuration and show optical activity. This structure is essential for functionality. The common denominator for ceramides is that all contain a sphingoid base in amide linkage with nonhydroxy, alpha-hydroxy or omega-hydroxy acids.

Synthetic ceramides have the ability to deposit on damaged hair locating in minute amounts in the cuticle layer. Increased protection against UV and visible radiation and limitation of the loss of water-soluble polypeptides are observable benefits.

The *phytosphingosine* base linked with a nonhydroxy acid (ceramide 3) may have more benefit in restoring the hair to its natural balance than other classes of ceramides, which have restorative benefits on the skin.

(e) Panthenol

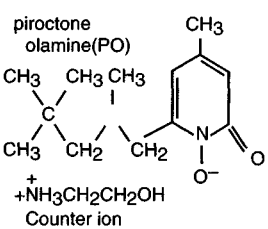
This is the provitamin of pantothenic acid or vitamin B5. Vitamin B5 is essential for normal hair growth and it has been found that use of panthenol in hair preparations can deliver vitamin B5 to the hair through its oxidation to the acid. Panthenol has also been shown to improve body and texture of hair together with a moisturizing capability.

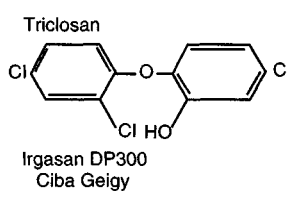
(f) Glutamic acid

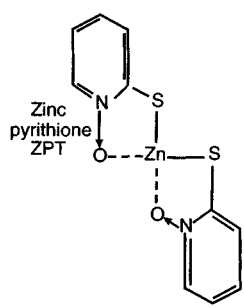
Glutamic acid derivatives are the subject of a Unilever Patent [23]. Research has shown that these derivatives are a source of hair growth energy and that significant linear growth stimulation can be obtained. Penetration enhancers can potentiate the benefit by enhanced delivery to the area of hair follicle in closest proximity to the dermal papilla, where the energy demand is greatest.

9.5 ANTIDANDRUFF AGENTS

Three agents associated with the treatment of scalp disorders have the following chemical structures. **Zinc pyrithione** (ZPT) was the first scientifically based organic therapeutic agent to offer alleviation of the scalp disorder known as dandruff. Dandruff manifests itself as the detachment of flakes of scalp skin. Almost contemporary with ZPT was another antidandruff agent, **piroctone olamine** (PO). Structurally it has little in common with ZPT except the presence of a pyridine ring. The relative and absolute effectiveness in shampoos of both







PO and ZPT was tested by Kligman *et al.* [24]. Their work established that both were effective, but that PO was marginally and consistently superior. Futterer [25] has largely confirmed the earlier work. He has used both shampoos and cream rinses as vehicles for the antidandruff agents. From a manufacturer's point of view shampoos are the most acceptable vehicle for an antidandruff treatment.

Futterer found that reductions in dandruff level of the order of 68% could be achieved for ZPT treatments but, under the same conditions, 82% when PO was the biologically active agent. The statistical significance of this difference in performance corresponds to $p < 0.05$. He also experimented with different concentrations of the biologically active materials and found that 0.5% PO gave only a marginally different antidandruff performance to 0.75% ZPT. The lower concentration of PO needed for the desired result makes it preferable to the formulator.

Boré and Goetz [26], like Breuer [3], are interested in the physical and chemical properties of sebum. They have compared the properties of healthy and seborrhoeic sebum and identified very large differences which are summarized in Table 9.3. The sebum samples were removed by a shampoo of the following constituents:

	%
Sodium lauryl sulphate	4.30
Betaine derivative	2.00
Lactic acid	0.24
Water	to 100.00

9.6 PREPARATION AND MANUFACTURE OF SHAMPOOS

Relative to most other personal-care products the preparation of shampoos is uncomplicated and straightforward. Nevertheless, extreme care at the development stage of the formulation is necessary to ensure that the long-term stability, microbiological integrity and regulatory compliance concerning consumer safety and consumer acceptability have been addressed. Shampoo preparation does, however, have some specific problems.

9.6.1 Shampoo preparation

Care must be exercised with regard to the solubility of various components. Stability tests can be made which will determine whether deactivation of functional additives through interaction between components is taking place.

Table 9.3 Properties of healthy and sebborhoeic sebum

Properties	*Sebum*	
	Healthy	*Seborrhoeic*
Quantity*	Less	Somewhat more
% Squalene	9%	12%
Iodine number	80	100
Palmitic/oleic acids†	1.0	0.7
Viscosity proportional to	1.5	0.7

*For the same extraction procedure.
† Ratio of saturated to unsaturated acids.

Example I
A typically straightforward case where functional ingredients are inert towards the other components.

1. The main detergent, foam booster, the hair functional additive and water are mixed together with gentle stirring to minimize frothing.
2. Citric acid is added carefully to the above mixture to adjust the pH to within the limits 5.6–6.2.
3. A consistency adjuster, say *N*-alkyl betaine, is added to the pH-adjusted blend with more vigorous stirring until the desired viscosity is attained.

Example II
Where some of the components are difficult to solubilize.

1. Dissolve the main detergent in the water.
2. Add the foam 'booster' to the above with stirring, and materials such as opacifiers and functional ingredients which present problems of dispersion.
3. Adjust the pH with citric acid to 5.6–6.2.
4. Adjust the viscosity with electrolyte additive (sodium chloride).

Example III
Where heat is needed to obtain solution.

1. Mix by propeller stirring the functional ingredient and the foam booster.
2. Using the same mixing regime add the main detergent to half the formulation water.
3. Add the mixture obtained in step (2) to that of step (1).
4. Separately use heat to disperse any difficult-to-dissolve ingredient in the remainder of the water.
5. Add the product of step (4) to that of step (3).
6. Adjust the pH of the product to 5.6–6.2 by means of adding citric acid.

Usually, with ingredients of the above solubility characteristics, no upwards adjustment of viscosity is needed.

Note that Examples I and III represent clear shampoos and Example II is an opaque product.

9.7 REPRESENTATIVE SHAMPOO FORMULATIONS

The major difference between the basic shampoo formulae is the level of surfactant used.

9.7.1 The Frequent Wash formula

This is intended for daily use and has the lowest active concentration because the sebum level on the hair must be balanced. Too high an active concentration would remove the sebum in total with gross detrimental effect to the hair. The

normal shampoo is designed for use every 3 or 4 days and has a correspondingly higher surfactant concentration.

	Frequent use *% w/w*	**Normal shampoo** *% w/w*
Sodium Laureth Sulfate (70%A)	7.70	13.50
Cocamidopropyl Betaine (30%A)	2.00	2.00
Tetrasodium EDTA	0.10	0.10
Preservative	q.s.	q.s.
Perfume	q.s.	q.s.
Colour	q.s.	q.s.
Citric Acid	to pH 6.0	to pH 6.0
Sodium Chloride	q.s.	q.s.
Water (deionized); Aqua (INCI)	to 100.00	to 100.00

9.7.2 Conditioning shampoos

These have grown considerably in importance in recent years. The newer formulations claim to wash and condition in one operation, leaving the hair easy to comb, lustrous and soft. Formulations of this type are complex, utilizing materials such as silicones and polyquaterniums. A great deal of care has to be taken to ensure that build-up on the hair is not excessive, and that silicone can be released on to the hair at the appropriate moment during rinsing.

2 in 1 Conditioning shampoo

	% w/w
Sodium Laureth Sulfate (70%A)	11.50
Cocamidopropyl Betaine (30%A)	5.00
PEG 3 Distearate	2.00
Polyquaternium 7	0.25
Dimethicone Copolyol	3.00
Panthenol	0.30
Tetrasodium EDTA	0.10
Preservative	q.s.
Perfume	q.s.
Colour	q.s.
Citric Acid	to pH 6.0
Sodium Chloride	q.s.
Water (deionized); Aqua (INCI)	to 100.00

9.7.3 Premium shampoos

These claim to thicken, balance or add volume to the hair and have also appeared in recent years. They utilize somewhat higher surfactant levels and contain a variety of conditioning and moisturizing ingredients, e.g. modified silicones, wheat proteins, panthenol and natural extracts.

Premium shampoo

	% w/w
Sodium Laureth Sulfate (70%A)	15.00
Cocamidopropyl Betaine (30%A)	5.00
Sodium Lauryl Sulfate and Glycol Distearate and Cocamide MEA	3.00
Guar Hydroxypropyltrimonium Chloride	0.20
Panthenol	0.30
Tetrasodium EDTA	0.10
Preservative	q.s.
Perfume	q.s.
Citric acid	to pH 6.0
Colour	q.s.
Water (deionized); Aqua (INCI)	to 100.00

9.7.4 Antidandruff shampoos

These are designed to alleviate dandruff, a scalp disorder which manifests itself as scaly flakes of scalp skin. There are various root causes for this complaint ranging from straightforward scalp irritations to eczema and seborrhoeic dermatitis. Zinc pyrithione was the first scientifically based organic therapeutic agent to offer alleviation of dandruff. Whilst being very effective in use, and substantive to hair and scalp, it is extremely irritant and has the disadvantage of being insoluble in water. More recently *pyroctone olamine* has been developed, a less irritant material which does have good aqueous solubility, thus enabling the development of clear antidandruff formulae.

Clear antidandruff shampoo

	% w/w
Sodium Laureth Sulfate (70%A)	11.50
Cocamidopropyl Betaine (30%A)	5.00
Piroctone Olamine	0.70
Polyquaternium 7	0.30
Perfume	q.s.
Colour	q.s.
Citric Acid	to pH 6.0
Sodium Chloride	q.s.
Water (deionized); Aqua (INCI)	to 100.00

Triclosan tends to be utilized in *medicated shampoos* where antimicrobial activity is desirable, but specific claims for dandruff alleviation are not made.

9.7.5 Baby shampoos

These require extreme care in formulating where low irritancy is the major need. Use of a nonionic detergent such as *polysorbate 20* can be recommended here. It

does not contribute to the foaming capacity significantly but does reduce the irritancy potential of the selected anionic. The balance between polysorbate 20 and *PEG 600 distearate* also controls viscosity.

Baby shampoo

	% w/w
Magnesium Laureth Sulfate (27.5%A)	11.00
Cocamidopropyl Betaine (30%A)	5.00
Polysorbate 20	1.00
PEG 600 Distearate	3.50
Preservative	q.s.
Perfume	q.s.
Citric Acid	to pH 6.0
Colour	q.s.
Water (deionized); Aqua (INCI)	to 100.00

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10

Hair colourants

Bryan P. Murphy

10.1 INTRODUCTION

Since the 9th edition of this book there has been much progress in hair colouring technology, although the basics have remained unchanged. We have seen advances in the gentleness of products, new thickening systems, and a growth in sales of men's products. For both men's and women's products the requirement to resist fading has almost become a cost of entry and, in fact, has been the basis of at least one new oxidation dye product in that time. Some of the advances in hair colour technology that we have seen are due to regulatory pressures, but many are due to development of superior ingredients. Because this field is large and diverse, this chapter will give only an overview of the field, an understanding of the chemistry of the major types of dye systems, and provide some practical applications. After having read this chapter the formulator should have a broad-based view of the basics of hair colouring technology, and be in a position to begin his own exploration of his particular area of interest. Due to the limited amount of space all the possible delivery systems for hair colouring products will not be reviewed in this chapter, since they will be covered thoroughly elsewhere in this book.

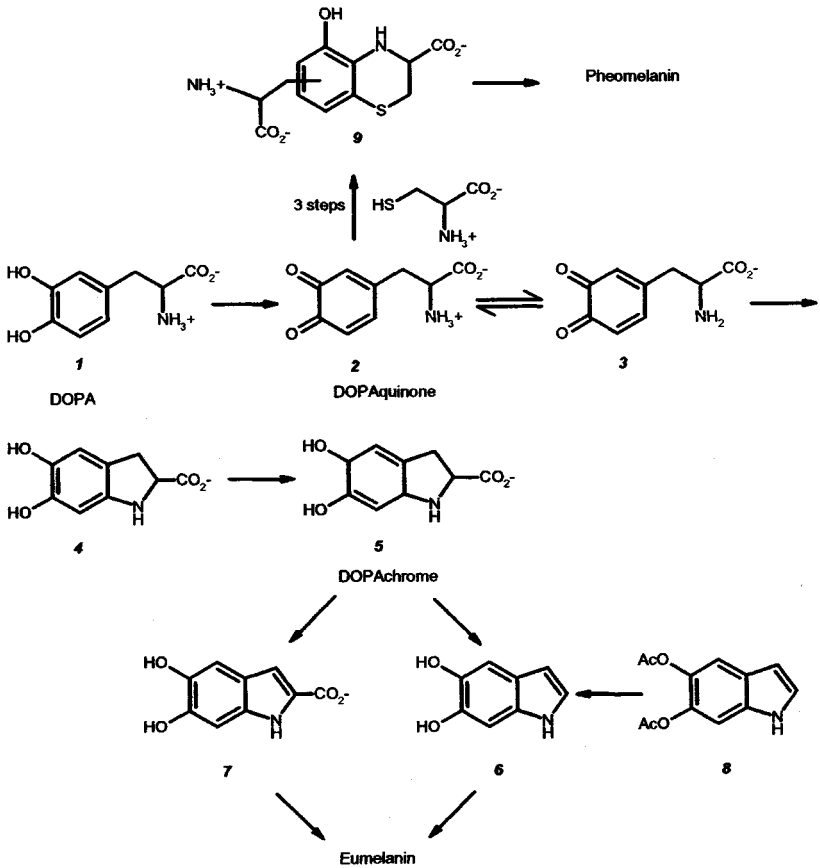
10.1.1 Natural pigmentation

Hair colours range from the very light blonds of the Scandinavian countries to the dark blacks found in the Far East. Interestingly enough, the endless number of colours is provided by a limited number of pigments (Scheme I): the pheomelanins (reds and yellows) and eumelanin (dark browns and blacks).

In both pathways dopaquinone (*2*), the oxidized form of DOPA (*1*), is the key intermediate. It reacts intramolecularly to produce eumelanin, or with cysteine to begin the process of pheomelanin formation. It is the various combinations of the two types of pigments, the amounts present, and the size and distribution of the pigment granules in the hair fibre that make for the variety of colours

Butler, H. *(ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn.*, 307–324

produced in nature [1]. This chapter deals not with colour as it exists in hair, though, but with modifying the colour that already is present in the fibre, or replacing colour that has been lost by greying.



Scheme I

10.1.2 Major categories

Hair colourants, as many other cosmetics, have a history that dates back thousands of years. Many good accounts of that history, such as that by Wall [2], are available, and the reader is encouraged to study them for some interesting background information. Trends aside, we can divide products that add colour to the hair into several useful major categories:

Temporary
Semipermanent (direct dyes)
Gradual colourants (auto-oxidative and metallic dyes)
Natural dyes

Demipermanent (oxidation dyes)
Permanent (oxidation dyes).

Within each of these product categories there are a number of variables: thickener, pH, and percentage of organic (dye) solvent being three of the most important parameters in defining the use and performance characteristics of the system. More on these points will be discussed with specific applications, as the need arises.

Another factor that relates to all the dyes and their performance, wearing properties, and feel on the hair, is the distribution within the fibre. In general, the semipermanent and permanent dyes are distributed throughout. (Notable exceptions to this are catalysed systems.) It is only the temporary colourants that remain on or near the fibre surface.

10.1.3 General considerations: hair structure relating to dye performance

At this point it is worthwhile to review briefly the structure of the average, undamaged hair fibre, and how the structure and ultrastructure relate to uptake and performance of dyes. The two major structural features to be considered are the cuticle, a crystalline protein structure, and the cortex, a more gelatinous material. The cuticle is formed in overlapping layers on the hair, and regulates entry of materials into the fibre both by physical and electrostatic means. In addition, modifications to its structure are responsible for the perception of hair damage (i.e. the rough feel). For the undamaged fibre, size and shape of the dye molecule are related to the rate, depth, and extent of penetration. As would be predicted from most diffusion equations, very large molecules diffuse more slowly than very small molecules. Damaged fibres, on the other hand, are more highly negatively charged and more porous. Thus the cuticle offers a less resistant barrier to absorption, and larger molecules are taken up more readily. In addition, this increase in the fibre's charge (and decrease in the apparent pK_a) can be responsible for increased dye–fibre interactions. Both of these are responsible for the differential wearing properties of dyes, and must be considered by the formulator when developing a product. In addition, the formulator can take advantage of the fact that at alkaline pH, or in the presence of materials such as urea, the fibre swells, thus increasing the potential for diffusion. Of course, after rinsing, the hair returns to its normal pH and state.

10.1.4 General considerations: absorption of dyes

As was mentioned earlier, there are a number of important considerations in formulation of a dye product. These include thickener, amount of organic solvent, pH, and surfactants. Besides aesthetics, one of the major reasons for their importance (for those products utilizing dyes that diffuse into the fibre) is that they determine the partition coefficient of the dye between the hair and the carrier. Obviously, for reasons of ease, efficiency, and raw material cost, the formulator

wants this number to be as large as possible. Since dye molecules generally are aromatic compounds that are not highly water-soluble, in the past there has been the need for some organic, water-miscible solvent to aid in their solubilization and delivery. So, for example, glycol derivatives or alcohols may be used to solubilize them, and may be used in combination with surfactants, fatty acids, amines, fatty amides and other cosmetic adjuvants. However, the formulator must take care that these systems favour release of the colourant to the hair, rather than keeping it in the vehicle.

10.2 TEMPORARY COLOURANTS

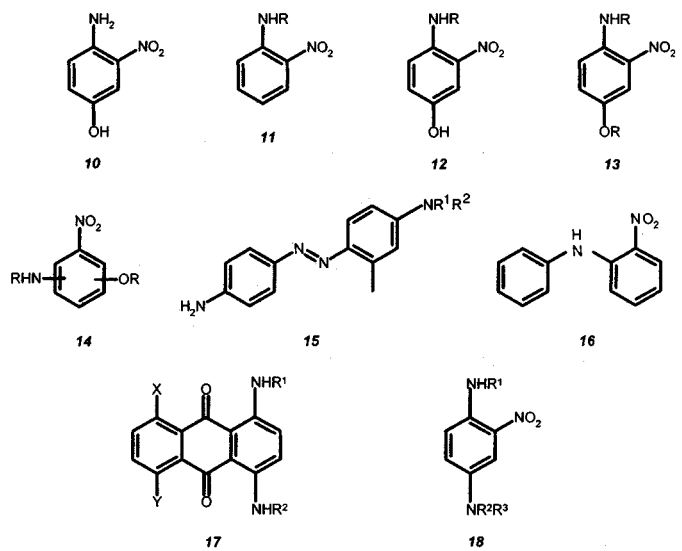
These products are based primarily on acid dyes. Although they are designed to be temporary, they are made longer-lasting in two circumstances: if the hair to which they are applied is significantly damaged, or if they are heated (e.g. with a hair drier) after application. These are different from almost all other products in that they are 'leave-in' products; that is, after application, the hair is not rinsed; removal is with the first shampoo. For this reason this is one of the most difficult products in which to balance propensity to deliver dyes and ability to give a product that imparts a pleasing feel to hair, with stability on the shelf. There must be enough dye to impart an even colour, and enough 'assistants' such as polymer and surfactant to give an even delivery. Too much, though, would leave the hair with an unappealing feel. Although there were several novel approaches mentioned in *Poucher's*, 9th edition, these have not been used to expand the temporary dye market, perhaps because these all have the potential to make the hair feel coated and unappealing.

10.3 SEMIPERMANENT DYEING SYSTEMS

Semipermanent dye products have been used for about forty years; not nearly as long as permanent products. They do, however, perform a function of which all other classes of dyes are incapable. They offer dark colours without the use of hydrogen peroxide. Hence there is no bleaching of the hair's melanin, only coverage. In addition, these products generally give some degree of highlighting effect. That is, the grey hair is coloured somewhat differently than the pigmented hair. These products wash out gradually, so there is no problem with roots or retouching. They are easy to use, and do not require mixing. Hence they are a good entry product. Finally, they are easy to fragrance, because there is no ammonia. They are popular as a hair colouring alternative for people who want to return grey hair to approximately its original colour, but for one reason or another do not want the change to be permanent. This method uses compounds that are already coloured, i.e. no chemistry occurs to form the dye compounds in the hair, as in oxidation dye products. The aim also is different from an oxidation dye; colour from these systems is designed to wash out gradually with time.

The delivery systems generally contain an organic solvent such as an alcohol or glycol derivative, a fatty acid, fatty acid amide, thickener, surfactant and perfume, besides water and the dyes. In addition, an aliphatic amine acts as a co-solvent and buffer, making it possible to take advantage of the swelling of the hair observed at pH 9–10. These parameters are adjusted to optimize the partition coefficient between the hair and the dye.

Although dyes such as 4-amino-3-nitrophenol (*10*) (Scheme II) have been known since the beginning of the twentieth century, a lack of good violet to blue dyes suitable for hair dyeing was one reason semipermanent dyeing was not seen as a commercial success until the middle of this century. In formulation of these products several classes of dyes are used currently: the *o*-nitroanilines (*11*), the aminonitrophenols (*12*) ethers of aminonitrophenols (*13* and *14*) and the azo dyes (*15*), all of which are responsible for the yellows and oranges; the nitrodiphenylamines (*16*) that give orange to red, the anthraquinones (*17*), which produce violet to blue shades, and finally, the 2-nitro-*p*-phenylenediamines (*18*), that give the red (HC Red 3; *18*; $R^1 = -CH_2CH_2OH$, $R^2 = R^3 = -H$) to violet colours (HC Blues 1 (*18*; $R^1 = CH_3$, $R^2 = R^3 = -CH_2CH_2OH$) and 2 (*18*; $R^1 = R^2 = R^3 = -CH_2CH_2OH$)).

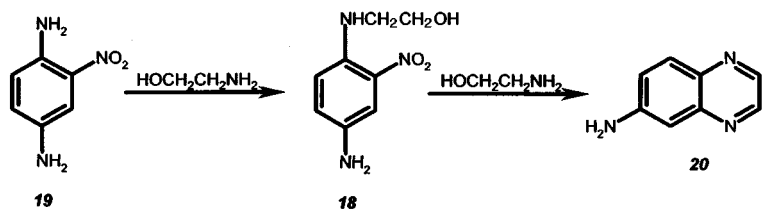


Scheme II

There are at least three advantages to the use of the 2-nitro-*p*-phenylenediamines. Their colours range from the reddish-orange ($\lambda_{max} = 474$ nm) of the parent compound of the series to the violet ($\lambda_{max} = 560$ nm) of the trisubstituted derivatives. This is a much larger range than for the analogous aminonitrophenols and

aminonitroanisoles. They have relatively high values for their extinction coefficients ($\log \varepsilon = 3.6$), and they have good photostability, unlike the *p*-nitroanilines.

Formulation of these materials is not as straightforward as one might imagine. Although they are not as susceptible to oxidation as the oxidative and auto-oxidative dyes, over time, exposure to oxygen still will result in loss of the more sensitive of these materials such as HC Red 3 and HC Blues 1 and 2, particularly in combination with other ingredients. In addition, the anthraquinone and azo dyes generally must be used in their dispersed forms. Finally, choice of the amine is not straightforward. In general, since these products are used at pH 9–10, the amine used as the buffer should have a pK_a close to that range, if it is to be an efficient buffer. There are some problems with this. Secondary amines will undergo nitrosamine formation. Primary amines on the other hand do not undergo nitrosamine formation, but one of the most useful, monoethanolamine, will mediate yellow quinoxaline formation from the 2-nitro-*p*-phenylenediamines [3]. Other amines can replace the group in position 1 of the aromatic ring, resulting in loss of the original dye and formation of a second dye [3] (Scheme III). This obviously has the potential to give stability problems. One way to avoid both problems is to use sterically hindered primary amines, such as 2-amino-2-methylpropanol.



19 *18* *20*

Scheme III

Since the semipermanent dyes not only diffuse into, but out of, the hair, consideration has to be given to ensuring that one colour is not lost preferentially, resulting in a change of shade, i.e. off-shade fading. Thus, when formulating, one generally uses dyes with a wide range of molecular sizes. This is necessary to obtain the full colour palette and to compensate for the fact that permeability and substantivity of the dyes differ for the porous tips of the hair and undamaged root end. Related to this, Han *et al.* have shown that there can be an interaction with the amino groups of the dye molecules with the hair [4]. Therefore, based on this interaction, when dyes such as HC Red 3 (*18*; $R^1 = CH_2CH_2OH$, $R^2 = R^3 = -H$), or 2-nitro-*p*-phenylenediamine are used, one would expect a reddening, or 'warm wearing' of the ends, i.e. the damaged hair. This is, in fact, the observation. This is counteracted by using large, amino-containing molecules, such as Disperse Blue 1 (*17*; $R^1 = R^2 = -H$; $X = Y = -NH_2$) and Disperse Violet 1 (*17*; $R^1 = R^2 = X = Y = -H$). These also are removed slowly from the end of the fibre. Thus, warm wearing is not a problem.

10.4 OXIDATIVE DYEING SYSTEMS: PERMANENT AND DEMIPERMANENT

Oxidative dyeing systems are divided into permanent and demipermanent. The permanent and demipermanent dye products must contain several, common, necessary ingredients:

- Surfactants
- Solvents
- Alkalizing agent
- Oxidant
- Dyes

The functions of the dyes and surfactants are obvious. The dye intermediates are common to the two, and the chemistry of the dye-forming reactions is the same. Solvents are employed in most systems to make a homogeneous solution from ingredients incompatible with water.

10.4.1 Permanent vs. demipermanent: alkalizing agent

The major difference between the two is the extent to which the system lightens the hair. Permanent products generally use ammonia or a high level of monoethanolamine to raise the pH. These alkalizing agents perform three functions vital to the performance of the product: they raise the pH to the correct value, generate the active oxidizing species from H_2O_2, and swell the hair fibres to facilitate penetration of the dyes. When monoethanolamine is used, it also helps dissolve some of the ingredients.

Among the factors that a formulator can control, the rate of bleaching of melanin is dependent on pH, H_2O_2 concentration, and the identity of the amine used. Rate of bleaching increases with increasing pH, and H_2O_2 and amine concentrations. Additionally, rates generally increase along the series:

$$\text{tertiary amine} < \text{secondary amine} < \text{primary amine} < \text{ammonia}$$

Therefore, ammonia usually is the alkalizing agent of choice for high-lift and permanent products. Some, though, do use entirely monoethanolamine at a high concentration or a combination of monoethanolamine and ammonia. For demipermanent products, which bleach somewhat, but require less lightening than a typical permanent product, monoethanolamine alone can be used. Where no bleaching at all is required, either hindered primary amines or secondary or tertiary amines can be used.

10.4.2 Permanent vs. demipermanent: oxidant

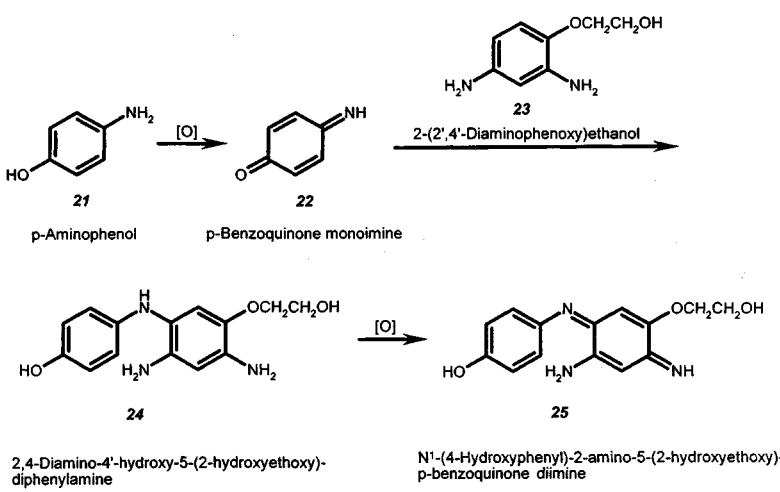
As mentioned above, the difference between the two is in the extent of bleaching of the hair that accompanies the dye-forming reactions. Therefore the chemistries of the two systems will be dealt with together. The oxidant begins

the coupling reaction by generating the first active coupling species, either a *p*-phenylenediimine or a benzoquinone monoimine, as will be shown later in Schemes IV and V. It is not the parent peroxide that is the electron acceptor to any great extent in the generation of the oxidized primary intermediates. The active oxidizing species is generated from H_2O_2 by the action of the alkalizing agent. In permanent and some demipermanent products the oxidant also is responsible for bleaching the hair's melanin. Besides giving lighter shades, the reason this bleaching is important is that it helps give a more level colour, so that there is not a large difference in colour between the grey and pigmented hairs.

10.5 PERMANENT SYSTEMS: DYES

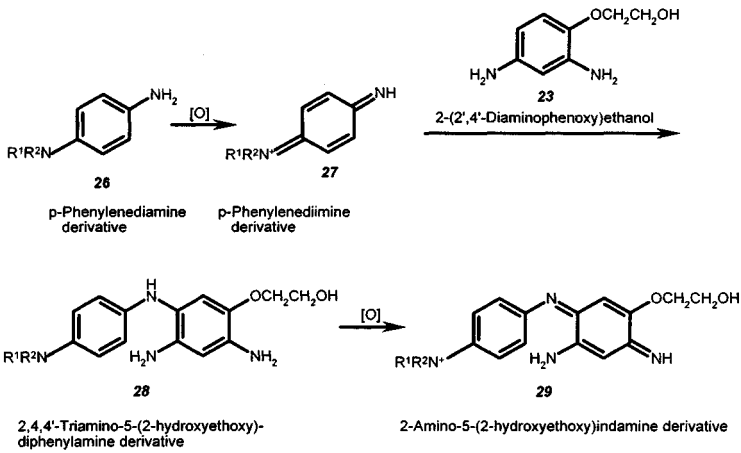
Oxidation dyes also are called permanent because of their stability to the normal wearing processes. Commonly it is growth of the hair, rather than fading, that dictates the need to re-colour or 'touch-up'. This loss of dyes is also unique, from the formulation aspect, in that, since they are permanent, there is the potential for more noticeable colour build-up on the re-dyed hair, than with other products. This can result in a striped appearance from repeated dyeing. They are also unique among all classes of hair colourants in their ability to give shades both lighter and darker than the untreated hair; that is, colours from light blonds to dark natural blacks are available. Also unlike the commercially available temporary and semipermanent systems, colour formation on hair is the result of chemical changes in the materials applied to the head; that is, it is precursors to the dyes, not the dyes themselves, that are applied.

To gain a better understanding of how we can use the materials to formulate shades, it is appropriate first to discuss a few important facts about the chemistry

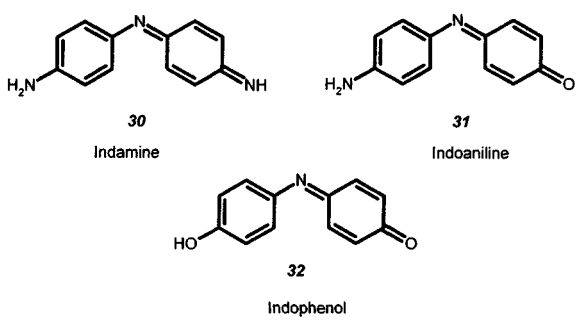


Scheme IV

and kinetics of the processes necessary to form these oxidation dyes, using the coupling of *p*-aminophenol (*21*; Scheme IV) and *p*-phenylenediamine derivative *26* (Scheme V) with 2-(2′,4′-diaminophenoxy)ethanol (*23*) as examples.



Scheme V



Scheme VI

There are three important components to this chemistry: the primary intermediate, the *m*-coupler or secondary intermediate, and the hydrogen peroxide. Oxidation of the primary intermediates *p*-aminophenol (*21*) and *p*-phenylenediamine derivative *26*, give *p*-benzoquinone monoimine (*22*) and *p*-phenylenediimine derivative *27* (Schemes IV and V, respectively). These couple with 2-(2′,4′-diaminophenoxy)ethanol (*23*) via electrophilic attack at the position *para* to the heteroatom of the coupler, to give leuco dyes (diphenylamines) *24* and *28*, which then rapidly oxidize to give indo dyes *25* and *29*. Therefore, using this chemistry, we can produce indamines (*30*), indoanilines (*31*), and indophenols (*32*). Although we

now understand quite a bit about these coupling reactions, particularly because of the extensive work on the subject by Brown and Corbett [5], the exact mechanistic details of the first step of the reaction (the oxidation of the intermediates by H_2O_2) are still unclear. Nevertheless, this chemistry has been useful in hair dyeing for over 100 years.

Rate data for the reactions of *p*-phenylenediamine show that both the oxidation and coupling steps are functions of pH. For the *p*-aminophenols, as pH is raised, oxidation occurs more readily, but coupling of *p*-benzoquinone monoimine is largely unaffected by changes in pH. However, it is not just the rates of oxidation and coupling that must be considered for product formulation. The rate of decomposition of hydrogen peroxide to the species active in oxidation dyeing also increases with pH. Therefore, at acidic to neutral pH, where the rate of uncatalysed H_2O_2 decomposition is slow, there is the potential for slow dye formation. However, this is only a consideration *in situ*. It is not a practical problem, since dye formation occurs faster in hair. In practice, though, the rate of melanin bleaching by peroxide does decrease with pH. Therefore, at pH 7, for example, the slow rate of melanin destruction does not allow one to lighten the hair significantly. Thus far, this has prevented the development of a product with significant bleaching formulated near neutral pH.

It is known that the formed indo dyes can undergo subsequent reactions [5]. So, the issue of stability of the dyes in the hair must also be considered, particularly to light, washing, and perspiration. This shows itself as the biggest problem in what is called 'warm wearing'; the blue indamine dye, for example, is slowly converted to a red, as it is transformed to a phenazine. There are a number of ways to retard this process, and these are discussed below.

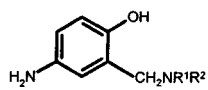
10.5.1 Primary intermediates

Substitution of the *p*-aminophenols or *p*-phenylenediamines with either electron-donating or electron-withdrawing substituents shifts the absorbance maximum of the indo dye formed, relative to the unsubstituted parent dye of the series. The caveat for the electron-withdrawing substituents is that if they are too electron withdrawing (e.g. a nitro group), the oxidation reaction will not occur in a reasonable time. Since there is only one aromatic amino group in the *p*-aminophenols, and since the nitrogen that undergoes electrophilic attack on the coupler must be unsubstituted, substitution is possible only on the ring. (The phenolic oxygen *para* to the nitrogen atom also must be unsubstituted so it can form the quinone species.) For *p*-phenylenediamines either ring or nitrogen substitution is possible. As we will see with the semipermanent dyes, the absorbance maxima of indo dyes formed from *p*-phenylenediamines increase as the degree of N-substitution increases. As with the *p*-aminophenols, though, the nitrogen that performs electrophilic attack on the coupler must be unsubstituted.

Besides the more usual derivatives such as alkyl and halogen, several more interesting analogues have been patented recently. These are the Mannich Base (*33*) [6] and benzyl alcohol derivatives of *p*-aminophenol. In addition, primary intermediates (*34*) containing the electron-withdrawing trifluoromethyl group also have been disclosed [7] (Scheme VII). It is interesting to note, though, that, at least in one series, higher temperatures have been used for the dyeing process.

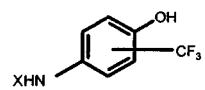
10.5.2 *m*-Couplers

The couplers fall into several fundamental categories: *m*-phenylenediamines (*35*), *m*-aminophenols (*36*), resorcinols (*37*), phenols (*38*), and heterocyclics, such as 2,6-diaminopyridine (*39*).



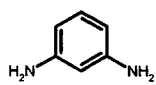
33

Mannich Base



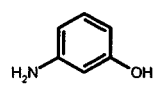
34

Primary intermediate containing trifluoromethyl group



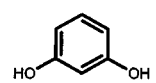
35

m-Phenylenediamine



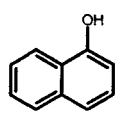
36

m-Aminophenol



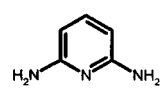
37

Resorcinol



38

Phenols



39

2,6-Diaminopyridine

Scheme VII

For the unsubstituted carbocyclic *m*-couplers, the general rule is that the more electron-donating the substituent, the higher the absorbance maximum of the indo dye formed. So, for example, with the same primary intermediate, the order of increasing value for absorbance maximum for the indo dyes formed from these couplers would be:

resorcinol < *m*-aminophenol < *m*-phenylenediamine.

For the unsubstituted carbocyclic *m*-couplers, with substituents *ortho* to the oxidized group of the indo dye, an electron-donating group shifts the absorbance

maximum hypsochromically (to a lower wavelength, i.e. to the violet end of the spectrum). There are, of course, some complicating factors, particularly the fact that, for the phenolic *m*-couplers, the indo dye formed will react with a second molecule of primary intermediate to form a trinuclear dye, which will be discussed later. Table 10.1 lists the colours of some of the common couplers and primary intermediates.

It is apparent from Table 10.1 that the *m*-phenylenediamines are important compounds for formulating the cooler and deeper shades, such as a natural blue-black. The biggest problem with these is that, although they are stable in a dry environment, in the presence of water there is an increased likelihood that the indo dyes formed from these materials will undergo a cyclization reaction leading to a phenazine, which is red, and is responsible for 'warm wearing' of shades containing *m*-phenylenediamine. However, introducing an electron-donating group such as alkoxy or hydroxyalkoxy in the position *ortho* to the incipient imino group, decreases the rate of the cyclization. So, for example, the indo dye formed from *23* should be more stable than the one formed from *m*-phenylenediamine.

The indo dyes formed from the *m*-aminophenols and resorcinols also have secondary reactions that result in colours different from the first-formed indo dye. Obviously coupling can occur *para* to either heteroatom in the molecule, still leaving a position *para* to the other heteroatom unblocked. This can result in formation of a trinuclear dye, which is somewhat drabber than the indo dye from which it is formed. This is not necessarily bad, since these materials provide part of the base colour, which the more brightly coloured dyes modify. However, we know that by blocking, for example, the position *para* to the nitrogen atom in a *m*-aminophenol, trinuclear dye formation is prevented, and bright colours can be generated.

Table 10.1 Colours produced by the reaction of some common primary intermediates and couplers

	PAP	*PPD*	*HE_2PPD*
m-Aminophenol	Warm brown	Red-brown	Medium violet
Resorcinol	Yellow green	Greenish-brown	Yellow-grey
2-Methylresorcinol	Ash brown	Yellow-brown	Grey-violet
m-Phenylenediamine	Orange-yellow	Blue	Greenish-blue
5-Amino-*o*-cresol	Orange	Purple-red	Purple
α-Naphthol	Red-orange	Violet	Blue
2-Methyl-5-(2-hydroxy-ethylamino) phenol	Orange-red		
23	Red	Violet-blue	
39		Blue	

PAP = *p*-aminophenol; PPD = *p*-phenylenediamine; HE_2PPD = N^4N^4-bis(2-hydroxyethyl)*p*-phenylenediamine.

So all this information can be summarized by a few statements.

1. The reactivity of a coupler towards an oxidized primary intermediate decreases with the introduction of electron-withdrawing groups. A recent exception to this rule has been seen in a coupler containing a nitro group patented by L'Oreal [8]. There are a number of theories why this particular coupler may work, including steric hindrance forcing the nitro group out of plane with the aromatic ring, and the conjecture that since the nitro group is in a position *meta* to the coupling position, it is not as deactivating.
2. Electron-donating groups in the 4-position of the *m*-coupler increase the rate of coupling.
3. The effects outlined above are the reverse for the primary intermediates. This of course makes sense when the mechanism is considered.
4. Although the electron-donating groups on the primary intermediate decrease the coupling rate, they increase the rate of oxidation relative to the parent compound of the series.

10.5.3 Formulation

Even with rate data and relative reactivities considered, prediction of an exact shade by knowing the pH of the mixture and the amounts and identities of the intermediates present, is still not possible in quantitative terms, particularly because the hair in which the colour is formed is not a passive reaction vessel. Neither is every hair on a person's head the same colour, and each hair contributes its own background colour to the shade. Also to be considered are the porosity of the individual fibres, the rates of diffusion, and the partition coefficients for the dye precursors. However, these data obtained from the mechanistic investigations are an excellent starting point and, given this knowledge, it is fair to say that much of what a formulator has to do, if this knowledge is applied correctly, is 'fine-tuning' of the desired shade.

This fine-tuning is the portion of product development in which we deal with the more nebulous variable of 'pleasing the consumer'. However, we still are able to apply what we have learned thus far to accomplish our goal. As with any of the dyes of which we speak, we are looking for colour, intensity, and brightness. Intensity is probably the most straightforward, as long as we have chosen our delivery vehicle so that we can get enough of the material into the hair. Brightness is addressed by considering the absorbance spectrum; in general, the narrower the absorbance band, the brighter the dye. Precise colour on hair is somewhat more difficult. Knowing that these materials have functional groups that ionize over the pH range in which we are working, and that the final pH in the hair will be in the range of 4–5, we can select our dye precursors, and make a good first approximation. First, of course, we know that there will be competition among all the oxidized primary intermediates for all the couplers, and vice-versa. Given that the reactive species for the couplers are the conjugate

bases, that the conjugate acid of the *p*-phenylenediimines and the uncharged *p*-benzoquinone monoimine are the reactive primaries, and that the rate of breakdown of H_2O_2 increases with pH, we know that it is best to work in the pH range of 9–11. In this range we can take advantage of the facts that:

1. *p*-Phenylenediamines with resorcinol give yellowish-green to brown dyes that are useful for background colour and 'ash' tonality.
2. α-Naphthol can be used as a second blue coupler. (At lower pH the solubility is not high.)
3. There is some background colour formation by *p*-phenylenediamine with itself and the couplers, by polycyclic dye formation.

10.5.4 Novel approaches: a follow-up

The relevant chapter in the 9th edition of this book mentioned several novel approaches to formation of indo dyes. L'Oreal patented the use of an iodide catalyst in combination with oxidation dyes. This not only has a catalytic effect, but appeared to lower the concentration of dyes necessary to obtain a given shade. Clairol developed a method for formation of indo dyes that did not require hydrogen peroxide; they utilized azide-containing primary intermediates. The chemistry involved in indo dye formation was initiated by light. This not only obviated peroxide use, but had the potential for increasing the number of shades, because there no longer seemed to be restrictions on what types of functional groups could be present in the primary intermediate. Based on the ingredient labelling of current products, it seems that neither of these has been utilized.

10.5.5 Oxidation dye product enhancements: formulations

The area that may have seen the most significant advances recently is probably thickening of permanent and demipermanent dyeing systems. Alkyl phenol ethoxylates have been a mainstay of thickening technology. These materials are formulated into a product at a concentration at which they act as a solvent and have a low viscosity. When they are diluted with water they thicken, to give a gel- or creme-like consistency. They are inexpensive, and aid in dissolution of the dyes and other ingredients. Polymeric thickeners now offer some advantages over the alkylphenol ethoxylates, and some producers have already begun to utilize them.

Patents by Pohl *et al.* suggest the use of polyacrylate thickeners [9–11]. This technology takes advantage of the fact that the dye-containing component is alkaline, and the peroxide component is acidic. These polymers are polycarboxylic acids, so neutralization with base activates them. At low pH these associative thickeners are in a more compact state. When combined with an alkalizing agent they uncoil ('swell') and thicken the solution in which they are

contained. Therefore, to utilize this technology, one must be able to dissolve or disperse the polyacrylate thickener in the low pH developer solution. The major caveat here is that the particular polyacrylate chosen must be stable to H_2O_2. Schmucker-Castner has also reported recently that the poly(acrylic acid) polymers offered by B.F. Goodrich meet these criteria and, as one might expect, have the added advantage of aiding in the buffering of the system [12].

10.5.6 Oxidation dyes: minimizing fading on the hair

One of the advantages of oxidation dyes has been related to one of their weaknesses. Oxidation dyes are designed to leave a 'permanent' colour on the hair. However, not all indo dyes have the same stability profile. Therefore, under certain conditions, some dyes may begin to fade (i.e. their original colour changes) within a hair fibre; others may retain theirs. This is the cause of one of the constant problems with oxidation dye products: off-shade fading. Red dyes are particularly susceptible to this. As the red dye fades (loses its tonal quality), the hair becomes less vibrant. Depending on the original shade, the hair can change more towards a brown colour.

One may recall that it was mentioned earlier that the blue indo dye formed from *m*-phenylenediamine cyclized to form a red phenazine, and the hair became brassy. Chemical modification of the parent *m*-phenylenediamine gave compounds that underwent this cyclization much less readily, and the tendency for brassiness or 'warm wearing' was minimized. A recent US Patent [13] outlined a similar approach to prevent degradation of red dyes, hence retaining the red colour on hair. In that case, 2-methyl-1-naphthol replaces α-naphthol as a coupler.

10.6 GRADUAL COLOURANTS

Hair can be coloured gradually over several days by application of heavy metals. This chemistry is relatively straightforward. Solutions of the lead or bismuth salts are applied to the hair, and with time form dark sulfides. This process has not changed significantly since the time of the Roman Empire, with the exception that their method of application was a lead comb dipped in acidic solution. However, during recent years heavy metals have fallen out of favour as colourants due to their potential effects on the health of the users.

10.6.1 Auto-oxidative dyes

The ability to use auto-oxidative dyes in a gradual colouring process has been known for 40–45 years. However, there have been a number of reasons why they have not been utilized until recently. One of the most important certainly may be the difficulty in manufacture and handling of the most useful dyes such as 1,2,4-benzenetriol, 2,3,5-trihydroxytoluene, 2,4-diaminophenol, 4-aminocatechol,

and 2,5-diaminoanisole. The idea of using them specifically as a men's product was certainly an important step towards their introduction, though. Because shades lighter than the starting colour of the hair were not available, there was a limited application as a permanent hair dye, but in a men's market this was not a major problem. They also offered the same advantages as the metallic dyes, in that the appearance of colour was gradual, hence it overcame the reluctance of men to colour their hair. Another problem with the auto-oxidative dye product was the inability to 'fine-tune' the shades the way that was possible with the normal oxidation dye products. However, this had been a minor one, and had not been a serious impediment to the launch and maintenance of successful products. Although there is still a small market for these products, they are being replaced by those that give more immediate results. More recently, improvements have been made to products that are similar to women's demipermanent products, and take only five minutes. This category continues to grow, and offers a real opportunity to the formulator that can combine the ease of use of the current products with the long-lasting performance that is lacking in current products for men.

10.7 NATURAL DYES

In the previous version of this chapter on hair colourants the interest in the use of natural dye products, particularly in systems that mimic the natural pigments of the hair, was increasing. Previously the major problem, though, was obtaining dark colours in a useful time. That is, colour could be developed from the purported monomer in eumelanin formation (5,6-dihydroxyindole; *6*) (Scheme I), but the time necessary to obtain darker shades was impractical. In addition, to obtain an intense black shade in a short time without repeated treatments, a second component, such as *p*-phenylenediamine, had to be added to the dye mixture. The problem seemed to be that 5,6-dihydroxyindole is inherently unstable at alkaline pH in the presence of oxygen. As a result, once it was applied to the hair, polymerization to the melanin could occur to a significant degree on the surface of the fibre. Although there was darkening in the dye bath, not enough of the material diffused into the fibre, and colour was not imparted to the hair to a significant enough extent for the black shades.

These problems were overcome by a Clairol invention [14] that mimicked more closely the natural pigment, because metal ions were incorporated into it. In nature, melanin acts as an effective ion exchange resin, and in the natural pigment-forming process, tyrosinase, a Cu^{2+}-metalloenzyme, mediates at least portions of the process. In fact, when hair was pretreated with a solution of Cu^{2+}, rinsed to remove surface metal ions, and treated with solution of 5,6-dihydroxyindole of 1% or less, dark black shades were obtained in five to ten minutes. When these materials were used in this manner, the pigment was distributed mainly in the periphery of the fibre [15]. This, combined with the presence of Cu^{2+} (which

catalyses the decomposition of hydrogen peroxide) in the polymer, made it very easy to modify or remove the colour with dilute aqueous peroxide solutions [15].

As one might imagine, formulation of such unstable materials might be difficult, since there is a great potential to lose the dye through polymerization during the formulation (manufacturing) process. This has also been addressed in several L'Oreal patents [16], that describe the approach of using *6* in an aerosol composition. The other approach that is a technical advance is to begin with a stable, protected version of *6*, such as 5,6-diacetoxyindole (*8*) (Scheme I), and to hydrolyse it *in situ* by including an excess of amine to mediate the hydrolysis or aminolysis of the precursor.

Technical ingenuity aside, none of the above approaches has produced a successful product. Most likely this is due to the difficulty in manufacture and the expense of the products, and because standard oxidation dye chemistry still produces superior colours with superior wearing properties. To address these issues a series of recent patents bases colour formation on the ferricyanide-mediated oxidation of DOPA (*1*) (Scheme I), an earlier precursor in the melanin biosynthetic pathway [17]. By combining these with oxidation dye precursors a range of shades is available, and the expense and manufacturing difficulties are avoided. However, this technology still suffers from the same drawback as any other that uses compounds in addition to the natural melanin precursors. The best that can be claimed is naturally based, rather than natural. Nonetheless, this is a very good first step in understanding the technology necessary to move eventually to colourant systems that completely mimic the natural processes.

Other types of hair colourants currently being marketed are based on plant pigments such as logwood, chamomile, and henna (the pure monomer of which is lawsone; 2-hydroxy-1,4-naphthoquinone). Generally, these are bought as powders that are mixed with warm water before application. This is presumably because stable products cannot be manufactured with these raw materials, which, in many instances, are the finely divided or powdered leaves of the plant. Although the monomers for these plant pigments are readily available, there have been no reports of using them successfully to develop commercial hair colourants, as with the melanin systems.

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11

Manicure preparations

Mitchell L. Schlossman

11.1 INTRODUCTION

The chief function of the nail in humans is that of protection. It protects the delicate end-of-finger bone, greatly helps in appreciation of fine touch and aids in picking up small objects. It is also, of course, used in scratching. Toe nails are equally important for protection.

The nails should receive regular treatment as an essential part of grooming to maintain them in good condition. They should be cut regularly, particularly if they show any tendency towards brittleness, and may be shaped, preferably with an emery board. Modern manicure preparations are designed to promote nail hygiene and often protect against the effects of solvents and detergents, or other materials which are normally handled during the daily routine. The general condition of the finger nails is also dependent on general physical conditions which affect their growth, such as nervous strain and alteration in glandular function, or dietary deficiencies of amino acids, vitamins and essential fatty acids.

The nail is composed of three layers: a soft layer known as the ventral nail, an intermediate layer of hard keratin, and an external layer known as the dorsal nail. The nail plate is composed of layers of flattened, keratinized cells fused into a dense but somewhat elastic mass [1]. Nails have their origin in the nail matrix, a living, highly proliferative epidermal tissue. The nail normally grows distally at the rate of about 0.1 mm per day and thus requires 4–5 months to regenerate completely after avulsion. It has been demonstrated that growth is slowed with increasing age, in cold conditions, in diseased states with reduced blood flow to the body's periphery, and in malnutrition. These all indicate that proliferative events in the nail matrix are sensitive to the local availability of nutrients [2]. The fibrous protein structure contains a high proportion of the sulfur-rich amino acid cysteine, a smaller proportion of methionine together

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 325–343

with other amino acids such as tyrosine, lysine, and histidine. The calcium content of the nail is very low – not more than 2 parts per 1000 by weight.

The nail also contains 12–14% of water and fatty materials, mainly in the form of cholesterol. Products designed as manicure preparations should, wherever possible, avoid use of materials which remove either natural fat or water-soluble substances, as these effects could interfere with the lattice-like structure and contribute to splitting or breaking. It is for this reason that fatty materials are often included in manicure preparations.

11.2 CUTICLE: CREAMS, OILS, AND REMOVERS

Partly covering the lunula or half-moon at the base of the nail plate is the membrane called the eponychium, more commonly known as the cuticle. When this overlaps too thickly, or becomes irregular and ragged, it spoils the appearance of the nails; hence the use of manicuring devices, including curved scissors, and cosmetic preparations designed to improve its appearance.

Cuticle creams soften the cuticle and at the same time prevent the nails from becoming brittle and ribbed. A lanolin- and protein-rich cream used as a nightly application is suitable for this purpose. The lanolin/protein formula has a marked softening effect on the cuticle [3].

Cuticle massage cream

	% w/w
Anhydrous lanolin	10.00
Isopropyl myristate	3.00
Stearic acid xxx (triple pressed)	2.00
Cetyl alcohol	2.00
Propyl paraben	0.20
Deionized water	70.55
Glycerol	4.00
Triethanolamine	1.00
Magnesium/aluminium silicate (Veegum HV)*	1.50
Hydrolysed animal protein	5.00
Methyl paraben	0.25
Imidazidinyl urea	0.20
Perfume	0.30
	100.00

* Veegum HV – R.T. Vanderbilt Co.

Lotion protein nail conditioner

	% w/w
Potassium coco-hydrolysed animal protein	5.00
Hydrolysed animal protein	5.00

Hydroxyethyl cellulose	0.50
Ethanol	30.00
Methyl paraben	0.15
Propyl paraben	0.05
Tocopheryl acetate	0.05
Laureth-23	2.00
Deionized water, perfume colour	q.s.
	100.00

Procedure

Add water to vessel. With agitation add hydroxyethyl cellulose and agitate until clear (a few drops of dilute NaOH hastens dissolution). In a separate vessel, dissolve parabens and perfume in ethanol. Add this blend to hydroxyethyl cellulose solution with agitation. Finally, add balance of ingredients and agitate until dissolution.

Cuticle oils are also used and these can be made with an oil-soluble liquid lanolin derivative diluted with a vegetable oil or a fatty acid ester.

Oil

	% w/w
Liquid lanolin derivative*	75
Castor oil or isopropyl myristate	25
	100

*Amerchol L-101 type mineral oil and lanolin alcohol – American Cholesterol Products, Inc.

Isopropyl lanolate can be used as an alternative type of liquid lanolin derivative. Regular use of a cuticle cream or oil loosens dead skin and cuticle, and helps to maintain it in a healthy condition. To improve the appearance it is usual to press the softened cuticle gently back and away from the nail using an orange stick tipped with cotton wool.

Cuticle removers

Cuticle removers are applied to the softened cuticle in similar fashion. They are generally water-based formulations containing alkalis, which act by causing hydrolysis and swelling of the softened cuticle to facilitate its removal. It is emphasized that this practice should be carried out with care, otherwise regular application of an alkali or acid may damage the nail bed and also cause dermatitis. A most effective type of solution is made with caustic potash and glycerol. A suitable product is made using from 2% to 5% potassium hydroxide as follows:

	% w/w
Potassium hydroxide	5
Glycerol	20
Water (softened or distilled)	75
	100

Methyl parahydroxybenzoate 0.2% and a water-soluble type perfume is normally added.

Trisodium phosphate is used in modern cuticle removers at a level of 8–10% with 15–25% glycerol. A surface-active material, such as sodium or triethanolamine lauryl sulfate, can also be included and small proportions of a soluble lanolin derivative have a softening effect without alkali harshness. A suitable formula is as follows:

	% w/w
Trisodium phosphate	10.0
Glycerol	20.0
Sodium lauryl ether sulfate*	3.0
Ethoxylated lanolin derivatives†	0.5
Water or rose water	66.5
	100.0

*Empicol ESB. 30 type – Albright Wilson Ltd.
†Solulan 75 type – American Cholesterol Products, Inc.

The amines, monoethanolamine, and triethanolamine, being less alkaline, should be used at a concentration of 10%, but even at this concentration they are not so effective as potassium hydroxide.

Lactic acid is another chemical used in cuticle softener/remover formulations and has a pH of 3–4. It works by dissolving the keratin of the stratum corneum and this removes the dead skin. Lactic acid available in 85% active solution may be used at 5–15%. Similar care must be taken when alkalis are utilized. Directions on usage must be carefully described to avoid harm to the nail bed and surrounding skin.

11.3 NAIL BLEACHES AND NAIL WHITE EDGING CREAM

Nail bleaches are used to whiten the nails and remove discolourations, nicotine and ink stains. Such stains may yield either to oxidizing agents, such as hydrogen peroxide, or perborate, or citric, tartaric or hydrochloric acids; or reducing agents such as sulfites with dilute acid. A 4% solution of concentrated hydrochloric acid in water and glycerol has been recommended. This is a formula for an abrasive nicotine stain remover:

	% w/w
Beeswax	10.0
Paraffin wax	5.0
Mineral oil	46.0
Borax	0.5

Pumice powder	8.0
Water	30.0
Perfume	0.5
	100.0

Procedure
The heated aqueous solution of borax may be added to the melted oils and fats and the pumice incorporated when the mixture is beginning to thicken. Homogenization or milling will improve the distribution of the pumice, but will cause wear on the homogenizer.

Nail white preparations
A nail white cream may be used to produce an even, white edge to the nails; a paste or cream, incorporating an inert pigment is often applied. The pigment is usually titanium dioxide or zinc oxide. Generally a fatty base is used as follows:

	% w/w
Titanium dioxide	30.0
White petrolatum or vanishing cream base	70.0
	100.0

This is prepared by milling the titanium dioxide into the petrolatum or base. Nail white pencils have largely replaced creams since they are easier to apply and less messy in use. They require moistening with water before application to the under-surface of the nail-free edge. A wax base is usually prepared by firms specializing in pencil manufacturing.

11.4 NAIL POWDERS

Powder nail polishes have largely been superseded by nail enamel or lacquer. A section of the public still uses the original preparations and they are suitable for use by men. They bestow a gloss on the nail surface by abrasive action. The formulations usually consist of newly powdered abrasives, and the gloss appears when the nails are buffed with a shaped chamois-leather pad after application. Stannic oxide, talc, silica, kaolin, and precipitated chalk have been used. Stannic acid is most effective.

	% w/w
Stannic Oxide	70
Talc	20
Zinc Oxide	10
	100

	% w/w
Stannic Oxide	90.0
Powdered Silica	8.0
Butyl Stearate	2.0
Pigment	q.s.
Perfume	q.s.
	100.0

The above formula with butyl stearate may be prepared by simple trituration or revolving mill. Mixtures of the powdered materials, by themselves, can be prepared in paste form by mixing with glycerol, tragacanth or starch mucilage, or they can be made into blocks by allowing such pastes to dry out at room temperature.

11.5 NAIL ENAMEL

Nail lacquers form the largest group of manicure preparations. They should be easy to apply, dry and harden rapidly, be waterproof, well-adherent, glossy, elastic, and resistant to chipping and abrasion. The raw materials employed should be non-toxic and dermatologically innocuous. The main constituents are the film-former, a resin, a plasticizer and solvents. In addition, pigments and suspending agent are usually present.

11.5.1 Raw materials

The resin

Nail lacquer or enamel is based on nitrocellulose which is derived from cellulose, a polymer made of several anhydroglucose units connected by ether linkages. Cellulose may be considered a trihydric alcohol. There are three different grades of nitrocellulose readily available. Nail polish uses the grade with a nitrogen content of 11.8–12.2 which is soluble in esters, ketones, and glycol ethers. Viscosity is a property which varies with the degree of polymerization of the nitrocellulose. The viscosity determines the amount required to produce a lacquer of given viscosity; it also affects the pliability of the film; the lower the viscosity the more brittle the resultant film. The viscosity of nitrocellulose solutions is measured by the falling-ball method and is expressed as the number of seconds taken for a standard ball to fall through a definite column of a standard nitrocellulose solution. The nitrocellulose is usually damped down for safety with isopropyl alcohol or ethyl alcohol. Special viscosity grades include 18–25 cp, 1/4 s, 1/2 s and 5–6 s. Most nail polish lacquers use a combination of 1/4 and 1/2 s grades of nitrocellulose to achieve the desired results. Lower viscosity grades have been used for special application, such as the nail polish pens [4] recently introduced onto the market.

Table 11.1 Solvents for nail enamels

°C		°C	
75–83	Ethyl acetate	150–160	Ethyl lactate
78	Ethanol	138	Xylene
80	Isopropyl alcohol	140	Iso-amyl acetate
86–90	Isopropyl acetate	135–172	Diacetone alcohol
124–129	*n*-Butyl acetate	65–69	Hexane
110.2–111	Toluene	94–99	Heptane
140–150	Amyl acetate	112–119	Isobutyl acetate

Solvents

A mixture of solvents is normally employed to dissolve non-volatile lacquer constituents. Nitrocellulose itself is water-insoluble and alcohols are generally not good solvents for nitrocellulose when used alone. The selection of solvents used as the volatile portion of the lacquer is important and consists of a mixture suitably balanced so that the rate of evaporation prevents changes which cause precipitation of the nitrocellulose taking place in the residual film as it dries on the nail. The boiling point of the solvents also influences the viscosity of lacquer solution. The lower the boiling point, the lower too is the viscosity of the resultant solution and the better the covering power. The solvent or solvents employed will therefore influence the ease of application of the nail lacquer, its rate of drying and hardening, and also the characteristics of the applied film. The preferred solvents for nail lacquers are consequently mixtures of low and medium boiling solvents. In order to assist the experiments a list of the most popular solvents used is given in Table 11.1 with their distillation range given in degrees centigrade.

The solvents used will also determine the gloss of films produced. A high boiling point solvent will usually give a brighter film than a low boiling point solvent.

Diluents

Diluents are organic solvents that are miscible with the nitrocellulose solvents but are not themselves solvents for nitrocellulose. They also help to lower and stabilize the viscosity of lacquers. There is a limit to the amount of diluent which can be tolerated by the nitrocellulose solution without causing precipitation of the latter.

There are three classes of diluents: the alcohols, aromatic hydrocarbons, and aliphatic hydrocarbons. Of these the alcohols, ethyl, butyl or isopropyl, are the most efficient diluents. The second class contains toluene and xylene. Toluene is preferred because it does not cause 'chilling' – cloudiness of the film produced by localized lowering of temperature due to the rapid evaporation of solvent and

resulting in the condensation of moisture with and upon the film. Toluene has been questioned as an unsafe ingredient for nail enamel during the past eight years. In 1991 toluene was added to Proposition 65 in the state of California, USA, as a reproductive toxicant. Toluene-free formulations are found chiefly in the USA among mass marketers of nail polish.

An example of a formula representing a toluene-free, formaldehyde-free system is as follows:

Toluene-free/formaldehyde-free nail enamel

	% w/w
n-Butyl Acetate	41.99
Ethyl Acetate	27.00
Nitrocellulose, 1/2 s (wet)	12.86
Saturated Polyester Resin*	8.50
Acrylates Copolymer	2.00
dl-Camphor	1.70
Stearalkonium Hectorite	0.85
Acetyl Triethyl Citrate	5.00
Benzophenone-1	0.10
Pigments and Pearlescence	q.s. to 100.00

* Diversol 09A-9514 – DVC Limited Inc., Duluth, GA, USA.

The third class of aliphatic hydrocarbons includes petroleum ethers, least efficient of all diluents. They cause a slight increase in the viscosity of nitrocellulose solutions and impart flow properties to the film applied.

Antidehydration w/o enamel

Additionally, although containing solvents, a study discussing the development of a w/o emulsion-type nail enamel to avoid dehydration from the nail by supplementing water to the nail was developed [5].

Additional resins for film improvement

A solution of 10–15% of nitrocellulose in a solvent blend provides the basis of a nail lacquer and such a mixture will dry out to produce a film. Such a film, however, would shrink on drying out and become brittle, and would not show much gloss. It is therefore necessary to add a suitable plasticizer to give the film flexibility, and resins to provide hardness and gloss and reduce the tendency to shrinkage. The resin now accepted as being the best available for use in conjunction with the nitrocellulose films for nail lacquers is a condensation product of *para*-toluene sulfonamide and formaldehyde and this is used at a concentration of 5–10% in the finished formulation, the exact proportion being dependent

on the concentration and composition of the solvents and other ingredients affecting film formation. This resin gives good gloss and good adhesion, and increases the hardness of nitrocellulose films. Relatively large amounts may be used without adversely affecting the ease of application. Firms that wish to make hypoallergenic claims for nail polish should eliminate the use of the formaldehyde resin which has been linked to allergy in some consumers. Most replace this resin with a polyester resin or an oil-free alkyd resin based on polyol dibasic acid ester. Another type derived from toluene sulfonamide is toluene sulfonamide epoxy resin [6]. Often the polyester resins yield nail enamels with poorer adhesion than the formaldehyde resin. Other resins compatible with nitrocellulose and used in nail lacquer in small amounts are maleic alkyd resins, acrylates, vinyls and polyamide resins. These resins help to improve gloss, hardness and adhesion.

Choice of plasticizer

The choice of a suitable plasticizer is most important as this material has a great effect on the viscosity of the enamel, the volatility or rate of drying, and most important on the gloss and flexibility of the nitrocellulose films. The most-used plasticizer for nail lacquer systems is dibutyl phthalate. Other common plasticizers are camphor and castor oil. Although it is volatile, camphor does not leave the film very quickly, but probably has other benefits. Castor oil is usually used as a carrier for other ingredients, but is also a plasticizer. Acetyl triethyl citrate, di-isobutyl adipate, butyl octyl adipate, sucrose acetate isobutyrate and ethyl toluene sulfonamide are also used as plasticizers in nail polish. These materials are used either singly or together in the preparation using about 5% of total plasticizers in the mix. Innumerable combinations of nitrocellulose resin, plasticizers, and solvents are theoretically possible in the formulation of nail enamel to give films which will vary in the degree of gloss, the thickness of the film and the rate of drying. It is, for example, possible to use a high content of nitrocellulose and plasticizer with a low resin content and a high proportion of solvent to give a fast-drying lacquer. Another recent innovation is in quick-drying suspension nail enamel. It is known that the solvent or solvents employed will influence the ease of application, its rate of drying and hardening, and also the characteristics of the applied film. A patent employing acetone provides for reduction in drying time from 50% up to about 70% over conventional nail enamel compositions [7]. On the other hand, if the proportion of plasticizer and resin is increased a slower-drying and thicker coating is obtained. The experimenter will soon discover the relationship of the composition of the solvent blend to the behaviour of the lacquer. Variations of volatile ingredients control both the viscosity and flow of the mix and the even drying out which must take place at a rate which gives a smooth even surface without precipitation of either the nitrocellulose or resins components. A recent patent describes a nail enamel

which does not contain either a formaldehyde resin, camphor or a phthalate plasticizer. In place of the aforementioned is found a triester such as glyceryl tribenzoate and a diester such as acetyl triethyl citrate [8].

Nail enamel colouring

The colouring of nail enamels must (a) impart to the clear lacquer an acceptable shade for cosmetic use, and (b) opacify the nail lacquer film so that even the most delicate of shades will cover the nail. All colouring materials used must be certified by the FDA. Of the many colourants used, the choice is limited to those which have good permanence and are insoluble in solvents in order to avoid staining and discolouration of the nails, as well as to avoid any chemical reaction to the lacquer. The most widely used organics are D&C Red No. 6 Barium Lake, D&C Red No. 7 Calcium Lake, D&C Red No. 34 Calcium Lake, D&C Yellow No. 5 Aluminium or Zirconium Lake and D&C Yellow No. 6 Aluminium Lake. Among the inorganics are cosmetic grades of yellow and red oxides, iron blue, iron black and purified titanium dioxide. Soluble dyes should not be used in nail enamel or, if used at all, sparingly, because of their staining effect on the skin and nails. They have generally poor light-fastness. Soluble dyes are generally used in tinting removers. The pigments, in order to be used in nail lacquers, should be dispersed in a ball mill or roller mill. The two-roll mill is preferred for the dispersion for nail lacquer [9]. The degree of dispersion has a major influence on the gloss of the enamel, its smoothness, and the ability of the pigment to remain in suspension. Generally, the pigment is mixed with nitrocellulose and plasticizer and passed through a two-roll mill. The final dispersion form of the colour is a hard plastic chip, which at any convenient time may be dissolved, in a clear base or solvents, to serve as a concentration from which a range of nail enamel shades may be formulated. Another method is to make a concentrated colour paste by dispersion in a ball-mill type of equipment. The total amount of colourant in nail enamel is usually 3–5%. Recently the use of hydrophobic pigments in nail lacquer has reduced settling problems by breaking and preventing the agglomeration of the heavier pigments suspended in the lacquer.

Cream-type enamels

Cream-type enamels are prepared by adding titanium dioxide as a filler to give opacity to the film.

Pearlized enamels

Nacreous pigments are important colourants for nail enamel and contribute to the making of the pearlescent type of enamel. Natural pearl essence or guanine (2-amino-6-hydroxy purine), bismuth oxychloride (BiOCl) and titanium dioxide-coated micas are chiefly used. These pigments are usually supplied in nitrocellulose lacquer bases.

Guanine is produced from the scales and bodies of various fish. The brilliance and lustre of the guanine crystals are produced during the coating of the nail surface and the drying of the film. Bismuth oxychloride has a much higher density and is less costly than guanine. It has a very high lustre and yields a mirror-like effect.

Enamels with UV absorbers

Ultraviolet (UV) absorbers such as the benzophenone derivatives are often used in the lacquer to protect the light stability of the BiOCl, nitrocellulose and other colourants. Titanium dioxide, a good UV absorber, and coated micas and mica colourants yield a softer lustre.

Water-based enamels

Water-based nail polish formulations have been the dream of every nail polish chemist. Many patents have been issued, but no major commercial products are water-based, because of problems such as poor adhesion. Several water-based [10–12] patents claim a 'peelable' film based on polyurethanes and/or vinyl and/or acrylic esters [13–15]. Another innovative product is prepared by pouring nail enamel onto an adhesive-backed sheet of paper. After a drying period it is packaged in a semisolid form [16].

The rheological goal of a nail polish formulation is to obtain a thixotropic system in which viscosity decreases with increasing shear rate. A thixotropic system becomes liquid upon agitation and reforms as a gel structure when at rest. Brushing nail polish would yield the proper application viscosity, while the remainder of the bottle remains relatively at rest, continuing to suspend pigments. Organically, modified clays are used universally as suspension agents for nail polishes. The process required to disperse the hectorite or bentonite requires mechanical and chemical energy. A Gaulin homogenizer, a sand, ball or pebble mill is utilized to produce a concentrated gel. Chipping as was described in the making of colourants is often used for the dispersion of these clays. Inorganic or organic acids are often additives used to activate the swelling of the clay, increasing its thixotropy.

11.6 FORMULATION

The following represent (Formula I) a cream and (Formula II) pearlescent nail lacquer [17], examples of ingredients being named according to their function in the formula.

Cream nail enamel (Formula I)

		% w/w
Solvent	*n*-Butyl acetate	28.23
Diluent	Toluene	24.54
Film-former	Nitrocellulose 1/2s (wet)	12.00

Solvent	Ethyl acetate	11.00
Resin	Toluene sulfonamide/formaldehyde resin	10.00
Secondary resin	Acrylates copolymer	0.50
Plasticizer	Dibutyl phthalate	5.00
Diluent*	Isopropyl alcohol, 99%	4.25
Suspending agents	Stearalkonium hectorite	1.00
Plasticizer	Camphor	1.50
Colour	D&C Red No. 6 Barium Lake	0.08
Colour	Titanium dioxide	0.75
Colour	Iron oxide	0.15
		100.00

* Isopropyl alcohol, 99%, also acts as a damper for the nitrocellulose.

Pearlescent nail enamel (Formula II)

	% w/w
Butyl acetate	34.04
Toluene	30.00
Nitrocellulose 1/2 s (wet)	14.90
Toluene sulfonamide/formaldehyde resin	7.10
Dibutyl phthalate	4.80
Camphor	2.40
Stearalkonium hectorite	1.20
Benzophenone-1	0.20
D&C Red No. 7 Calcium Lake	0.08
D&C Red No. 34 Calcium Lake	0.05
FD&C Yellow No. 5 Aluminium Lake	0.08
Iron oxides	0.15
Bismuth oxychloride (25%)	5.00
	100.00

Manufacture

The manufacture of nail lacquers should consist of two separate operations: (a) the manufacture and compounding of the base lacquers and, (b) the colouring of such lacquers to give cosmetically acceptable shades. A mechanical stirrer or turbomixer is used. The diluent is added first, followed by solvents, plasticizer and resins. Stainless steel or aluminium vessels, electrically grounded, are used to prevent lacquer discolouration. Agitation is continued for several hours until solution is complete. The suspension base is left overnight to develop viscosity and thixotropy. The clear lacquer is passed through a filter to remove any insoluble matter and is finally passed into a storage tank. Pigment or coloured lacquers are prepared by adding, under agitation, the appropriate amount of pigment solution or colour concentrate to the clear lacquer in the mixing tank.

A description of the manufacturing process and safety considerations may be found in a chapter on the subject which appeared in 1957 [18]. A laboratory evaluation of nail enamels includes viscosity–thixotropy relationships, gloss, solids, colour matching to a laboratory standard, brushability, drying rate, hardness, stability, adhesion and wear resistance. For consistent results it is necessary to follow exact quality control procedures [19].

Base coat enamel

A base coat is sometimes applied to the nails before the coloured nail enamel. This consists of a clear concentrated lacquer base, forms a firm, even surface on the nail and enables the subsequent application of coloured lacquer to be distributed evenly without showing streaks or variations in colour intensity in a relatively thin film, which is less liable to chip than several separate applications of a coloured lacquer. Many base coats are either the same as, or very similar to, a colourless base lacquer. Some experimenters have tried to product a tackier film by utilizing the aryl sulfonamide resin and/or polyvinyl butyral at higher levels; other resins may also be used.

Final top coat

Finally a top coat or hardener is used over the coloured lacquer. This consists of a clear lacquer base containing a lower proportion of plasticizer and a higher proportion of resin to give a hard surface film and high gloss. The complete manicure procedure is intended to enhance the final appearance of the nails and decrease wear characteristics such as the tendencies towards chipping from the edge of the nail, effects of abrasion and resistance to materials such as water, solvents and detergents.

Strengtheners and hardeners

Strengtheners and hardeners work by either penetrating the nail or providing a strong protective coating. A recent innovation is a quick-drying top coat and hardener containing cellulose acetate butyrate resin in place of nitrocellulose and a mixture of solvents in order to produce a top coat which dries in 60–90 seconds [20]. Formaldehyde is an effective nail hardener.

Use of nail enamel dryer

A nail enamel dryer is used to reduce the period of waiting time for the nail enamel to dry out and set after application. Nail polish dryers traditionally have been drying oils that provide a protective layer to a wet nail polish film. This protects the polish from inadvertent marring or smudging prior to the film hardening. Modern formulations often contain volatile silicone copolymers such as cyclomethicone or dimethicone. Aerosol products, which apply a highly volatile

propellant and small portion of oil, give only a satisfactory 'quick-dry' effect when sprayed on to freshly applied enamel.

Nail enamel dryer

	% w/w
Mineral Oil, 70 Vis.	85.00
Cyclomethicone	10.00
Isopropyl Myristate	5.00
	100.00

Nail polish 'thinner'

Nail polish thickens primarily either because the more volatile solvents escape during use or because of improper sealing of the bottle. A combination of solvents, approximately the ratio found in nail polish, is used as a 'thinner'. Usually, a slightly greater proportion of the faster-evaporating solvents is desirable. The following formula is representative:

	% w/w
Ethyl Acetate	25.00
n-Butyl Acetate	20.00
Ethanol (anhydrous)	20.00
Toluene	35.00
	100.00

11.7 ENAMEL REMOVERS

Enamel removers may consist of any suitable solvent such as acetone or ethyl acetate, or a solvent blend based on toluene similar to that used as the solvent of the nail enamel. Most solvents, particularly low boilers, cause dehydration and remove natural oils from the nail. Such damaging effects are reduced to some extent by using solvent blends and by including some fatty or oily material. Formulae are as follows [21]:

Oily nail lacquer remover

	% w/w
Ethyl Acetate	98.00
Castor Oil	2.00
Colour, Perfume	q.s.

Non-smear lacquer removers

Non-smear lacquer removers may be formulated containing water. The water content must be about 10%. Since the water increases the removal time, only an active solvent such as acetone is usually employed.

Water-containing lacquer remover

	% w/w
Distilled Water	10.00
Acetone	90.00
Colour	q.s.
Perfume	q.s.

Clear gel polish remover

		% w/w
A	Methylethyl Ketone	78.00
	Distilled Water	9.75
	1,3-Butyleneglycol	9.75
B	Carbopol 940	0.50
C	Di-2-ethylhexylamine	2.00
D	Perfume, colour and UV absorber, q.s.	q.s.
		100.00

Procedure

Make a solution of A. Add B slowly, dispersing well. Now add C. Product thickens. Avoid aeration. Now add D. When dissolved, product may be packaged.

A nail enamel remover in 'cream' form can be prepared by dissolving waxes in the solvent to give a product of desired consistency. The following formulae are suggested:

Cream nail enamel remover I [23]

	% w/w
Ethyl Acetate	38.30
n-Butyl Acetate	40.00
Castor Oil	4.00
Perfume	0.10
Ethyl Cellulose (60–80 s)	2.80
Stearic Acid	11.00
Ammonium Hydroxide (concentrated)	3.80
	100.00

Procedure

The above ingredients (with the exception of the ammonium hydroxide) are mixed until complete solution is

obtained (heating at 50–60°C will hasten the rate of solution). When the composition forms a clear liquid the ammonium hydroxide is slowly added and the mixture is stirred.

Cream nail enamel remover II [25]

	% w/w
Stearic Acid	9.50
Triethanolamine	3.50
Mineral Oil	10.00
n-Butyl Acetate	50.00
Butyl Stearate	5.00
Carbitol	5.00
Water	17.00
	100.00

Procedure

(A) Melt waxes and esters. Heat to 60–70°C. (B) Add the triethanolamine to the water. Heat to 40°C. (C) Add the carbitol. (D) Mix the two phases and allow to cool.

11.8 NAIL EXTENDERS

Nail extenders or elongators (US Patent 2 558 139) consist essentially of a mixture of methyl methacrylate polymer which is mixed either immediately before use or during application to the nail. The low molecular weight monomer is presented in liquid form mixed with 1.0% of a polymerization promoter such as *p*-phenyldiethanolamine or *m*-tolyl diethanolamine, and the polymethyl methacrylate in granular form is mixed with a peroxide catalyst, generally benzoyl or lauroyl peroxide. The materials are mixed in the proportion of 2 parts of solid polymer and 1 part of the liquid monomer to form a paste which is applied to the nail, when polymerization takes place in about 10 minutes to form a hard plastic film. It should be recorded that the materials used for this type of product are all potential skin sensitizers.

Appendix: Ingredients

Materials	*INCI*	*Supplier*
(1) Anhydrous lanolin	Lanolin	
(2)	Isopropyl Myristate	
(3) Stearic acid (triple pressed)	Stearic Acid	
(4) Cetyl alcohol	Cetyl Alcohol	
(5) Propyl paraben	Propylparaben	
(6) Deionized water	Water, Aqua	
(7) Glycerol	Glycerin	
(8)	Triethanolamine	

(*Continued*)

Materials	*INCI*	*Supplier*
(9) (Veegum HV)	Magnesium Aluminum Silicate	R.T. Vanderbilt Co.
(10) Hydrolysed animal protein	Hydrolyzed Collagen	
(11) Methyl paraben	Methylparaben	
(12) Imidazidinyl urea	Imidazidinyl Urea	Nipa, Ltd.
(13) Perfume	Parfum, Fragrance	
(14) Potassium coco-hydrolysed animal protein	Potassium Cocyl-Hydrolyzed Collagen	
(15) Hydroxyethyl cellulose	Hydroxyethylcellulose	Goodrich
(16) Ethanol	Alcohol Denat.	
(17) Tocopheryl acetate	Tocopheryl Acetate	Roche Vitamins
(18)	Laureth-23	
(19) Amerchol L-101	Mineral Oil (and) Lanolin Alcohol	American Cholesterol Products, Inc.
(20) Castor oil	Castor (Ricinius Communis) Oil	
(21) Potassium hydroxide	Potassium Hydroxide	
(22) Water (softened or distilled)	Water, Aqua	
(23) Trisodium phosphate	Trisodium Phosphate	
(24) Empicol ESB.3	Sodium Lauryl Ether Sulfate	Albright Wilson Ltd
(25) Solulan 75	PEG-75 Lanolin	American Cholesterol Products, Inc.
(26)	Beeswax	
(27) Mineral oil	Mineral Oil (Paraffinum Liquidum)	
(28) Paraffin wax	Paraffin	
(29)	Borax	
(30) Pumice powder	Pumice	
(31) Titanium dioxide	Titanium Dioxide	
(32) White petrolatum or vanishing cream base	Petrolatum	
(33) Stannic oxide	Tin Oxide	
(34) Talc	Talc	Whittaker, Clark & Daniels
(35) Zinc oxide	Zinc Oxide	
(36) Powdered silica	Silica	
(37) Butyl stearate	Butyl Stearate	
(38) *n*-Butyl acetate	Butyl Acetate	
(39) Ethyl acetate	Ethyl Acetate	
(40) Nitrocellulose, 1/2s (wet)	Nitrocellulose	

(*Continued*)

Materials	*INCI*	*Supplier*
(41)	Acrylates Copolymer	
(42) *dl*-Camphor	Camphor	
(43)	Stearalkonium Hectorite	
(44)	Acetyl Triethyl Citrate	
(45)	Benzophenone-1	BASF
(46) Pearlescence	C I 75170 (or) Guanine	
(47)	Toluene	
(48) Toluene sulfonamide/ formaldehyde resin	Tosylamide/Formaldehyde Resin	
(49)	Dibutyl Phthalate	
(50) Isopropyl alcohol, 99%	Isopropyl Alcohol	
(51) Iron oxide	Iron Oxide	
(52)	D&C Red No. 6 Barium Lake or C I 15850 : 2	
(53)	D&C Red No. 7 Calcium Lake or C I 15850 : 1	
(54)	D&C Red No. 34 Calcium Lake (or) C I 15880 : 1	
(55)	FD&C Yellow No. 5 Aluminium Lake (or) C I 1940	
(56) Bismuth oxychloride (25%)	Bismuth Oxychloride (or) C I 77163	
(57) Mineral oil, 70 Vis	Mineral Oil (Paraffinum Liquidum)	
(58) Cyclomethicone	Cyclomethicone	
(59) Ethanol (anhydrous)	Alcohol	
(60) Acetone	Acetone	
(61) Methylethyl ketone	MEK	
(62) 1,3-Butyleneglycol	Butylene Glycol	
(63) Carbopol 940	Carbomer	Goodrich Performance Chemicals
(64) Di-2-ethylhexylamine	Di-(2-Ethylhexyl) Amine	
(65) Ethyl cellulose (60–80 s.)	Ethylcellulose	
(66) Ammonium hydroxide (concentrated)	Ammonium Hydroxide	
(67) Stearic Acid	Stearic Acid	
(68) Carbitol	Ethoxydiglycol	

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12

Men's toiletries

Paul Paniccia

12.1 INTRODUCTION

For a long time the toiletry industry saw the male market as offering a major potential for growth because of the low usage of personal-care products amongst men compared to women. Until recently it proved a difficult market to succeed in, but there are clear signs that there is now real and significant growth in this segment of the industry. However, the growth is not uniform in all markets; the European market has grown more, with higher *per-capita* consumption, than the US [1]. The activity undertaken by a majority of men on a daily basis, namely shaving, has proved to be the entrée into a wider male toiletries franchise for a number of brands. Shaving-related products probably account for the male-oriented skin-care sector and those positioned for sensitive skin have a particular appeal as a significant portion of men both in the UK and a number of European countries perceive themselves to have sensitive skin. While the structure of skin is described in the chapter on skin preparations it suffices here to describe differences between the skin of males and females. While skin does thin with age, men have a thicker dermis that helps to give their skin greater elasticity as they get older. The thinner skin of females, when subjected to the elements, UV radiation and pollution, is more affected by the resultant cumulative damage thereby accounting for the more pronounced deterioration with age. Males exhibit greater sebum production than females and possibly this accounts for the propensity of male skin to form spots. Sebum production increases until middle-age for both men and women, falling off after about the age of forty. This rate of decline is similar for both, though women have a much lower production rate at all ages past puberty. In short, gender differences in skin relate to the action of the sex hormones testosterone and oestrogen which become particularly active from the onset of puberty onwards [2].

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 345–375

Table 12.1 Market size 1996 and change since 1992

Country	Year	Razors and blades	Shave preparations	Fragrances	Skin conditioners	Hair care	Deodorants	Bath, shower, talc
	1992	1443	540	3714	241	95	268	74.2
France (Ff million)	1996	1803	680	4008	244	129	456	103.6
	% Change	25%	26%	8%	1%	35%	70%	40%
	1992	252	133	596	23	72	111	34
Italy (L billion)	1996	277	128	602	23	70	117	38
	% Change	10%	−4%	1%	0%	−3%	6%	10%
	1992	109	49	253	3	26	100	30
UK (£ million)	1996	171	69	240	10	27	158	36
	% Change	57%	41%	−5%	233%	3%	58%	23%
	1992	457	184	861	140	148	335	84
Germany	1996	629	173	848	139	153	365	88
(DM million)	% Change	38%	−6%	−1%	−1%	4%	9%	5%
	1992	21333	6348	31820	1305	1200		
Spain (Ptas million)	1996	21632	6822	33045	2514	1250		
	% Change	1%	7%	4%	93%	4%		

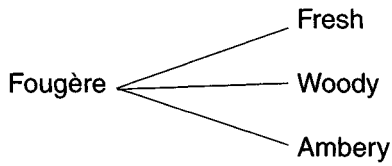
Table provided by courtesy of Euromonitor plc.

It is difficult to obtain accurate figures for the male toiletries market as some brands have both female and male variants while others have unisex-positioned products. However, estimates for 1996 in major European markets and the growth since 1992 are shown in Table 12.1. The figures include pre-shave and post-shave preparations, male-specific deodorants, body care and hair care, razors and blades.

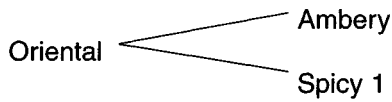
12.2 MEN'S FRAGRANCES

Fragrances for men are generally called 'after-shaves' in order to link them to a very masculine activity and so be more acceptable to the male user. In the past the fragrance content of such products has been around 1%. However, *eau de toilette* and *eau de cologne* fragrance products can also be positioned for the male market. Essentially all fragrance products are fragrance compounds blended in aqueous alcoholic mixtures which may also have a low level of an emollient ester. *Eau de colognes* tend to contain fragrance compounds at concentrations in the range 2–4% while *eau de toilettes* tend to have higher fragrance compound concentrations, possibly up to 10%. While each fragrance product has a unique odour due to the composition of the particular compound used the odours can be characterized into a limited number of categories.

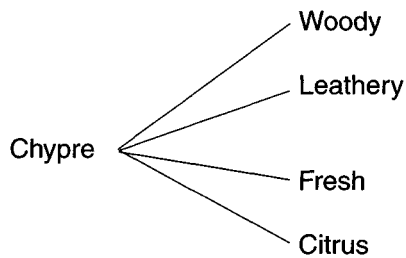
Masculine fragrances can largely be classified into the three major categories of fougère, oriental and chypre. Each of these can be further classified as follows:



Fougère types have a warm powdery character which can be modified to provide either a specific fresh or woody or ambery twist to particular fragrances in this category.



Oriental fragrances tend to have a 'heavy' character either skewed to amber or, more particularly, spice-like overtones.



Chypre, a fragrance classification also common with fragrances for females, consists of woody, leathery, fresh and citrussy notes.

Kolnisches Wasser, the original *eau de cologne*, dating back to the early eighteenth century, is a citrus fragrance under the chypre category. Around the turn of the century fougère-type fragrances were marketed; 'Fougère Royale', a woody fougère, in 1882 and 'English Lavender', a fresh fougère, in 1910. 'Old Spice', first introduced in 1937, is a well-established oriental spicy perfume which gave its name to one of the best-known male toiletry ranges. In the 1960s 'Brut' from Fabergé, with an amber-like fougère character, also established a mass market position for both fragrance and male toiletry products. 'Aramis', a leathery chypre perfume, made its debut in 1965 in a more up-market position. 'Eau Savage' introduced in 1966 represented a modern citrus fragrance type. 'Paco Rabanne pour homme' introduced in 1973, had a woody fougère character and it was around this time that male fragrance product introductions started to increase rapidly in number. 'Polo' in 1978 established a position for leathery chypre perfume. Trends are carefully watched and a successful introduction is often followed by other products with a fragrance character in a similar

category. Key products initiating trends were 'Drakkar Noir' in 1982 and 'Cool Water' and 'Jazz' in 1988, all in the fresh fougère area, whilst 'Armani', in 1984, and 'Fahrenheit' in 1988, represent key introductions in the fresh chypre category. In the 1990s 'cK One' continued the popularity for fresh, light scents and, more specifically, was positioned as a unisex product.

Contemporary male fragrance trends can be discerned along three lines and provide a wider fragrance spectrum for men than ever before. Firstly, there are the modern classics which are characterized by freshness provided by watery, citrussy or new green top notes with woody dry down. Recent fragrances representative of this trend are 'Ô de Lancôme pour Homme', Dior's 'Dune pour Homme' whilst 'Opium pour Homme' by Yves Saint Laurent has a spicy character within this modern classic category. Secondly, there is a discernible trend with a casual fresh approach with invigorating and exhilarating top notes drying down to a woody note. 'Tommy', a leading fragrance in the US market, with citrussy, fruity and marine notes providing the fresh invigorating character, is representative of this class along with 'Hugo Boss' which is a dominant fragrance in the European market. The third line is an ultra-creative trend incorporating either ingredients associated with food or spicy, oriental themes twisted to provide more innovative characters thereby breaking the classical freshness trend. Some introductions have moved closer to characters more associated with feminine fragrances. 'The Dreamer' from Versace has a warm woody, spicy, floral character while Largerfeld's 'Jako' also takes up the innovative spicy positioning. The gourmand (edible or food-like) character is represented by 'A* men' with a caramel note or 'What about Adam' having a rhubarb note along with warm, green florals. Men, particularly younger ones, are becoming more discerning and willing to wear fragrances which are outside the traditional fragrance character that previous generations of men would have known.

Fragrancing of functional products is of particular importance in giving a male ethos as well as brand identity to the product. Fragrances for such products are often of a similar character to fine fragrances such as the ones mentioned above which have become widely known and accepted by the male consumer.

12.3 SHAVING PRODUCTS

Shaving is an age-old art viewed as a chore by most men but, at the same time, seen as an important part of good grooming and as a social necessity. Some men prefer to grow beards, the number rising or falling according to fashion, but for a small minority of men who suffer from certain skin problems which are exacerbated by shaving, the growth of a beard may be a last resort. Some men may suffer from razor bumps or *pseudofollicullitis barbae* [3], which results from ingrowing beard hairs. These are curved hairs which grow out and re-enter the skin like a small splinter, resulting in inflammation and in some instances pustule formation. The most common problem associated with shaving is skin

irritation, which includes nicks and cuts. Some skin irritation is unavoidable because of the removal of some stratum corneum along with removal of beard hair. The degree of irritation is dependent on factors such as blade sharpness, angle of incidence of blade, pressure exerted on blade and beard wetting and lubrication. In a study of the mechanism of shaving [4] irritation has been assessed in relation to the amounts of shaved particles of beard hair and stratum corneum.

The growth of male beard, axillary and pubic hair is a secondary sex characteristic, which begins at puberty influenced by increase in the male sex hormones. Paradoxically this same hormone is also responsible for the later development of male-pattern baldness, although a genetic factor is also believed to be involved. Hair growth of the beard is similar to that of the eyebrow, the nose, the ear and the body except in the pubic and axillae regions. The rate of growth of facial hair is about 0.3–0.4 mm/day. It is estimated that during 55 years of adult life the average male shaves off a whisker length of about 27.5 feet of hair [4]. An average man has about 30 000 hairs on his face.

A dark-haired beard is readily visible as soon as it emerges from the skin, leading to '5 o'clock shadow', and this often means more frequent shaving. Lighter-coloured hair is not so readily visible in the early stages of emergence. In the past it was believed that shaving increased the rate of hair growth and the coarseness (diameter) of facial hair. This was based on the theory that irritation of the skin by shaving caused mild hyperaemia, leading to increased mitosis and stimulated growth rate. While it is accepted that removal of the outer layers of stratum corneum during shaving induces an accelerated turnover of skin cells [5], there is no evidence for increased rate of hair growth or hair diameter overall [6].

An effective shave is dependent on the following:

1. Preparation of the beard, i.e. hydration of the hair by the use of soap and warm water. Ideally the preparation time is reported to be 4 minutes at 49°C [6].
2. Application of a good shaving aid.
3. Sharpness of blade.
4. Angle of incidence of blade to hair.
5. Pressure exerted on the razor.

Wetting of the hair fibre allows it to swell and soften and to lower the force required to cut the hair, reducing discomfort during shaving. It is generally accepted that some degree of lubrication of the skin is necessary for a reasonably comfortable shave, since the frictional force of the dry skin is reported [7] to be higher than for wet skin. A good shaving preparation should provide some lubrication. An individual will obviously adjust the angle of incidence of the blade and pressure on the blade, to minimize the risk of cutting the skin while shaving effectively.

In practice most men do not prepare their beards in the best way. Fortunately advances in blade technology with highly improved blade edges and effective lubricant films on blade mountings, compensate for inadequate preparation to ensure a comfortable and effective shave.

12.3.1 Lather shaving cream

Convenience and economy in use probably gives rise to the popularity of lather shaving creams. They are based on a mixture of sodium and potassium soaps, except for aerosol shaving foams which may have triethanolamine as the cation. Potassium soaps are more readily soluble than sodium soaps and they help to generate foam more quickly. The formation of bubbles ensures a ready supply of water to the beard hairs, keeping them in a hydrated condition. A properly formulated product should therefore provide a copious lather of small bubbles, which break slowly and remain on the beard throughout the duration of the shave to provide sufficient emolliency.

Shaving creams normally contain 30–50% of soaps. Formulations based on stearic acid alone do not give sufficient lather. It is therefore usual to combine it with some coconut oil fatty acid. The ratio of stearic acid to coconut oil may vary, but a satisfactory ratio would be 25% coconut oil to 75% stearic acid. An acceptable sodium hydroxide/potassium hydroxide ratio would be 1 : 5. A humectant such as glycerol, sorbitol or propylene glycol is usually included at 10–15% to minimize drying out of the cream and to make the cream slightly softer.

Lather shave creams have some free fatty acid although their pH is about 10. The reason for this is that pockets of unneutralized alkali remain even under well-controlled manufacturing conditions [7]. The level of free fatty acid should be checked as part of routine quality control. Also a test on a small sample for free alkali must be carried out in the cold. (Heating during the test would complete the reaction and so give a negative result.) If free alkali is present this indicates that soap formation had not been completed in the main batch because of too low a temperature during manufacture.

A small percentage of free fatty acids in excess of the calculated amount of alkalis needed for neutralization is added to lather cream formulations to ensure complete saponification, to help to overcome the harshness of soap on the skin, to act as plasticizer, and to contribute to the characteristic pearlescence of these products. It is normal practice to store them for some time before filling to allow the pearliness to develop.

A typical basic formulation follows on page 351.

In the past it was usual to control the consistency by adding an electrolyte. These have certain disadvantages, e.g. potassium chloride can lead to corrosion in aluminium tubes, and borax is now subject to legislative control. Electrolytes based on calcium and magnesium must be avoided because of incompatibility with alkali soaps. Antimicrobials such as sodium borate have been used both to

Formula I Lather shave cream

	% w/w	
Stearic acid	30.00	
Coconut oil	9.00	A
Potassium hydroxide (50%)	3.75	
Sodium hydroxide (100%)	1.50	
Glycerol	10.00	B
Water	36.50	
Potassium hydroxide strength as above	3.75	C
Stearic acid	5.00	D
Perfume	0.50	E

Note: The selected perfume must be compatible with the high pH of the product.

Procedure

1. Part A. Melt the stearic acid with the coconut oil in a jacketed pan with steam heat and raise the temperature to 80°C; maintain that temperature.
2. Part B. Mix the caustic soda and potassium hydroxide of B with the glycerol and water and heat to 50°C.
3. Run B into A with slow stirring taking about 10 min for the addition. Continue for a further 5 min. Heat is evolved in the reaction.
4. Part C. Add C with further mixing. The addition of the potassium lye in two equal amounts ensures that the harder soda lye is all saponified first.
5. Part D. Heat D to 70°C and add to the batch.
6. Part E. Cool slowly while mixing to 45°C, and add the perfume.
7. Store the batch for 1 month before filling and packing.

stabilize the product and prevent infections arising from cuts during shaving, though the widespread use of after-shave products supplies this latter benefit.

12.3.2 Lather shaving stick

This type of product contains a much higher level of soap (about 80% compared to creams, 35%). Of this 20–25% are made from coconut or palm kernel oils. Other ingredients are glycerol 5–10% and water 8–10%. The fatty acids ratio and the sodium/potassium ratio are similar to those of the lather shaving cream.

After saponification the mass is dried, formed into chips, and milled with other ingredients such as perfume, colour and opacifier as required. The soap chips are moulded to the desired shape using a soap plodder.

12.3.3 Aerosol shaving foam

Aerosol shaving foams have been on the market for more than 30 years and they are probably the most popular shaving aid today. The formation of foam is based on the following principle. The aerosol can is filled with a soap solution, the concentrate, together with liquid propellant added under pressure. The propellant, formerly a mixture of chlorofluorocarbons, is now being replaced by 'ozone-friendly' hydrocarbons. On shaking, some of the propellant becomes temporarily emulsified in the concentrate. When the valve is actuated the propellant pushes the concentrate up the dip tube and out of the valve. On reaching atmospheric pressure the emulsified propellant expands to form an instant foam. This foam, applied to the pre-wetted beard, is sufficiently stable to last throughout the shaving process.

Formula II represents the foundational formula for an aerosol shave foam concentrate.

Formula II Aerosol shaving foam

	% w/w	
Stearic acid	6–7	A
Lauryl or Stearyl Alcohol	0.5–1.0	
Sodium Lauryl Sulfate	3–5	
Glycerol	1–5	B
Triethanolamine	3.2–3.6	
Water; Aqua	to 100	
Perfume	q.s.	C

Filling: 97% of above concentrate, 3% hydrocarbon propellant

Procedure

1. Charge main vessel with water and add other ingredients in B while heating to 70°C.
2. In separate vessel melt fatty acid and alcohol together to 70°C (Part A).
3. Add A to B, stir to uniformity before commencing cooling.
4. Add perfume when the mix is below 40°C.
5. Fill into aerosol cans when the mix is at ambient temperature and charge with propellant gas according to standard procedure.

Note: The perfume must be soap-compatible. Other ingredients may be added, if required for specific purposes; some of these are listed below:

Lubricants such as silicone fluid or mineral oil (at 1–2%).

Polymers such as polyvinyl pyrrolidone and sodium carboxymethyl cellulose are also useful for increasing viscosity (body) of the products.

Menthol is widely used at about 0.1%, as a cooling agent. One disadvantage is that its strong odour is difficult to mask; and another is that above a certain threshold it causes a burning sensation.

Preservatives and colour are not normally necessary, but can be added if required.

Allantoin is sometimes used at 0.05% to promote healing of wounds.

It has been claimed that certain materials cause contraction of the hair follicile muscles (*arrectores pilorum*) and thus push the hair further above the skin surface and hold it erect. The theory is that, on cutting such erect hair and on subsequent relaxation of the follicle muscle, the hair will retract below the skin surface giving a closer shave. In practice this is probably difficult to achieve, because the muscles lie too deep in the skin to be affected significantly by short-term application.

12.3.4 Aerosol barrier pack

This pack is described in Chapter 13 under Specialized Containers where the liquid concentrate is contained in an inner bag separated from the propellant. This prevents any unwanted reaction between concentrate and propellant and allows foam to be dispensed consistently throughout the life of the product without a drop in pressure as the contents are used up.

12.3.5 Post-foaming gel

Post-foaming gels, now well established, represent a more recent innovation in the shave preparation market although the seminal patent for this technology dates back to 1970 [8]. These gels call for some form of compartmentalized packaging such as the barrier pack described in Chapter 13 that allows the propellant (driving gas), which expels the contents, to be separated from the gel itself. The gel, a soap-based system, stabilized with a water-soluble polymer, blended with lipophilic ingredients contains a hydrocarbon with a suitable boiling point so that when the gel is manipulated between the hands, prior to application to the face, the heat from the skin, aided by the mechanical action, vaporizes the hydrocarbon component transforming the gel into a dense creamy foam. The dispensing of a clear product is part of a trend for clear products which is indicative of mild skin-caring attributes while the generation into a dense creamy foam conveys rich moisturizing properties.

Formula III [9]

	% w/w	
Stearic Acid	6.00	A
Myristic Acid	2.00	
Steareth-2*	1.00	
Water (Deionized) Aqua	to 100	B
Sorbitol 70%	10.00	
Propylene Glycol	3.50	
Triethanolamine 99%	4.20	
Hydroxypropyl Cellulose† (1% aqueous solution)	5.00	C
Carbomer 984‡ (2% aqueous solution)	10.00	
Perfume, preservative, colour	q.s.	

Filling: 97% of above concentrate, 3% isopentane.
* Volpo S2 from Croda.
† Klucel HF from Hercules.
‡ Carbopol 984 from B.F. Goodrich.
Formula supplied by Croda Oleochemicals (now Croda Chemicals) based on a system described in detail by US patent 3 541 581.

Procedure

1. Heat steareth-2, stearic and myristic acids to 65–70°C.
2. Dissolve sorbitol, propylene glycol and triethanolamine in water; heat to 65–70°C.
3. Add hydroxypropyl cellulose and carbomer solutions. Stir to cool.
4. When cool, fill into containers, add pentane and agitate to disperse.

12.3.6 Brushless shave cream

Brushless shave creams are oil-in-water emulsions and similar to vanishing creams. The main difference is that the levels of oil and emulsifying agents tend to be higher in shaving creams. A basic formula is as follows:

Formula IV Brushless shave cream

	% w/w	
Mineral (Paraffinum Liquidum) Oil	10.0	A
Stearic Acid	15.0	
Cetyl Alcohol	1.0	
Carbomer 934	0.6	B
Water (demineralized); Aqua	20.0	
Triethanolamine	2.0	C
Triethanolamine Lauryl Sulfate	1.0	
Water; Aqua	45.4	

Propylene glycol	5.0	
Preservative	q.s.	D
Perfume, Fragrance	q.s.	E
	100.00	

Procedure

1. Disperse with high-speed mixing the carbomer in the water of B at room temperature. (About one-third total water.) Allow to stand to ensure that the mixture is smooth and clear.
2. Heat A in a jacketed pan to 75–80°C and maintain temperature.
3. Heat the water of C to 75–80°C; add the ingredients of C with stirring.
4. Add (2) to (3) at this temperature while stirring for 5 min or longer to ensure saponification. Allow to cool.
5. Add B to the batch (through a fine screen), while stirring.
6. Dissolve the preservative(s) in the propylene glycol (D) with heat if necessary, cool to the temperature of the batch and add it while stirring.
7. Continue mixing until the temperature is 45°C. Add perfume (E).

Brushless shave creams have a pH of 7.5–8.5 and are thought to cause less irritation than lather shave creams. However they have certain disadvantages. More product is required per shave; it is difficult to rinse them from the razor; the beard-softening action is less effective than a foam due to slower uptake of water from the emulsion by the hair; and they leave the skin greasy.

12.3.7 Shaving oils

Shaving oils have recently come onto the shave preparation market, particularly in the UK, in an attempt to introduce to the market something significantly different in form and mode of application. They are blends of naturally occurring oils either alone or in combination with emollient ingredients such as fatty esters, silicone or hydrocarbon oils to provide a lubricating effect during shaving. A particular characteristic is the small amount of product that is required for an application prior to shaving. These are normally clear liquids so do not provide a marker on the face like a foam or lather to enable the user to distinguish the areas he has shaved from those he has not.

12.3.8 Dry shaving preparations

These are pre-shaving preparations for use with electric razors. It is generally known that electric shavers do not cut the beard as close to the skin as razor

blades in wet shaving. In a study of particles collected from shaving [10], microscopic examination showed that the ends of hair fragments shaved with a blade were of uniform length, and straight and clean, whereas those from an electric razor were of irregular length and showed ragged ends that were fibrillated (vertically split).

Many users prefer the convenience of the dry shave with an electric razor, even though for most of them it does not give quite such a satisfactory shave as is obtained in wet shaving. The proportion of razor blade users (wet shavers) to electric razor users (dry shavers) is approximately 70 : 30.

Whereas comfortable and efficient wet shaving requires the hair to be soft and swollen to minimize cutting forces, shaving with an electric razor is believed to be efficient if the hair is stiff and dry. This is achieved by removal of the film of perspiration from the face by the use of an alcoholic pre-shave lotion. In addition to being antiseptic, the alcohol also imparts a mild astringent effect which tightens the skin.

Astringency can be increased using zinc phenosulfonate, aluminium chlorhydrate or lactic acid [7]. These preparations sometimes contain emollients to reduce the drag of the cutting head against the skin. Lubricants such as silicone oils help to reduce the friction between the skin and the blade.

The following formulation [11] is an example of an emollient type of pre-shave lotion.

Formula V Pre-electric shave lotion

	% w/w
Di-isopropyl Adipate*	12.00
Benzethonium Chloride†	0.10
Ethanol‡	87.90
Perfume and colour	q.s.

* Crodamol DA – Croda.
† Hyamine 1622 – Rohm & Haas.
‡ Ethanol-denatured alcohol, US grade SD Alcohol 40.

Procedure
Blend all ingredients, chill, filter, and fill.

For historical reasons mention must be made of certain oily products promoted at one stage as dry shaving preparations for use with ordinary razors. These products were not successful because they did not provide the required wetting for a comfortable shave with a razor blade.

12.4 AFTER-SHAVE PRODUCTS

Both wet and dry shaving results in removal of hair and skin, the quantity removed varying from one individual to another. The amount of skin in shaving debris can vary from 25% to 75% [7]. This coupled with the degreasing effect of soap and surfactant used in shaving products results in the familiar after-shave skin trauma. After-shave preparations are intended not only to alleviate this but also to cool and refresh the skin and exert a mild astringent effect. They also protect it from bacterial infection while it recovers from the slight injury.

The most popular types of product have been, and continue to be, clear lotions containing about 40–50% of ethanol and the appropriate level of water. The ethanol/water ratio may be adjusted depending on the type and level of perfume. In some instances it is necessary to use a perfume solubilizer. Other ingredients used are various combinations from the following examples of raw materials: propylene glycol as humectant; menthol as cooling agent; witch hazel as astringent; quaternary ammonium compounds as biocides; di-isopropyl adipate as emollient.

Formula VI After-shave lotion

	% w/w
Ethanol (denatured), SD Alcohol 40	50–65
Deionized water, Water, Aqua	to 100
Propylene Glycol	4–6
Fragrance, Parfum	1–2
Colour	q.s.

Procedure

Mix perfume and propylene glycol and dissolve in alcohol. Add water slowly with stirring. Possible clouding may be avoided at this stage by the addition of small amounts of water at a time with stirring in between each addition.

Cool to about 4°C and filter through a fine filter to give a sparklingly clear product.

12.4.1 After-shave gel

An after-shave product in the form of a gel can be made by using a combination of a carboxyvinyl polymer (A) and a base (B). The stiffness of the gel can be altered by varying the amount of the polymer and the triethanolamine addition. Helpful graphs indicating the relationship between A and B to give varying consistencies are shown in the brochures of the suppliers of Carbopol 934 [12].

Formula VII After-shave gel

	% w/w
Carbomer* 934	1.00
Menthol	0.10
Ethanol (denatured)	48.00
Triethanolamine	1.00
Water	to 100.00
Perfume	q.s.
Colour	q.s.

* Carbopol 934 from Goodrich.

Procedure

1. Disperse the Carbopol 934 in one-third of the water with high-speed mixing. Allow to stand until smooth and free from bubbles.
2. Dissolve triethanolamine, menthol and perfume in the ethanol.
3. Add B to A in small amounts while stirring to disperse any cloud which might form temporarily.
4. Dissolve the colour in the remaining water and add to the batch slowly, still stirring slowly.

12.4.2 Quick-breaking after-shave foams

These are dispensed from the aerosol as a foam which, on application to the skin, breaks easily. They have declined in popularity since they were first introduced but the following is an example of a formulation [11] in which the triclosan acts as an antiseptic.

Formula VIII Quick-break after-shave foam

Concentrate	% w/w	
Nonionic emulsifying wax*	3.34	
Ethanol (denatured)	95.34	
Menthol	0.06	A
Triclosan†	0.06	
Allantoin	0.10	
Di-isopropyl Adipate‡	1.10	
Perfume	q.s.	B

* Polawax A 31 – Croda.
† Irgasan DP 300 – Ciba-Geigy.
‡ Crodamol DA – Croda.

Aerosol pack formulation for formula	%
Concentrate from Formula VIII	92.00
Butane	8.00
	100.00

Procedure

Blend ingredients of A in concentrate VIII together, and warm to 60–65°C. Cool to 40°C and add the perfume. When cool fill the aerosol pack with concentrate and introduce propellant under pressure with safety and quality control procedures necessary for this type of package.

12.4.3 After-shave balm

For shavers with sensitive skins, after-shave products with high levels of alcohol can be more irritating than refreshing. In such cases an after-shave cream or balm is useful. These are oil-in-water emulsions, similar to vanishing or moisturizing creams. They may contain no alcohol, or only a low level. The following is an example [13].

Formula IX After-shave balm

	% w/w	
Carbomer 934 (3%)*	6.6	A
Water (deionized); Aqua	20.0	
Methyl Gluceth-20-Distearate†	2.0	B
Cetearyl Alcohol (and) Ceteareth 20‡	2.5	
Isopropyl Palmitate	1.5	
Triethanolamine (10% aqueous)	2.0	C
Water; Aqua	50.4	
SD Ethanol 40	15.0	D
Preservative	q.s.	
Perfume§	q.s.	

* Carbopol 934 from Goodrich.
† Glucam E 20 from Amerchol.
‡ Promulgen D from Amerchol.
§ Parfum, Fragrance (INCL)

Procedure

1. Disperse the carbomer 934 in the water of A with high-speed stirring. Allow to stand until mixture is smooth and free from air bubbles.
2. Heat B in a jacketed pan to 80°C.
3. Heat C to 80°C.
4. Add A to C stirring until thoroughly mixed. Maintain temperature at 75°C.

5. Emulsify by adding B to the batch and mixing at high speed for 5 min and then reducing speed while cooling to 45°C.
6. Dissolve the preservative and perfume in the alcohol of D and add to the batch carefully when at 30°C.

12.4.4 After-shave powder

This form of after-shave product is not popular but could be useful for those with certain skin conditions such as acne. It is based on talcum powder to give a smooth, matt appearance, with additives such as menthol for a cooling effect, colour and a bactericide, e.g. cetrimide.

12.5 HAIR-CARE PREPARATIONS FOR MEN

Preparations for the hair and scalp are mainly concerned with tidying and fixing the hair. These include:

1. lotions and tonics;
2. hair dressings;
3. hair-styling gels;
4. gloss aerosol packs.

12.5.1 Hair lotions and tonics

Hair lotions and the so-called tonics with a light fixative effect are for use as a daily application to keep the hair tidy. These were, in the past, expected to help to grow hair on balding heads. The claims that have been made to arrest baldness and to restore fallen hair were not supported by clinical evidence. One claim for tonics that might be advanced is that their regular use would help to keep the scalp in good condition; and the friction produced by the fingers on the scalp, or by the use of a fairly stiff brush, would stimulate the blood flow to the hair follicle and thus contribute to their better condition.

The normal loss of hair was a useful factor in persuading men to use a hair lotion, because daily use of a brush or comb showed fewer hairs each day and thus appeared to indicate reduced hair loss, merely because the hairs were removed regularly.

When profuse loss of hair occurs at the temples and on top of the head with little indication of replacement, follicular activity has stopped and baldness occurs. The factors responsible for male-pattern baldness (also seen in females) can be influenced genetically and by the presence of male hormones, and exacerbated by stress or anxiety and follicular damage if the hair is not cared for. Excessive production of sebum leading to excessive oiliness is a contributory factor which can be corrected.

Several raw materials have been promoted over the years for the formulation of hair tonics and lotions. Some of these were intended to enhance only the

appearance of combed hair, while others contained active ingredients and were intended to maintain the scalp in good condition, since a healthy scalp is one essential requirement for shining healthy hair.

Any effects on hair growth must be viewed in relation to the comments already made concerning hair loss. Except for oily preparations, these tonics were based on mixtures of water and denatured ethanol. The following formula for bay rum is included for historical reasons. Bay rum originally contained rum as a solvent for the bay oil, but this was later replaced by an ethanol/water mixture. A typical perfume was a mixture of Oil of Bay 80% and Oil of Pimento 20% suitable for Formula X.

Formula X Hair tonic

	% w/w
Perfume; Fragrance	2.5
Ethanol 95%	60.0
Glycerin	2.0
Water (deionized); Aqua	35.5

Procedure

Dissolve the perfume in the ethanol. Add a solution of glycerol, water and any required colour, in small amounts, mixing well after each addition. Filter through a fine filter using talc or kieselguhr as a filter aid, to obtain a sparklingly clear product.

Claims have been made for a large number of materials for use as 'active ingredients' in hair lotions and tonics. Among these are:

1. Materials which act as rubefacients, i.e. which bring blood to the skin surface. These were claimed to stimulate growth in hair follicles. These include:
   (a) cantharides, not now allowed in cosmetics under the EC directive, and Prescription only under Medicine (UK) Act at 0.1%;
   (b) capsicum extract, allowed for external use at 2.5% as capsicum;
   (c) pilocarpine, not now allowed in cosmetics under the Consumer Protection Regulation (CPR) of 1984 (UK), and Prescription only under the Medicine Act (UK);
   (d) quinine can be used at 0.2% calculated as quinine base;
   (e) ammonia, allowed at 6% calculated as NH_3 (if more than 2% the label must say 'Contains ammonia';
   (f) resorcinol, allowed in cosmetics for shampoos and lotions at 0.5%, subject to the combination rule which states that the sum of the actives must not exceed 1%;

(g) salicylic acid is allowed for external use in liquids at 0.05% other than for the treatment of 'corns';
(h) turpentine oil; and
(i) rosemary oil.

2. Sulfur and some of its derivatives. Colloidal sulfur has been widely used as an antidandruff agent in hair tonics. Some sulfur derivatives are claimed to be useful agents for promoting hair growth, and for maintaining the scalp in a healthy condition.
3. Nutrients which are claimed to help cell synthesis, e.g. vitamins A and E, the vitamin B group and vitamin F. Vitamin factors such as pantothenic acid and panthenol have also been used.
4. A number of other miscellaneous compounds have been reported [7].

Examples of formulae follow.

Formula XI, XII Men's hair tonics

	% w/w	
	XI	*XII*
Ammonia solution	5.0	–
Oil of rosemary	1.0	–
Quinine hydrochloride	–	0.2
Ethanol	25.0	5.0
Glycerin	5.0	5.0
Water	64.0	89.8

The following illustrates the use of pantothenic acid. The water-soluble calcium salt of pantothenic acid is used.

Formula XIII Pantothenic acid tonic

	% w/w
Calcium pantothenate	0.5
Glycerin	3.0
Ethanol denat.	27.5
Water	69.0

Procedure

Dissolve calcium pantothenate in glycerol and ethanol and add to water in small amounts stirring between each addition to avoid a lasting cloud formation. Adjust the pH to 5.0–6.0 with lactic acid. A preservative methyl *p*-hydroxybenzoate at 0.15% may be used. Filter and pack into opaque bottles to prevent photo-oxidation.

12.5.2 Antidandruff lotions

These lotions can be described as hair tonics by virtue of the fact that any preparation which corrects or alleviates seborrhoea must contribute to a healthier condition of the scalp and reduce the tendency for hair loss. They may be oily or non-oily depending on the particular form of dandruff which is being treated. If a purely alcohol-based product is to be used to correct a greasy condition, it is advisable to include some oily material to reduce the degreasing action of alcohol to an acceptable level.

Several antimicrobial agents have been reported as active materials for medicated shampoos and some of these are used in the following lotions.

Formula XIV	**Antidandruff lotion**
	% w/w
Salicylic Acid	0.05
Resorcinol	0.20
Oleyl alcohol	20.00
Alcohol	79.25
Perfume	0.50

The level of oleyl alcohol may be varied according to the degree of oiliness required.

Sulfur preparations have a fungicidal action when applied externally. In the following lotion a combination of sulfur and salicylic acid is used.

Formula XV	**Antidandruff lotion**
	% w/w
Salicylic acid	0.05
Precipitated Sulfur	3.00
Glycerol	0.30
Ethanol	10.00
Water	86.65

A preservative, methyl *p*-hydroxybenzoate, may be used at 0.15% and perfume at a low level of 0.2%.

The sulfur remains as a suspension in this lotion. For a more cosmetically acceptable form of sulfur therapy solutions of polythionic acids and their salts are used. Quaternary ammonium polythionates are also suggested for treatment

to combine the properties of sulfur and those of quaternary ammonium compounds (US Patent 2 815 344). The object of using soluble sulfur compounds was to promote penetration of the tissues with a view to enhancing their effect. These lotions tend to be drying on the skin and dosage should be kept low and controlled. Although there is little clinical evidence that solutions of some of the active materials listed under tonics give greater effectiveness there is some evidence for improved efficacy for elemental sulfur [7]. A report [14] pointed to renewed interest in dried colloidal sulfur as an effective ingredient in antidandruff formulations.

Lotions can also be prepared with quaternary ammonium compounds, provided the concentration of the solution is controlled to prevent overdosage, since this is likely to cause irritation. The lotion should be formulated to give 0.01–0.02 g of active material per application. They have been suggested for use with fatty acids to prepare conditioning creams for men. Such mixtures are claimed to give complexes with certain desirable properties, which vary according to the fatty acid chain length.

The following is an example of this type:

Formula XVI Hair conditioning cream for men

	% w/w	
Isopropyl Palmitate	2.5	
Lauric Acid	2.5	A
Stearyl Dimethyl Benzyl Ammonium Chloride	10.0	
Preservative	q.s.	B
Water	85.0	

Piroctone olamine and climbazole, more recent ingredients, are claimed to be highly effective antidandruff agents and offer the possibility of formulating clear products because of their high solubility characteristics in surfactants and alcohol. The recommended dosage in tonics is 0.1% for piroctone olamine and 0.3% for climbazole.

Formula XVII Antidandruff hair tonic with climbazole [15]

	% w/w	
SD-Alcohol 39-C	50.00	
Fragrance	0.30	
Di-isopropyl Adipate	1.00	A
PEG-40 Hydrogenated Castor Oil (and) Propylene Glycol*	0.30	
Climbazole†	0.30	

Water; Aqua	42.30	
Panthenol	0.50	
Cetrimonium Chloride‡	0.20	B
Allantoin	0.10	
Glycerin	2.00	
Propylene Glycol (and) Ethoxydiglycol (and) Birch (Betulae Alba) Leaf Extr.§	3.00	

* Cremophor RH 455 from BASF.
† Crinipan AD from Haarman & Reimer.
‡ Dehyquart A from Henkel.
§ Cremogen Birch 739004 from Haarman & Reimer.

Procedure
Blend ingredients in part A and then add B. Blend ingredients in part C and then add to rest of formula. Adjust pH of completed mix to 6.5.

Shampoos are a way of controlling the development and prevention of dandruff, and those based on quaternary ammonium compounds are reported to have been used successfully for the treatment of seborrhoea. When used in conjunction with conventional anionic detergents, however, there would be a problem of incompatibility with a resultant loss in efficacy. If used with nonionic or amphoteric surfactants the foaming would not be good and additionally, in the latter case, the cost of the shampoo would be rather high. Most antidandruff shampoos contain zinc pyridine thiol-*N*-oxide (ZnPTO) as the active agent along with conventional shampoo detergents. This and related salts are reported to have a strong antibacterial effect in addition to slowing down the rapid turnover of epidermal cells [7]. The zinc salt, being insoluble in water and surfactant solutions, requires formulation in a system containing a rheological additive such as magnesium aluminium silicate to provide sufficient viscosity to enable the salt to be uniformly suspended in the formula. Hence, only opaque shampoos are possible.

More recently, piroctone olamine has been employed as an antidandruff agent in shampoos. Given its solubility characteristics in surfactants this material allows the formulation of clear products which are aesthetically elegant as well as being efficacious. The recommended dosage for this active is around 0.75%. Climbazole is another antidandruff ingredient that also allows formulation of clear shampoo products although the required process in formulating with this material is less straightforward. The recommended dosage in shampoos for climbazole is 0.7–1.0%.

Another product that is becoming popular with men is the conditioning shampoo which cleans the hair and gives a slight degree of conditioning which is sufficient for men's hair. A combination of silicone and the other emollients are incorporated into the shampoo formulation. These products can be opaque or clear. The following is an example [16] of this type.

Formula XVII Conditioning shampoo for men

	% w/w	
Trimethylsilylamidimethicone*	2.0	A
Lauramide DEA (and) Linoleamide DEA†	6.0	
Sodium Laureth Sulfate‡	30.0	B
Water	37.0	
PEG-120 Methyl Glucose Dioleate§	2.5	C
Water	22.5	
Citric acid	q.s.	D

* Dow Corning Q2-8220.
† Monamid 1007 from Mona Industries.
‡ Empicol ESB3 from Albright & Wilson.
§ Glucamate DOE-120 from Amerchol.

Procedure

1. Mix together ingredients of A in a vessel large enough for whole batch.
2. Mix ingredients of B and add to batch.
3. Heat the mixture of C to obtain solution and add to batch.
4. Adjust pH to 6.8 with D in a little water and well stirred into the batch before testing.

Earlier in this chapter mention was made of hair loss and baldness. The materials that have been described so far help to maintain the scalp and hair in good condition and perhaps provide nutrients to promote healthy hair. However a 'cure' for baldness is still the subject of much interest. The only material which has emerged in recent times as a hair promoter is 'minoxidil', which is a powerful vasodilator [17]. In a number of clinical trials, cited in ref. 17, minoxidil is reported to have increased visible hair on the vertex of about one-third of male subjects with male-pattern baldness.

12.5.3 Hairdressings

Hairdressings are preparations intended to give good control, good set and lustre to the hair without making it greasy. Application of water will give an initial set allowing the hair to be combed into position, but this does not last long as the water soon evaporates. If oil is used on its own, it helps when combing the hair and imparts lustre but does not give a good set without the presence of water. This is why users of brilliantine apply water before the brilliantine. The ideal product would therefore be an emulsion which combines the properties of water and oil. Certain lotions and gels can also impart the properties of these two materials.

Hairdressings have changed over the years, and the various product types are classified below.

(a) Pomades and solid brilliantines

Because of their greasiness, the popularity of pomades and brilliantines has declined considerably in Europe. They are still being used by some African-Americans in the United States and are used widely in Africa and Asia. Based on mineral oil or vegetable oil, thickened with one or more waxes, and thus being semi-solid, they offer convenience in use. Products based mainly on petroleum jelly tend to drag and are dull in appearance.

Formulae XIX, XX, XXI, XXII Brilliantines and pomades

	% w/w			
Ingredients	*XIX*	*XX*	*XXI*	*XXII* [18]
Petroleum jelly; (Petrolatum)	94.0	75.0	60.0	87.0
Beeswax (Cera Alba)	6.0	–	–	–
Microcrystalline wax	–	–	15.0	–
Paraffin wax	–	5.0	5.0	3.0
Lanolin	–	–	–	4.0
Polysorbate 85	–	–	–	1.0
Mineral oil	–	20.0	20.0	5.0
Colour, perfume	q.s.	q.s.	q.s.	q.s.

Procedure

Heat the ingredients except for the perfume together in a steam-heated jacketed pan to 75°C; mix slowly, and add the oil-soluble colour. Allow to cool to 45–50°C and add the perfume. While still liquid fill into suitable containers.

The next formulation gives good gloss and, being water-miscible, is less tacky on the hair and gives less build-up than traditional solid brilliantines.

Formula XXIII Water-miscible solid brilliantine

	% w/w
Acetylated Lanolin	10.0
Isopropyl Lanolin	5.0
Mineral (Paraffinum Liquidum) Oil	30.0
Polyethylene Glycol 400 Monostearate	5.0
Petroleum jelly; (Petrolatum)	45.0
Ethoxylated Cetyl/Oleyl Alcohol (e.g. Empilan KL type)	5.0

With the addition of colour and perfume the preparation is as for the three previous pomades. In some African countries pomades are applied as hair straighteners using a hot metal comb.

(b) Liquid brilliantines

These are meant to deposit a fine film of oil on the hair without the heavy greasy appearance of a pomade. They are simple mixtures of mineral oil and alkyl myristate.

Formulae XXIV, XXV, XXVI Liquid brilliantine

	% w/w		
	XXIV	*XXV*	*XXVI**
Mineral oil	85.0	75.0	–
Isopropyl Myristate	15.0	25.0	15.0
Ethanol denat.	–	–	85.0
Perfume, Fragrance	q.s.	q.s.	q.s.

*This is an aerosol concentrate which can be developed to be dispensed from an aerosol pack, using suitable propellants.

(c) Non-greasy hair creams

The early type of non-greasy hair creams were made with gum tragacanth. These had good fixative properties but tended to give a dull effect on the hair, and the dried film of gum flaked off when the hair was combed, giving the impression of dandruff. This effect can be reduced by using a polyol and a small quantity of an oily material. It is essential to use a preservative to prevent microbial decomposition of the mucilage. The degree of opacity may be varied by adding about 0.5% of tincture of tolu or benzoin.

Formula XXVII Non-greasy hairdressing

	% w/w	
Gum tragacanth	1.5	A
Ethanol	5.0	
(Mineral oil)	(2.0 or 3.0)	
Perfume, Fragrance	0.5	
Glycerin	5.0	
Methyl *p*-hydroxybenzoate	0.2	B
Water (deionized); Aqua	40.0	
Water (deionized)	45.8 or 44.8	

Procedure
Mix the gum in the alcohol and add the perfume and oil (if used). Dissolve the preservative in the glycerol, add to the water of B. Gradually mix B with A and finally add the remaining water with stirring and allow to thicken. Filter and pack.

Similar but more acceptable aqueous gels can be prepared by using a carboxyvinyl polymer such as Carbopol 940. Neutralization of this polymer with triethanolamine gives a gelled product. Additives such as water-soluble lanolin derivatives may be included.

Formula XXVIII Aqueous gel hairdressing

	% w/w	
Carbomer 940	0.20	
Water	20.00	A
Propylene glycol	2.00	
Preservative	q.s.	B
Triethanolamine	0.20	
Soluble lanolin derivative	0.50	C
Water	77.10	
Perfume	q.s.	

Procedure
1. Disperse the Carbomer 940 in the water of A with high-speed stirring. Allow to stand until mixture is smooth and free from air bubbles.
2. Heat B in a jacketed pan or water bath to dissolve the preservative.
3. Dissolve the lanolin derivative in the water of C with heat if necessary, and add triethanolamine with stirring.
4. Add A to C stirring until thoroughly mixed.
5. Add B to C stirring until thoroughly mixed.
6. Perfume when batch has cooled to 45°C.

Graphs showing viscosity against concentration of Carbopol and the variation of viscosity with the amount of neutralizer can be obtained from the supplier so that the thickness of gel required can be manipulated.

(d) Emulsion-type hairdressing

These can be either oil-in-water or water-in-oil emulsions. When applied to the hair, a water-in-oil emulsion does not lose its water as easily as oil-in-water emulsion. It gives an immediate gloss effect with ease of combing. In the case of an oil-in-water emulsion, the hair is duller with the outer film of water, which reduces the glossy appearance. The gloss effect of the oil becomes evident only after the water has evaporated.

Water-in-oil emulsions. A water-in-oil hairdressing emulsion must have a good balance between thermal stability for adequate shelf-life and mechanical instability so that it breaks easily when rubbed on the hands and on the hair. If this emulsion breakdown is not rapid, the emulsion will remain white when rubbed on the hair. The required balance is achieved when calcium soaps are used as emulsifiers. Thermal stability can be increased using cholesterol or wool-wax alcohols at levels of up to 0.5%.

Formula XXIX W/O hairdressing

	% w/w	
Beeswax	3.0	
Stearic Acid	0.5	
Mineral Oil	34.0	A
Petroleum jelly	2.5	
Cholesterol	0.2	
Lime water (freshly made)	to 100.0	B
Perfume	0.3–0.5	C

Procedure

1. Heat A in a steam jacketed pan to 65–70°C, and maintain temperature.
2. Prepare lime water. Use immediately.
3. Add B to A and mix with a high-speed stirrer to form the emulsion.
4. Cool to 45°C and add the perfume (C) stirring to ensure good dispersion.

To prepare lime water, a 1% concentration of calcium hydroxide in deionized water is mixed thoroughly and repeatedly, and allowed to stand until a clear supernatant liquid is obtained. This can be used as required. Freshly prepared lime water should contain not less than 0.15% w/v of calcium hydroxide (British Pharmacopoeia).

Oil-in-water emulsions

Formulae XXX, XXXI, XXXII O/W hairdressings

	% w/w			
	XXX	*XXXI*	*XXXII*	
Mineral (Paraffinum Liquidum) Oil	25.0	44.0	35.5	
Beeswax (Cera Alba)	5.0	1.0	–	A
Stearic Acid	6.0	4.4	2.5	
Glyceryl Monostearate	–	–	2.0	
Triethanolamine (TEA)	1.0	0.6	1.0	B
Water; Aqua	63.0	50.0	54.5	
Preservative(s)	q.s.	q.s.		
Propylene Glycol			4.5	
Preservative(s)			q.s.	
Perfume	q.s.	q.s.	q.s.	

Suggested preservative(s) mixture, methyl paraben 0.15%; ethyl paraben 0.02%, but tests for microbiological status must be carried out.

Procedure

1. Heat A in a steam jacketed pan to 70°C and maintain heat.
2. Heat B to 70°C.
3. Add A to B at 70°C while mixing and continue mixing for 5 min.
4. Formula XXXII: dissolve preservative in the propylene glycol and add to B.
5. Cool to 45°C and add the perfume.

(e) Gels

Certain gels were popular at one stage. One was the microgel, which is an oil-in-water emulsion which is clear because the oil droplets are so small. Another type was based on aqueous polyethylene glycol gelled with a cellulose thickener. Both types of gel [7] are miscible with water and are less greasy than hair creams, but do not give gloss to the hair.

(f) Lotions

Certain lotions were also marketed, based on solutions of resins in a volatile solvent such as ethanol. The presence of a plasticizer was essential to make the resin more flexible and less brittle. Among other materials included were lustre aids for gloss without making the hair too greasy. A British patent [19] describes the use of certain lustre aids, which with the resin give both gloss and fixative properties.

(g) Aerosol hair gloss

A modern, simple formulation [20] which imparts sheen without a heavy oily feel follows:

Formula XXXIII Aerosol hair gloss

	% w/w
Phenyl Trimethicone*	4.0
Glycereth-26†	0.5
Mink oil (light fraction)	0.5
Isobutane and propane	95.0

* Dow Corning 556.
† Volpo G26 from Croda.

Procedure
Blend the first three ingredients together at room temperature. Fill the aerosol can with 5% of this concentrate and propellant at 95% by weight.

12.5.4 Hair colour restorers

These products are based on sulfur and a lead salt and are used to restore the original colour to grey hair. When the mixture is applied, the sulfur which is deposited on the hair shaft gradually darkens with the formation of lead sulfide. The product is applied daily to build up the colour until the required shade is obtained. Application is then repeated at intervals to maintain the colour. Lotions were used at one time, but these had poor stability. More acceptable and convenient product forms are a cream and a pomade [9].

Now that modern men are going to 'hairdressing salons for men', and using the services previously only offered to women, the up-to-date colouring methods are being used by them.

12.5.5 Modern hair-styling products

The women's products aimed at setting, styling and conditioning of hair are examples, suitably perfumed for men, which are being formulated. The same palette of ingredients is used to give any combination of these three treatments. Setting/styling or setting/conditioning gels can be applied to give a wet look or combed through the hair to give a dry appearance. Mousses can be formulated to give light hold and styling or firm hold and styling, etc.

Formula XXXIV Hair setting gel [21]

	% w/w	
Carbomer 940*	1.0	
Water (deionized)	30.0	A
Vinyl Caprolactam/PVP/Dimethylaminoethyl Methyacrylate Copolymer†	10.0	
Sodium hydroxide (20%)	1.4	B
Water (deionized)	56.6	
Polyoxyethylated fatty alcohol [2]‡	1.0	C
Perfume, colour, preservative	q.s.	D

* Carbomer 940, Goodrich.
† Copolymer VC-713, ISP.
‡ Mulgofen ON-870, Rhône-Poulenc.

Procedure

Part A. Disperse Carbomer in water of A.

Part B. Add the Copolymer and sodium hydroxide to the water of B. Add Part A through a strainer to batch and mix.

Part C. Warm part C to liquefy but cool slightly before adding to the batch.

Finally, add the perfume, colour and preservative. The total weight of these three must be deducted from the water so that the total is 100%.

The following are examples of formulae for styling mousse.

Formulae XXXV, XXXVI Hair-styling mousse

	% w/w		
	XXXV [16]	*XXXVI* [16]	
Polyoxyethylated Fatty Alcohol*	0.50	0.50	
Water (deionized)	81.38	73.88	A
Polyquaternium-11†		4.70	
Vinyl Caprolactam/PVP/Dimethylaminoethyl Methacrylate Copolymer‡	6.00	8.80	B
Ethanol	12.00	12.00	
Amodimethicone (and) Tallowtrimonium Chloride (and) Nonoxynol-10§	0.12	0.12	
Perfume, preservatives	q.s.	q.s.	

* Mulgofen – ON-870 from Rhône-Poulenc.
† Gafquat 755 N from ISP.

‡ Copolymer VC-713 from ISP.
§ DC 929 Cationic emulsion from Dow Corning.

Aerosol Fill:	Solution	90–95%
	Propane/butane	5–10%

Procedure
Formula XXXV. A. Dissolve the Mulgofen in water. B. Add Copolymer VC-713 and stir until uniform. Add other ingredients and stir.
Formula XXXVI. A. As above. B. Add the Gafquat before the Copolymer VC-713.

12.6 OTHER PRODUCTS

Other products, described in other chapters of this book, can be adapted by using suitable fragrances for men. Formulations have been suggested [22] as part of a total men's range and include sunscreen moisturizing gel, protective barrier lotion, facial cleanser, skin cleanser, shower gel, and moisturizer for sensitive skins. There has been a crossover of skin-care ingredient technology from female-orientated products with the introduction of male skin-care products containing active ingredients such as AHA's (alpha hydroxy acids) which exfoliate the top layers of skin [23]. Formulations for alternative bronzing compositions have been proposed [24].

12.7 SUMMARY

A number of changes have occurred in the male toiletries market over the past few years. Sales of shave preparations, male fragrances, hair-care products and skin-care products have not only increased in volume but there is a marked increase in penetration in the younger age groups with certain trends discernible. For instance, the establishment of post-foaming shave gels as a significant sector in the shave-preparation category has been largely due to their widespread use by males under 35. In the UK market, for example, over 60% of shave gels are used by men under 35. In the introduction mention was made of the high proportion of men considering themselves to have sensitive skin. It is pre- and post-shave preparations positioned for sensitive skin which appear to resonate with the male consumer in matching skin type with product as opposed to the usual skin type classification of dry, normal, greasy and combination skin.

The change in the male hair-care market has been to move from male-specific products such as brilliantines, pomades and emulsion-type dressings to styling products which, in formulation terms, are little different from those marketed for the female sector. Such male-orientated products are essentially distinguished by fragrance and packaging. In the body-care sector there has been a significant increase in usage of body sprays, with or without deodorant active ingredients,

mainly as a consequence of the introduction of new fragrance variants, which maintains consumer interest in this sector. Shower gels are another category in the body-care area which has enjoyed growing usage. Sometimes such products are positioned to reflect particular lifestyles such as sports activities. Here again, the usage of body sprays and, to a lesser extent, shower gels is skewed to the younger age group. The trend towards greater penetration of the younger age sector of the male population augurs well for the future of the male toiletries market. As these consumers mature they will consider the use of personal-care products as more routine and normal than their forebears. This comes at a time with changing demographics; as the 'baby boom' generation passes into middle age it is important that there is greater penetration of toiletry usage in the less numerous younger age groups to maintain volume sales. The challenge which faced the industry a decade or more ago will have changed from one of persuading men to use toiletries at all to providing more innovative, efficacious and higher-quality products.

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13

Pressurized dispensers

Jim McAllister

13.1 INTRODUCTION

Before examining the topic in detail it is important to define clearly the term 'Pressurized dispenser'.

> In simple terms a pressurized dispenser is a packaging form, which can store the product under pressure until required and then, on demand, discharge the product. To do this there must obviously be a source of internal pressure (a propellant), and a means of discharging the product and propellant (a valve).

This definition obviously excludes pump packs, which have a valve, but do not have any permanent internal pressure.

Pressurized dispensers, or aerosols as they are more popularly known, were first used by the public at large soon after the end of the Second World War and it is from this point that the world aerosol industry has developed.

13.2 HISTORICAL DEVELOPMENT OF PRESSURIZED PACKS

Pressurized dispensers, although perhaps not recognizable as such, have been known for many years. However, the basis of modern pressurized packs, or the aerosols, was introduced by Rotheim, who was granted a patent in 1929. His invention was a pressurized container fitted with a valve to enable the product to be dispensed in a controlled manner. The main use was for spray paint, but it was also used for fire extinguishers and cosmetics.

The scope for aerosols was realized during the Second World War, when insecticides were developed to help to reduce the effect of insect-carried diseases, on the fighting performance of the troops.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 377–391

Following the end of the war the potential of this packaging system for general use was soon realized and the modern aerosol industry was born. There are now few products which cannot be presented in an aerosol format. World aerosol production has increased steadily and in 1997 had risen to *c.* 9 billion units. European production accounted for over 4 billion units and the United States over 3 billion units. This growth is testimony to the fact that aerosols are a unique product form, that is easy to use, convenient, safe and relatively inexpensive.

13.3 AEROSOLS AND COSMETICS

During 1997 personal-care products accounted for over 60% of European aerosol production, based on the number of cans produced. A breakdown by product type of aerosol cosmetic products manufactured in Europe is shown in Table 13.1.

13.4 THE COMPONENTS OF AN AEROSOL PRODUCT

Unlike a liquid product the packaging of an aerosol product is not simply a container, but is a functional part of the product. The components of an aerosol can be detailed as follows:

1. Concentrate
2. Propellant
3. Container
4. Valve and actuator
5. Dust cap.

These various parts will now be examined in more detail.

13.4.1 Concentrate

The concentrate is essentially the 'active part' of the aerosol product. Thus for a hairspray it could be an alcoholic solution of a resin. The type of and amount of resin in the solution will depend on the effect that the product is designed to give to the consumer.

Table 13.1 1997 European production by cosmetic product type

	Units (millions)	*Percentage of European production*
Hair spray	685	30.0
Hair mousse	290	12.6
Deodorant body spray/antiperspirant	950	41.7
Shaving foam	286	12.6
Shaving gel	5.6	0.2

For an antiperspirant the concentrate will be a suspension of aluminium chlorhydrate, whilst for a deospray it could be simply an alcoholic solution of a fragrance.

The amount of a particular active material that is required for a product is determined by the relative proportions of concentrate and propellant, which cause a dilution effect, and also the valve/actuator combination, which controls the discharge rate.

13.4.2 Propellant

The propellant is the source of internal pressure by which the concentrate is expelled from the can. The sealed aerosol can is under internal pressure from the propellant and when the valve is opened this internal pressure drives the concentrate from the can. Thus an essential property of any propellant is that it can exert a pressure inside the can, which is greater than the pressure on the outside. However, there are other properties which should also be considered.

Ideally a propellant should be non-flammable, it should be odourless, it should be of low toxicity and be chemically inert.

In recent years, as the problems of ozone depletion and global warming have become more understood, the stability of the propellant after it has been released from the can has also become an important property of a propellant.

Additional properties which are important to the formulator are solvent power and availability in a wide range of pressures.

Today there is no single propellant which meets all of these criteria. The most commonly used propellant is 'butane', which is a blend of *n*-butane, *i*-butane and propane. It is the relative proportions of these three ingredients which result in a particular pressure rating for the propellant. The common grades of butane are identified by the pressure, in terms of psig, which they exert at 21°C. *viz.* 30, 40, 48 and 70. Butane 40 is the most widely used of these.

Butane is a liquefied gas such that in an aerosol container it can exist almost entirely in its liquid form. It is the liquefied propellant which provides a pressure reservoir as the can is discharged and thus maintains a constant pressure during the life of the can.

However, compressed gases are also used in aerosol products. These are mainly compressed air, nitrogen and carbon dioxide. Unlike a liquefied propellant, a compressed gas does not provide a pressure reservoir and the internal pressure falls during the life of the can. Typically for a can pressurized with nitrogen the initial pressure will be in the order of 10 bar, but will fall to 3 bar during the life of the can.

13.4.3 Container

Aerosol containers can be made from a range of materials such as tinplate, aluminium, glass and plastic.

Tinplate containers are made from tin-plated steel and are constructed from three pieces. These are as follows:

1. the container body
2. a base, also known as the cone
3. a top, also known as the dome.

The body is printed in a flat sheet form, with several individual bodies printed on the same sheet. The sheets are then cut to the size of the container and the individual pieces formed into a straight-sided cylinder with a side weld. The base and top are then crimped into place. Depending on the formulation to be packed, the internal surface of the can may need to be given one or more lacquer coats to give protection against corrosion.

The diameter of the aperture on the neck is 2.5 cm and valves are fixed by an internal crimp.

Aluminium cans are made in one piece from an aluminium pellet, which is shaped like a coin. The diameter and thickness of the pellet is determined by the size of the can to be produced. The pellet is shaped into a straight-sided tube, which is given an internal lacquer coating, formed into an aerosol can and printed on the same machine.

The neck aperture can be of various sizes and the crimping may be internal or external depending on the actual aperture diameter. Thus a 2.5 cm neck will have an internal crimp as with a tinplate can, whilst a 20 mm or less neck will have an external crimp.

Glass containers, which are generally used for fragrance products, are often coated with a protective envelope of plastic to prevent the risk of flying particles of glass if the container is accidentally broken. All glass containers are externally crimped.

Plastic containers are made from PET and are not widely used, but like glass containers are externally crimped.

Irrespective of the material of construction, the container, when sealed by the valve, must be capable of withstanding the internal pressure of the propellant. Since different formulations using different pressure propellants will exhibit different internal pressures, it is important to select a container suitable for the particular formulation.

Tinplate and aluminium containers are identified by a pressure rating, which may be 10, 15 or 18 bar. EC Regulations require a 10 bar container to withstand 10 bar of internal pressure without exhibiting any permanent deformation.

The correct pressure rating for a container to be used for a particular product is determined from the formulation pressure at 50°C. For a formulation pressure of P bar at 50°C the container must not deform below an internal pressure of $1.5 \times P$ bar and must not burst below an internal pressure of $1.8 \times P$ bar.

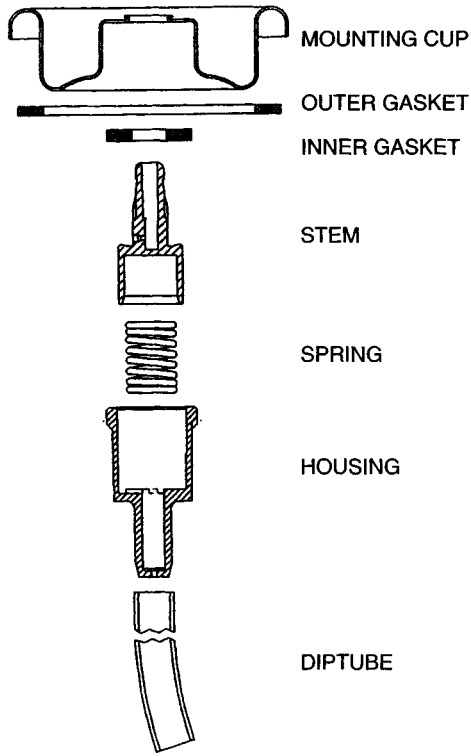

Fig. 13.1 Components of a standard 2.5 cm aerosol valve.

13.4.4 Valve and actuator

The valve is perhaps the most important part of the aerosol packaging, since it is the means by which the product is released from the can. Not only does it control the time at which the product is released, but also the rate at which it is released.

The valve is composed of several components (see Figs. 13.1–13.3). The components are: actuator, valve cup, outer gasket, stem, gasket, spring, housing and diptube. The actuator is the button on the top of the valve and although it is used as a safe and easy means of operating the valve it also controls the characteristics of the spray. It may contain an insert which can cause mechanical break-up of the product as it is released from the can. This will result in a finer spray.

The valve cup, which can be made from tinplate or aluminium, is the support for the actual valve housing and the means by which the housing is securely attached to the can during the crimping operation. The valve cup is crimped on to the can and a secure seal is achieved by the presence of the outer gasket.

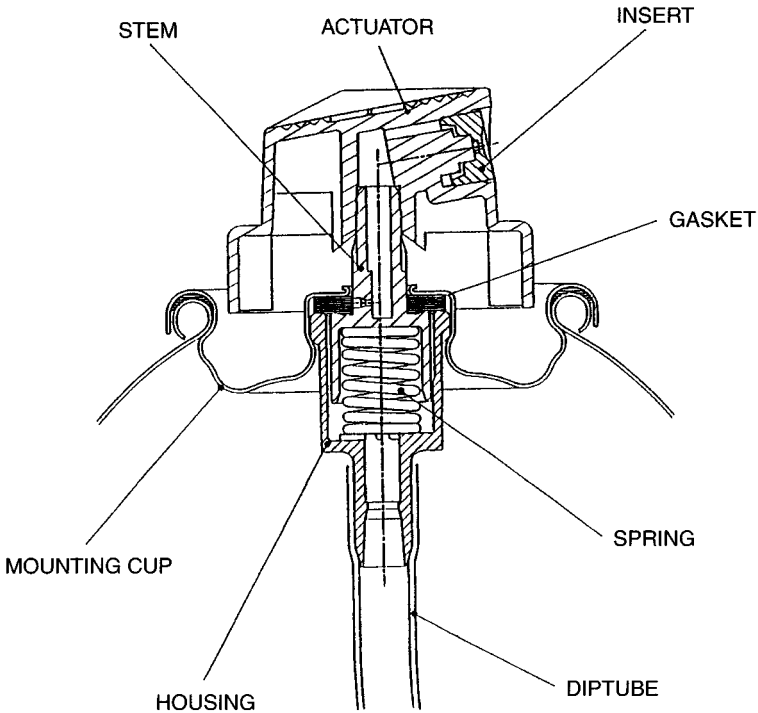

Fig. 13.2 Aerosol valve in closed position.

The stem is the part of the valve which is visible above the valve cup and to which the actuator is fitted. The product enters the stem via the stem orifice, which is a small hole through the stem at right angles to the axis of the stem. The stem orifice is normally covered by the inner gasket, when the aerosol is not being operated (see Fig. 13.2). The inner gasket is the barrier between the high-pressure environment within the can and the outside. When the valve is operated the stem orifice descends below the inner gasket (see Fig. 13.3) and product and propellant can escape into the stem and be sprayed out through the actuator.

The inner gasket is held against the inside surface of the valve cup by the housing, which is crimped permanently in position. The spring, which fits below the stem inside the housing, is present to force the valve closed by pushing the stem upwards when pressure on the actuator is released. This allows the stem orifice to again rise upwards and be covered by the inner gasket.

The diptube delivers product to the valve housing.

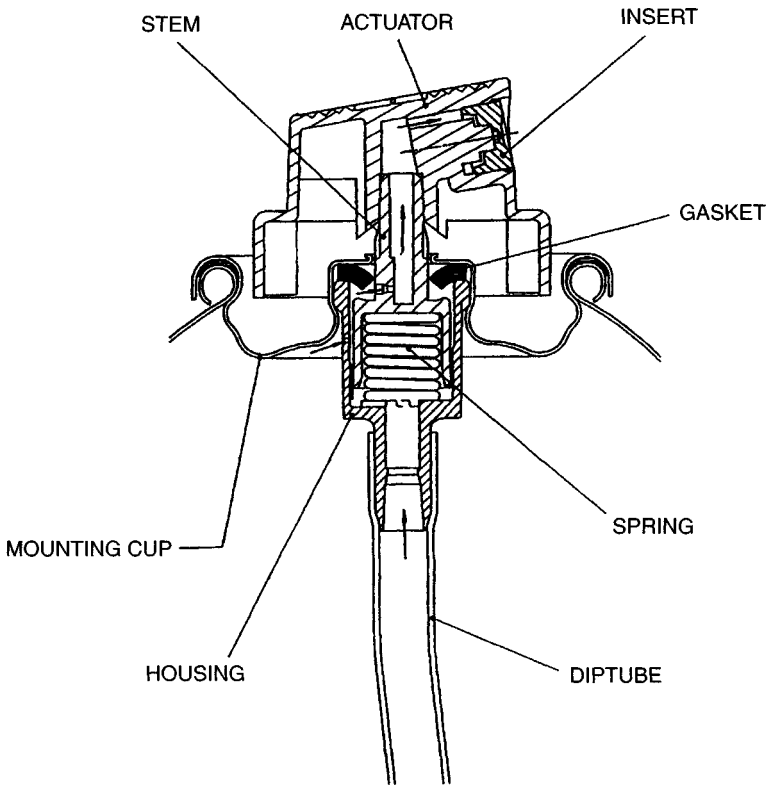

Fig. 13.3 Aerosol valve in open position.

13.4.5 The dust cap

The dust cap is present to protect the valve against accidental operation during transport or storage.

13.5 AEROSOL MANUFACTURE

The manufacturing operation is identical to a bottle-manufacturing operation in that it comprises filling the product, closing the pack, and finally testing to show compliance with specification. However, the specific operations at each stage are more complex.

The filling is done in two parts, with the concentrate and the propellant being added in separate operations. The closure involves permanently crimping the valve cup to the can, rather than attaching a cap with a screw fitting.

Testing is also more complex since, in addition to the typical checks that are carried out on a bottle product, the integrity of the pack, which is under pressure, must be proven to ensure that the can will be safe to use.

The filling and closure operation has four stages:

(a) Product filling, which is similar to any liquid filling operation.
(b) Valve placement, which may be a manual or automatic operation.
(c) Crimping, which is the operation by which the valve cup is permanently attached to the can. At this stage a partial vacuum may be applied to the can as part of the crimping operation and, if required, takes place immediately prior to the actual crimping stage. Application of a vacuum removes, at least in part, the air in the headspace. The vacuum operation reduces the internal pressure in the can after the propellant has been added since the air, which would have been trapped, will compress and not liquefy. The operation also removes oxygen and thus helps prevent product deterioration. Since moisture is also removed this can help to reduce corrosion. If, however, a high vacuum is applied it can reduce line speed.
(d) Propellant filling, where the propellant is forced through the valve into the can. There are other means of gassing, but today this is the most common method.

The finished product testing is in two parts.

The first part is typical product fill checks, which are part of any production operation. For aerosols it is more complex since there are two separate filling operations, concentrate and propellant, both of which must be checked individually.

The second part of the testing is specific to aerosols and is designed to confirm the integrity of the pack. Physical measurements must be made of the dimensions of the crimp to ensure compliance with the dimensions specified by the valve manufacturer. Crimps outside specified tolerances could lead to leaking cans. This would lead to cans which will not spray due to having no internal pressure and, more seriously, the possibility of a fire or an explosion. To confirm the integrity of each and every can the filled cans are passed through a bath of water maintained at a temperature of 55°C. The purpose of this operation is not, as is commonly believed, so that bubbles will be spotted escaping from leaking cans, which can then be removed from production. The primary function of water bath testing is to stress the cans by raising the internal pressure due to the temperature of the water. This will cause cans which have an inherent weakness to deform or even disintegrate. Thus cans which could be a potential danger are not sold to the public.

There are other off-line checks which are generally carried out. These would typically include pressure and discharge rate.

13.6 PRODUCT DEVELOPMENT

In developing any new product it is essential to consider not just the consumable but also the packaging and potential interactions between the two. This is

particularly true for an aerosol product, in which product performance, consumer acceptability, stability of formulation and pack and safety are all very much interconnected.

Other than product performance, consideration should be given to the choice of can (pressure rating and internal protection), internal gasket (a gasket swell check is vital to ensure valve failure is eliminated) and flammability (as indicated by a flame extension test).

As with any product it is essential that a full stability exercise is carried out on the total package. The actual test protocol will obviously vary between product types, but the ultimate safety of the product must always be paramount, because of the potential inherent hazard that exists with every aerosol product.

13.7 AEROSOLS AND SAFETY

Aerosols are potentially hazardous products. The packs are under pressure and for the most part contain flammable materials, a particularly hazardous combination. However, the risk of injury to the consumer or damage to property from using an aerosol product is very low. Incidents do happen, and when they occur can be very serious. However, the number of incidents which occur is small in relation to the total number of aerosols sold.

The caring attitude of aerosol manufacturers, who build safety into their products during the development stage, is responsible for this situation. This is further demonstrated by the aerosol industry communicating necessary safety information to the consumer as part of the pack copy.

Within the EC there is specific wording which is mandatory for inclusion in the pack copy. For any aerosol product the following statement is required:

> Pressurized container: protect from sunlight and do not expose to temperatures exceeding 50°C. Do not pierce or burn, even after use.

If the product contains flammable material, then unless the manufacturer can prove that the product is not flammable, the pack must contain the statement 'HIGHLY FLAMMABLE' and the Flame Symbol. The following statements should also appear on the can:

- 'Do not spray on naked flame or any incandescent material'
- 'Keep away from sources of ignition – No Smoking'
- 'Keep out of reach of children'
- Obligatory operating precautions to warn consumers of specific dangers of the product.

13.8 FORMULARY

There are many different cosmetic products which are now available as aerosols. The main product types are hairspray, mousse, antiperspirant, deospray, shave foam and shaving gel. Typical examples will now be indicated.

The following formulations are intended only as guidelines. There is no express or implied warranty against patent infringement, product stability nor fitness for purpose.

13.8.1 Hairspray

A typical formulation will contain an alcoholic solution of a resin, a neutralizing agent for the resin, a plasticizer, a fragrance and, of course, a propellant. The concentrate is relatively easy to manufacture with the resin being dissolved in the alcohol. The neutralizing agent, typically an organic amine, is then added to the solution, followed by the plasticizer and fragrance. The type of hold which can be expected from a product will depend on the amount and type of the resin used.

A typical hairspray using propane/butane as propellant is shown in Formula I. The resin used in this formulation is marketed under the name of Amphomer 28-4910, by National Starch and Chemicals Limited.

Formula I Hairspray

	% w/w
Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer	3.00
AMP 95	0.52
Silicone DC193	0.10
Ethanol	61.38
Propane/Butane	35.00
	100.00

It is generally difficult to formulate successfully with both high levels of resin and propane/butane, because the resin is not particularly soluble in the propellant. Resins have been developed that can tolerate much higher levels of propane/butane. This allows the formulator more options and the opportunity of producing lower-cost formulations. A typical example is given in Formula II.

Formula II Hairspray

	% w/w
Acrylates/Octylacrylamide Copolymer	2.25
AMP 95	0.57
Dimethicone Copolyol	0.10
Ethanol	46.98
Fragrance	0.10
Propellant (Propane/Butane)	50.00
	100.00

Formula II is a low-cost formulation which has a high level of propellant. This requires the use of a special resin, which has a high tolerance for propane/butane. The resin in this formulation is marketed by National Starch and Chemical Limited under the name of Amphomer HC.

13.8.2 Hair mousse

This product category became firmly established during the early 1980s. A hair mousse was initially a conditioning product, but latterly styling has become much more important.

The formulations are based on cationic conditioning polymers. This type of formulation tends to cause corrosion problems with tinplate cans and so most formulations are packed into aluminium cans. It is possible to produce a mousse formulation which can be packed into tinplate cans but such formulations are not easy to develop and require extremely careful stability testing.

Since the normal means of dispensing a mousse is from an inverted can, mousse valves do not have a diptube. This is because in the inverted position the end of the diptube would be clear of the product concentrate and on opening the valve only propellant would be discharged. Since mousse products contain only *c.* 10% propellant, this action would quickly deplete propellant levels to the point at which foam quality would be impaired and eventually the can would not spray.

Formula III Mousse

	% w/w
Polyquaternium 4	1.00
Dehyquat A	0.20
Isopropyl Myristate	0.10
Cocamidopropyl Betaine	0.40
Stearamidopropyl Dimethylamine	0.60
Water	87.70
Propellant (CAP40)	10.00
	100.00

13.8.3 Antiperspirant

Antiperspirants are unusual in that they are marketed in several product forms. Today, along with aerosols, roll-on and stick products are all widely used. Aerosol antiperspirants have a very real benefit over other delivery formats in that there is no direct contact between the product and the user's skin.

Unfortunately, the efficacy of aerosol antiperspirants has always been less than for both stick and roll-on products. However, it is now possible to use

activated forms of aluminium chlorhydrate, which can substantially increase the performance of aerosol products.

A typical formulation, a suspension of aluminium chlorhydrate, is shown in Formula IV.

Formula IV Antiperspirant

	% w/w
Aluminium Chlorhydrate	5.10
Bentone Gel DOA	5.10
Triclosan	0.05
Fragrance	0.50
Silicone DC345	4.25
Propellant (CAP40)	85.00
	100.00

13.8.4 Deospray

Deosprays have become the major product category for aerosol toiletry and cosmetic products. They are simple to formulate and easy to manufacture.

In the simplest form a deospray can be quite simply an alcoholic solution of a fragrance. Such products simply mask body odour, although the presence of the alcohol will give some short-term deodorancy. However, many formulations also include a bactericide which can give long-lasting protection against the development of body odours. A typical material used for this purpose is triclosan.

Formula V Deospray

	% w/w
Ethanol	40.0
Fragrance	1.0
Triclosan	0.1
Propellant (CAP40)	59.9
	100.0

13.8.5 Shaving foam

Typical shaving foams are based on triethanolamine soaps of stearic and myristic acids. There are many additives which can be included in the basic formulation. Silicones or polymeric materials are used to reduce the drag as the razor moves over the skin.

Owing to the occurrence of skin problems, sensitive skin variants have become increasingly important. Formula VII shows an example of a sensitive skin shaving foam, using Polyquaternium 10, which can help to relieve specific problems associated with sensitive skin.

Formula VI Shaving foam (regular variant)

	% w/w
Stearic Acid	7.2
Triethanolamine 99	3.1
Laureth-23	0.9
Sodium Laureth Sulfate	3.2
Fragrance	0.1
Germaben II	0.5
Deionized Water	75.0
Propellant (CAP40)	10.0
	100.0

Formula VII Shaving foam (sensitive skin variant)

	% w/w
Stearic Acid	1.5
Palmitic Acid	5.7
Triethanolamine 99	4.0
Hydroxyethylcellulose	0.2
Polyquaternium 10	0.2
Laureth-23	0.9
Sodium Laureth Sulfate	3.2
Fragrance	0.1
Germaben II	0.5
Deionized water	73.7
Propellant (CAP40)	10.0
	100.0

13.8.6 Shaving gel

Over the past few years this product has become increasingly important in terms of the market volume of the shaving products market.

The base formulation is essentially similar to that of a shave foam, but it contains a small percentage of a volatile hydrocarbon such as *n*-pentane, whose function is to act as a post-foaming agent. Although part of the concentrate, this material cannot be added into the blending stage, because of its inherent volatility. It is mixed with the concentrate at the point of filling.

The product is not filled in a typical aerosol can, but uses a bi-compartmental system. This system consists of an aerosol can and a flexible internal bag, which contains the product concentrate.

The propellant (CAP40) occupies the volume around the outside of the bag and is introduced through the base of the can after the product has been filled into the bag. Thus the propellant operates by causing a pressure on the outside of the bag, which forces the product out when the valve is opened.

A example of this type of packaging is Bi-can from Carnaud Metal Box. Formula VIII shows a typical base formulation for a shaving gel.

Formula VIII Shaving gel

	% w/w
Palmitic Acid	8.40
Stearic Acid	2.80
Triethanolamine 99	6.50
Sorbitol 70%	2.50
Propylene Glycol	1.50
Ceteareth 2	1.00
Hydroxyethylcellulose	0.02
Fragrance	0.30
Pentane	2.25
Deionized Water	74.73
	100.00

Materials	*INCI*	*Supplier*
(1) Ethanol	Alchohol	
(2) Propane/Butane	Propane/Butane	Calor Gas
(3) Fragrance	Fragrance	
(4)	Dimethicone Copolyol	
(5)	Polyquaternium-4	
(6) Dehyquart A	Cetrimonium Chloride	
(7) Isopropylmyristate	Isopropyl Myristate	
(8) Cocamidopropyl Betaine		
(9) Stearamidopropyl dimethylamine	Stearamidopropyl Dimethylamine	
(10) Deionized Water	Water, Aqua	
(11) Propellant (CAP40)	Propane/Isobutane/*n*-Butane	Calor Gas
(12)	Aluminium Chlorhydrate	
(13) Bentone Gel DOA	Dioctyl Adipate (and) Quaternium-18 Hectorite (and) Propylene Carbonate	Elementis
(14)	Triclosan	Ciba Specialty Chemicals
(15) Silicone DC345	Cyclomethicone	Dow Corning
(16)	Stearic Acid	
(17) Triethanolamine 99%	Triethanolamine	
(18)	Laureth-23	

(Continued)

Materials	*INCI*	*Supplier*
(19)	Sodium Laureth Sulfate	
(20)	Palmitic Acid	
(21)	Hydroxyethylcellulose	
(22)	Polyquaternium-10	
(23) Sorbitol 70%	Sorbitol	
(24)	Propylene Glycol	
(25)	Ceteareth 2	
(26)	Pentane	
(27)	Octylacrylamide/Acrylates/ Butylaminoethyl/Methacrylate Copolymer	
(28) Silicone DC193	Dimethicone Copolyol	Dow Corning
(29) AMP 95	Aminomethyl Propanol	
(30) Germaben II	Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben	Sutton

14

Skin preparations

Grace Abamba

14.1 INTRODUCTION

Just as paper is a substrate for the artist, the skin is that for the cosmetic scientist. For this reason it is extremely important that we acquire a reasonable understanding of the skin's structure, function and response to various stimuli. Only then should we begin to develop formulations to maintain or improve it.

The information on the skin which has been collected from medical and biophysical research is vast. The skin cannot be treated as a separate entity as it contributes to and is affected by the whole physiology of the body. To complicate things further, the skin of different individuals often reacts differently to similar conditions or stimuli. For example, one individual may break out into a rash, yet another may experience a more serious allergic reaction. There are still a number of structures in the skin whose functions are not known or completely understood and so the research continues.

The first part of this chapter aims to provide the reader with a simple guide through the skin in its normal state.

In the rest of the chapter the biology of two of the most common skin complaints, namely dry skin and oily skin, and typical cosmetic formulations which have been developed to alleviate them, will be discussed.

More detailed studies of the skin can be found elsewhere [1,2].

14.2 BIOLOGY OF THE SKIN

Our skin is our body's first point of contact with the outside world. A closer look reveals that the skin is not a completely smooth covering as suggested by photographs of fashion models. Instead it is covered by lines, furrows, wrinkles, dents and, in many places, hair. This can be confirmed with the help of a mirror and magnifying glass.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 393–452

In an average adult, skin covers a surface area in excess of $2\,m^2$. With the exception of the skeletal muscles the skin is the heaviest organ of the body.

The skin varies in thickness between the palms and soles of the feet, where it is very thick, to the fine delicate skin on the face. There are two types of skin, **glabrous** and **hairy**.

Glabrous skin, found on the palms and soles of the feet, lacks hair follicles and sebaceous glands but has a very thick epidermis and encapsulated sense organs in the dermis. In hairy skin, hair follicles and sebaceous glands are both present, but there are no encapsulated sensory organs. Facial skin has large sebaceous glands associated with fine vellus hairs, contrasting sharply with the scalp, which contains large hair follicles. The structure and function of hair is described in more detail in Chapter 8.

14.2.1 Function

(a) Protection

The skin's pH is naturally acidic, ranging from pH 4 to 6 compared with pH 7.2–7.5 found within the body's internal environment. This lower pH results from the production of certain amino acids and lactic acid by the epidermis, combined with acidic substances present in sebum and sweat. This **acid mantle**, as it is known, along with resident microflora, resists chemical and microbial attack by acting as a chemical buffer, detoxifying agent and bacteriostat.

In addition, the skin's viscoelastic nature offers a high degree of resistance to mechanical trauma. In its capacity as a protective barrier the skin also guards the body against damage by ultraviolet light from the sun and other sources, and prevents excessive loss of water from the body which would otherwise lead to dehydration. Such protective properties are greatly reduced or destroyed if the skin is in contact with water, solvents or solutes for long periods of time.

(b) Communication and control

The skin communicates pressure, pain, temperature, odour and sexual stimuli to the body through the brain which then co-ordinates the signals. For example, the body's temperature and water content are controlled via the vascular system and the production of sweat. All these functions are crucial to our survival in a constantly changing environment.

14.2.2 Structure

The key to a better understanding of the skin's functions is to take a closer look at its structure. A vertical section of the skin reveals three distinct layers, namely the outermost epidermis, the dermis and finally the hypodermis or subcutaneous layer (Fig. 14.1).

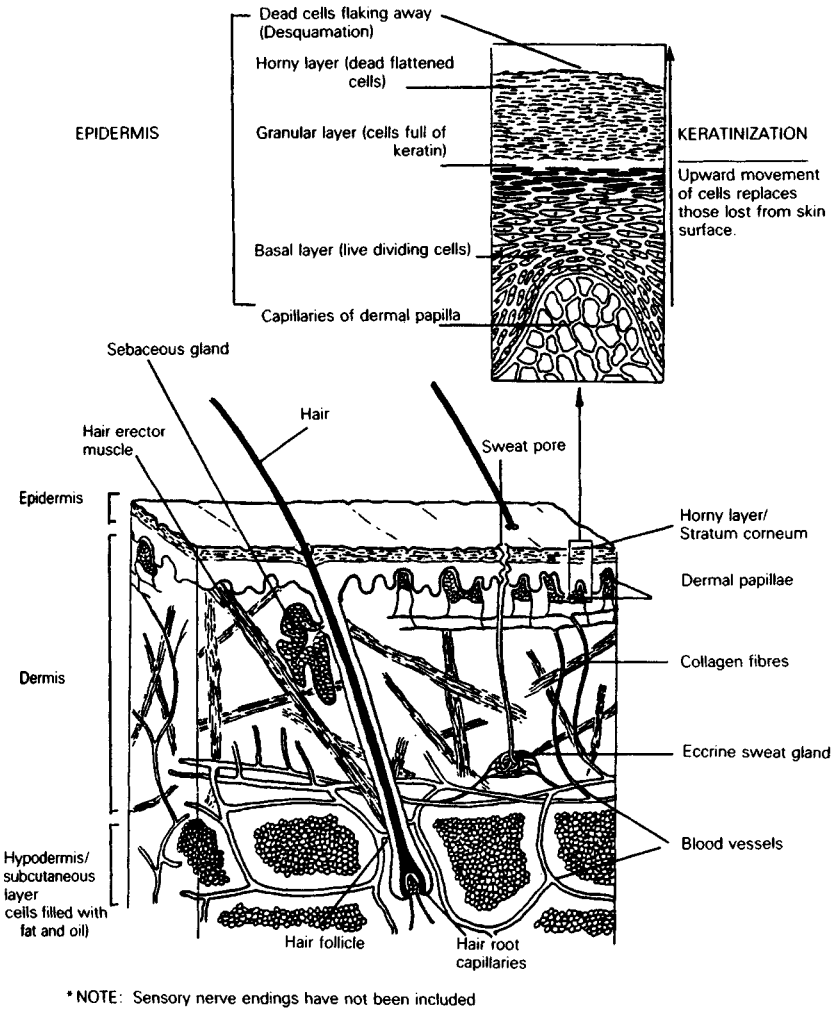

Fig. 14.1 Structure of the skin.

(a) Epidermis

The epidermis is an avascular structure, made up of many layers of cells. The special structure of the epidermis is classified as stratified squamous epithelium and is typical of vertebrate animals. It is responsible for producing the main barrier known as the **horny layer** or **stratum corneum**, which forms the outermost part of the epidermis. The horny layer is made up of water-resistant dead cells, called corneocytes, which are segmented together with a complex lipid material.

The epidermis varies in thickness from 75 to 150 micrometres (μm) in most areas to 4 mm on the palms of the hands and the soles of the feet. In terms of cells the epidermis consists of about 35 cell layers of which 15–20 layers make up the horny layer. It rests on the connective tissue component of the skin known as the dermis, which contains blood vessels and lymphatic vessels. The epidermis itself is avascular. The area of contact between the epidermis and the dermis is an undulating surface, which helps to secure attachment, increasing the surface area for the supply of nutrients to the epidermis via the blood vessels, known as dermal papillae.

The lower living layers of the epidermis can also be subdivided as follows:

1. the germinative or basal layer;
2. the stratum spinosum or prickle cell layer;
3. the stratum granulosum or granular layer, which is characterized by the presence of distinctive keratohyalin granules.

Keratinization

The dynamic process of epidermal renewal is known as keratinization. It begins in the basal layer where the cells, known as keratinocytes, multiply by mitotic cell division and are continually pushed upwards whilst producing the protein, keratin. By the time these keratinocytes reach the outer layer they are dead, water-resistant flakes which are segmented together with a complex lipid material. Due to wear and tear, these cells in the horny layer are lost to the environment in a process called desquamation.

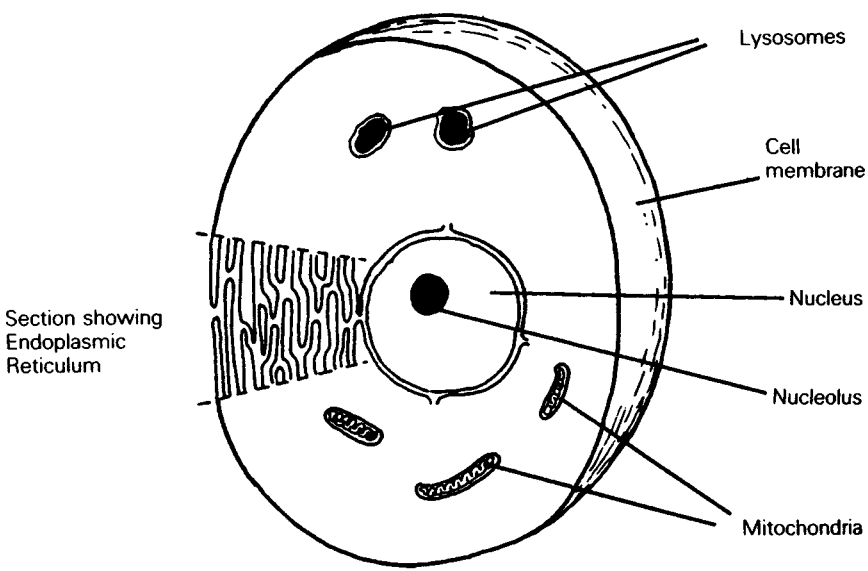

Fig. 14.2 Simplified diagram of an animal cell.

Production of keratinocytes in basal layer. Active cell division (mitosis) generates the keratinocytes in the basal layer at the same rate as they are desquamated at the surface. These keratinocytes contain nuclei and active organelles such as mitochondria, endoplasmic reticulum and Golgi complexes. This means that these cells are living and also capable of replicating themselves.

When the epidermis is physically separated from the dermis and turned upside down, one sees a highly undulated surface, which is produced by contours of individual keratinocytes projecting into and conforming to the contours of the dermis. In aged skin these undulations are gradually flattened out.

The keratinocytes which are cuboidal in shape are held together mechanically by fibres called desmosomes. The undulations together with the desmosomes increase the strength of attachment between the epidermis and dermis via the epidermal–dermal junction. The arrangement also provides a large surface area for transport of nutrients into the basal layer via a network of blood capillaries known as the dermal papillae.

Prickle cell layer. The dividing keratinocytes move outwards into the prickle cell layer and assume a more flattened or polyhedral shape. They are described as prickle cells because when they are isolated they have numerous tiny projections. These cells synthesize a network of keratin filaments within the cytoplasm, called tonofibrils.

Granular layer. As the keratinocytes move into the granular layer they become more flattened and synthesize a compact amorphous material called keratohyalin. The latter bunches up to enclose the tonofibrils.

Degradation of cell organelles. The next stage involves the degradation of the cell organelles, namely the mitochondria, ribosomes and ultimately the nucleus. The cells are markedly flattened and are filled with keratohyalin masses and filaments. At the same time an insoluble keratinized envelope surrounds the cells.

The degraded cell organelles contribute to the formation of a hygroscopic amino acid pool commonly referred to as the **natural moisturizing factor** (NMF). The NMF acts as a water resevoir in the horny layer, which keeps the latter pliable, and feeling soft. The composition of the NMF is detailed in Table 14.1.

Table 14.1 Composition of the NMF

Components	%
Free amino acids	40.0
Lactate	12.0
2-Pyrrolidone carboxylic acid	14.0
Urea	4.0
Mineral salts	16.0
Sugars, organic acids, peptides	11.0
Urocanic acid	3.0

Formation of stratum corneum. The keratinized cells, now known as corneocytes, pump out lamellar granules, which are thought to be arranged into lipid bilayers between the cells of the lower stratum corneum. These intercellular lipids contribute to the maintenance of healthy skin in several ways; namely, hydration, corneocyte adhesion and reduction in transepidermal water loss. The composition of these lipids is shown in the following list.

Components	%
Ceramides	55
Cholesterol esters	10
Free fatty acids	20
Cholesterol	15

Desquamation. In the upper stratum corneum this series of lipid bilayers becomes progressively more haphazard. This process, together with the degradation of the desmosomes, is involved in the poorly understood mechanism that is associated with the desquamation of the superficial cells into the environment.

The human epidermis is able to maintain its functions by virtue of the structure plus its ability to renew itself constantly. It has been reported that the whole epidermis renews itself once every 2 months.

Control of epidermal activity

The study of the controlling factors in epidermal growth and renewal has proved to be extremely complex. The compounds which seem to be important in this process include epidermal growth factor, cyclic nucleotides, prostaglandins, glucocorticoids, calcium and antimitotic agents often described as chalones. Further details about the possible role of these materials have been discussed by Goldsmith [2].

Melanocytes and Langerhans' cells

There are two other important types of cells in the epidermis: the melanocytes and Langerhans' cells. The melanocytes manufacture a pigment called **melanin** which is injected into keratinocytes during keratinization. Melanin is involved in protecting the skin from ultraviolet light, thus acting as the body's natural sun screen. There are two types of melanin: eumelanin (brown/black) and phaeomelanin (red/yellow) which contribute to the basic colour of the skin, hair and eyes. The role of melanin and synthetic filters in suncare products will be discussed more fully in Chapter 16. Figure 14.3 shows a flow diagram of the biosynthesis of melanin.

The skin represents the first line of defence of the body's non-specific defence system. It has a whole host of immune cells, proteins and specific responses, the most important being the **Langerhans' cells**, resident immobile

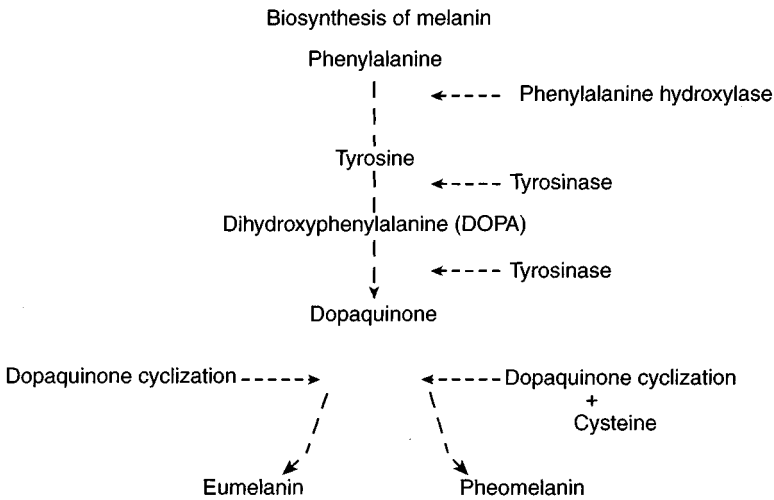

Fig. 14.3 Biosynthesis of melanin.

phagocytes which engulf and digest foreign objects. Other immune system cells include B cells, T cells, macrophages and cytokines.

Langerhans' cells were discovered over a century ago but it was not until recently that experimental research confirmed their function in the skin's immunosurveillance system.

(b) The dermis

The dermis functions as a supporting frame to the epidermis, supplying it with nutrients via the blood capillaries. It also supports the sensory nervous system, secretory glands and hair follicles.

Unlike the epidermis, which is a cellular structure, the underlying dermis consists of connective tissue. Other examples of connective tissue in the body include bone, cartilage and loose areolar tissue. In skin, the connective tissue consists of a fairly dense network of protein fibres embedded in a hydrophilic viscoelastic gel called the ground substance. Cells known as fibroblasts carry out synthesis, maintenance and replacement of this connective tissue.

Collagen and elastin. Collagen forms the major constituent of the fibrous protein which gives the skin its tensile strength. These collagen fibres make up 30% of the wet weight of the dermis and are arranged largely as interwoven strands or bundles that lie in a plane which is parallel to the skin's surface. The second type of protein fibre is called elastin; this makes up a smaller percentage and tends to be interwoven among the collagen bundles. These elastic fibres allow the skin to deform and return to its original state once the pressure or tension is removed.

Ground substance. The dermal ground substance consists of salt, water and glycosaminoglycans. The latter form complexes with protein molecules known as proteoglycans. The best-known examples of 'glycosaminoglycans' are hyaluronic acid and chondroitin sulfate. Hyaluronic acid is known to play a vital role in the hydration of tissues since it carries with it a large volume of water.

Mast cells. The mast cells, which are the second major cell type in the dermis, can be found close to the small blood vessels. They are responsible for synthesis and secretion of (a) heparin, which is an anticoagulant, and (b) and (c) histamine and prostaglandins, both of which have vasoactive properties.

Sweat glands. Sweat glands are found only in mammals. There are two distinct types of sweat glands: the eccrine and apocrine glands. The apocrine glands are associated with the hair follicles in the dermis and are found in the axillae, breasts, ear canal and anogenital region. Their function is not well understood. They are under the control of the sex hormones and, like the sebaceous glands, become active around puberty; in particular, they respond to emotional stress. Apocrine sweat is produced in minute quantities, about 1 μl/day, and expelled by contraction of the smooth muscle around the apocrine duct, as a milky viscous fluid. The latter is sterile and odourless but is then quickly broken down by the skin bacteria (diphtheroids) to produce more than one hundred volatile substances. The result is the production of socially unacceptable odours, particularly in the axillae. This presents a challenge to formulators of deodorant and antiperspirant products (see Chapter 3).

Human beings are homeothermic, which means that they need to maintain a constant body temperature of about 37°C to ensure that all internal processes work properly. This process is co-ordinated by the nervous system via the production of eccrine sweat and the regulation of blood flow to the peripheral blood vessels in the skin. The eccrine sweat is a free-flowing, salt-water secretion which is produced by about 3 million sweat glands that are distributed all over the body. Each gland is a discrete, coiled tube which is embedded in the dermis and supplied by a rich network of nerves and blood vessels. A long duct carries the salt water from the secretory coil through the epidermis and onto the skin surface via an opening, or pore, in the horny layer. As the sweat evaporates from the surface of the skin, it cools the body (Fig. 14.3). The sweat glands become functional only after the first 12 months of a baby's life and can produce from 3 to 10 litres of sweat per day in an adult. All the eccrine sweat glands respond to thermal stress. In addition, those found in the palms of the hands, the soles of the feet and the axillae respond to emotional stress.

Sensory skin receptors. Human skin is the largest sensory organ of the body, and within this function it serves to maintain an open communication channel between the body and the external environment. The cosmetic scientist knows

that the perceived texture of, say, a moisturizing lotion before, during and after use is a very important factor which helps the consumer to decide which to pick from a dozen others on the shelf. For instance, a person with dry skin may prefer to use the heavier texture of a cream because he/she perceives it to be more efficacious than a light milk. This may not be true technically but it is necessary also to appeal to the consumer's perception.

External stimuli usually result in sensations which can be classified into two groups: thermal and/or tactile; pleasurable or unpleasant.

Sensory receptors in the skin pass incoming information to the brain via nerve fibres which travel through the spinal cord to the cortex of the brain. The latter then relay a series of responsive motor impulses in a system described as a feedback mechanism. In general, the sensory nerves all arise from the spinal nerve branches. These branches are arranged in such a way that one branch serves an area called a dermatome. There are numerous types of sensory receptors in the skin, some of which are described in Table 14.2.

When evaluating products with consumers, questionnaires have to be developed using a language which will help the consumer to describe the sensory perception of the tactile properties of a product. Such language can include words such as: rough, smooth, sticky, soft, slippery, wet, dry, oily, watery, silky and velvety. All this must be tied in with the other information generated by our other senses such as the visual, auditory, gustatory and olfactory senses. The process of consumer panel selection is extremely important since factors such as previous experience, conditioning, and physical and mental state will contribute to the subject's assessment of the product. See Chapter 18 for further details.

Table 14.2 Common sensory receptors in human skin

Sensory/receptor	*Location/sensory function*
Free nerve terminals	Just below epidermis Pain and itch
Hair follicle endings	Surround hair follicle Sensitive mechanoreceptors
Pilo-Ruffini corpuscles	Associated with hair follicle Slow-reacting mechanoreceptors
Miessner's corpuscles	Hands, fingers, soles, toes Touch and pressure
Mucocutaneous corpuscles	The skin and mucous membranes, e.g. lips, tongue, eyelids, penis, clitoris Pressure receptor corpuscles
Vater-Pacinian corpuscles	Lower dermis near bones and fingers, breast, genitalia – vibration, pressure
Hederiform endings	Glabrous skin – mechanoreceptor for touch

(c) The hypodermis

Below the epidermis is a layer of fatty or adipose tissue called the hypodermis. The cells in this layer synthesize and store fat as an energy reserve. This is to help insulate the body from low external temperatures and to act as a buffer against trauma. On a more familiar note, the hypodermis provides the body with its contours, whether they are attractive curves or unwelcome bulges.

14.2.3 Skin permeability

In normal intact skin it has been established that the keratinized corneocytes and the largely non-polar lipid intercellular cement of the horny layer are the major factors involved in the maintenance of an efficient barrier. The function is lost if the stratum corneum is removed by tape-stripping techniques but is re-established again after a few days when the stratum corneum grows back. In addition, dietary deficiency of essential fatty acids such as linoleic acid results in skin with poor barrier properties. The vast number of products and chemicals that come into contact with the human skin make it of vital importance that the horny layer is well looked after.

Many raw materials which are commonly found in cosmetic and toiletry products permeate into and through the stratum corneum; some can also act as penetration enhancers for other specific materials. Examples of penetrants include water, glycerol, ethanol, phenol urea, aluminium salts and essential oils. Common penetration enhancers include water, organic solvents such as propylene glycol, surfactants and dimethylsulfoxide (DMSO). Occlusive dressings are often used to increase the hydration of the stratum corneum. This is used to promote the penetration of topically applied steroids. Permeation tends to occur through the intercellular matrix, but hair follicles, sebaceous glands and the sweat ducts have been shown to provide a faster alternative route for transport of highly polar molecules.

The thickness of the stratum corneum varies throughout the body and this, in turn, affects its permeability to various substances. Paradoxically, palms and soles which have the thickest stratum corneum show high diffusivity (to water in this case). Nevertheless, this property is compensated for by a long lag time on the onset of diffusion caused by the thicker horny layer. In this steady state, however, small molecules diffuse very quickly through the skin in the palms and soles compared to other parts of the skin.

The culprits most often involved in disrupting the stratum corneum are surface-active agents which, despite their use at low concentrations, have a cumulative effect. Other materials which can cause problems include perfumes, preservatives and sunscreen agents. Therefore it is desirable in the development of new products to minimize damage to the skin's natural barrier since cosmetics are primarily employed to improve the appearance of the consumer's skin.

Damage to the skin may be caused by: mechanical stress, chemicals, light and micro-organisms (bacteria, yeasts, moulds and viruses). To the cosmetics manufacturer chemical- and light-induced damage are the most important considerations. Appropriate safety tests ensure that the potential for a product or its component raw materials to cause adverse reactions is reduced to a minimum. Adverse reactions include skin irritation and sensitization which results in varying degrees of inflammation of the skin. Inflammation of the skin is known as **dermatitis**, of which there are many types.

Inflammation involves all the changes which take place in an injured living tissue, provided that the injury does not immediately kill the cells or destroy the tissue structure.The visual signs of this activity, known as the **triple response**, are:

1. erythema – redness;
2. oedema – swelling;
3. flare – more extensive reddening and swelling.

Each stage of the triple response can be measured objectively, but these changes are accompanied by subjective manifestations (burning, itching, and stinging) which must also be taken into consideration.

14.2.4 Biology of human (a) racial, (b) newborn and infant skin and (c) ageing skin

(a) Racial skin types

Skin colour and hair type account for the major differences in the skin of the various ethnic groups which make up the human race as we know it. These two differences mean that cosmetics which suit one group may not suit another; especially colour cosmetics which may not blend with a skin's colouring. The differences depend on gene heritage, living standards and different climatic exposure.

The following divisions are recognized by researchers: Caucasian, Asian, Hispanic, African, African Caribbean and African American. The colours in these racial groups range from white and cream through yellow to light and dark brown to black, and there are differences of shade within each race. The various types of darker skins in countries already marketing products for their special needs have led the cosmetic industry worldwide to develop and market them as 'ethnic' products.

The primary determinant of skin colour is the pigment, melanin. However, the presence of yellow carotenoids and light reflected from the blood vessels and different layers of the skin influence the final colour. As outlined above in *Epidermis* (p. 398) melanin is produced by melanocytes found in the basal layer of the epidermis. Figure 14.3 is a flowsheet of melanin production. The granules are transported via the melanosomes from the melanocytes into the keratinocytes

as the latter are pushed upwards in the keratinization process. The amount of melanin within the keratinocytes depends on the size, density, quantity and distribution of melanosomes present. This in turn accounts for the differences in pigmentation of different races in addition to the patterns of light and dark skin within each race. There are approximately thirty-five different shades of black skin based on undertones ranging from yellow-pink to blue-black. Asian skin, compared to say African skin, contains relatively little melanin, but substantially more B-carotene. Ethnic skin is often treated as problem skin, but increasing research in the 1990s is discovering the physiological functional differences, for instance, between white and black in both skin barrier and response to irritants [3,4]. However, like Caucasian skin, it falls into the four major skin types listed under the section on basic skin care, although one group may be predominantly associated more with one type than another.

In the development of skin preparations it is important for the formulator to be aware of the functional and anatomical differences between the various skin types. Inclusion of people with ethnic skin on the test panel during product evaluation and safety tests will help to address many of the problems resulting from the use of inappropriate raw materials. Problems include hypopigmentation, hyperpigmentation, acne and eczema.

(b) Newborn and infant skin

The skin of a full-term newborn baby is well developed and exhibits excellent barrier properties. In premature babies the stratum corneum is thinner and consists of fewer layers. In both cases the skin makes up approximately 13% of the body weight compared with 3% in an adult. Therefore, damage to the skin can magnify the effects of increased transepidermal water loss, heat loss and susceptibility to infection. There is also a greater risk of toxicity from the percutaneous absorption of topically applied materials because of the higher skin area to weight ratio.

Newborn babies and infants can experience dry skin owing to environmental factors, such as the climate and central heating. In addition young children may receive large doses of ultraviolet light because they spend so much time in many outdoor activities. All these factors should be taken into consideration when formulating products for this group of people.

(c) Processes affecting ageing skin

There are two distinct processes which lead to the cutaneous changes associated with ageing: namely intrinsic natural ageing and extrinsic photo-ageing. Intrinsic ageing is genetic in origin and is significantly affected by hormonal and vascular changes, facial expression lines and the effects of gravity. Extrinsic ageing can be defined as the acceleration of intrinsic ageing caused by various environmental conditions – especially exposure to ultraviolet radiation from the

Table 14.3 Comparison of extrinsic and intrinsic effects on ageing

Extrinsic (photo-ageing)	*Intrinsic (natural ageing)*
Coarse, deep, fine wrinkles (permanent)	Fine, shallow wrinkles (disappear with stretching)
Rough, dry, scaling (xerosis) texture	Smooth, dry texture
Pigmentation is mottled with freckles, melasma, dark 'liver' or 'age' spots known as solar lentigines, on hands, face and chest	Pigmentation is pale on lighter skins
Thick, leathery skin	Smooth, thin skin
Red, finely branched capillaries (telangiectasia)	
Pores are dilated with comedones (blackheads and whiteheads)	Pores are not dilated
Growths can include pre-cancerous lesions: seborrhoeic and solar keratoses; cancerous lesions: melanomas and carcinomas	Soft, red, raised papule, senile angioma
Thickened stratum corneum	Thinned stratum corneum
Basal pigment cells are increased in number and clumped together	No change in basal pigment cells
Elastic fibres are increased in number, clumped and disoriented (solar elastosis)	Degeneration of elastic fibres
Increased amount of mucopolysaccharides	Degeneration of mucopolysaccharides
Degradation of collagen	Collagen becomes highly cross-linked
Fibroblasts increase in activity	Fibroblasts decrease in number and activity
Blood vessels dilated and increased in number	Blood vessels not dilated and decreased in number
Inflammation present	No inflammation, suppressed immune system
Hair follicles are dilated and filled with horny debris	Degeneration of hair follicles (alopecia)
Sebaceous glands are enlarged	Degeneration of sebaceous glands
Decrease in subcutaneous fat	Decrease in subcutaneous fat
Reduction in number of active sweat glands	Reduction in number of active sweat glands

sun and sun lamps. Other contributory factors include the effects of wind, smoke, pollutants and central heating. The resultant effects are summarized in Table 14.3.

14.3 BASIC SKIN CARE

Apart from hair care, the skin-care category forms the largest sector of the cosmetics and toiletries market and continues to grow. Over the years, with the introduction of many new raw materials plus advances in surfactant/emulsion

Table 14.4 Some consumer needs in skin care

Protection (from)	*Repair (of)*
Ultraviolet radiation	Dry skin
Infrared radiation	Sunburn
Wind	Acne
Central heating	Trauma – stress, smoking –
Chemicals	burns, illness
Cold	Wrinkles
Pollution	Puffy eyes
Insects	Razor bumps
	Stretch marks
	Cellulite
	Skin cancer
	Patchy pigmentation
	Freckles, age spots
	Scars

technology, products with good functionality and aesthetic appeal have been developed.

The condition of the face, neck and hands is often used by the consumer as an indication of the general condition of the skin. These exposed areas readily show the signs of ageing caused by the sun and the repeated use of strong chemicals such as detergents on the hands. A healthy glowing skin reflects general mental and physical well-being. For this reason, consumers will spend enormous sums of money every year on skin-care products to try to achieve this.

Consumer needs can be roughly divided into two areas: protection and repair/treatment. Some of these needs are listed in Table 14.4. Other factors influencing the marketing of skin-care products are:

1. environmental issues – Green consumerism;
2. increase in an ageing population;
3. increase in disposable income;
4. animal welfare issues with respect to product safety tests;
5. increase in numbers and spending power of ethnic minority groups.

Skin is often classified into four types according to the activity of the oil-producing sebaceous glands. This classification is commonly used for facial skin because the skin type can vary in the individual depending on age, body site, season and state of health.

1. Dry skin.
2. Oily skin.
3. Normal skin is not particularly oily or dry. It is smooth and firm to touch and the skin pores are barely noticeable.

4. Combination; this type of skin has a tendency to be greasy in the central T-zone of the forehead, nose, central cheeks and chin. The skin on the other areas is normal or dry.

14.3.1 Dry skin

The function of the epidermis is to produce and maintain an efficient barrier called the stratum corneum (horny layer). Skin is continuously losing moisture to the atmosphere by diffusion of water vapour through the stratum corneum and the sweat glands (below the thermal threshold of sweating). The keratinized cells, NMF and intercellular lipid keep this **transepidermal water loss** (TEWL) to an acceptable minimum.

It has been established that water keeps the horny layer supple and ensures neutralization of acids and alkalis. A water content of 10–20% in the stratum corneum is said to be required to keep it soft and pliable. An alteration of the barrier (by repeated exposure to surfactants for instance) can cause an increase in TEWL to the extent that water is lost faster than it can be replaced from the underlying tissues. This results in the horny layer drying out, precipitating dry skin conditions.

Dry skin feels taut, rough and itchy. Closer observation reveals the presence of very fine wrinkles and, at a more advanced stage, large scales. The surface of severe dry skin is cracked and is reddened (erythema) as a result of the dilated peripheral blood capillaries in the dermis. Environmental factors, sunlight and ageing, plus numerous skin diseases and dietary deficiencies, all produce dry skin. The environmental factors include low relative humidity caused by central heating, wind, cold weather and repeated contact with water, surfactants and solvents. Since many conditions can cause symptoms of dry skin it is virtually impossible to give a universally accepted definition of the condition. Seitz and co-workers [5] developed a useful set of photographic reference standards as a clinical tool to quantify visual changes in scaling, cracking and erythema.

(a) Dry skin development

Water. Although water is important in maintaining the flexibility of the horny layer, repeated contact of the skin with water does, in fact, dry out the skin. One possible mechanism for this phenomenon is that the stratum corneum absorbs water and expands, creating stresses which result in the formation of cracks in the surface. The water-soluble fraction of the NMF is also lost. When the skin is no longer in contact with water the horny layer dries out and is unable to return to its original state because of the cracks. Thus, groups of corneocytes are left to protrude from the skin's surface giving it a rough, unacceptable texture.

Surfactants and solvents. Repeated use of surfactants and solvents disrupts the barrier functions of the skin. For example, surfactants are able to absorb at

surfaces and therefore will interact with biological membranes such as the skin. In doing this, surfactants de-fat the skin by emulsification of the lipids, resulting in an increase in TEWL and permeability for chemicals. In addition, surfactants may be absorbed onto, and denature, proteins (keratin) in the stratum corneum, resulting in marked changes in structure and function. The resultant effect is skin which is dry, rough and scaling.

Facial skin which has been washed with a surfactant-based product can often experience a temporary sensation of tightness. It is thought that this tightness is caused by the residual film of surfactant remaining on the skin after washing [6]. The highest potential for damage is shown by the anionics such as saturated C10–C12 alkyl chains in soaps, alkyl sulfates and alkyl benzene sulfonates. Cationics like nonionics show good skin compatibility at normal use levels but are severe irritants at high concentrations. Amphoterics are well known for the mildness on the skin, hence their use in baby shampoos. They have also been shown to reduce the irritation potential of anionics [7].

14.3.2 Oily skin

Oily skin results from the excessive activity of sebaceous glands which produce the lipid secretions known as **sebum.** There are several factors which can cause and/or contribute to oily or greasy skin; genetic inheritance, hormonal changes, diet, stress and external agents (chemicals, ultraviolet light). Changes in hormone levels which occur during puberty, the menstrual cycle, use of oral contraceptives and pregnancy tend to influence the activity of the sebaceous glands which can result in a flare-up of oily skin.

(a) Sebaceous glands

The sebaceous glands are holocrine glands which are often associated with hair follicles and are found all over the body except in the palms and soles. In some scattered locations, such as the mucosa and the nipples, the sebaceous glands are found independent of the hair follicle. The highest population of sebaceous glands is found on the scalp, forehead and face (400–900/cm^2). Sebum production begins in the small cuboidal reproductive cells in the outermost layer of the glandular sac. As the cells mature and progress towards the space in the centre of the sac, or lumen, lipid synthesis accelerates, resulting in an increase in cell volume of up to 150 times. Eventually the cells rupture, discharging differentiated lipid plus cell remnants (sebum) to the skin surface.

Sebum consists mainly of triglycerides plus some free fatty acids, wax esters, squalene and a small amount of cholesterol and its esters. Sebum secretion is under hormonal control and increases significantly at the time of puberty, when there is a marked rise in the level of circulating male hormones (androgens) such as testosterone. Sebum secretion reaches a maximum at about 20 years and decreases by approximately 28% per decade after this age.

(b) Function of sebum

In birds and fur-bearing animals, lipid-secreting glands function as a natural emollient and often have pheromonal activity. In humans, however, the function of sebum is less clear. Sebum has been shown to have mild antibacterial and antifungal properties but these activities have not been shown to be important in humans. The presence of some lipid on the surface of the horny layer does help to maintain skin smoothness and suppleness, but this is not a significant effect because in young children the glands are underdeveloped and yet the skin is still smooth and supple. In addition, mild de-fatting of the skin *in vivo* does not decrease barrier function.

(c) Acne vulgaris

Highly active sebaceous glands can and often do result in an inflammatory disorder, called *acne vulgaris*. This is commonly described as 'teenage spots' in the large number of adolescents who suffer from it. Acne is characterized by clogged pores (hyperkeratinization of the sebaceous duct and hair follicle), blackheads (open comedones) and whiteheads (closed comedones) or inflammatory lesions which we call pimples.

The pathogenesis of *acne vulgaris* can be summarized as follows. Excess sebum plus an increased rate of keratinization results in the formation of an occlusive plug or comedone in the pores leading to the hair follicle. Accumulation of stagnant sebum encourages the proliferation of anaerobic bacteria, especially the species *Proprioni bacterium acnes, Staphylococcus albus* and *Corynebacterium acnes*. These bacteria produce enzymes called lipases which hydrolyse the triglycerides in the sebum to produce free fatty acids and glycerol. The former causes further irritation which results in further hyperkeratinization and inflammation.

Factors which can aggravate acne include heat, humidity, ultraviolet light, constant friction, the application of heavy moisturizers and make-up, and the excessive use of soap or detergent scrubs.

Comedogenicity. In the 1970s the cosmetic industry received adverse publicity which suggested that certain materials used in cosmetic products could cause and aggravate acne, particularly in adult women. These materials were described as being 'comedogenic' and Dr Kligman invented the term 'acne cosmetica' for this type of acne. A frenzy of research produced a long list of such comedogenic ingredients, some of which are shown in Table 14.5. Various companies capitalized on these findings by labelling their products as 'non-comedogenic'. After further research, however, it was found that the condition found both in adult women and in adolescents is *acne vulgaris* which can develop by several different mechanisms. In addition, it was realized that a lot of exaggerated claims were being made; the term comedogenic has been superseded by the more accurate description 'acnegenic'.

Table 14.5 Some materials which have been shown to be acnegens

Isopropyl myristate	Butyl stearate
Isopropyl palmitate	Isopropyl isostearate
Octyl palmitate	Grapeseed oil
Myristyl myristate	Octyl dodecanol
Oleic acid	Oleyl alcohol
Cocoa butter	Lanolin
Coconut oil	Isostearic acid

Acnegenic covers the potential of a material to cause and aggravate both comedones and pimples. Although the list of acnegenic materials helps reduce the risk of formulating a product which may cause acne-related problems, it is still advisable to test the finished product. More often than not, individual materials which may have acnegenic properties produce a finished product which is non-acnegenic; of course, the converse can also be true.

14.3.3 Care of mature, ageing skin

With the market emphasis on prevention, skin care for the elderly is only starting to receive adequate attention. Elderly, mature skin tends to be very dry, thin, wrinkled and inelastic. Considerations when formulating cleansers, moisturizers and products for protection against over-exposure to UV radiation are summarized below.

Cleansers

Aged skin retains its ability to reduce transepidermal water loss but damage to the stratum corneum barrier by physical or chemical agents may result in a greater than normal water loss. In addition it takes longer to repair the stratum corneum.

The use of mild surfactants, with refatting properties, is recommended to prevent excessive dryness. Examples of such surfactants include decyl polyglucosides, amphoterics, betaines and sulfosuccinates.

Moisturizers

Use of moisturizers is particularly important for the exposed parts of the body, especially during dry, cold weather. Actives can include more occlusive oils and waxes such as hypoallergenic lanolin, paraffin, petrolatum, wheatgerm oil and long-chain fatty alcohols, humectants such as urea, hyaluronic acid, and plant-derived amino acids. Other actives which include lecithin and ceramides will help to protect and maintain adequate barrier function.

Photo protection

Mature skin needs adequate protection from overexposure to UV radiation to prevent further damage, hence the inclusion of UV sunscreens in daily

moisturizers for the skin and bald areas of the head. Physical blockers such as titanium dioxide, along with a blend of antioxidants, may also help to reduce the damaging effects of UV radiation.

14.4 SKIN-CARE REGIMEN

A balanced diet and sensible social habits such as abstinence from smoking or excessive drinking, plus taking adequate rest, give the skin an excellent start. However, there is a generally accepted daily regimen for external skin care which usually involves three steps: cleansing, toning and moisturizing/nourishing/protecting.

Cleansers. The cleansing of the skin removes dirt, dust, loose corneocytes, micro-organisms, sebum and sweat residues and make-up.

Toners. The use of a toner (also called a freshener) removes final traces of dirt and soap residues. It also temporarily reduces pore size and makes the skin feel refreshed and invigorated. Products which are called astringents tend to be used for oily skin to remove the excess sebum.

Moisturizers, nourishing and protective products. Frequent application of moisturizers helps the skin to maintain the moisture content of the stratum corneum, keeping it smooth and pliable. In this way moisturizers act as a supplement to the NMF and intercellular lipid. They also form a protective base for the application of make-up. All skins, whether dry or oily, require a moisturizer at least twice a day.

14.5 CLEANSING PRODUCTS

14.5.1 Soap and (surfactant-based) synthetic detergent-based products

Today there is a wide choice of cleansing formulations for the consumer to use. This choice is based not only on the infinite combinations of active agents and other additives but also on product form. Traditionally, soap and emulsion-type cleansing creams represented the two basic ways of cleansing the skin. Soap is the product which results from the neutralization of a mixture of fatty acids (usually tallow–coconut combination) in a process called saponification. The chemistry, formulation and manufacture of bar soaps are given in Chapter 15. Although soap is effective in removing grime, and is relatively inexpensive, it does have certain drawbacks. The washing solution formed by soap is extremely alkaline and can cause irritation, dryness and scaling. Although the skin compatibility of soaps has been improved by the incorporation of various superfatting agents, they are gradually losing their popularity to synthetic detergent-based products. The latter provide mild cleansing systems which can be in the form of bars called syndets and gels, liquids and aerosol mousses.

(a) Syndet bars

Although syndet bars are more expensive to manufacture than soap bars, they have a better skin compatibility profile, they produce a rich creamy lather and do not leave scum deposits in the bath or washbasin in hard water. They can also be formulated to a pH close to that of the skin.

Many different types of additives can be incorporated into a syndet base to suit a wide range of applications. For example, the formula shown below uses soya lecithin as a skin-conditioning agent. Lecithin is a natural constituent of plant and animal cells and is a popular additive in anti-wrinkle creams. Oatmeal is incorporated as the active in a syndet bar for oily skin (Formula 1).

Formula 4 (Croda C1550) is a clear cleansing bar which is essentially less aggressive to the skin than conventional toilet soaps. It is based on a combination of soap (sodium stearate) and synthetic detergents. Cocoyldiethanolamide/cocoyl sarcosine blend is a surface-active material specially designed for use in combination with sodium stearate to improve clarity of the bar. Almond oil PEG complex is incorporated to enhance the skin-conditioning properties of the preparation, functioning as a superfatting agent. High levels of humectant, lactamide MEA/acetamide MEA blend, propylene glycol and glycerol are used as skin moisturizers.

Formula 1 Syndet base* *(to be used in formulae 2, 3 and 4)*

This product is sold commercially and bought by manufacturers to produce syndet bars.

		% w/w
Surfactants	C12–C18 Fatty Alcohol Sulfate*	35.40
	Disodium Fatty Alcohol Sulfosuccinate	1–14
Refatting agents	Fatty Alcohols	10–20
Plasticizers	Stearyl Mono/Diglyceride	0–10
Filler	Starches	0–10
Whitener	Titanium Dioxide	0–0.2
Deionized Water		to 100%

	Syndet bars		
	% w/w	*% w/w*	*% w/w*
Formulae	**2** Dry skin	**3** Oily skin	**4** Conditioning/ cleansing
Syndet base* (**Formula 1**)	91.0	85.0	–
Soya Lecithin†	5.0	–	–
Oatmeal	–	9.3	–
Sodium Stearate‡§	–	–	24.00
TEA-Lauryl Sulfate (40%)§‖	–	–	18.00

	% w/w	% w/w	% w/w
Formulae (*continued*)	**2** Dry skin	**3** Oily skin	**4** Conditioning/ cleansing
Acetamide MEA (and) Lactamide MEA[¶l]	–	–	10.00
Almond Oil PEG-60 complex[¶l]	–	–	5.00
Cocoyl DEA/Cocoyl Sarcosine blend** [l]	–	–	20.00
Propylene Glycol[l]	–	–	8.00
Glycerin[‡‡]	–	–	12.85
Urea[§]	–	–	2.00
Ethylene Diamine Tetra Acetic Acid (EDTA), Disodium Salt[s]	–	–	0.15
Deionized water, Aqua	3.0	5.0	–
Preservative, colour, perfume[s/l]	1.0	1.0	q.s.

[*] Zetasap 813A. Zschimmer and Schwartz (GmbH & Co).
[†] Emulthin M35 (Lucas Meyer).
[‡] Witco, Ltd.
[§] (40%), Empicol TL40/T (Albright & Wilson).
[¶] Incromectant Lamea (Croda Inc.).
** Crodasinic CAC (Croda Inc.).
[‡‡] Croderol GA7000 (Croda Inc.).
[s] Ingredients are solid.
[l] Ingredients are liquid.

Formulae 2 and 3

1. Mixing: Feed Zetasap 813A into amalgamator (toilet soap mixer), then add other ingredients. Finally add perfume and colour.
2. Refine, extrude, cut and stamp as for toilet soap.

Formula 4

1. Combine all liquids (l) and heat with agitation to 70–80°C.
2. Slowly add the sodium stearate maintaining mild agitation while avoiding excessive foaming.
3. Heat to 90–100°C until the sodium stearate is completely dissolved.
4. Add the rest of the solids (s) while mixing and maintain temperature between 85 and 90°C.
5. When all the rest of the solids have dissolved, stop agitation and maintain temperature to allow for de-aeration.
6. Skim off and pour into suitable moulds.

(b) Other synthetic detergent-based cleansers

Rinse-off, liquid surfactant-based products have made a significant impact on the cleansing market. The category includes shower gels which are used all over the body; liquid hand soaps, foam baths, shower shampoos (for hair and body) and

facial cleansers. These types of products have brought versatility to the formulator and are available as liquids, gels, aerosol mousses and impregnated tissue wipes. It is obvious that consumers (and particularly men) still enjoy the sensation of washing the face with water rather than with an emulsion. Emulsion-based products are not popular with men because they perceive them to be feminine.

Facial cleansers must be able to effect a mild yet thorough cleansing of the skin. Such formulations normally contain a mixture of surfactants which work synergistically; a refatting agent, a thickener, perfume and water. The appearance of the product can be modified by using water-soluble dyes. Pearlescent agents such as the ethylene glycol stearate derivatives or opacifying agents such as titanium dioxide or copolymer latex emulsions are other possible additives.

In the past, anionic surfactant systems such as fatty alcohol ether sulfates combined with fatty acid diethanolamides were popular. However, the use of diethanolamides was plagued by their potential to cause adverse skin reactions and to generate nitrosamines. This resulted in the move to use anionic/amphoteric systems; examples of amphoterics are the alkyl betaines, amido alkyl betaines, sulfobetaines and N-alkyl-amino propionates. Other milder anionic systems that may be used include fatty acid carboxylates, sarcosinates, isethionates, taurates, sulfosuccinates and more recently the mono-alkyl phosphates. Nonionics such as the amine oxides are also commonly used.

Clear, coloured gel systems are becoming very popular where the surfactant can be thickened with sodium chloride. Other viscosity modifiers, which also provide a pleasant silky feel to the lather, can be used. These include cationic guar gums, cellulose derivatives, polyethylene glycol (PEG) esters, xanthan gum, guar gums and their derivatives and polyacrylic acid resins, known commercially as the carbopol resins.

The list of refatting or skin-conditioning agents which can be used in these formulations is endless. Humectants that can be used include glycerol, propylene glycol and ethoxylated sorbitol. Hydrolysed proteins are very substantive to the skin. Silicone derivatives have increased in popularity because of their ability to impart smoothness to the skin without stickiness. Examples of silicones which can be used include dimethicone copolyol and diquaternary polydimethyl siloxane, as shown in the formulae.

Natural products appeal to many consumers concerned with environmental issues. Natural oils and extracts are easy to incorporate as skin conditioners with the aid of nonionic emulsifiers.

Facial cleansers incorporating proteolytic enzymes such as papain seem to be gaining widespread acceptance as keratolytic agents.

The formula below describes a clear gel cleanser which uses a mixture of mild surfactants, often used in baby products to provide copious foam, mildness as well as superior cleansing and rinsing properties. Dimethicone copolyol is a silicone surfactant which offers good skin feel and skin-conditioning properties plus foam stability. Polysorbate 20 and PEG-40 castor oil are used as co-solubilizers and PEG-150 distearate is the thickening agent.

Formula No. 5 Foaming gel cleanser

		INCI/CTFA name/chemical description	*% w/w*
A	Miranol BT*	Disodium Lauroamphodiacetate (and) Sodium Trideceth Sulfate	18.00
	Mirataine CBS*	Cocoamidopropyl Hydroxysultaine	12.00
	Miranol C2M CCRC* NP	Cocoamphodiacetaate	10.00
	Kessco PEG-6000DS†	PEG-150 Distearate	1.00
		Polysorbate 20	1.00
		Dimethicone Copolyol	1.00
		Preservative	q.s.
		Water (deionized); Aqua	to 100%
B	DE Surfactol 365‡	PEG-40 Castor Oil	0.50
		Propylene Glycol	0.50
C		Perfume	q.s.

*Miranol Inc. †Stepan Company. ‡Caschem, Inc.

Procedure

1. Heat (A) to 75°C under agitation.
2. Continue mixing while allowing to cool.
3. At 45°C, adjust pH to 6.8 and add (B).
4. Add C.

More recently, sugar-derived alkylpolyglucosides when combined with alkyl ether sulfate provide a synergistic effect in terms of foaming and mildness. A mild facial wash gel is given in Formula No. 6.

Formula No. 6 Mild facial wash gel

	INCI/CTFA name/chemical description	*% w/w*
Plantaren 1200*	Lauryl Glucoside	10.00
Texapon NSO*	Sodium Lauryl Sulfate	3.60
Gluadin W40*	Hydrolysed Wheat Gluten	0.20
	Panthenol	0.20
	Allantoin	0.20
	Sodium Chloride	1.00
	Water (deionized); Aqua	84.50
	Preservative	q.s.
Perfume	Parfum	q.s.

*Henkel KGaA.

Procedure

1. Add the ingredients in the order shown.
2. Mix at room temperature.

A solution for the preparation of freshening and cleansing towelettes/wipes is shown in the next formula. Methyl gluceth-10 provides soft 'feel', and PEG-75 lanolin and oleth-20 provide gentle cleansing. The alcohol produces a cooling sensation. Microbiological testing of this type of product must be carried out extensively and monitored carefully during manufacture and after marketing.

Formula No. 7 Skin cleansing towelette/wipe solution

	INCI/CFTA name/chemical description	*% w/w*
	Water (deionized); Aqua	to 100%
Glucam E-10*	Methyl gluceth-10	5.00
Solulan L-575*	PEG-75 Lanolin	3.60
	Citric Acid	0.20
Omeroxol OE-20*	Oleth-20	1.00
Ethanol (98%) (denatured)	Alchohol Denat.	15.00
	Preservative	q.s.
Perfume	Parfum; Fragrance	q.s.

* Lipo Chemicals, Inc.

Procedure

1. Combine all the ingredients, except alcohol.
2. Stir until homogeneous.
3. Add alcohol and stir until homogeneous.
4. Pack in sealed sachets ensuring that the towelettes are completely saturated. If this is not done the parts which are only dampened might develop mould growth. Tests for microbiological safety are essential (Chapter 21).

The following liquid hand soap uses Tegopearl B-48 from Th. Goldschmidt to provide a rich pearlized appearance. This material contains the pearlizer, glycol distearate, which has been blended into anionic surfactants thus allowing it to be added directly to a formula without prior heating.

Formula No. 8 Moisturizing liquid hand soap

		INCI/CTFA name/chemical description	*% w/w*
A		Water (deionized); Aqua	to 100%
	Tego Betain L 7*	Cocamidopropyl Betaine	7.00
		Sodium Laureth Sulfate	25.00
	Antil 111*	PEG-55 Propylene Glycol Oleate	2.00
B	Abil B88183*	Dimethicone Copolyol	0.60
	Tego Pearl B-48*	Cocamidopropyl Betaine (and) Glycol Distearate (and) Cocamide MEA (and) Cocamide DEA	4.50
		Preservative	q.s.
	Perfume	Parfum; Fragrance	q.s.

* Th. Goldschmidt AG.

Procedure

1. Heat the water to 60°C. Add ingredients in (A) in order and mix between each addition.
2. Cool to 30–35°C. Add the ingredients in (B).
3. Mix well, avoiding air-entrapment.

14.5.2 Cleansers for oily skin

Frequent and effective cleansing is recommended for oily skin in order to reduce the amount of sebum left on the skin to an absolute minimum and so avoid the development of spots and pimples. Emulsion cleansers are to be avoided since they tend to leave a layer of oil on the skin. Face masks and exfoliating lotions are used for exfoliation of acne-prone skin rather than facial scrubs since the latter can cause disruption of the comedones, which exacerbates the condition.

Synthetic detergent systems can be used for cleansing oily skin where an astringent such as ethanol or witch hazel may be included as shown in the next formula. This is an unusual oil-controlling cleanser compounded with pyridoxine tripalmitate (oil-controlling) and panthenol (soothing and moisturizing) for use in oily/sensitive skin. This lotion cleanser may be applied with a cotton ball or impregnated into a wipe fabric as a total product.

Formula No. 9 Oil-controlling cleanser

		INCI/CTFA name/chemical description	*% w/w*
A	Deltyl prime*	Isopropyl Palmitate	10.00
		Polysorbate 65	3.00
		Pyridoxine tripalmitate	0.50
B		Water (deionized); Aqua	to 100%
	Myristocor†	Myristamidopropyl Dimethylamine Phosphate (and) Propylene Glycol	0.25
C		Ethanol 95% Denatured	25.00
	dl-Panthenol†	Panthenol	0.50
	Eucalyptus 70/75*	Eucalyptus	0.05

*Givaudan. †Roche vitamins/fine chemicals.

Procedure

1. Heat (A) to 70–75°C.
2. Heat (B) to 70–75°C with mixing.
3. Add (B) to (A) with mixing.
4. Add (C)when mixture has cooled to 35°C.

The following formulation makes use of the keratolytic properties of salicyclic acid as the exfoliating agent. Chamomile is used for its anti-inflammatory properties.

Formula No. 10 Exfoliating lotion

INCI/CFTA name/chemical description	*% w/w*
Water (deionized); Aqua	to 100%
Denatured Ethanol (95%), Alcohol, Denat.	10.00
Propylene Glycol	2.00
Preservative	q.s.
Chamomile Extract	1.00
Salicylic Acid	0.25
Parfum, colour	q.s.

Procedure

1. Dissolve preservative in propylene glycol.
2. Blend all ingredients except water.
3. Add water slowly, dispersing cloud (if any found), before repeating the additions, and mix well.
4. Add perfume.

Gels have become a popular product form for cleansing and post-cleansing products. A carbopol gel is used in the next formula where the alcohol provides antiseptic and astringent effects; allantoin is added as a soothing agent.

Formula No. 11 Medicated clear cleansing gel

	INCI/CTFA name/ chemical description	*% w/w*
Carbopol 940*	Carbomer Carboxyvinyl resin	1.00
Deionized water	Water, Aqua	to 100%
Ethanol (98%) (denatured)	Alcohol Denat.	50.00
Croderol GA7000†	Glycerin	3.00
	Allantoin	0.20
	Menthol	0.08
Preservative		q.s.
Diisopropanolamine		to pH 6.5–7.0
Perfume	Parfum; Fragrance	q.s.

* B.F. Goodrich. † Croda.

Procedure

1. Hydrate carbopol in water/ethanol mixture.
2. Add remaining ingredients.When completely homogeneous, neutralize to pH 6.5 with diisopropanolamine solution.

14.5.3 Emulsion cleansers

Cleansing creams, lotions and milks can be oil-in-water or water-in-oil emulsions which combine the solvency of water and oils to effect cleansing of the skin. In doing this they also leave a layer of emollient oil on the skin, leaving it feeling smooth, in contrast to the dry sensation often felt after the use of soaps and other synthetic detergent systems. Emulsion-based cleansers are recommended for people with dry skin.

(a) Cleansing cream

The original cleansing cream was based on one of the oldest-known emulsions and is commonly known as a cold cream. It was traditionally based on a mixture of natural waxes and vegetable oils (beeswax and olive oil) stabilized with borax. At the turn of the century, mineral oil replaced the more unstable vegetable oils as shown in the formula. In a cold cream the proportion of fatty and oily material predominates, but application to the skin results in a cooling effect which is produced from slow evaporation of the water contained in the emulsion (Formula 12).

The preservative of choice for cold creams used to be a combination of methyl parahydroxybenzoate (methylparaben) and propyl parahydroxybenzoate (propylparaben). Nevertheless, challenge testing must be conducted during the development stages to ensure that the product is adequately preserved and complies with microbiological guidelines.

Replacement of part of the mineral oil with up to 15% of petroleum jelly can be used to produce different textures and consistencies. Further substitution with fatty acid esters such as isopropyl myristate improves the thixotropic behaviour of the cream, thus improving its spreading properties. A modified cold cream formula is as follows (Formula 13).

Although the beeswax–borax system is still frequently used there are other emulsion systems which are also widely employed. The triethanolamine stearate and glyceryl stearate (self-emulsifying) systems have been used to develop lighter oil-in-water creams which tend to have better aesthetic properties. Cetyl alcohol acts as an emollient and, like carbomer 934 (carbopol 934), it increases the viscosity of the cream. Other hydrocolloids such as cellulose derivatives, alginates and magnesium aluminium silicate may be used to thicken the external phase of oil-in-water creams (Formulae 11, 15). Reduction of the oil phase will produce a lotion rather than a cream. Formula 11 is a cream whereas Formula 15 is a lotion.

(a) Rinse-off emulsions

Rinse-off emulsions are applied or massaged into the face and rinsed off with water rather than wiped off with a tissue. Some of these products will generate a

Formula Nos. 12–16 Cleansing creams

	% w/w				
	Borax		*TEA-soap*	*Lotion*	*Cream*
INCI	**12** *W/O*	**13** *W/O*	**14** *O/W*	**15** *O/W*	**16** *O/W*
A Mineral (Liquidum Paraffinum) Oil	45.0	40.0	30.0	20.0	–
Beeswax (Cera Alba)	16.0	16.0	–	10.0	–
Stearic Acid	–	–	10.0	–	1.0
Petroleum jelly, Petrolatum	–	5.0	–	–	–
Cetyl Alcohol	–	–	–	–	4.0
Lanolin	–	–	–	3.0	–
Isopropyl Myristate	–	5.0	–	–	–
Sorbiton Stearate*	–	–	–	5.0	–
Ethylene Glycol Monostearate†	–	–	–	–	3.0
Octyl-12-Hydroxy Stearate†	–	–	–	–	2.0
Lauric Isopropanolamide	–	–	–	–	3.0
Stearic Isopropanolamide	–	–	–	–	3.0
B Glycerin	–	–	1.0	–	–
Carbomer 934§, Carbomer	–	–	0.5	–	–
Tween 60*, Polysorbate 60	–	–	–	2.0	–
Sodium Cocoyl Isethionate ‡					
Fenapon HC 78	–	–	–	–	30.0
Borax	1.0	–	–	–	–
Triethanolamine	–	1.0	q.s.	–	–
Preservatives	q.s.	q.s.	q.s.	q.s.	q.s.
Water (deionized); Aqua	←		to 100		→
C Perfume, Parfum	q.s.	q.s.	q.s.	q.s.	q.s.

* ICI Speciality Chemicals. ‡ISP (Europe) GAF (GB) Ltd. † Croda Chemicals Ltd.
§B.F. Goodrich.

Procedure

Formulae 12, 13, 15, 16

1. Heat ingredients of phase A to 75°C in a jacketed vessel large enough for the whole batch and maintain heat.
2. In a separate container dissolve the ingredients of B in the water and heat to 75°C.

3. Slowly add B to A at 75°C with mixing.
4. Cool to 35°C and add perfume.

Formula 14

1. Hydrate the carbomer in water/glycerol mixture (B) and heat to 70°C.
2. Dissolve preservative in B and add triethanolamine. The amount must be derived by experimentation to give required final pH and consistency of cream. Maintain heat at 70°C.
3. Heat ingredients of A to 70–75°C and add B at 70°C.
4. Cool to 35°C while mixing slowly and add perfume.

small amount of lather whilst being washed off and are known as foaming cleansers. Such products incorporate some synthetic detergent to achieve this action. Consumers who enjoy using soap and water will prefer to use such products; they can still rinse with water but avoid the drying effects of soap or detergent-based cleansers.

Formula 16 is designed to be worked into a lather with water, massaged gently onto the facial skin and rinsed off.

(b) Cleansing fluid emulsions

Fluid emulsions are known as either milks or lotions. They can be described as low-viscosity alternatives to cleansing creams. They are applied to the skin with a tissue or cottonwool pad and so are often more economical than creams. In general these products contain mineral oil or other oils such as jojoba and other vegetable oils, plus fatty acid esters such as isopropyl palmitate. The introduction of nonionic emulsifiers gave the formulator a great deal of flexibility. These emulsifiers can either be used to supplement the type of systems described above or they can be used on their own. In this way anything from a textured cream to a stable pourable milk can be produced, as shown in formulations 17 and 19. Compare with Formula 15.

The next formulation (19) contains distilled lanolin alcohols (available as Super Hartolan from Croda Chemicals Ltd) which have excellent emulsifying properties especially in water-in-oil systems. They contain a high level of cholesterol which occurs naturally in the skin and provide emulsifying plus emollient attributes.

Formula 20 incorporates a sebum-absorbing material called polycocamido protein lipid sulfate (Polymer SBOCP from Brooks Industries). It serves to reduce the surfactant-loading required in oily-skin cleansers.

Cleansing milks

Formulae	% w/w			
	17	**18**	**19**	**20**
A Mineral Oil (Light Liquid Paraffin. BP) or Paraffinum Liquidum (INCI)	10.00	–	–	21.0
Mineral Oil (Heavy Paraffin Oil. BP) or Paraffinum Liquidum (INCI)	–	–	8.40	–
Stearic Acid	3.00	–	4.20	4.0
Cetyl Alcohol	0.50	–	0.40	–
Cetostearyl Alcohol	–	1.0	–	–
Distilled Lanolin Alcohols*	–	–	1.10	–
Steareth-100 (Brij 700)†	–	3.0	–	–
Diethylene Glycol Stearyl Oxide (Brij 72)†	–	3.0	–	–
PPG-15-Stearyl Ether (Arlamol E) †	–	3.0	–	–
Heptamethylnonane (Arlamol HD)†	–	7.0	–	–
B Carboxyvinyl Polymer (1342 Carbomer)‡	0.50	–	–	–
Hydroxyethyl Cellulose§	–	q.s.	–	–
Polyoxyethylene Sorbitol (Atlas G-2330)†	–	3.0	–	–
Sodium Cocoyl Isethionate (Arlatone SCI)†	–	10.0	–	–
Glycerin	1.00	–	–	–
Triethanolamine	1.80	–	2.10	1.5
Preservative	q.s.	q.s.	q.s.	q.s.
(Deionized) Water, Aqua	← to 100 →			
C Sodium Polycocamido Protein Lipid Sulfate (Polymer SBOCP)¶	–	–	–	5.0
D Perfume, Fragrance	q.s.	q.s.	q.s.	q.s.

Note that sodium polycocamido protein lipid sulfate is sebum absorbing.

* Croda Chemicals Ltd.
† ICI Speciality Chemicals.
‡ B.F. Goodrich.
§ Natrosol, Hercules. Can be used to achieve desired consistency.
¶ Brooks Industries Inc.

Procedure

Phase A

Formulae 17–20. Heat phase A to 70–75°C and maintain heat.

Phase B

Formula 17. Hydrate carbopol in water/glycerol mixture and heat to 70°C. Add rest of B and dissolve.

Formula 18. Heat water to 90°C to dissolve the Arlatone SCI completely. Cool to 70°C. Add predetermined amount of Natrosol solution. Add rest of B and dissolve.
Formulae 19 and 20. Heat water to 70°C to dissolve preservatives and add triethanolamine.

Emulsification

Formulae 17–20. Add B to A at 70°C while stirring. Continue stirring while cooling to 35°C.

Phase C

Formula 19. Add Polymer SBOCP while stirring.
Formulae 17–20. Add perfume while stirring

14.6 SKIN TONERS

Skin toners are called by a variety of names which include fresheners, clarifying lotions, tonics and astringents and are available as liquids, gels and creams. When applied onto the skin with a cottonwool pad, toners remove the final traces of grime, residues from soap or emulsion cleaners plus any loose flakes of dead skin. They leave the skin feeling clean, fresh and invigorated before a moisturizer or liquid foundation make-up is applied.

The active component of these products is astringent and so will exhibit the following properties to varying degrees: sensation of skin tightening, erection of hairs, temporary reduction of pore size, removal and reduction in skin oiliness, antiperspirancy, rapid coagulation of blood from a fresh wound and skin healing.

Materials with astringent properties can be classified as follows:

1. Short-chain alcohols – ethanol, isopropanol.
2. Organic acids with low molecular weight – lactic acid, citric acid.
3. Metal salts of organic or inorganic acids – aluminium sulfate and aluminium lactate.
4. Vegetable extracts containing tannins – witch hazel.

Basic skin toners will contain the astringent material, water, moisturizer and preservative.

Denatured ethanol is commonly used as the astringent material at levels of 5–25%.

14.6.1 Astringent lotions

Astringent lotions are useful in the control of very oily or acne-prone skin. These products often contain high levels of ethanol and sometimes isopropanol which exhibits stronger solvent properties. As well as its astringent properties, ethanol is an effective germicide/antiseptic and its evaporation from the skin provides a pleasant cooling sensation. In products for acne, antibacterial agents such as chloroxylenol, triclosan and benzalkonium chloride can be included to

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minimize bacterial proliferation. Keratolytic agents, such as salicyclic acid, are incorporated as exfoliants (Formula 21).

14.6.2 Toners and fresheners

Toners for dry and normal skin are often based on lower alcoholic strengths. At the present time alcohol-free toners are often preferred since alcohol can leave the skin feeling dry and does not project a natural image. Menthol can be used instead of ethanol to provide similar cooling sensations. A traditional skin tonic is shown in Formula 22.

Formula 23 shows a non-alcoholic formula which uses alternative moisturizers to glycerol which can leave an unpleasant sticky feel. In recent years a multitude of moisturizers have become available for these systems such as sodium hyaluronate, silicone derivatives such as dimethicone copolyol, jojoba ethoxylates, panthenol and water-soluble vitamin E derivatives. Formula 23 contains sodium pyrrolidone carboxylate (sodium PCA from A&E Connock Ltd) which is one of the constituents of the skin's natural moisturizing factor, NMF.

Skin toning lotions

	% w/w		
Formulae	**21**	**22**	**23**
CTFA/Chemical/INCI	Astringent (oily skin)	Normal/ dry skin	Ethanol-free for dry skin
Denatured ethanol, Alcohol Denat. (INCI)	20.00	5.00	–
Polyethylene oxide sorbitan monolaurate (Crillet 1)*, Polysorbate 20 (INCI)	–	1.25	–
Propylene Glycol	5.00	–	2.0
Glycerin	–	10.00	–
Preservative	–	q.s.	q.s.
Methyl *p*-hydroxybenzoate Methylparaben (Nipagin M)†	0.15	q.s.	q.s.
Pyrrolidone carboxylic acid sodium salt (Sodium PCA)‡	–	–	2.0
Witch Hazel (Hamamelis Virginiana) Extract‡	–	–	5.0
Cucumber (Cucumis Sativus) Extract‡	–	–	3.0
Polyoxyethylene (PEG) Glycol Oleyl Ether*	0.50	–	–
Perfume, Parfum, Fragrance	q.s.	q.s.	q.s.

(*Continued*)

Formulae	% w/w		
	21	**22**	**23**
CTFA/Chemical/INCI	Astringent (oily skin)	Normal/ dry skin	Ethanol-free for dry skin
Colour: water-soluble dye	q.s.	q.s.	q.s.
Hydrolysed Silk Proteins (Crosilk liquid)*	–	1.0	–
Water (deionized); Aqua	←	100	→

*Croda Chemicals Ltd. †Nipa Laboratories Ltd. ‡A&E Connock (Perfumes and Cosmetics) Ltd.

Procedure

Formula 21

1. Disperse the perfume in the PEG oleyl ether with gentle warming.
2. Add the ethanol; stir until clear.
3. Dissolve the Nipagin M in the propylene glycol and add to the main mixture.
4. Stir well and add water and colour.

Formula 22

1. Blend the silk protein and glycerol in the water.
2. Dissolve the Crillet 1 in the ethanol.
3. Add (2) to (1) while stirring.

Formula 23

1. Add all the ingredients to the water while stirring.

Toning solutions can be thickened to form attractive gels with carbomers, cellulose derivatives or isostearic acid. A clear toning gel can be prepared as shown in Formula 24.

A more sophisticated toning gel may be prepared with a variety of natural extracts in a hydroxypropyl methyl cellulose gel (Methocel 40-202E from Dow Corning).

Skin toning gels

Formulae	% w/w	
	24 Tonic normal/ oily skin	**25** Toning
Water (deionized); Aqua	← to 100	→
Carboxyvinyl Polymer Carbomer 940 (CTFA) (Carbopol 940*)	1.0	–

(*Continued*)

Formulae	% w/w	
	24 Tonic normal/ oily skin	**25** Toning
Hydroxymethyl cellulose (Methocel 10-202E)**	–	1.5
Glycerin	3.0	–
Sorbitol (70%)	3.0	–
Propylene Glycol	–	3.0
Preservative	q.s.	q.s.
Quaternium-15 (Dowicil 200**)	–	0.2
Deionized Water	–	3.0
Orange Flower Water†	–	5.0
Aloe vera (1–1)§ Aloe Barbadensis	–	5.0
Witch Hazel‡ (Hamamelis Virginiana) Distillate	–	15.0
Allantoin¶	–	0.2
Dimethicone Copolyol†	–	2.0
Menthol	–	0.5
Perfume, Parfum	q.s.	q.s.
Tween 20¶, Polysorbate 20	–	1.0
Triethanolamine	1.00–1.35	–
Lactic acid	–	to pH 5.0–6.0

*B.F. Goodrich. †Dow Corning. ‡William Ransome. §S. Black & Co.
¶Merck. ¶ICI Speciality Chemicals. **Dow Chemicals.

Procedure

Formula 24

1. Hydrate the carbomer 940 in water.
2. Dissolve the preservative in the glycerin, add to the carbopol solution.
3. Add the remaining ingredients.
4. Add the triethanolamine to the desired consistency.

Formula 25

1. Disperse the Methocel 40-202E in water with high-speed stirring.
2. Blend the next six components together and add to (1), while stirring.
3. Blend the preservative in the remaining water and add to the main batch while stirring.
4. Mix the menthol and perfume in the Tween 20, stir until clear and add to the batch.
5. Adjust pH to 5.0–6.0 with lactic acid.

14.7 POST-CLEANSING PRODUCTS

14.7.1 Care for dry skin

Since dry skin lacks water there are a number of ways that cosmetic formulations can temporarily reverse this by a process called moisturization. This is the ability of a preparation to increase the water content of the non-viable epidermis, that is the stratum corneum. Moisturizing creams, gels and lotions are applied for the relief of the signs and symptoms of dry skin, leaving it soft and smooth. The skin scales become more pliable and transparent and therefore less visible, and the appearance of the skin shows a dramatic improvement.

There are several methods of achieving moisturization, the most popular being the use of emollients and humectants (Table 14.6).

(a) Emollients

Application of a thin film of occlusive materials such as an oil or waxes makes the skin feel soft and smooth. These materials, commonly known as emollients, often reduce TEWL (transepidermal water loss) which tends to increase the water content of stratum corneum. Their rapid reversal of dry skin symptoms can be largely attributed to their ability to fill the cracks in the horny layer and glue down the protruding corneocytes. A list of commonly used emollients is given in Table 14.6, e.g. hydrocarbons, lanolin alcohols.

(b) Humectants

Certain hygroscopic materials known as humectants can draw water to the horny layer and hold it in the intercellular lipid matrix. This water would come from the water in the finished formulation and the lower epidermal layers rather than the external environment.

Controversy still surrounds the basis for the efficacy of a humectant. For example, work done by Batt and co-workers [10] shows that the application of a 10% aqueous solution of glycerol significantly increases TEWL. However, the application of 15% aqueous glycerol to the forearm significantly decreased TEWL for up to 4 hours and reduced skin roughness. Note that 98% solution of glycerol will absorb water from the skin in a dry atmosphere until it reaches a 30% active equilibrium mixture when it exhibits its humectant properties. One could postulate that topically applied glycerol may become involved in various biochemical processes in the stratum corneum which are not clearly understood at present.

(c) Hydrophilic matrices

Materials such as hyaluronic acid and colloidal oatmeal act as a type of blanket which provides protection as well as moisture to the skin.

Table 14.6 Raw materials commonly used in moisturizing formulations

Function	*Class*	*Examples*
Moisturizer	Hydrocarbons	Mineral oil, squalane, petrolatum
	Polyols (humectants)	Propylene glycol Glycerin, sorbitol
	Lanolin derivatives	Lanolin, lanolin alcohols
	Silicones	Dimethicone, cyclomethicone
	Fatty acids	Stearic acid, linoleic, isostearic acid
	Fatty alcohols	Cetyl alcohol, stearyl alcohol, cetearyl alcohol
	Esters	Isopropyl myristate, isopropyl palmitate, jojoba oil
	Triglycerides	Sesame oil, sweet almond oil, Cocoa butter
	Amino acids	Hydrolysed animal protein, collagen, milk protein, silk amino acids
	Miscellaneous	Urea, lecithin, aloe vera,
Antioxidants/stabilizers		Butyl hydroxy anisole (BHA) Butyl hydroxy toluene (BHT) Tocopherol
Emulsifying agents	Soaps	Stearates (NH4, K), Myristates (Na, TEA) Isostearates Beeswax/borax
	Esters	Glyceryl stearates Sorbitan stearates PEG stearates
	Fatty alcohols	Cetyl, Stearyl, Cetearyl alcohols
	Polymers	Carbomers, Xanthan Gum, Cellulose Gum, Polyglyceryl Methacrylate
	Sterols	Lanolin alcohol, Cholesterol, Soyasterol
	Esters	PEG 40-caster oil, Steareth-21, Ceteareth-5, Isosteareth-20
	Silicones	Cetyldimethicone Copolyol
	Anionics	Lauryl Sulfates (Na, TEA)
	Cationics	PEG15-Cocamine Stearylalkonium Chloride
	Amphoterics	Sodiumlaurimino Dipropionate
	Others	Lecithin

14.7. 2 Basic components of moisturizing/nourishing products

Unfortunately the majority of effective moisturizing actives cannot be applied without some modification because they are difficult to apply and can leave the skin feeling tacky. For this reason they are formulated into cosmetic emulsions and microemulsions which can be stabilized with an appropriate emulsifier system. As a result of the wide choice of emulsifiers, moisturizing products, like emulsion-based cleansers, are available as milks, lotions, creams, clear gels and aerosol mousses.

On the whole a good moisturizing formulation is non-irritant, easy to spread over the skin, easy to rub in without 'soaping up', able to leave the skin feeling soft rather than sticky, and pleasantly perfumed. If the product is to be unperfumed there should be no fatty base odour. The basic components of a moisturizing product include moisturizer(s), emulsifier system, water, preservative and antioxidants if necessary. Examples of commonly used components are listed in Table 14.6. Emulsifiers are dealt with in Chapter 19. It becomes obvious that the extensive catalogue of components can generate an infinite number of formulations. Resulting formulations will therefore depend on the choice and experience of the formulation chemist. Therefore the examples of formulations given here represent a basic guide and not an exhaustive account.

Moisturizing preparations can be classified into five groups.

1. Day preparations.
2. Night preparations.
3. Hand and body lotions.
4. All-purpose products.
5. Barrier creams.

14.7.3 Day preparations

Day moisturizing products tend to be light, oil-in-water emulsions which are designed to spread easily and rub into the skin quickly. They, like liquid foundation creams, have evolved from the traditional vanishing cream system which is an oil-in-water emulsion that is based on high-quality stearic acid as the oil phase. Commercial triple-pressed stearic acid consists of a mixture of stearic and palmitic acid with a tiny amount of oleic acid. Partial neutralization of the fatty acid (16–20%) with a base such as triethanolamine or potassium hydroxide produces a soap which constitutes the emulsifier system. The nature of the neutralizing base plus the degree of saponification will determine the consistency and texture of the cream. For instance, potassium hydroxide will produce harder soap than triethanolamine.

Examples of simple vanishing creams are shown in Formulae 26 and 27.

These soap-based oil-in-water creams give a wet feel on the skin when first applied. They do not rub in well and appear soapy and white. Traditionally

excess stearic acid was used to counteract this but left a tackiness on the skin when the 'vanishing' cream's water had dried out. It also tended to make the cream thixotropic and appear thin when applied. The addition of dimethicone copolyols is another method of overcoming the soapiness.

Secondary emulsifiers such as self-emulsifying glyceryl monostearate and other nonionic surfactants such as polyethylene glycol esters and fatty alcohol ethers can be used to prevent any skin dryness which may result from use of the alkali-stearate soaps. Other emulsion stabilizers include the carbomers and fatty alcohols such as cetyl alcohol. Cationic surfactants, such as stearalkonium chloride, are used to a lesser extent as emulsifiers. Because of their substantivity to the skin, they may be used to give an additional smooth skin feel after application.

Day creams

	Formulae	**26**	**27**	**28**	**29**
	CTFH/Chemical/INCI names		*% w/w*		
A	Stearic Acid (triple-pressed)	20.00	23.00	–	2.00
	Isopropyl Palmitate	–	3.00	–	–
	Mineral Oil, Paraffinum Liquidum (Light liquid Paraffin)	–	–	4.00	2.00
	Cetyl Alcohol	–	–	3.00	2.00
	Glyceryl Monostearate (Self-emulsifying)	–	–	12.00	–
	Polyoxyethylene (fatty ester (Arlatone 983S))*	–	–	–	4.00
B	Glycerol	4.00	6.00	12.00	1.50
	Propylene Glycol	–	–	–	2.00
	Preservative	q.s.	q.s.	q.s.	q.s.
	Potassium Hydroxide	1.40	–	–	–
	Triethanolamine	–	1.40	–	–
	Deionized water (Aqua)	←	100	→	86.50
C	Perfume	q.s.	q.s.	q.s.	q.s.

* ICI Speciality Chemicals.

Procedure

1. Heat A and B independently to 75°C.
2. Add A to B slowly with continuous stirring.
3. Cool to 35°C and add perfume.

Note: (ICI Speciality Chemicals) Formula 29. To alter the viscosity from 120 000 mPas (measured 7 days after manufacture. Brooktield LVT,TF spindle, 6 rpm, 1 minute) vary the percentage of stearic acid and/or cetyl alcohol.

The combined use of nonionic emulsifiers and the HLB system gives the formulation chemist a great deal of flexibility in the development of stable emulsions for varying oil/water combinations. Number 29 is a cream, number 30 is a milk.

Formula No. 30 Moisturizing milk

		INCI/CTFA name/chemical description	*% w/w*
A	Arlatone 983S*	PEG-5 Glyceryl Stearate	1.50
	Brij 76*	Steareth-10	1.50
		Cetyl Alcohol	0.80
	Light liquid paraffin oil (Mineral oil)	Mineral (Paraffinum Liquidum) Oil	9.00
	Miglyol 812†	Caprylic/Capric Triglyceride	4.00
B	Hygroplex HHG‡	Hexylene Glycol (and) Fructose (and) Glucose (and) Sucrose (and) Urea (and) Dextrin (and) Alanine (and) Glutamic Acid (and) Aspartic Acid (and) Hexyl Nicotinate	5.00
Preservative			q.s.
Deionized water		Water, Aqua	to 100%
C	Carbopol 941§	Carbomer	0.15
Deionized Water		Water, Aqua	15.00
D		Triethanolamine	0.15
Deionized water		Water, Aqua	8.00
E	Perfume	Parfum, Fragrance	q.s.

*ICI Speciality Chemicals Ltd. †Dynamic Nobel. ‡Chem Lab Dr K. Richter.
§B.F. Goodrich.

Procedure

1. Heat (A), (B), (C) and (D) to 70°C independently.
2. Add (B) slowly to (A) whilst stirring thoroughly.
3. Add (C) followed by (D) whilst stirring.
4. Homogenize the mixture.
5. Cool to 35°C add (E).
6. Cool to 30°C.

(a) Natural additives

In the past decade the demand by the consumer for 'natural products' has increased. Although a general consensus as to what constitutes a natural product has not yet been agreed, it is very difficult to develop a completely natural product. The cosmetic industry has responded in a number of ways. The most common method is to add small amounts of oils or hydroalcoholic extracts from

plants and, less often, animal extracts. Although the list of naturals are endless they tend to be fruit and vegetable extracts, vitamins and amino acids. Some examples of natural plant additives are given in Table 14.7. The natural theme runs through many skin-care products today.

The next formula uses fresh plant extracts, hyaluronic acid and the biofactor iniferine to deliver essential nutrients to the skin. Tocopherylacetate is included as an emollient and free radical scavenger. The formulation is stabilized by

Table 14.7 Some plant extracts commonly used in skin-care products and their properties

	Main actives	*Properties*
Cucumber	Glycosides, amino acids, sulfur compounds, enzymes	Moisturing, refreshing
Burdock	Inulin, mucus, resins, tannins	Antimicrobial
Hops	Essential oils, bitter substances, vegetable hormones	Invigorating, toning
Marigold	Carotinoids, saponins, triterpene, polysaccharides	Stimulating, moisturizing for oily skin
Birch	Essential oils, tannins	Astringents, stimulate blood circulation
Watercress	Mustard glycosides, essential oils with raphanol	Antimicrobial, cosmetics for greasy skin, freckles, spots
Gentian	Glycosidic bitter substances, essential oils	Antimicrobial, astringent, stimulating
Fir	Oily resins, tannins, Vitamin C	Toning, softening, deodorizing, antimicrobial
Daisy Flower	Saponin, tannins, essential oils	Anti-inflammatory (in cosmetics for spots)
Witch Hazel	Mucilages, flavonoids, gallic acid	Cooling astringent, stimulates blood circulation; ideal for sensitive skin, including baby's
Indian cress	Mustard glucosides, glycotropaeolin	Invigorating, antimicrobial, antiseborrhoeic
Rosemary	Essential oils, tannins, flavonoids	Toning, astringent, stimulates blood circulation
Sage	Essential oils, tannins, saponin, flavenoids	Astringent, antimicrobial
Horsetail	Silicic acid, saponin, flavonoids	Astringent
Thyme	Essential oils with thymol, bitter substances, tannins	Astringent, deodorizing

nonionic emulsifiers and Aloe Moist, which is a gelling agent based on Aloe vera and polyglycerylmethacrylate.

Formula No. 31 Stimulating day cream

		INCI/CTFA name/chemical description	*% w/w*
A	Naturchem GMHS*	Glyceryl Hydroxy Stearate	4.00
	Naturchem THS 200*	PEG-200 Trihydroxy Stearin	4.30
	Waxenol 816*	Cetyl Palmitate	2.00
	Waxenol 801*	Arachidyl Propionate	4.00
	Wickenol 171*	Octyl Hydroxy Stearate	8.00
		Tocopheryl Acetate	1.00
B	Aloe Moist†	Aloe Vera Gel (and) Polyglyceryl Methacrylate (and) Propylene Glycol	20.00
	Deionized water	Water, Aqua	to 100%
C	Iniferine‡	Water (and) Lactoferrin (and) Thioxanthine (and) Uric Acid	
	Bio-Hyaluronic Acid‡	Hyaluronic acid	0.02
	Mallow Fresh Plant Extract PG‡	Mallow (Malva Sylvestris) Extract	2.50
	Cucumber Fresh Plant extract PG‡	Cucumber (Cucumis Sativas) Extract	2.50
D	Perfume	Parfum	q.s.
	Preservative		q.s.

*Caschem Inc. †Terry Corporation (USA): S. Black (UK). ‡Rahn.

Procedure

1. Heat (A) and (B) separately to 75°C.
2. Add (B) slowly to (A) whilst stirring.
3. Cool to 35°C with stirring.
4. Slowly add (C) and (D).

A skin cream for sensitive skin, described below, contains the vegetable oils, sunflower and wheat germ plus the vitamin, d-panthenol, which act as gentle yet effective moisturizers.

Formula No. 32 Day cream for sensitive skin

		INCI/CTFA name/chemical description	*% w/w*
A	Brij 721* Polyoxyethylene-(21) stearyl alcohol	Steareth-21	2.0
	Brij 72*	Steareth-2	3.0

Formula No. 32 (*Continued*)

	INCI/CTFA name/chemical description	*% w/w*
Polyoxyethylene-(2) Stearyl Alcohol		3.0
Silicone fluid		2.0
	Beeswax (Cera Alba)	2.0
Lorol C16†	Cetyl Alcohol	1.0
Sunflower oil	Sunflower (Helianthus Annus) Seed Oil	6.0
Mineral oil	Mineral (Paraffinum Liquidum) Oil	4.0
Wheat Germ Oil	Wheat (Triticum Vulgare) Germ Oil	1.0
Arlamol D4* Octamethyl cyclotetra siloxane	Cyclotetrasiloxane	3.0
B	Glycerin	5.0
D-Panthenol‡	Panthenol	2.0
	Deionized water, Aqua	to 100%
Preservative		q.s.
C	Collagen	3.0
D Perfume	Parfum	q.s.

* Uniqema (ICI Speciality Chemicals). † Henkel GmbH. ‡ Roche.

Procedure

1. Heat (A) and (B) separately to 70°C.
2. Add (B) to (A) whilst stirring.
3. Homogenize the mixture.
4. Add (C) and (D) below 35°C with stirring.

Formula No. 33 Cream for oily skin

	INCI/CTFA name/chemical description	*% w/w*
A	Stearic Acid	1.00
	Cetyl Alcohol	1.00
Arlamol E*	PG-15 stearyl alcohol	1.00
Brij 72*	Steareth-2	3.50
Brij 721*	Steareth-21	1.50
Precipitated sulfur USP	Sulfur	4.00
B	Propylene Glycol	3.80
Nigapin M†		0.20
Methyl-*p*-hydroxy benzoate	Methylparaben	0.20
	Salicylic acid	1.00
C	Deionized Water, Aqua	to 100%
Perfume	Parfum	q.s.

* Uniqema (ICI Speciality Chemicals). † Nipa Laboratories.

Procedure

1. Heat (A) and (B) to 70°C separately.
2. Add (B) slowly to (A) whilst stirring continuously.
3. Homogenize the mixture.
4. Cool to 35°C, add (C).
5. Cool to 30°C.

14.7.4 Special additives/nutrients

The special additives or nutrients have become very sophisticated and expensive. Because of the expense, many of these additives are not incorporated at a high enough level to become truly functional within the product, unless it is sold at a premium price.

(a) Vitamins

The dietary importance of vitamins is well established. However, there is a growing interest in their topical application. The most commonly used vitamins include E, A, C and panthenol. Vitamin E (*dl*-alpha-tocopherol) is employed as an antioxidant/free radical scavenger. In this role it has been shown that levels of about 5% reduce membrane phospholipid peroxidation. Peroxides are involved in the cellular damage caused during photo-ageing. Vitamin E acetate, a more stable form, is often used as an emollient in skin creams and gels.

The group of chemicals derived from vitamin A, known as retinoids (all-*trans* retinoic acid or tretinoin) have been most widely used in the treatment of photo-damaged skin. Renova, an emollient-based form of tretinoin, has received FDA approval for the cosmetic treatment of ageing skin. Structural improvements brought about by this material include normalization of epidermal activity, formation of new collagen and blood vessels, and reduction in pigmentary changes. A typical regimen would use 0.025–0.05% of tretinoin as a starting concentration. It is important to note that this material is a photosensitizer and is recommended for use during the night. Also, initial side-effects can include dryness, erythema and itching, which are supposed to diminish after the first three months. Recent developments suggest that aromatic retinoids could present a non-irritant alternative to tretinoin.

Another derivative of vitamin A, its palmitate, can be incorporated into creams to help maintain the skin's barrier properties by stimulating the epidermal cells to produce glycolipids. The latter are important in the formation of the intercellular lipid lamellar structure.

Vitamin C (ascorbic acid) is another natural antioxidant which regulates collagen biosynthesis and is involved in the wound-healing process of the body. It also helps to regenerate vitamin E to its parent form and therefore its ability to scavenge free radicals. Ascorbic acid is claimed to inhibit the photo-induced damage of the skin.

(b) Proteins

Protein derivatives such as hydrolysed protein, amino acids and proteoglycans are very substantive to the skin, leaving it feeling soft and smooth. The most popular types include collagen, hyaluronic acid, milk proteins, silk proteins and amino acids, and (more recently) marine proteins.

(c) Essential fatty acids

γ-Linolenic acid (GLA) is an essential fatty acid which occurs naturally in many vegetable seed oils such as evening primrose oil (9–10%) and borage oil (23–25%). GLA is said to improve the skin's efficiency as a barrier to transepidermal water loss. In addition it is thought to become incorporated into the skin's structural lipids thus increasing the suppleness and flexibility of the epidermis.

(d) Hydroxy acids

The use of α-hydroxy acids and more recently β-hydroxy and α-keto acids in the treatment of ageing skin has attracted much interest over the past decade. These organic acids are normally synthesized but can be derived from natural sources such as sugar cane, sour milk and citrus fruits. They include lactic, glycolic, malic, tartaric, citric, gluconic, mandelic and salicylic acids.

These materials possess epidermal renewal properties such as reduction of corneocyte adhesion at the base of the stratum corneum and an increase in skin hydration, so that when applied in a cream to rough dry skin, accumulated corneocytes are shed as cell turnover rate increases, leaving smoother skin.

This is also accompanied by a reduction in hyperpigmentation. In the long term these materials have been shown to increase collagen and elastin synthesis. The most effective α-hydroxy acids tend to be lactic and glycolic and are used at 1–5% in mass products. Higher levels (up to 15%) can be used under the supervision of a dermatologist or trained beauty therapist. Alpha-hydroxy acids can often cause irritation because of their low pH and are supplied as buffered solutions of pH 4.5.

Recent *in-vitro* studies show that conjugating α-hydroxy acids with amino acids could significantly reduce irritation. Examples of conjugated materials include arginine (pH 6.8) and arginine lactate (pH 6.0).

The β-hydroxy acid, salicylic acid, has been used as a peeling agent by dermatologists for many years. It is longer-acting and less irritating than the α-hydroxy acids.

(e) β-Glucans

β-Glucans are polysaccharide materials derived from natural oats, wheat and baker's yeast. They are chemically modified to make them water-soluble; for example, yeast β-glucans undergo partial carboxymethylation to form carboxy

methylated-β(1-3),(1-6)-glucan. They are used in medicine in the management of wound healing. In skin-care and sunscreen products β-glucans have been shown to reduce oxygen radical formation and stimulate the Langerhans' cells in UV-radiated skin. Oat β-glucans, at 1% in topical creams, also exhibited the following properties: stimulation of collagen synthesis, increase in epidermal turnover rate, reduction of fine wrinkles, reduction in skin damage caused by a detergent challenge [11].

14.7.5 Additives which aid delivery of actives

As skin-care systems increase in complexity, new methods of delivering chemically incompatible cocktails of actives to the skin have grown in importance. Initially they were presented as marketing gimmicks but with a growing number of educated and demanding consumers they have become a serious formulation tool. Delivery systems have expanded from emulsions and microcapsules to multiple emulsions, liposomes, cyclodextrin, polymeric systems and patch technology. Several of these systems are summarized below.

(a) Microcapsule

Microcapsules represent the oldest controlled-release techniques utilized in topical formulations. They are composed of a hollow vesicle containing an active ingredient.

(b) Liposomes

Liposomes can be defined as microscopic spherical vesicles in which the membranes consist of a bilayer of amphiphilic molecules.

The membranes of true liposomes consist of phospholipids which are important building blocks for biological cell membranes. Vesicles which consist of nonionic surfactants are called niosomes. For this reason liposomes have been termed membrane-mimetic structures, which because of their biocompatibility and size (15–3500 nm), efficiently penetrate the skin, unlike classical emulsions. Plant phospholipids (lecithin) tend to be used because of their high content of esterified polyunsaturated fatty acids such as linoleic acid. As a type of microencapsulation technology, liposomes represent a safe way of delivering actives such as moisturizers and vitamins to the deeper layers of the skin [9]. The latter can adhere to the corneocyte, releasing the actives either by diffusion or during the fusion of the liposome walls with the lipids or proteins of the stratum corneum.

Formula No. 34 shows a light moisturizer based on liposomes (lecithin) that delivers evening primrose oil which is rich in γ-linolenic acid. The acrylates/C10-30 alkyl acrylate cross-polymer is used as the emulsifying agent.

Formula No. 34 Liposome moisturizing lotion

		INCI/CTFA name/chemical description	*% w/w*
A	Pemulen TR-I*	Acrylates/C10-30 Alkyl Acrylate Cross-polymer	0.25
	Carbopol Ultrez*	Carbomer	0.20
		Caprylic/Capric Triglycerides	3.00
		Octyl Stearate	8.00
		Mineral (Paraffinum Liquidum) Oil	7.00
B	Deionized Water	Water, Aqua	75.55
		Glycerin	2.00
C		Sodium hydroxide (18%)	0.50
D		Lecithin (and) evening primrose oil	3.00

* B.F. Goodrich.

Procedure

1. Combine the ingredients in part A in final vessel. Mix the ingredients with rapid stirring to disperse the polymers.
2. Combine the ingredients of part B and mix until homogeneous.
3. Add three-quarters of part B to part A slowly with strong mixing. Mix for about 20 minutes to swell the polymers.
4. When the emulsion is smooth and white, add part of the sodium hydroxide and bring the pH to 7.0 then continue to mix until smooth and uniform.
5. Slowly add the remainder of part B with moderate mixing.
6. Add the remaining sodium hydroxide.
7. Add the preservative and mix. Add the liposomes using slow agitation to avoid rupturing them.
8. Mix until uniform.

(c) Cyclodextrins

Cyclodextrins are starch derivatives which consist of a unique three-dimensional structure. They have the ability to incorporate other so-called 'guest molecules' into their cavity. They reduce skin penetration and thereby protect the skin from the undesirable properties of the active material.

(d) Porous polymeric systems

Porous polymeric systems act like human cells but instead of being surrounded by a membrane wall they are open to the external environment, allowing movement of molecules in and out. Release of the active ingredient occurs on the skin surface mainly by the partitioning of the active between the polymer and the skin.

14.7.6 Night preparations

Products which are supposed to be left on the skin overnight serve to provide vital nutrients to the skin which may have been lost during the day. Some examples of

nutrients which can be used will be discussed later in this section. These products, like massage creams, tend to be water-in-oil emulsions which are available as creams and viscous lotions. Water-in-oil emulsions tend to be less cosmetically elegant than the oil-in-water types because of the difficulty of rubbing them in; in addition they are apt to leave a feeling of stickiness on the skin. These effects can be attributed to the presence of waxes in the formulations necessary to provide a rigid rubbing-in time needed, the greater the reinforcement of a consumer's perception of the product being 'nutritive' to the skin. One of the advantages that water-in-oil systems have over their oil-in-water counterparts is that the continuous oil phase has direct contact with the skin and forms a protective film immediately without any detergent action. In this way the dispersed water particles are trapped in the oil by the water-in-oil emulsifiers and the product is more resistant to being washed off. Therefore such products have remained popular with people with dry skin.

Traditional night creams were originally based on the beeswax, borax and mineral oil systems. Today other waxes, vegetable oils and silicone oils (instead of mineral oil) can be used as emollients and co-emulsifiers, such as quaternary ammonium salts or the volatile silicones such as cyclomethicone.

Distilled lanolin alcohols (Super Hartolan-Croda Ltd) are excellent water-in-oil emulsifiers especially when formulating milks and lotions as shown in the next formula.

Formula No. 35 Replenishing night lotion

		INCI/CTFA name/ chemical description	*% w/w*
A	Cropure apricot kernel*	Apricot (Prunus Armeniaca) Kernel Oil*	8.00
	Mineral Oil 25cS at 25°C	Mineral (Paraffinum Liquidum) Oil	4.00
		Squalene	3.00
	Satulan*	Hydrogenated Lanolin	2.00
	Volpo L23*	C12-13 Pareth-23	2.00
	Cropure avocado oil*	Avocado (Persea Gratissima) Oil	1.50
		Stearic Acid	1.50
	Cithrol GMS N/E*	Glyceryl Stearate	1.50
	Crodacol C90EP*	Cetyl Alcohol	1.00
	Crodamol GTCC*	Caprylic/Capric Triglyceride	1.00
	Super Hartolan*	Lanolin Alcohol	0.50
	Calendula oil Monarom*	(Soybean Oil (and) Calendula Officinalis Extract (and) Tocopherol)	0.50
	Arnicaflower oil Panarom*	(Soybean Oil (and) Arnica Montana Extract (and) Isopropyl Myristate (and) Tocopherol	0.50

Formula No. 35 (*Continued*)

		INCI/CTFA name/ chemical description	*% w/w*
	Vitamin E acetate†	Tocopheryl Acetate	0.50
B	Deionized water	Water, Aqua	to 100
		Propylene Glycol	4.00
	Carbopol 981§	Carbomer	0.15
		Preservative	q.s.
C		Triethanolamine	q.s.
D	Collasol (2% Collagen)	Soluble Collagen	3.00
	Deionized water	Water, Aqua	3.00
E	Perfume	Parfum, Fragrance	q.s.

*Croda Oleochemicals Ltd. †Roche. §B.F. Goodrich.

Procedure

1. Hydrate carbopol in hot water (65–70°C). Dissolve preservative in propylene glycol and add to carbopol solution (B).
2. Combine components of (A) and heat to 70°C.
3. Add (B) to (A) whilst stirring.
4. Adjust pH to 5.5–6.5 with (C).
5. Cool to 35°C, add perfume (E).
6. Cool to 30°C, add collagen in water of (D).

A new range of silicone emulsifiers such as lauryl methicone copolyol (Q2-500 from Dow Corning) and cetyl dimethicone copolyol (Abil EM90 from Th. Goldschmidt) have recently become available. These can be used to produce stable water-in-oil formulations with up to 74% water with little or no waxes. Therefore the resulting formulations exhibit excellent moisturizing properties combined with improved aesthetics. Examples of formulations using this technology are given below. Formula No. 37 is particularly interesting since it contains a high level of avocado oil which tends to be rather difficult to emulsify.

Formula No. 36 Night cream

	INCI/CTFA name/chemical description	*% w/w*
A (hot)		
	Mineral (Paraffinum Liquidum) Oil	11.00
Dow Corning 200/50*	Dimethicone	2.00
Ceraphyl 424†	Myristyl Myristate	2.00
Crodomol IPM‡	Isopropyl Myristate	2.00
Dow Corning Q2-500*	Lauryl Dimethicone Copolyol	2.00
Witconol APM§	PPG-3 Myristyl Ether	0.50

Formula No. 36 (*Continued*)

	INCI/CTFA name/chemical description	*% w/w*
B (cold)		
Glycerol	Glycerin	5.00
	Sodium chloride	2.00
Deionized water	Water, Aqua	to 100%
Preservative		q.s.
C (cold)		
Dow Corning 1101*	Cyclomethicone (and) Dimethicone	2.00
D Perfume	Parfum	q.s.

* Dow Corning Corporation. † Van Dyke. ‡ Croda Chemicals Ltd. § Witco.

Procedure

1. Heat (A) to 40°C. Dissolve preservative in glycerol/water. Add salt.
2. Using a homogenizer add 1% of (B) into (A). Agitate until uniform.
3. Add remaining (B) slowly to (A) with moderate agitation.
4. Cool to 30°C, add (C).
5. Add (D).

Formula No. 37 Night cream with avocado oil

	INCI/CTFA name/chemical description	*% w/w*
A (hot)		
	Avocado (Persea Gratissima) Oil	25.50
Abil EM 90*	Cetyl Dimethicone Copolyol	2.50
	Hydrogenated Castor Oil	0.80
	Beeswax (Cera Alba)	1.20
B (cold)		
	Sodium chloride	0.50
Deionized water	Water, Aqua	to 100%
Preservative		q.s.
Perfume	Parfum, Fragrance	q.s.

* Th. Goldschmidt.

Procedure

1. Heat (A) to 75°C. Dissolve preservative in glycerol/water. Add salt.
2. Add (B) slowly to (A) whilst stirring.
3. Cool to 35°C, add perfume.
4. Homogenize once the cream has cooled to 25°C.

14.7.7 Hand and body lotions

Products for use on the hands and body tend to be similar in formulation to the day moisturizers. They are usually lotions and sometimes aerosol mousses rather than creams, for ease of application. This can be achieved by increasing the viscosity of the water phase with agents such as the carbomers and cellulose derivatives.

The formula described below contains a high level of the humectants, glycerol and sorbitol. The distilled lanolin alcohols may be added to improve the barrier-forming properties on the skin.

Formula No. 38 Hand and body lotion

		INCI/CTFA name/chemical description	*% w/w*
A	Light Liquid Paraffin B.P.	Mineral (Paraffinum Liquidum) Oil	10.00
	Super Hartolan*	Lanolin Alcohol	2.00
	Cetyl Alcohol		2.00
	Stearic Acid		20.00
	Arlacel 83†	Sorbitan Sesquioleate	2.00
B	Glycerin	Glycerin	7.50
	Sorbitol 70% solution	Sorbitol	2.50
	Propylene Glycol	Propylene Glycol	5.00
	Deionized water	Water, Aqua	to 100%
	Triethanolamine		5.00
	Preservative		q.s.
	Perfume	Parfum, Fragrance	q.s.

* Croda Chemicals Ltd. † ICI Speciality Chemicals.

Procedure

1. Heat (A) and (B) independently to 75°C.
2. Add (B) to (A) slowly with continuous stirring.
3. Cool to 35°C, add perfume.

The following formula uses a cationic emulsifier, distearyl dimonium chloride, to leave a smooth dry afterfeel. A castor oil derivative, methyl cetate ricinoleate, is used instead of mineral oil to give a non-greasy product. Methyl cellulose (Methocel E4M – Dow Chemical Company) is used to increase the viscosity of the external water phase as described above.

Formula No. 39 Hand and body lotion

		INCI/CTFA name/chemical description	*% w/w*
A	Methocel E4M* (2%)	Methylcellulose (2% solution)	10.00
	Deionized water	Water, Aqua	to 100
B		Propylene Glycol	1.00
	Methyl-*p*-hydroxybenzoate	Methylparaben†	0.25
	Propyl-*p*-hydroxybenzoate	Propyl paraben†	0.10
C	Arosurf TA-100†	Distearyldimonium Chloride	1.50
	Naturechem GMHS§	Glyceryl Hydroxystearate	2.00
	Naturechem MAR§	Methyl Acetate Ricinoleate	10.00

Formula No. 39 (*Continued*)

		INCI/CTFA name/chemical description	*% w/w*
	SF 96-350[¶]	Dimethicone	1.00
D		Perfume	q.s.

* Dow Chemical Company. † Nipa Labs. ‡ Sherex Chemical Company. § CasChem, Inc. ¶GEC Silicone Products.

Procedure

1. Heat (A) to 80°C.
2. Heat (B) until preservatives are dissolved.
3. Heat (C) to 80°C and add to (AB) whilst stirring.
4. Cool to 35°C, add perfume (D).

The next formulation includes jojoba oil which is a liquid wax as an emollient and allantoin for its soothing properties.

Formula No. 40 Jojoba hand and body lotion

		INCI/CTFA name/chemical description	*% w/w*
A	Petroleum Jelly	Petrolatum	0.50
	Stearic Acid	Stearic Acid	0.75
	Cetyl Alcohol	Cetyl Alcohol	1.00
	Glyceryl Monostearate	Glyceryl Stearate (SE)	1.00
	Isopropyl Myristate	Isopropyl Myristate	2.40
	Mineral oil, Light Liquid Paraffin	Mineral (Paraffinum Liquidum) Oil	0.20
	Jojoba liquid wax*	Jojoba Wax	2.00
	Cremaphor A†	Ceteareth-6 (and) Stearyl alcohol	2.45
B	Allantoin	Allantoin	0.15
	Glycerol/Glycerin	Glycerin	1.50
	Preservative		q.s.
	Deionized Water	Water, Aqua	to 100%
	Triethanolamine	Triethanolamine	0.30
	FD&C yellow No. 5‡ (0.1% aq.solution)	FD&C Yellow No. 5 C I 19140	0.10
C	Perfume	Parfum, Fragrance	q.s.

* A & E Connock (Perfume and Cosmetics) Ltd. † BASF. ‡ D.F. Anstead

Procedure

1. Heat (A) and (B) independently to 70°C.
2. Add (B) to (A) whilst stirring.
3. Cool to 35°C and add perfume (C).

The following formulation uses cocoa butter and lanolin oil, which is rich in cholesterol, to provide excellent emolliency. The emollient ester glyceryl tricaprylate/caprate (Crodamol GTCC – Croda Ltd) is a reconstituted vegetable oil that improves the spreading properties of the cream on the skin. An antioxidant should be included to prevent any rancidity.

Formula No. 41 Cocoa butter lotion

		INCI/CTFA name/chemical description	*% w/w*
A	Caprylic/C	Caprylic/Capric Triglyceride	2.00
	Cocoa butter (refined)	Cocoa (Theobroma Cacao) Butter	2.00
	Fluilan*	Lanolin Oil	1.00
	Stearic acid	Stearic Acid	2.00
	Polawax GP200*	Proprietary nonionic wax blend	0.75
	GMS S/E GE802*	Glyceryl Stearate SE	2.00
	Silicone oil F111/100†	Dimethicone	1.00
B	Deionized water	Water, Aqua	to 100
		Glycerin	4.00
		Triethanolamine	0.93
		Preservative	q.s.
C	Perfume	Parfum	q.s.

* Croda Oleochemicals Ltd. † ICI Speciality Chemicals. Unichema (ICI Chemicals)

Procedure

1. Heat (A) and (B) independently to 70°C.
2. Add (B) to (A) whilst stirring.
3. Cool to 35°C, add perfume (C).

14.7.8 All-purpose products

As their name suggests, all-purpose creams and lotions can be used as a moisturizer or a cleansing cream on the face, hands and body.

A simple, all-purpose cream can be formulated with polypropylene glycol (PPG) stearyl ether (Arlamol E, ICI Speciality Chemicals) as the emollient and stabilized with stearyl alcohol and nonionic emulsifiers (Formula 42).

Formula 43 describes a cream with a high mineral oil content. The latter combines efficient soil removal with emolliency. The magnesium sulfate is added as an emulsion stabilizer.

All-purpose milks have become popular because of their light texture and ease of spreading. In Formula No. 44 heptamethylnonane and PPG-15 stearyl ether/cyclomethicone (Arlamol HD and Arlamol S3 – Uniqema (ICI Speciality

Chemicals)) together with paraffin oil are used for their emolliency. Urea is included for its moisturizing properties.

An attractive microemulsion gel, No. 45, can be formulated using an emulsifier with a high HLB number such as ceteareth-30 (Emulgin B3 – Henkel). The octyldodecanol and PEG-7 glyceryl cocoate exhibit both emollient and emulsifying properties.

All-purpose products

		% w/w			
	INCI names (commercial names bracketed) **Formulae**	**42** Cream	**43** Cream	**44** Milk	**45** Microemulsion gel
A	PPG-15 Stearyl Ether (Arlamol E)*	20.00	–	–	–
	Steareth 21 (Brij 721)*	1.60	–	–	–
	Steareth 2 (Brij 72)*	3.40	–	–	–
	Stearyl Alcohol	4.00	–	–	–
	Lanolin Alcohol (Super Hartolan)†	–	1.00	–	–
	Cholesterol†	–	1.50	–	–
	Petrolatum	–	7.50	–	–
	Paraffin (Paraffin Wax)	–	5.00	–	–
	Mineral (Paraffinum Liquidum) Oil	–	20.00	10.00	–
	Isohexadecane (Arlamol HD)*	–	–	6.00	–
	PPG-15 Stearyl Ether (and) Cyclomethone (Arlamol S3)*	–	–	3.00	–
	Ceteareth 30 (Emulgin 3)‡	–	–	–	13.00
	PEG-7 Glyceryl Cocoate (Cetiol HE)‡	–	–	–	2.00
	Octyldodecanol (Eutonal G‡)	–	–	–	5.00
B	Glycerin	–	5.00	–	20.00
	(Preservative)	q.s.	q.s.	q.s.	q.s.
	BHA (Butylated hydroxyanisole)§	–	0.002	–	–
	Sorbeth 30 (Polyoxyethylene sorbitol, Atlas G-2330)*	–	–	3.50	–
	Panthenol¶	–	–	1.50	–
	Urea	–	–	4.00	–
	Magnesium Sulfate	–	–	0.50	–
	Water, Aqua (Deionized Water)	70.70	to 100	to 100	42.00
C	Quaternium-15 (Dowicil 200)‖	0.10	–	–	–
D	Parfum (Perfume), Fragrance	0.20	q.s.	q.s.	q.s.

*ICI Speciality Chemicals. †Croda Ltd. ‡Henkel GmbH. §Nipa Laboratories.
¶Roche Products. ‖Dow Chemical Company.

Formulae 42, 43, 44
1. Heat (A) and (B) independently to 65–70°C.
2. Add (B) to (A) slowly with stirring.

Formula 42
3. Cool emulsion to 50° C. Add (C) (preservative).
4. Cool to 35° C and add (D).
5. Homogenize after emulsification.

Formulae 43, 44
3. Cool to 35°C and add (D).
4. Homogenize after emulsification.

Formula 45
1. Heat (A) in a jacketed pan to 95°C.
2. Heat (B) to 90°C and add to (A).
3. Cool to 60°C and add perfume.
4. Stir until homogenization is complete and then stop while cooling to allow the mixture to deaerate.

Note: To obtain the desired transparency it is necessary to observe the specified temperatures.

14.7.9 Protective products

(a) Simple hand lotions

Hand preparations are available as creams, lotions and gels, having replaced the glycerin and rosewater type of products which were very popular about 50 years ago. The skin on the hands, like that of the face, is continuously exposed to the environment as well as constant immersion in hot detergent solutions. If adequate protective measures are not taken then the hands can become extremely scaly, dry and inflamed, resulting in an increased TEWL and impaired barrier properties. Hand-care products are applied to rehydrate, smooth and leave a residual non-tacky protective film on the skin. In addition to emollients, they can incorporate a healing or soothing agent, such as allantoin or lanolin which confers some barrier properties to the product. Two examples of hand preparations are described below.

(b) Barrier creams

Barrier creams, like hand creams, are protective products. In addition, however, to acting as moisturizers, they prevent external materials from permeating the skin, such as water, defatting solvents, soil and dirt. The formulation of barrier creams will be determined by the type of external materials from which the end-user requires protection.

Formula No. 46 Hand lotion

	Commercial names	*INCI/CTFA name/chemical description*	*% w/w*
A		Mineral (Paraffinum Liquidum) Oil	5.0
		Stearic Acid	2.5
	Glyceryl monostearate (self-emulsifying)	Glyceryl Stearate SE	2.5
	Lanolin, anhydrous	Lanolin	1.0
B	Glycerol	Glycerin	2.0
		Triethanolamine	1.0
	Deionized water	Water, Aqua	to 100%
	Preservative		q.s.
C	Perfume	Parfum, Fragrance	q.s.

Procedure

1. Heat (A) and (B) separately to 75°C.
2. Add (B) to (A) slowly with continuous stirring.
3. Cool to 35°C, add perfume (C).

Formula No. 47 Conditioning hand lotion

	Commercial/common names	*INCI/CFTA name/chemical description*	*% w/w*
A	Quatrisoft Polymer LM-200	Polyquaternium-24	1.00
		Triethanolamine	0.95
		Propylene Glycol	4.80
	Deionized water	Water, Aqua	to 100%
	Preservative		q.s.
B	Mineral Oil (Light liquid Paraffin)	Mineral (Paraffinum Liquidum) Oil	2.40
		Isopropyl Myristate	2.40
		Stearic Acid	2.90
	Amerchol C	Petrolatum (and) Lanolin (and) Lanolin alcohol	0.50
	Cetal*	Cetyl Alcohol	0.40
		Glyceryl Stearate	1.00
	Bisabolol†	Bisabolol	0.80
C	Perfume	Parfum, Fragrance	q.s.

* Amerchol Corporation. † Dragoco Ltd.

Procedure

1. Heat (B) to 70°C.
2. Add Quatrisoft Polymer LM-200 to the water in a separate container.

3. Once the polymer is hydrated, add the remaining water-soluble ingredients and heat to 70°C.
4. Add (A) to (B) while stirring rapidly.
5. Cool to 40°C, and add perfume.

Protection from water

Formulations which exhibit water repellency may be based on petroleum jelly and lanolin and silicones. An aerosol mousse, as an alternative, offers a product which is hygienic and easy to apply. Kaolin may be included as a skin protectant. Glyceryl monostearate (self-emulsifying grade) allows the product to be easily washed off after use.

Formula No. 48 Barrier cream

Common names	*INCI/CTFA name/chemical description*	*% w/w*
A	Mineral (Paraffinum Liquidum) Oil	10.0
	Glyceryl Stearate SE	5.0
	Stearic Acid	0.5
	Silicone fluid	5.0
B	Glycerin	5.0
Deionized water	Water, Aqua	to 100
Preservative		q.s.
C	Kaolin	36.0
D Perfume	Parfum, Fragrance	q.s.

Procedure

1. Heat (A) to 70°C.
2. Dissolve preservative in the glycerol and add water, heat to 75°C.
3. Add (B) to (A) with constant stirring.
4. Gradually add kaolin, continuing stirring until a smooth consistency is obtained.
5. Add perfume (D).

Formula No. 49 Aerosol barrier mousse, intermediate

Commercial/Common names	*INCI/CTFA name/chemical description*	*% w/w*
A GMS S/E GE802*	Glyceryl Stearate	3.20
Corona Lanolin*	Lanolin	1.40
	Silicone	2.80
	Stearic acid	1.00

Formula No. 49 (*Continued*)

Commercial/Common names		*INCI/CTFA name/chemical description*	*% w/w*
B	Deionized water	Water, Aqua	to 100
	Preservative		q.s.
C	Perfume	Parfum	q.s.

* Croda Oleochemicals Ltd.

Procedure

1. Heat (A) and (B) independently to 75°C.
2. Add (B) to (A) with rapid stirring.
3. Cool to 40°C, add perfume, and fill.
4. Fill 90% product with 10% propellant.

(c) Protection from soil and oils

Non-oil soluble film formers such as gum acacia and tragacanth or sodium alginate can be used to provide oil repellency. Glycerin helps to plasticize the gum film.

Formula No. 50 Barrier cream

Commercial/Common names		*INCI/CTFA name/chemical description*	*% w/w*
A	Gum acacia	Acacia Catechu (or) Acacia Farnesiana (or) Acacia Senegal	5.00
	Deionized water	Water, Aqua	5.00
B	Glycerol	Glycerin	2.00
	Gum tragacanth	Tragacanth (Astragalus Gummifer) Gum	5.00
		Preservative	0.2–0.5
	Deionized water	Water, Aqua	82.8–82.5
C	Perfume	Parfum, Fragrance	q.s.
			100.00

Procedure

1. Dissolve the acacia in the water (A).
2. Disperse the gum tragacanth in the glycerol and disperse the preservative.
3. Add (A) to (B) with continuous stirring.
4. Stir until homogeneous.

(d) Deep engrained dirt on hands

A vanishing cream-type formula can be used to prevent the hands becoming ingrained with dust and dirt. The effect is achieved by rubbing the soap into the pores, which ultimately helps in the removal of soil when the hands are washed.

Formula No. 51 Barrier cream

		CTFA name/chemical description	*% w/w*
A		Stearic Acid	10.00
		Beeswax (Cera Alba)	2.00
	Petroleum jelly	Petrolatum	4.50
B	TEA	Triethanolamine	1.50
		Glycerin	8.00
	Deionized water	Water, Aqua	54.00
	Preservative		q.s.
C		Magnesium Stearate	20.00

Procedure

1. Heat (A) and (B) independently to 75°C.
2. Add (B) to (A) stirring slowly. Cool to 35°C and add perfume.
3. Add (C) and stir slowly until cold.

Note: All formulations provided are prototypes for further evaluation. There is no express or implied warranty against infringements, merchantability or fitness of purpose.

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Formulation index

Formula No	*Type*	*Supplier*	*Reference*
1	Syndet base	Zschimmer & Schwarz	Z&S Booklet
2	Syndet for dry skin	Zschimmer & Schwarz	Z&S Booklet
3	Syndet for oily skin	Zschimmer & Schwarz	Z&S Booklet
4	Skin-conditioning bar	Croda	C&T, 1989, **104,** 12, 93
5	Foaming gel cleanser	Miranol	C&T, 1989, **104,** 3, 125
6	Mild facial wash gel	Henkel GaA	C&T, 1989, **104**, 11, 9
7	Cleansing towelette/ wipe	Amerchol	C&T, 1989, **104**, 12, 91
8	Moisturizing liquid hand soap	Goldschmidt	C&T, 1989, **104**, 12, 86
9	Oil-controlling cleanser	Roche	C&T, 1989, **104**, 12, 91
10	Exfoliating lotion	G. Abamba	
11	Medicated clear cleansing gel	Croda	Croda Catalogue (C1259)
12	Cold cream cleanser	G. Abamba	
13	Cold cream cleanser	G. Abamba	
14	TEA stearate cleansing cream	G. Abamba	
15	Cleansing cream (nonionic emulsifiers)	G. Abamba	
16	Facial wash cream	Croda	Croda Catalogue (C1159)
17	TEA-soap lotion	G. Abamba	
18	Cleansing lotion	Uniqema (ICI)	Uniqema (ICI Speciality Chemicals)
19	Cleansing beauty milk	Croda	Croda Catalogue (C334)
20	Cleansing milk	Brooks	C&T, 1989, **104**, 11, 91
21	Skin tonic	W.A. Poucher	
22	Glycerol and silk toning	Croda	Croda Catalogue (C1093)
23	Alcohol-free skin freshener	G. Abamba	
24	Toning gel	G. Abamba	
25	Toning gel	S. Black	Dow Chemicals Co. Booklet
26	Skin Cream	G. Abamba	
27	Skin Cream	G. Abamba	
28	Skin cream	G. Abamba	

Formula No	*Type*	*Supplier*	*Reference*
29	Skin cream	Uniqema (ICI)	ICI Catalogue
30	Moisturizing milk	Uniqema (ICI)	ICI Catalogue (F41-44)
31	Stimulating day cream	Rahn	Rahn formulary
32	Day cream for sensitive skin	Uniqema (ICI)	ICI Catalogue F45-4-9
33	Anti-acne cream	Uniqema (ICI)	ICI Catalogue (F41-2-3)
34	Liposome moisturizing lotion	B.F. Goodrich	
35	Replenishing night lotion	Croda	Croda Catalogue (C1366)
36	Night cream (silicone)	S. Black	Dow Chemical Skincare 4/11877
37	Night cream with avocado oil	Th. Goldschmidt	Th. Goldschmidt Abil. EM Booklet
38	Hand and body lotion	G. Abamba	
39	Cationic hand and body lotion	S. Black	Caschem Booklet
40	Jojoba lotion	A&E Connock	Formula P2/35
41	Cocoa Butter lotion	Croda	Croda Catalogue (C1418)
42	Multipurpose cream	Uniqema (ICI)	C&T, 1987, **102**, 113(10)
43	All-purpose cream	W.A. Poucher	Perf., Cos. Soaps, 8th edn, 1974 volume 3, revised by George Howard
44	General-purpose milk	Uniqema (ICI)	ICI Catalogue (F42-4-10)
45	Skin gel microemulsion	Henkel	C&T, 1987, **102**, 10, 113
46	Hand lotion	W.A. Poucher	
47	Hand cream, conditioning	Amerchol	
48	Barrier cream (oil repellent)	W.A. Poucher	
49	Aerosol barrier mousse (Water-Repellent)	Croda	Croda Catalogue (C1333)
50	Barrier cream (soil and mineral oil)	W.A. Poucher	
51	Barrier cream (dust and dirt)	W.A. Poucher	

15

Soap

Michael Willcox

15.1 INTRODUCTION

Soap is undoubtedly the oldest product to be produced specifically as a surfactant and in its many forms continues to play a major role today. Within this highly competitive marketplace soap is presented in a multitude of forms both solid and liquid, and the object of this chapter will be to identify the many ways in which soap has developed from earliest times to a product which, today, we most probably take for granted.

From a strictly chemical viewpoint, any compound that results from the reaction of an insoluble fatty material with a metal radical or even an organic base could be described as a soap. If the metal radical is sodium, potassium or even ammonium, soluble soaps are formed. Where the radical is a heavy metal, insoluble 'metallic soaps' result and this explains the formation of hard-water scum around the bath or washbasin caused by calcium or magnesium soaps. Other 'metallic soaps', in which the radical is zinc, lead, manganese, cobalt or tin, may require a reaction at elevated temperatures or by double decomposition with sodium or potassium soaps and a salt of the relevant heavy metal. These soaps have uses in other industries.

In conclusion, the basic reaction in soap making between a neutral fat and an alkali is to produce a soap and glycerol.

$$\underset{\text{Neutral fat}}{C_3H_5(O_2CR)_3} + \underset{\text{Alkali}}{3MOH} \rightarrow \underset{\text{Soap}}{3RC_2OM} + \underset{\text{Glycerol}}{C_3H_5(OH)_3}$$

15.2 HISTORICAL BACKGROUND

The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in Ancient Babylon. Inscriptions have been discovered that indicate that the inhabitants boiled fat with ashes. It is unclear precisely

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 453–465

what these products were used for, although it is probable that their use was restricted to garment washing until Roman times. It has been suggested that the word soap was derived from Mount Sapo, which was a location for animal sacrifice. Melted animal fats and wood ashes would be washed down from the mountain and, in the clay along the banks of the River Tiber, a crude soap would form.

From these very tentative beginnings the product became progressively more refined as better-quality raw materials were used. The general use of soap as a washing medium probably dates back 1000 years or so, when the countries around the Mediterranean were producing modest quantities of soap, using a variety of locally available fatty raw materials. In addition to animal fats, vegetable oils such as olive oil would have been used. This limited production continued without significant modification until the breakthrough in the nineteenth century brought about by the availability of cheap soda. The French chemist Leblanc is credited with the invention of the process to convert common salt into soda ash, the same material that is derived from wood ash. The development by the Belgian chemist, Solvay, of the ammonia process further reduced the cost of soda and, at the same time, improved both the quality and quantity of this material which was vital to support the growth of the soap-making industry.

Throughout the nineteenth century the chemistry of soap-making became better understood with the discovery of the different fatty acids present in neutral fats and oils and this, in turn, led to the establishment of the fundamentals of the modern-day process involving the saponifications of neutral fats or fatty acids with the appropriate caustic material. Caustic soda will produce a harder sodium soap whilst caustic potash will yield the softer potassium soaps. The selection of specific fats and oils will yield a liquid soap.

Although production methods and techniques may have changed drastically from those earliest days it is worth remembering that the basic chemistry of soap remains virtually unchanged.

15.3 PRODUCTION OF SOAP BASE

The production of soaps in general, and toilet soap in particular, was always surrounded with an aura of mystery; the master soap-boiler would serve a long apprenticeship before earning respect as a skilled artisan. Even today's sophisticated chemical engineering approach to soap-making retains the need for a high degree of specialized process knowledge.

The very early soap may have been relatively crude and would most certainly have been fairly offensive in terms of smell and appearance. The improvements in both product and production techniques have resulted from a better understanding of the process and the availability of raw materials of a significantly higher quality. Chemical engineering skills have provided an opportunity for some producers to move away from pan boiling to the most modern continuous saponification process.

In the most basic of chemical terms, soap is the result of the reaction of a fatty material and alkali to produce a fatty soap which has surfactant properties. The choice of fatty materials in the earliest days would have been limited to neutral animal fats (suet or tallow), vegetable oils (olive oil or rapeseed oil) and possibly fish oils. As mentioned earlier, the alkali would have been wood ash, possibly mixed with lime. Modern practice would use either neutral fats (animal or vegetable) or blended fatty acids with the appropriate caustic alkali.

The formulations of individual soap-makers vary widely. In Europe, however, there is a general belief that a blend of fat/fatty acids based on tallow and nut oils in the ratio of 4 : 1 produces a product of wide acceptability and optimum performance.

The choice and selection of fatty materials has a significant bearing on the finished product, as do the fat ratios; specific requirements either increase or reduce the level of nut oils according to the requirements of the individual producer. It should also be understood that the choice, selection and pre-preparation of the fats will have a bearing on the colour and odour of the finished base soap.

Cosmetic scientists will be only too aware of the many problems surrounding the use of tallow and tallow derivatives caused by the concerns over BSE.

Tallow is derived from a number of sources (cattle, sheep and goats) and although the process conditions used to render tallow have been demonstrated to inactivate any risk materials, soap-producers have found themselves enmeshed within a complex bureaucratic minefield which has seriously limited the choice of raw materials depending on their origin and the ultimate point of sale of the finished product.

Tallow or its fatty acid derivatives continue to be the preferred principal raw material in Europe and most of America, but the use of the alternative vegetable-derived materials in other parts of the world has become of greater interest as the problems surrounding BSE continue. Indeed it is only now, as a direct result of these problems, that the general public has become aware of the raw materials used in soap production. Vegetable-based products are considered later in the chapter.

Whatever the choice of the principal raw material, the secondary nut oil content is usually derived from either coconut oil or palm kernel oil. Again the appearance of the final soap is dependent on the quality and degree of refining of these oils.

The producer can often further improve the quality of the fats and oils by bleaching and hydrogenation of the feedstock. This ensures continuous supply of consistent quality; as, with any natural product, the fats and oils will vary from year to year and crop to crop. The use of fatty acids also provides a consistent feedstock which can be used for the partial or total substitution of the neutral fats.

It is essential that the soap-boiler has a detailed knowledge of the chemistry of the fatty feedstock so that the correct amount of alkali to ensure complete saponification is used.

15.4 SOAP BOILING

15.4.1 Kettle boiling

The traditional process of pan boiling in large open kettles is time-consuming and requires relatively large amounts of energy. The process involves a number of distinct stages starting with the initial boiling or preliminary saponification. Once this saponification has been completed a soap layer is formed when salt is added. The soap layer, known as 'neat' soap, consists of about 65% real soap with about 35% water and contains traces of glycerin, salt, etc.

Boiling continues with the careful addition of further quantities of caustic soda to ensure the removal of excess fat and other impurities. The pan is then allowed to stand to facilitate the complete separation of the soap layer from the residual liquid. The soap is further washed to remove excess salt when it is available to be processed by a variety of different methods. This forms the basis of the production of commercial bars, flakes, granules and powders. Cosmetic and toiletry companies can buy these forms in bulk and make their own specialized branded products, e.g. toiletry and bath tablets, baby soaps, etc.

The processing of soaps from neutral fats also results in the formation of glycerin and this valuable raw material can be recovered from the residual liquid left after the boiling process. Normally a proportion of glycerin is retained within the soap layer; this is considered essential to produce a high-quality product.

15.4.2 Continuous process

While pan boiling is still widely used, it tends to be the method of manufacture favoured by the smaller specialized producer. Continuous process production is considered to have many advantages, being much quicker, taking up less space and using less energy. The switch to continuous process also facilitates the use of fatty acids in place of neutral fats although both raw materials are used extensively. The resulting base soaps tend to have characteristically different odour profiles, often leading to interesting discussions regarding which is the 'best' product.

The fats are first converted into fatty acids and glycerin by high pressure at 500°C in a continuous, fat-splitting process. There are companies specializing in this operation which sell fatty acids and purified glycerin to soap base manufacturers.

15.4.3 Base using vegetable materials

As mentioned earlier, the problems associated with BSE have created a great deal of interest in soaps which have no animal content.

For cultural, religious and economic reasons vegetable-based products are widely used throughout Africa and Asia, and one has seen a rapid improvement in the quality of these alternatives.

The techniques for production mirror those of animal-derived soap bases but the availability of ever-increasing volumes of palm oil, palm kernel oil and coconut oil has led to a significant reduction in costs, when compared with the historic differentials that existed between these different types of base.

Indeed forward projections might indicate that the availability of animal-derived materials might, at best, remain fairly static but the availability of alternative vegetable raw materials is set for a significant increase over the next 10 years driven by the levels of production in the Far East.

Palm oil fatty acid and palm stearine are the principal raw materials that replace tallow and its derivatives in vegetable-based soaps, whilst the minor constituents remain the fatty acids of either coconut oil or palm kernel oil. Fatty acids are tending to replace the neutral oils, and palm oil in particular is quite dark in colour compared with tallow and is liable to make the final soap base a creamy yellow colour.

As indicated previously, the selection of good-quality raw materials is essential for the production of a soap base with good colour and odour.

15.5 CONVERSION TO FINISHED BARS

In the very early days the basic soap would be separated and it might have been coloured and/or perfumed by adding materials directly to the liquid soap. After mixing, this liquid soap would have been run into large block moulds to solidify. Once solid the block would then have been cut by wire into blocks of soap of the desired size. Some simple decoration might also have been applied by pressing an engraved block into one face of the tablet.

There is still a market for bar soaps as laundry and scrubbing soaps; these are produced in a manner similar to the early method. The basic liquid contains approximately 63% of soap and this mass is coloured and perfumed as above. The mass is then run onto a large chilling roller and the semi-solid soap is scraped off in the form of ribbons which are passed directly to an extruder where the soap emerges as a continuous bar. This bar is cut into blocks by an automatic wire cutter. The blocks are then passed through a conditioning tunnel to harden the surface prior to stamping and final packaging. In this form the soap block is still very soft and is prone to surface damage. The tablets still have a high level of moisture and will gradually harden as they are stored. It was often the practice to leave soap bars to dry out for some time after purchase, to ensure that they lasted longer when they were used.

15.5.1 The milling process

The next significant advance in processing was the introduction of milling prior to extrusion to produce a better-quality, more consistent regular bar. The base

material is checked to ensure that there is no significant excess of salt and the level of free caustic alkali is reduced to a minimum.

At this time one does have the opportunity to introduce other additives (the concept of superfatted soaps will be discussed later). Suitable preservatives are added to the liquid soap to guard against rancidity; individual producers will have their own particular favoured combination of preservatives. Normally, this will include the capacity to chelate any trace of free ferrous metal that might be present from the process, along with a suitable antioxidant to ensure no degradation of the fatty constituents.

The liquid soap would again be run onto a large chilling roller and converted into semi-solid ribbons which are then passed through a drier when the moisture content of the base would be reduced to approximately 13%. The dried ribbons can then be used to produce the finished bars.

A pre-weighed quantity of base will be introduced to a ribbon mixer and other ingredients will be added either in liquid or powder form. These will consist typically of titanium dioxide, which acts as an opacifier, perfume and pigments or dyestuffs to achieve the desired end-product. The other formulation options are mentioned later in the chapter.

The soap mass is mixed to ensure that all of the additives are evenly coated onto the soap ribbons. This is then passed through a roll mill a number of times or, alternatively, a series of roll mills to produce a homogeneous soap mass in which the additives are evenly distributed. This mass is then passed to an extruder where it is compressed into a continuous bar of soap which can be cut into individual billets prior to stamping and final pack-off.

The process involves no external heat; in fact it is necessary to remove some of the heat generated by the process by having water cooling both of the roller mills and the barrel of the extruder. The surface finish of the bar can be enhanced by applying heat to the extruder head, which in turn heats up the surface layer of the bar as it passes through the extruder plate.

The continuous evolution of processing techniques has modified and in many cases replaced some of these steps as modern production methods move to greater speed and efficiency. A modern soap plant will probably use a continuous saponification process with in-line washing of the soap to remove much of the glycerin (a valuable by-product). The liquid soap will then be passed through an in-line heat-exchanger prior to being sprayed into a vacuum drier when the soap is deposited on the walls. It is then scraped off and is passed through an extruder refiner to emerge as a noodle product ready for the next stage of processing.

Mixing and milling will have been replaced by in-line dosing of perfume, the colouring system and any other additives and the use of multi-screw extruders/refiners. The final extrusion is carried out in two or three stages with the use of vacuum between each stage. The final extruded bar is cut automatically and fed into high-speed multicavity pressing equipment, linked directly to

packaging machines capable of line speeds in excess of 300 tablets per minute for a regular-sized bar.

Whatever combination of processing techniques is used the finished bar should have a good, consistent texture and be capable of being moulded into a wide variety of shapes from the simple rectangular bar to the most highly sculptured novelty soap.

15.6 SOAP PERFUME AND ADDITIVE SYSTEMS

Soap is a very versatile basic material which is capable of accepting a highly diverse range of liquid and solid additives. The only real limitations are placed on additives that might degrade the product chemically, might cause physical damage to the process equipment or might cause harm to the process worker or end-user. Outside of these limitations the choice is endless. Even relatively high levels of additives (up to 20%) are possible with the correct choice of base soap along with specialized processing but these would probably be restricted to highly fragranced soaps.

As always the quality of the basic raw material has a significant effect on colour and fragrance and it is essential to choose the correct grade of soap for the desired end-use. There is little point in seeking to produce a delicately fragranced pastel coloured soap if the base material is creamy yellow in colour with a strong odour.

As soap is a relatively harsh chemical (pH 10) the skill of the perfumer is required to ensure that the final formulation will have excellent stability throughout the life of the bar. It is also essential that the perfumer has access to the actual base material that will be used as different soap bases react in slightly different ways. This is even more noticeable when one compares the performance of the same perfume in bases produced from neutral fats with bases produced from fatty acids.

Similarly the choice of pigment or dyestuff has to be made with greatest care to ensure that the finished product has adequate stability. Although the use of pigments is probably preferred because of their greatly increased stability, particularly to light, it is often necessary to make use of a limited range of approved dyestuffs because of the restrictions forced upon the producer by particular regulations in certain countries. Japan is a typical example.

The addition of other fatty/oily materials is often undertaken to provide a superfatted product with improved lathering properties and enhanced skin feel. These products can be introduced either into the liquid soap prior to drying or at the mixing/dosing stage. The original choice of such materials would have been restricted to petroleum-based products (oil and/or jelly), lanolin and fatty acids/oils such as coconut.

More recently the wide availability of other fatty chemicals has presented the soap formulator with a bewildering choice of options.

A typical formulation for a regular toilet soap would be:

Soap base	
Titanium dioxide	0.2–0.4%
Perfume	0.5–1.0%
Colour	q.s.

In more luxurious formulations the level of perfume could rise to 4.0% and they would also incorporate superfatting agents as mentioned above. These types of soap become increasingly difficult to process and invariably require hand pressing to ensure good finished tablet quality.

Perfume, colour and superfatting systems will represent the major additives one might expect to find in regular soap tablets but the way in which the market has become ever more diverse can be demonstrated by the availability of soaps that contain antibacterial materials to enhance deodorant claims. Soaps with mild abrasives such as pumice, oatmeal, maize meal, groundnut kernels and even herbs, dried flowers and dried seaweed, are natural products gaining much favour within the marketplace, as are pure soaps that contain no additives at all.

As pointed out at the beginning of this section soap is a highly versatile material and it is likely that many more, as yet untried, additives will find their way into soap in the future.

15.7 OTHER TYPES OF SOAPS

In addition to the animal- and vegetable-based regular soaps which have been discussed in detail above, there are a number of other related products manufactured by similar techniques.

15.7.1 Shaving soaps

Shaving soaps differ from toilet soap in the main by the addition of caustic potash to the saponification process; in combination with the correct choice of fatty acids, this creates a softer soap base with enhanced lathering characteristics. The control of free alkali is crucial and these soaps are often given a free fatty acid finish to minimize the risk of irritation in use. Processing is very similar to regular toilet soap and again the choice of a suitable superfatting material is essential to provide a good after-feel to the skin.

Lather shave creams are normally produced from stearic acid and coconut oil and saponified with a mixture of caustic soda and caustic potash. Glycerin will also be added to aid product texture and skin feel. Although the product

formulation is relatively straightforward the product can prove difficult to process and does require specialized mixing equipment.

15.7.2 Translucent soaps

Translucent soaps are a relatively recent innovation although it has long been known that soap can pass through a translucent phase during processing. It has been the ability to control the production of this translucent phase with the addition of glycerin and other polyol-type materials, linked with specific modifications to processing, that has allowed the soap producer to develop a whole range of soaps that exploit this novel form of presentation.

As with regular toilet soap these soaps are available in both animal- and vegetable-based variants capable of being handled by the remilling process to produce tablets of reasonable clarity. This clarity is usually enhanced during storage. These soaps are processed using conventional equipment, are extruded in exactly the same way as regular toilet soap and are capable of being moulded into a variety of complex shapes.

It should be noted that soaps produced from translucent base are more difficult to mould due to the surface texture of the extruded billets, and also that the shrinkage characteristics are significantly different from those of opaque soaps. The stamping tools for translucent soaps are normally constructed using special alloys to allow for adequate chilling of the stamping surface, and are designed to accommodate the specific shrinkage characteristics of the base.

The selection of perfumes and colours for these products is of prime importance as it is essential to ensure that they do not adversely affect the translucency of the finished tablet. Any competent perfumer will be able to provide the soap formulator with an interesting selection of fragrances for the development of new and interesting alternatives.

A typical formulation for a translucent soap will be relatively simple, but one should note that the level of fragrance is normally no higher than 1.5% as this can affect translucency.

Translucent soap base		
Perfume	Parfum, Fragrance	1.0–1.5%
Colour		q.s.

Translucent soaps can also be enhanced by the addition of mica-coated pigments to produce a pearl effect or solid, natural particulate materials such as seaweed, loofah, poppy seeds, etc. This again demonstrates the wide versatility of soap as a medium for creative design.

15.7.3 Transparent soap

As with the translucent soaps mentioned above, the market has seen a growing interest in clear products generally, and transparent soaps are a variant that is of increasing interest. Formulation and production methods vary considerably and one of the oldest methods involves dissolving a good-quality soap in alcohol with gentle heating to form a clear solution which is then coloured and perfumed.

The bulk of the alcohol can then be removed by distillation and the transparent liquid soap is cast into blocks or moulds and allowed to set. The moulded product is cut to the required size of billet and pressed to roughly its final shape. The tablets then have to be conditioned for up to 3 months before being packed off, and during this period characteristic distortion may take place, resulting in some of the shapes that have been familiar in the marketplace for many years.

Although the resulting bars have excellent clarity and do not require any special style of wrapping this whole process is labour-intensive and time-consuming, and has tended to be superseded by other product variants.

Rather than using a pre-saponified base material it is more convenient to saponify the oils and fats *in situ* and then add the combination of glycerin and sugar required to stabilize the clear phase. There is also a lower percentage of alcohol present so that the soaps do not have to be left to condition.

The selection of the fatty raw materials used to produce transparent soaps is very similar to that undertaken for regular soap production and the quality and colour of the individual fats/oils or fatty acids will have a direct effect on the colour of the finished product. Castor oil is an important ingredient to include in the mix of oils and fats as it does aid with product clarity but does have the disadvantage of producing a distinct yellow colour in the finished tablet. This limits the range of colours capable of being produced from this type of base material.

A typical formulation for such a transparent soap base would be:

	INCI names	*% w/w*
Tallow fatty acids	Tallow Acids	27.00
Coconut oil	Coconut (Cocos Nucifera) Oil	7.00
Castor oil fatty acids	Castor (Ricinus Communis) Oil	5.00
Ethanol	Alchol	10.00
Sodium Hydroxide	Sodium Hydroxide	6.20
Sugar	Sucrose	15.50
Glycerol	Glycerin	9.00
EDTA*	EDTA	0.25
Water	Water, Aqua	to 100.00

*EDTA = Ethylenediamine tetraacetic acid.

Fats are premelted in one vessel and in a second vessel water, sugar, glycerol and preservatives are heated. In a third vessel an alcoholic solution of caustic

soda is prepared and the three phases are reacted to form the basic soap. Other alkaline materials (e.g. triethanolamine) may be used to effect saponification, although the resulting bars are often much softer than those produced with caustic soda.

The soap mass is checked for setting characteristics and adjusted as necessary. It is then transferred to a holding tank when the formulation quantities of colour and perfume are added.

This product can then be dosed into separate moulds or cups and passed through a conditioning tunnel to emerge as a single billet. Once the billets have been allowed to cool for 24 hours they can be moulded and film-wrapped. The resulting tablets have good clarity but some form of film-wrapping is considered essential to overcome any tendency of surface blooming which can detract from the appearance.

One possible disadvantage of this type of formulation is the presence of alcohol which necessitates controlled, low-flash production areas. More recently transparent soaps have been developed by combining soap with detergents and these formulations give excellent clarity and have a low odour.

A typical formulation for this type of soap would be:

	INCI names	*% w/w*
Stearic acid	Stearic Acid	15.00
Coconut oil fatty acid	Coconut (Cocos Nucifera) Oil	6.00
Propylene glycol	Propylene Glycol	18.00
Glycerol	Glycerin	8.00
Sodium hydroxide	Sodium Hydroxide	4.20
Sugar	Sucrose	10.00
Sodium laureth sulfate	Sodium Laureth Sulfate	16.00
Sodium lauryl sulfate	Sodium Lauryl Sulfate	12.00
Tetrasodium EDTA	Tetrasodium EDTA	0.20
BHT[†]	BHT	0.20
Water	Water, Aqua	to 100.00

[†]BHT = Butylated Hydroxylated Toluene; an antioxidant.

As with other bases it is possible to enhance both the lathering characteristics and the skin feel with the inclusion of suitable additives. As mentioned above it is essential to film-wrap the finished bars to avoid any risk of surface crystallization due to deposits of sugar as the bars lose moisture.

The formulator can experiment with the relative proportions of propylene glycol, glycerol and sugar to adjust the hardness of the final bar to suit individual requirements. The method of manufacture follows similar lines to that given above.

The use of low-colour raw materials results in a base which is almost water-white, capable of accepting reasonably high levels of fragrance (up to 5%).

For both formulation types it is essential to select the perfumes and other additives to take account of process conditions (typically up to 2 hours at 70°C). Colouring is best achieved using organic dyestuffs which give brighter, cleaner shades than can be obtained using inorganic pigments, although light stability can be a problem and the addition of an ultraviolet screen can help to minimize fading.

The only possible disadvantage of this product compared to the extruded translucent soaps mentioned previously is the restriction placed upon tablet shape by the process and the texture of the base material itself. The tablets tend to be reasonably regular in shape with flat backs, but can be moulded with slight distortion rather than being shaped into the highly sculptured forms that are available from an extruded bar.

15.8 DETERGENT/COMBINATION BARS

Although this class of product is not a soap in the strict sense of the word the rapid increase of cream/cleansing bars places these products in a major category within the overall bar soap market.

Modern detergent systems now provide raw materials which can be used singly or more usually in combination with a proportion of regular soap to produce a solid bar with significantly reduced pH levels that mimic those of the skin. Although the basic raw materials are more expensive than regular soap these products have perceived benefits which allow for higher prices in the marketplace.

Some of the more specialized formulations require special process equipment and indeed many of these formulations are covered by patents. However, it is possible to process commercially available, fully formulated base materials on regular soap-making equipment that has had some minor adaptations made to allow for precise temperature control. This is essential to ensure that the process mass is maintained in a suitable plastic condition without becoming too mobile. Also it is necessary to ensure that the extrusion equipment has a suitable worm capable of the correct degree of compression for detergent materials.

Combination bars are normally formulated using a ratio of soap to detergent of around 50:50. They are necessarily less expensive in terms of raw material cost but the pH values are only slightly reduced at around 9.0–9.5.

15.9 LIQUID SOAPS AND HANDWASHES

Traditional liquid soaps are saponified using oils and fats that have a high oleic acid content, and a proportion of caustic potash is used in combination with caustic soda to produce a liquid which is normally quite dark in colour and often

has a strong smell. These soaps still have industrial and sanitarian uses but are no longer considered relevant as consumer products in today's even more sophisticated market.

It is also possible to produce true liquid soaps with better colour and odour by using a combination of the higher chain-length fatty acids, and sarcosine has been found to be a very effective starting material. One drawback with these products is the relative high cost of the fatty acids.

Some products which are described as 'liquid soaps' may indeed contain small proportions of true liquid soaps in a detergent-based system but increasingly the market is moving towards the concept of liquid handwashes that are formulated from only detergent-based surfactants.

In formulation terms these products are closely related to bubble baths and body shampoos, and the details on formulation options given elsewhere in this book can be used as a basic guide. The products are normally enhanced with additional moisturizing raw materials to counteract their frequent use as a handwash in place of regular soaps. Whilst targeted towards the kitchen shelf these products are also finding their way into the bathroom. Indeed many of the cleansing bars mentioned above have liquid-based companion products that contain identical additive systems to support some of the more popular claims regarding the percentage of moisturizers present.

The basic handwash formulations are also used to create antibacterial variants which can be considered more effective for a kitchen environment. The careful choice of one of the many suitable antimicrobial agents is necessary to provide adequate support for the specialized claims made for these products.

This concludes what, by its very nature, can only be a fairly brief overview of a highly complex industry, but should provide the development chemist with some degree of guidance for future soap development projects.

16

Sun damage and sunscreen preparations

Michael Brown and Nicola Fardell

16.1 INTRODUCTION

In recent decades the standard of living in the developed countries of the world has advanced enormously. We are all enjoying increasing leisure time together with increasing wealth with which to appreciate it. For northern Europeans, where the home climate is often mixed, the attraction of a foreign holiday with virtually guaranteed sunshine has become not only irresistible, but also readily affordable to much of the population. The benefits of such a holiday are well known. Endless sunshine promotes a strong feeling of well-being whilst relaxation helps to relieve stress and generally improve health. But for many, the greatest benefit derived from a hot climate is the psychological one provided by the appearance of a good suntan as dictated by modern fashion. A suntan shows the world that its wearer is 'fit and healthy' as well as being affluent enough to indulge in the pursuit of leisure.

How very different from not too long ago, when a suntan was the sign of an outdoor working peasant forced to struggle to live off the land. Constantly exposed to the sun, the peasant's skin became thick, leathery and brown. In contrast, the gentry were able to avoid the sun's rays and maintain the fine white skin characteristic of the 'English Rose'. In Victorian times, elegance and fashion dictated that skin should be white and that brown skin was indicative of hard labour and poverty. It was only at the end of this era that fashion gradually began to change. This gradual change became cataclysmic in the 1930s when fashion guru Coco Chanel returned from a foreign holiday sporting a deep tan. Overnight, the whole Caucasian population desired the new fashion, tanned skin.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 467–503

There is some element of truth in the belief that a suntan is beneficial. There can be no doubt that the feeling of well-being it brings is real and of emotional benefit. In addition, sunlight promotes the synthesis of vitamin D and reduces the symptoms of the modern ailment SAD (Seasonal Affective Disorder). However, the adverse effects of excessive sun exposure are also very real and seriously damaging. Recent upsurges in the incidence of skin cancer mirror increases in leisure time and the availability of inexpensive package holidays abroad. Countries such as Australia and South Africa with non-native Caucasian populations living in extremely hot climates also show extreme incidence of skin cancer. This link between sun exposure and skin cancer is too significant to ignore. In addition, more and more people are now suffering from dermatological disorders brought about from sunlight overexposure, and we are all aware of the leathery wrinkled appearance of the skin of the middle-aged Californian lady lazing beside her pool. Her premature skin ageing is a direct consequence of excessive sun exposure. Also, who amongst us has not at some time suffered the pain of sunburn? Whilst the pain and redness are transient, the underlying skin damage is almost certainly permanent and may manifest itself in later years in potentially lethal ways. In this chapter we will look at the causes of the adverse effects of sunlight and what can be done to prevent or minimize them.

16.2 SUN-INDUCED SKIN DAMAGE: ITS CAUSES AND MEASUREMENT

16.2.1 The electromagnetic spectrum

Our sun emits a constant flow of energy in the form of electromagnetic radiation spanning an enormous range of wavelengths from 10^5 metres (m) down to 10^{-6} nanometres (nm) (Fig. 16.1). The lowest energy radiation takes the form of electric and radio waves with wavelengths up to 10^5 m, whilst the highest energy is represented by gamma and cosmic rays with wavelengths as small as 10^{-6} nm. In the middle of this scale lies the region we call sunlight, comprising intermediate energies with wavelengths ranging from 1000 nm to 1000 nm. Sunlight is subdivided into a number of smaller regions, each categorized by the specific physiological effect it exhibits. Radiation between 1000 nm and 750 nm is the near-infrared, detectable as heat. Wavelengths from 750 nm to 400 nm are observed as visible light, giving us the seven colours of the rainbow and enabling us to see objects. Between 400 nm and 100 nm lies the ultraviolet (UV) region of the solar spectrum which is directly responsible for many adverse biological reactions such as sunburn, skin ageing/tanning, photodermatoses, immunosuppression and skin cancer.

Fortunately, the Earth's atmosphere absorbs virtually all wavelengths of electromagnetic radiation below 295 nm or thereabouts. Consequently, the surface of our planet is not exposed to cosmic rays, gamma rays or x-rays, each of which is

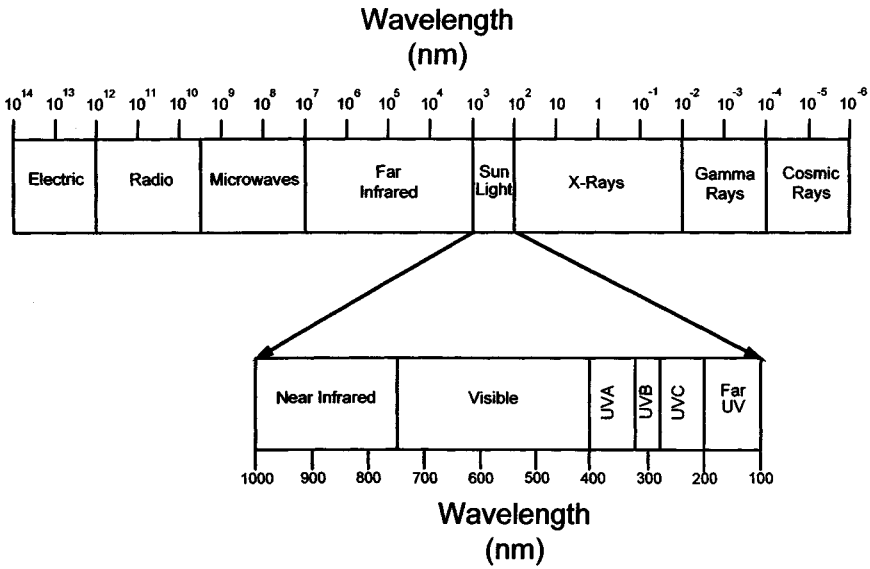

Fig. 16.1 The solar electromagnetic radiation spectrum.

potentially lethal. Of the wavelengths of radiation which do reach the Earth's surface, ultraviolet has the highest energy, making it the most important in relation to sun exposure. Over the years, photobiologists have arbitrarily described different sub-regions of the UV spectrum each defined by a somewhat indistinct physiological activity. They are, in descending order of energy: far-UV radiation (100–200 nm), UVC (200–280 nm), UVB (280–320 nm) and UVA (320–400 nm).

The far-UV and UVC region

This region is described as the germicidal UV because of its ability to kill single-cell organisms. We are fortunate that some five thousand million years ago, when our planet's upper atmosphere was created, far-UV and UVC were prevented from reaching the Earth's surface by the formation of the ozone layer. Consequently life evolved and thrived, and will continue to do so as long as the ozone layer remains intact. Recently much controversy has surrounded our ozone layer with suggestions that it is being depleted. Whilst evidence clearly shows that ozone 'holes' have been detected at the Earth's poles, it is still too early to speculate whether this represents a true depletion of the ozone layer or whether this is simply normal fluctuation. However, since UVC radiation is both cytotoxic and capable of producing severe sunburn at very low exposure levels, any true evidence of ozone depletion will need to be viewed as very serious.

The UVB region

As an aide-memoir, UVB is often over-simplistically identified as UV-'B' for burning. This is because it is the primary initiator of sunburn, contributing approximately 85% of summer sunburn reaction. However it is also responsible for the initiation of certain skin cancers, many photodermatoses, premature skin ageing and for the generation of the photoprotective pigment known as melanin which gives our skin its suntanned appearance. On a positive note, UVB is also responsible for synthesis of vitamin D in the skin.

The UVA region

UVA is often over-simplistically identified as UV-'A' for ageing. This is because its long-term effects on the dermal layers of human skin manifest themselves as visual wrinkling and ageing of the skin. However, UVA is also capable of generating both immediate skin pigmentation and delayed pigmentation, the latter being the tanning response. UVA also contributes approximately 15% of the sunburn reaction which occurs as a result of overexposure to summer sunshine. Many photodermatological skin conditions such as polymorphic light eruption (PLE), solar urticaria and chronic actinic dermatitis (CAD), occur as a direct result of exposure to UVA light, whilst several 'photo-active' substances can also produce abnormal skin reactions as a result of exposure to UVA light. Recent work indicates that UVA is also implicated in skin cancer [1,2].

The variations in energy of the different UV regions lead to the visualization of effects at different times. Immediate pigmentation due to UVA develops after only a few hours and thus may afford the skin some minimal initial protection. Reddening due to UVA, however, may not take place for up to 72 hours after exposure. UVB erythemal reactions develop after as little as 8 hours and may persist for 24 hours and longer. Tanning may or may not appear, depending on the skin type of the individual and his or her capacity for producing melanin. The severity of all responses to UV light depends upon the intensity and total dose of the sunlight received. This may be modified by latitude, altitude, season, time of day, cloud cover, atmospheric pollutants, etc. It is also noteworthy that whilst UVB will not penetrate window glass, UVA may do so and therefore exposure to UVA may continue even when indoors or whilst driving for example.

16.2.2 Penetration of UV radiation and interaction with skin components

When UV light penetrates skin, it can interact with biological molecules, give up its energy and cause transient and/or permanent changes in those biological molecules. Any molecule which is capable of absorbing light is referred to as a chromophore and biological systems such as human skin contain many potential chromophores. Exactly which chromophores actually absorb light, and how this manifests itself as skin damage, is dependent upon both the energy of the

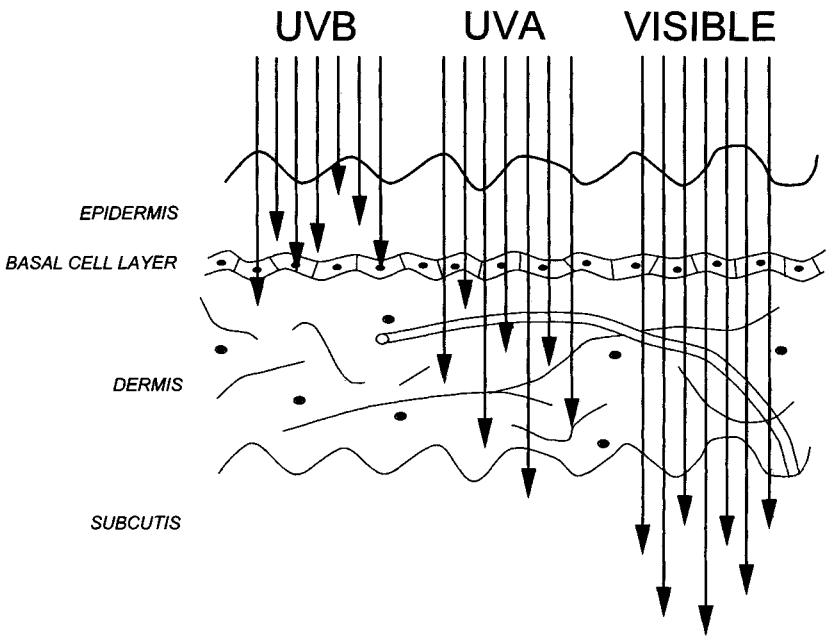

Fig. 16.2 Penetration of solar radiation into skin.

incident light and its depth of penetration into skin. Figure 16.2 shows the comparative depth of penetration of the different ranges of sunlight radiation.

UVB penetrates only as far as the basal cell layer and possibly into the upper margins of the dermis. Most adverse effects of UVB light on skin arise from the absorption of UVB by chromophores in the living and actively dividing cells of the lower epidermis and basal cell layer, i.e. the keratinocytes, melanocytes and Langerhans' cells. UVA, on the other hand, will penetrate far deeper into the skin, penetrating through the epidermis and deep into the dermis where it can initiate photochemical reactions within structural components of the skin such as collagen and elastin.

Consequently it can be seen that the epidermis with its basal cell layer is invaded by both UVB and UVA wavelengths, whilst the dermis suffers primarily from UVA aggression. The cells of the epidermis and the basal cell layer contain many constituents which may act as UVB chromophores. However, the major epidermal chromophore is deoxyribonucleic acid (DNA). The high energy contained within a photon of UVB light is sufficient to induce permanent structural changes in DNA and, in so doing, will disrupt the genetic coding of individual cells. In most cases this damage is corrected by cellular 'repair' mechanisms, but occasionally 'repair' is not 100% accurate or complete and this may ultimately lead to the degenerative process of malignancy. Whilst the subject of

malignant melanomas, carcinomas and solar keratoses is beyond the scope of this chapter, it is worth noting that epidemiological evidence links high UVB exposure (i.e. lower latitudes) and low natural skin pigmentation, with increased incidence of melanoma.

The first sign of UVB skin damage is the erythemal or skin-reddening response which in severe cases becomes sunburn. The mechanisms by which UV radiation initiates erythema are poorly understood. Several theories exist including: a direct effect on blood vessels, photochemical generation of migratory chemical mediators in the epidermis or cytokine release by epidermal cells damaged by direct or indirect action of UV radiation. Whatever the mechanism, the end-results are: localized increase in blood content (brought about by vasodilation), pain, inflammation and ultimately skin blistering followed by peeling. At this stage protective mechanisms come into operation. The skin thickens, notably the outer horny layer and the epidermis, to protect the formative basal layer of cells by increasing the distance between them and the source of UV radiation. This explains the leathery appearance of the skin of individuals constantly exposed to the sun. More importantly the mechanism of delayed pigmentation is initiated, resulting in a suntan, brought about by the increased production of a protective UV chromophore, namely melanin. Melanin is produced in the melanocyte cells of the epidermis following stimulation by UVB radiation and is inserted into newly developing keratinocytes. Keratinocytes flatten and migrate to the skin surface where they make up the outer keratin horny layer. In so doing they carry melanin to the skin surface where it forms the protective suntan. A suntan will take about 4 days to develop and will only last for the lifetime of the epidermis, which will be approximately 14–21 days after the stimulatory effect of the UV radiation source has subsided. The protection it affords is about four times that of non-tanned skin. Levels of protection will be dealt with later in the chapter.

All the effects of UVB radiation on the epidermis described above may also be brought about, to a much lesser extent, by UVA. Consequently, UVA will contribute approximately 15% to sunburn, may stimulate some tanning, may cause DNA damage indirectly via intermediary chromophores and will initiate all manner of photoallergenic responses and photodermatoses. In addition, UVA can penetrate deeper into the skin, reaching well into the dermis where it can initiate photochemical reactions which lead to premature skin ageing visualized as excessive wrinkling and loss of elasticity. These changes are thought to be brought about by oxidative free radicals produced by UVA light. These free radicals cause photochemical reactions within the structural proteins of the dermis resulting in a breakdown of the elastin fibres which give skin its elasticity and a decrease in soluble collagen. The deeper penetration of UVA into skin is due to the lack of suitable natural UVA chromophores in the epidermis. Only the bleached precursor of melanin is able to absorb UVA in any real quantity and, by an oxidative reaction, this leads to the immediate pigmentation phenomenon already mentioned.

16.2.3 Skin types and the choice of sun product

Individuals may be classified into one of six skin types, as described by Fitzpatrick [3], according to the way their skin behaves on exposure to UV radiation:

I Always burns easily; never tans
II Burns easily; tans minimally
III Burns moderately; tans gradually
IV Burns minimally; tans easily
V Rarely burns; tans profusely
VI Never burns; deeply pigmented.

Skin types vary from the type I fair-complexioned, light-haired Caucasian of Celtic origin to the type VI deeply pigmented, dark-haired Negroid races. Skin Type III is typical of 'normal' northern Europeans. In the case of skin types I and II, the amount of radiation required to initiate melanin production is far greater than that which will cause erythema. Therefore these individuals suffer the pain of severe sunburn long before a protective melanin shield can be generated. For skin types IV and above the reverse applies, in that the erythemal dose of UV radiation is greater than the melanogenic dose and so these types tan well before burning. Such a tan then serves to increase their protection from burning even further. Clearly the choice of appropriate sunscreen protective formulation by an individual depends heavily on that person's skin type, with skin types I and II requiring considerably greater protection than skin types IV and V.

Other factors also need to be taken into account when choosing a sun protection product. Generally, the first priority of a sun product is to protect the skin from erythemal radiation and hence sunburn. This can be achieved by protecting primarily against UVB wavelengths which, as previously stated, contribute about 85% of the sunburn reaction. However, it is common practice for consumers to use the additional protection which a sunscreen provides as a means of extending their time in the sun and not, as would be more appropriate, as a means of providing additional protection for the same length of time. If sun exposure is increased in this way, a sun product which provides only UVB protection will actually allow the skin to be exposed to increased amounts of UVA radiation, leading to the previously described problems associated with UVA exposure. Thus the consumer should be wary of high sun protection formulations which do not contain significant levels of UVA sunscreens and should be aware of his or her skin type and the benefits of products which screen against both UVA and UVB. Manufacturers, on the other hand, need to be clear exactly what they wish to achieve when developing a sun product. It is true to say that many major sunscreen manufacturers now produce products which provide a good balance of both UVA and UVB protection but consumers should

be wary of lesser-quality products. The ways in which protection levels of sun products are identified are now discussed.

16.2.4 Sun protection factors (SPFs) and SPF testing

The level of protection from sunburn afforded by a sun product is described by the sun protection factor (SPF). Since SPF measures sunburn it is predominantly, but not entirely, a measure of UVB protection. The SPF is measured *in vivo* using human volunteers following a strict method. Over the past twenty years national SPF methods have been published and revised in Germany, USA/Canada, South Africa, Australia/New Zealand and Japan. In addition, a new and widely used pan-European method, 'The COLIPA SPF Test Method' has recently been published [4]. Historically, the individual national methods were substantially different, which resulted in differences between SPFs determined in different countries. However, in recent years manufacturers throughout the world have worked together to harmonize procedures so that, today, the essential components of all methods are more or less the same, resulting in consistent SPF numbers. The similarities between the world's leading SPF test methods are shown in Table 16.1.

SPF testing is based on the fundamental premise that sunscreen effectiveness can be assessed by exposing an individual to a source of UV radiation and comparing the lowest dose of UV that is needed to redden the unprotected skin (the minimum erythemal dose or MED), with that required to redden skin protected with a fixed quantity of sun product.

Table 16.1 Similarities between international SPF test methods

	FDA (American Standard)	*SAA & NZ (Australian/NZ Standard)*	*COLIPA (European Standard)*
Standard sunscreens	SPF4 – Homosalate	SPF4 – Homosalate SPF15 – Octyl Dimethyl PABA + Oxybenzone	SPF4 – Octyl methoxycinnamate SPF15 – Octyl Dimethyl PABA + Oxybenzone
Quantity applied	2 mg/cm^2	2 mg/cm^2	2 mg/cm^2
Test area	50 cm^2	50 cm^2	Minimum 35 cm^2
Light source	Xenon arc	Xenon arc with continuous UVA	Defined match to solar spectrum
Successive exposure times	1.25 ×	1.25 ×	1.25 ×
Time before visual evaluation (hours)	16–24	16–24	16–24

Minimum erythemal dose (MED)

The MED is defined as the minimum quantity of radiant energy of specific wavelength or range of wavelengths which produces the first unambiguous reddening of human skin, 24 hours after exposure. Under constant-intensity conditions the total quantity or dose of radiant energy is directly proportional to total time of exposure and hence MEDs are often described as either total energy dose or exposure time at a stated constant energy flux. Depending upon wavelength and intensity of the source of irradiation, an MED time (or dose) can vary from a few minutes (high-intensity UVB) to many hours (sunlight-intensity UVA). Within this range, minor variations will also occur between individual skin types.

Having defined MED, we can now define the sun protection factor (SPF) as the ratio of the dose of energy required to produce a MED on protected skin (MED_p) to that required to produce an MED on unprotected skin (MED_u).

$$SPF = \frac{\text{exposure time to produce erythema (protected skin)}}{\text{exposure time to produce erythema (unprotected skin)}} \quad (1)$$

Similarly,

$$SPF = \frac{MED_p}{MED_u} \quad (2)$$

So, taking a simple example, a person using an SPF10 product will be able to remain exposed to the radiation for ten times longer than without protection, before a reddening of the skin will occur. Alternatively, and perhaps more appropriately, the individual would receive only one-tenth of the exposure using an SPF10 product than he or she would have received in the same time if unprotected. One must bear in mind, though, that a skin type I person will be protected for much less absolute time than a skin type IV person using the same SPF product, due to their greater sensitivity to UV radiation and therefore lower MED times, both protected and unprotected.

SPF testing in vivo

In vivo SPF testing is typically carried out on the skin of the backs of between ten and twenty human volunteers of skin types I–IV. Initially the MED_u for each individual is determined by exposing a number (usually 5 or 6) of 1 cm^2 test sites on the skin to increasing doses of radiation from a solar simulator. The solar simulator emits a spectrum of UV light (290–400 nm) matched as closely as possible to midday, midsummer sunlight at 40°N latitude.

The irradiated test sites are examined either visually or by reflectance colorimetry, approximately 24 hours after exposure, and the lowest dose increment which produced the first unambiguous redness is defined as the MED_u for unprotected skin.

The sun product under examination is then applied to a separate area of the volunteer's back at precisely 2.0 mg/cm^2, this being representative of a typical average in-use application rate. The test is then repeated using a new series of increasing radiation doses in which the middle exposure is equal to the previously determined MED_u multiplied by the anticipated SPF number for the product. Again the exposure dose required to generate the first sign of redness on product-protected skin (MED_p) is assessed. From these values the SPF is calculated according to equation (2).

Since the SPF test uses human volunteers, it is vulnerable to a certain degree of biological variability between individual volunteers, due to factors such as skin type, skin condition (sweating, temperature, wrinkling, etc.) and evenness of product spreading. Systematic variability can also arise from factors such as solar simulator lamp variation, environment (temperature, humidity, airflow, etc.) and accuracy of MED assessment. Because of this, most SPF methods define limits of acceptable variability within individual test results, which ensures a reasonably robust test when 10 to 20 volunteers are used. As a final note, it is also worth mentioning that product performance on the beach under natural sunlight will be affected by additional factors such as application rate, spreadability, product formulation type, presence of photosensitizing impurities, substantivity of product, percutaneous absorption, skin temperature, wind velocity, swimming, etc. Consequently, SPF numbers should be viewed as only a guide to protection level and not as absolute.

Measuring SPF in vitro

When it comes to product labelling, the safety of the consumer is paramount and so human volunteer studies are always used to determine the SPF labelled on a marketed sun product. However, *in vitro* instrumental methods are widely used in the sun product development process to screen out potentially poor formulations early in the cycle, thus allowing those with a better chance of success to be submitted for *in vivo* studies. Companies adopting *in vitro* techniques are therefore spared the considerable time and expense of repeatedly submitting products for human volunteer tests which may not achieve the desired SPF. In addition, *in vitro* techniques can help to eliminate some of the biological variability of *in vivo* testing and are also particularly advantageous in situations in which lack of suitable biological end-points prevents the use of an *in vivo* technique, as with UVA measurement for example.

The physical absorbance of a sunscreen agent can readily be measured spectrophotometrically. Whilst this will predict which wavelengths of radiation are likely to be protected against, it will not accurately predict the SPF of any product which contains it. This is due to many factors, the most important of which are solvent effects of the base formulation into which the sunscreen is added, the rheological properties of the final preparation and the surface topography of

the medium on which the sun product is spread. For these reasons, *in vitro* techniques need to utilize finished formulations applied to simulated skin substrates, or excised skin itself.

One of the first techniques reported which recognized these essential features involved the use of skin replicas made from UV-transparent resin [5]. The intensity of narrow-band UV irradiation transmitted through the replica was measured using a broad-band UVB detector, both before and after product application. From these measurements an estimate of SPF could be calculated. Whilst reasonably effective, this method was UVB-specific and therefore of only limited value for the newly evolving sun products containing significant levels of UVA sunscreen. The technique was therefore further developed into a new method [6], in which a textured UV-transparent adhesive tape is used as the substrate to which the product is applied. Broad-band (UVB and UVA) light is directed onto the surface of the tape following application of the test sun product. A scanning spectroradiometer is then used to measure transmission through the product-treated substrate in 5 nm wavelength intervals from 290 nm to 400 nm. These individual transmission measurements can then be used to calculate a series of wavelength-specific protection factors or monochromatic protection factors (mPF) which, when plotted against wavelength as in Fig. 16.3, gives a visual representation of product protection across the whole UVB/UVA spectrum.

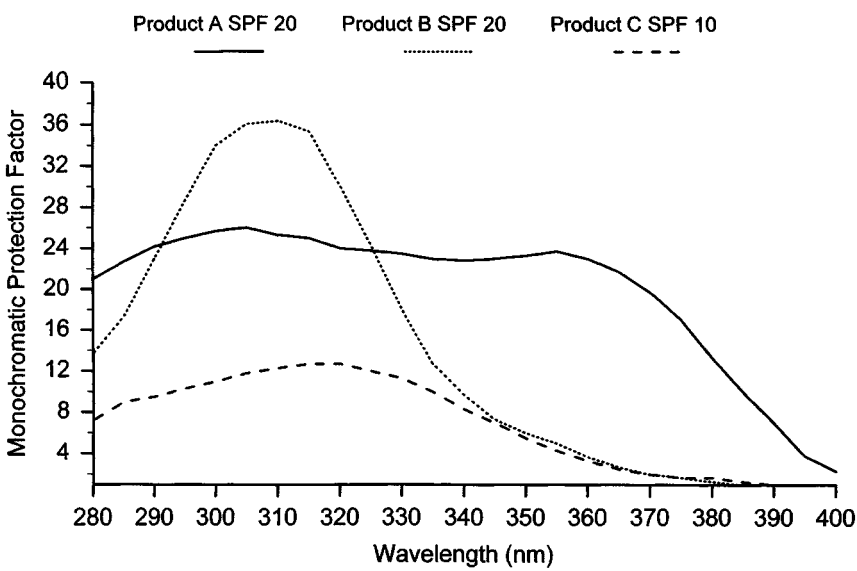

Fig. 16.3 Monochromatic protection factors for three sun products.

It can be seen that the quality of protection afforded by sun products claiming the same SPF can vary considerably, especially in their degree of protection against UVA.

Monochromatic protection factors can be used to estimate SPF by applying adjustments, via a computer program, for the spectral irradiance of terrestrial sunlight and for the relative effectiveness of each wavelength of radiation in generating an erythemal reaction. Whilst this method lends itself more readily to emulsion systems, it can be used with care for some oil-based or alcohol-based formulations and has fast become a widely used technique throughout the world.

More recently, reflectance spectrophotometry has been considered as a possible technique for estimating SPF. This *ex vivo* technique measures the reflectance of UV light from within the skin, after passage through sunscreen which has been applied directly to the skin surface. Unfortunately, this technique is fraught with difficulties since the UV radiation has to traverse the sunscreen film twice, whilst scattering at the skin's surface may also occur, making measurement very complex.

Measuring UVA protection

For a long time, educated opinion was that whilst UVB was clearly harmful, UVA was 'safe' or even advantageous, since it delivered the benefits of a suntan with no negative effects. Recent research has clearly proven this not to be the case and UVA is now implicated in many serious adverse effects in skin. In recognizing this, manufacturers have developed sun products which provide additional protection against UVA wavelengths. With this improvement in product performance comes the need to inform the consumer of the amount of UVA protection offered. To this end, many techniques have been considered for measuring the level of UVA protection [7]. Unfortunately, the biological effects of UVA all tend to be chronic, manifesting themselves after very long or multiple exposures to UVA. There is no easily measurable, acute and immediate response to normal sunlight levels of UVA which would serve as a measurement end-point in an *in vivo* human volunteer test. Consequently most proposed *in vivo* UVA measurement techniques rely on abnormally high doses of UVA radiation and/or biological end-points which do not occur naturally. Such techniques include the UVA erythema method which is, in essence, the same technique as the SPF test but uses UVA radiation to induce erythema in either patients with clinical photosensitivity to UVA light, normal volunteers with chemically (psoralins) induced photosensitivity or normal volunteers exposed to high doses of UVA light. Whilst effective, this method is not popular due to the dubious ethics of deliberately photosensitizing volunteers or generating UVA sunburns with high-energy doses.

A second *in vivo* method which is perhaps more popular utilizes an immediate photo-oxidation reaction in type III and type IV human skin, in which existing

brown-coloured reduced melanin or pre-melanins are converted into their blue-grey oxidized forms. This colour change forms the basis of the technique in which, much as with the SPF method, the minimum dose of UVA energy necessary to generate the first perceivable pigmentation forms the basic unit of measurement. Two subtly different techniques have now evolved. In the immediate pigment darkening (IPD) version, high-energy UVA produces a colour change in skin which is visible immediately after irradiation but is transient, fading after only a few minutes or hours. In the persistent pigment darkening (PPD) version, the UVA energy is increased ten-fold and again a pigmentation response in skin is observed immediately after irradiation. This colouration is more persistent, lasting many hours or even days, making it easier to measure.

In vivo UVA methods are even more time-consuming and expensive than SPF testing and may not deliver particularly meaningful measures of protection. Because of this, their popularity is waning in favour of spectrophotometric methods such as that previously described as the *in vitro* method of measuring SPF. Since this technique generates monochromatic protection factors throughout the UVB and UVA spectrum, the data produced can be used in a number of ways to generate indices of UVA protection. This *in vitro* technique, together with a unique symbolic method of categorizing UVA protection, has already been adopted in the UK by many major companies following the lead of the country's leading sunscreen retailer, Boots the Chemists. The system indicates UVA protection levels by means of a star rating symbol. In this system a product is awarded a number of stars (up to a maximum of four) depending on the relative amount of UVA absorbance delivered by the product as compared to its UVB absorbance. The measurement technique, if not the labelling system, has grown in popularity and is now the front-runner to become the standard UVA measurement method for Europe. In the USA, the Food and Drug Administration (FDA) are actively considering its suitability for inclusion in their sunscreen monograph, following recommendation by the Cosmetics, Toiletries and Fragrance Association (CTFA).

In Australia the Standards Authority of Australia has published a method for testing sun product performance which incorporates an *in vitro* measure of 'broad-spectrum' protection. Broad-spectrum refers to protection throughout the UV spectrum and so includes UVB and UVA. This technique also relies on a spectrophotometric measurement of transmission of UV light through a thin film of sun product. A broad-spectrum product is defined as one which transmits less than 10% of UV wavelengths between 320 nm and 360 nm.

Other measures of sun product performance

As the sunscreen market becomes more and more sophisticated, many additional performance claims are being made of sun products. With each claim comes a specific test method designed to substantiate the claim. Examples of

additional performance claims now applied to sun products include: photostable, water-resistant, waterproof, sweat resistant, all-day protection, etc. Whilst raising awareness of these methodologies, this chapter will not attempt to describe them all.

16.3 PRODUCT INGREDIENTS

16.3.1 Sunscreen agents

To be considered as a potential UV screening agent a chemical entity must have the following attributes:

1. It must absorb UV light over a broad or specified part of the spectrum without any chemical breakdown which would lead to a reduction in efficacy or the production of toxic or irritant by-products.
2. It must possess suitable characteristics to allow it to be readily formulated into cosmetic vehicles and should be absorbed easily into the skin.
3. It must be resistant to removal by water or sweat.
4. It must not require too-frequent re-application to be effective.
5. It must be highly effective at low concentrations.
6. It must be non-toxic, non-irritant and non-sensitizing.

There are innumerable chemical compounds which absorb in the UV region. We have heard earlier that DNA itself is capable of absorbing UVB radiation; however, this could never be considered a sunscreen agent as it can readily break down under high-energy radiation. Similarly, urocanic acid which is found in the stratum corneum is able to absorb energy between 300 and 325 nm and may have some physiological screening properties. However, this material undergoes a photochemical isomerism from the *cis* to *trans* form and rapidly loses its efficacy. More significantly, its use in cosmetic products is now banned in Europe. Even melanin itself can provide protection equivalent to a SPF of only 4–5 in Caucasians, but this material is difficult and expensive to obtain from either natural or synthetic sources and is difficult to formulate with. So, in general, natural materials are not good UV screening agents. Some natural oils recently suggested as UV screens, such as mink oil or avocado oil, give only very low levels of protection, though they may be reasonably stable. For the moment formulators have to be satisfied with the extensive list of synthetic chemicals which are the principal sunscreen agents in use worldwide.

Organic sunscreens

There are indeed many organic screening agents available today. A great deal of time, effort and money has been spent in searching for the perfect material which will satisfy the list of requirements detailed above. All allowable UV

screening materials are categorized by both the FDA in the United States and the EC in Europe, according to their acceptability. This acceptability depends largely on the level of toxicological data available for each compound, the most important requisite of a sunscreen being its safety in use. However the FDA and EC categories are by no means identical; what is acceptable on one side of the world may not necessarily be so on the other.

Based on our list of requirements for a sunscreen agent, the following chemical materials are considered to be acceptable and to satisfy those requirements. They function primarily by absorbing UV energy and converting it into heat. This list is by no means exhaustive, but contains those chemicals most often used.

p-*Aminobenzoic acid (PABA) and its derivatives.* These are well-known UVB screening agents, still popular in the USA but uncommon in Europe. Apart from PABA itself, the most commonly used derivative is 2-ethylhexyl-*p*-dimethylaminobenzoate (Octyldimethyl PABA) at allowable levels up to 8.0%. It has an absorption peak at 311 nm.

Cinnamates. Cinnamic acid esters are more popular in Europe than the PABA compounds. The best known is 2-ethylhexyl-*p*-methoxycinnamate (Octylmethoxycinnamate) at levels up to 10%. This also has an absorption maximum at 311 nm (Fig. 16.4). Other well-known cinnamates are isoamyl-*p*-methoxycinnamate and 2-ethoxyethyl-*p*-methoxycinnamate.

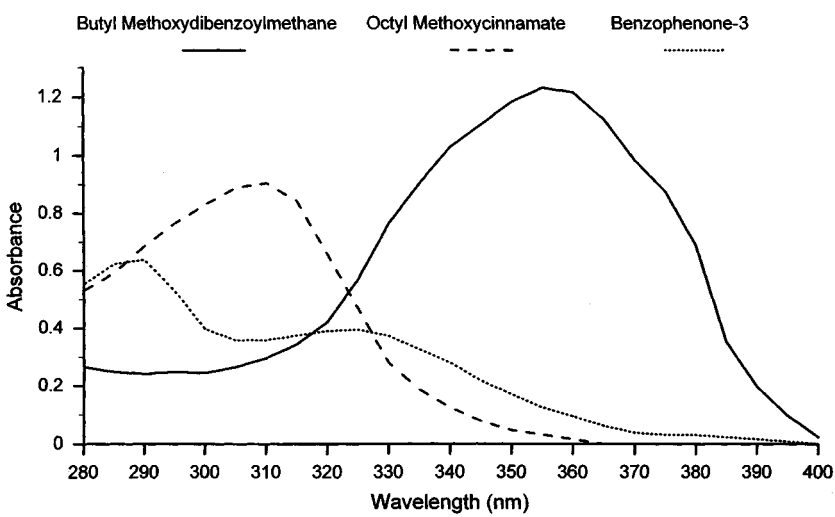

Fig. 16.4 Absorbance of a selection of organic sunscreen materials.

Salicylates. Well known and often used, octyl salicylate has an absorption peak at 307 nm and can be used at levels up to 5%. Its overall protective effect, however, is poor, its absorbance being far less than PABA or cinnamate derivatives of equivalent concentration. It is often used as a synergist with other sunscreens since it aids their solubility. Homomenthyl salicylate (homosalate) has similar characteristics but may be used at levels up to 10%. It is used as a standard in some SPF determinations *in vivo.*

Anthranilates. Menthyl anthranilate has an absorption peak at 336 nm and is therefore employed as a UVA screen at up to 5% concentration in the USA. It is not permitted in Europe.

Camphor derivatives. 3-(4-Methylbenzylidene) camphor is becoming much more widely used in European countries as a UVB sunscreen, despite its comparatively low peak absorbance wavelength of 300 nm. This is primarily because sun product photostability, and therefore sunfilter photostability, has become an issue in recent years. This camphor derivative is reported to have superior photostability [8] compared with many other sunfilters and, in addition, can improve the photostability of other filters when used in combination with them. It is allowed up to a maximum concentration of 6%; 3-benzylidene camphor is also allowed up to the same maximum level.

Benzophenones. The benzophenone sunscreens have absorption peaks at wavelengths greater than 320 nm and are frequently employed as UVA screens. 2-Hydroxy-4-methoxy-benzophenone (benzophenone-3 or oxybenzone) is widely used at up to 10% concentration in combination with UVB screens to give broad-spectrum protection. This is particularly the case in the USA where, until recently, benzophenones were the only allowed UVA filters apart from methyl anthranilate.

Dibenzoylmethanes. These materials are the most commonly used UVA-absorbing materials, particularly in the EU where they have been allowed for many years. The most widely used derivative is 4-*t*-butyl-4′-methoxydibenzoylmethane, which has its peak absorbance at 358 nm, right in the middle of the UVA range. This material was until recently not allowed in the USA, but it has recently been added to the permitted list at levels between 1% and 3%. In Europe it can be used at concentrations up to 5%.

4-Isopropyldibenzoylmethane is another useful filter with its peak of absorbance around 345 nm.

Octocrylene. This is a relatively new sunfilter which is allowed in both the EU and the USA at levels up to 10% (expressed as acid). Chemically, it is 2-cyano-3,3-diphenyl acrylic acid, 2-ethylhexyl ester. It has its peak absorbance at 303 nm.

Others. There is a small body of opinion favouring water-soluble sunscreens at present. Although this contradicts our previously stated requirement of resistance to removal by water or sweat, it is suggested that water-soluble materials may be more effective by virtue of their skin penetration properties. Such compounds are readily available, the two most notable being the soluble benzophenone, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (benzophenone-4), and 2-phenylbenzimidazole-5-sulfonic acid. The benzophenone is a UVA screen allowed at up to 10% in the USA and up to 5% in the EU. The benzimidazole is a UVB filter allowed up to 4% in the USA and up to 8% in Europe. Both are solubilized by neutralization with a suitable base such as triethanolamine.

The suitability and effect of any of these compounds depend on the requirements of the product and its vehicle formulation. It is common to use combinations of sunscreens to achieve the desired effect, with the majority of today's commercial products containing two, three, four or more different filters. It is likely that new chemical agents will be developed; however the expense of toxicological studies needed to achieve positive listing for use in sun products, is likely to limit seriously the number.

Inorganic (physical) sunscreens

Taken to extremes the ideal physical sunscreen would be to stay indoors, brick walls being good protection against UV radiation (but not glass, which reflects UVB but allows UVA to pass through). More acceptably, one may use a parasol or wear reflective clothing. It is frequently recommended that small children wear a sunhat and a T-shirt on the beach and this is good advice, although radiation can penetrate the weave of some cloths. Our interpretation of a physical sunscreen is an inorganic compound which has radiation scattering and reflective properties due to its physical form. We include here largely natural minerals and pigments – talc, mica, kaolin and metal oxides. The criterion for choice then becomes their cosmetic acceptability. Iron oxides are frequently used in facial colour cosmetics at relatively low levels. To achieve any kind of radiation protection the levels required would result in a product sadly lacking in aesthetic properties, even if the iron oxides were good reflectors to begin with. Mica, or titanium dioxide-coated micas, are used as pearlescent pigments in colour cosmetics and these either reflect or transmit light depending on the wavelength of the light and the crystal dimensions of the physical sunscreens. Talc, being a white powder, is able to reflect light. The most common choices as physical sunscreens, however, are zinc oxide and titanium dioxide.

Zinc oxide is often used in pharmaceutical creams and ointments for purposes other than sun protection. Its use as a sunscreen lies in its good light-barrier properties, which extend across the whole of the UVA and UVB wavelength range and, indeed, the visible spectrum. Therefore products containing zinc oxide offer a very broad UV protection, but also tend to give some visible light protection which may result in a white appearance of the product on the skin.

This led to the very white sunblock products which found favour for skiing and other outdoor sports. In the past few years, however, zinc oxide has been found to give greater protection in the UVA region around 370 nm, particularly as smaller particle size grades have become available. This has led to products containing zinc oxide having less of a tendency to whiten the skin and, consequently, being more cosmetically acceptable. More mainstream formulations now contain zinc oxide in combination with either organic filters or titanium dioxide. In both cases the zinc oxide boosts protection in the higher UVA region whilst incurring only minimal skin whitening.

A great deal of research and effort has gone into tailoring the use of titanium dioxide as a physical sunscreen. Titanium dioxide has similar light-scattering and reflective properties to zinc oxide, thus preventing the transmission of UV and visible radiation. Hence, whilst it gives good protection from UV light, it too gives a white colour to the skin if used in its standard pigmentary form. Fortunately, its cosmetic acceptability and usefulness have been dramatically improved by the manufacture of micronized forms with much smaller particle sizes than standard pigmentary forms.

Pigmentary titanium dioxide used in the paint industry and in colour cosmetics contains large particles in excess of 200 nm in diameter. These reflect radiation across the whole spectrum including the visible. Consequently, they are a vivid white colour when applied to a surface. As the particle size of the material decreases, however, more of the longer wavelength light is transmitted until little or no reflection occurs. Products which contain such low particle size material no longer reflect visible light and so do not appear white on the skin. This improves cosmetic acceptability for the majority of consumers. Titanium dioxide exhibits low reflection of visible wavelengths at particle sizes of about 50 nm diameter and commercial grades around this size are now available.

As the particle size decreases further, the amount of UVA radiation reflected decreases and the reflection of visible wavelengths decreases further to almost zero. Commercial grades are available down to about 15 nm and these give very minimal skin whitening whilst retaining fairly broad-spectrum protection. If the particle size is decreased still further, then skin whitening disappears but so does the broad UV protection since most UVA light is then transmitted. The shorter UVB radiation continues to be reflected from physical barriers down to molecular dimensions, and this is shown by the UVB screening properties of the liquid crystal structure of ordinary window glass (Fig. 16.5).

The efficiency of titanium dioxide as a physical screen hence depends greatly on its particle size. Decreasing the particle size decreases skin whitening, but makes the UV protection less broad. The formulator needs to choose the particle size of titanium dioxide carefully so that the product has the benefits and aesthetics desired by the particular consumer for whom it is intended.

High SPFs can be achieved using metal oxides alone, but formulation is difficult since high levels of powders need to be incorporated into the formulation

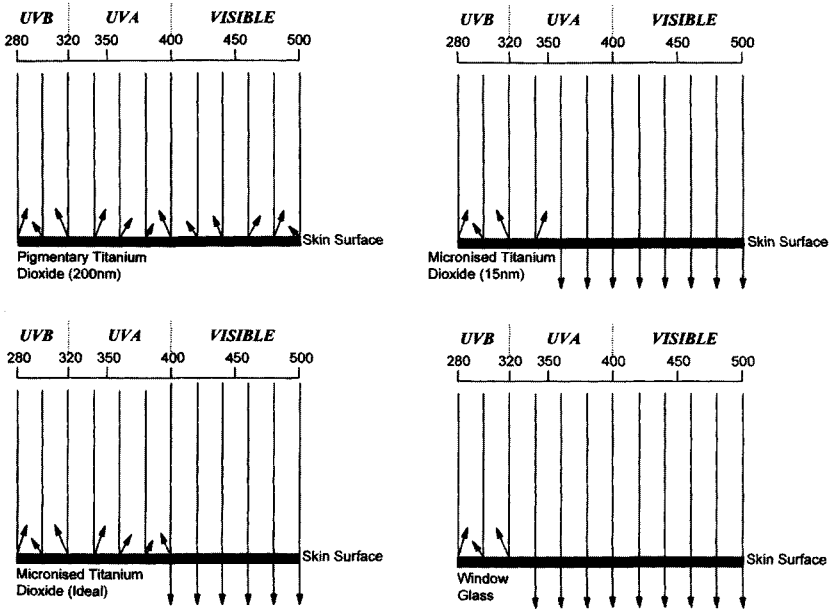

Fig. 16.5 Particle size effect of physical sunscreen materials.

and some degree of skin whitening is likely. However, for sensitive skins the hypoallergenic alternative of a product containing inorganic sunscreens only, is a good choice or even a necessity. Surface-treated titanium dioxides are commercially available which assist the production of either oil-in-water or water-in-oil emulsions, depending on the surface coating.

Metal oxides can also be used in combination with organic filters to give broad-spectrum protection whilst maintaining good aesthetics. This option is becoming increasingly popular, particularly with the current trend towards higher SPF products.

Some theories implicate the reflective properties of titanium dioxide with an increase in photo-instability of potentially vulnerable organic sunscreens. In other words, radiation scattered by metal oxides within the product may accelerate potential photodegradation of any adjacent chemical. Similarly it is suggested that titanium dioxide may be photo-activated to produce oxidative free radicals which may actually accelerate the very skin ageing process it is often used to protect against. Neither of these theories is proven, but the formulator must be aware of some of the controversies and choose his or her ingredients carefully to minimize the likelihood of such events.

16.3.2 Waterproofing agents

An important requisite of any sunscreen product is that it should withstand water, either in the form of sweat, or from the sea or a swimming pool. During bathing the skin continues to be exposed to high levels of irradiation as UV light readily penetrates the water's surface. It is highly desirable therefore that the product is not easily washed off. Naturally one can and should re-apply the product after immersion, especially as it is likely to have been towelled off during drying, but this is often inconvenient or forgotten. Waterproofing characteristics should therefore be built into formulations.

There are official tests for standards of water resistance which involve an *in vivo* SPF measurement before and after immersion for a fixed period in water. If a product is to be described as water-resistant it should retain at least 50% of its SPF following moderate activity in water, or the SPF should remain within the same protection category of either minimal, moderate, extra, maximal or ultra protection as defined by the FDA, depending on the test method used.

Water resistance can be achieved in a number of ways. Oil-based formulations or stick formulations have inbuilt water repellency due to their non-aqueous nature. In these cases the product sits on the skin as an oily or waxy film which is not easy to dislodge. The majority of sun protection products, however, are emulsions which can contain very high levels of water. Water-in-oil emulsions are usually inherently water-resistant. The low levels of water present as the dispersed phase are readily lost on application to the skin to leave the continuous oil phase smoothly spread over the surface to give a water-repellent film. Water-in-oil emulsions though, are not very acceptable to the consumer because they often have a heavy, greasy feel.

Oil-in-water systems are cosmetically more elegant and have a better skin feel. These also deposit an oily film on the skin once the high levels of water have evaporated but, by nature of their surfactant systems, they are easy to re-emulsify in the presence of water from a pool or the sea and consequently are easier to remove. An ideal system would be one which has the elegance of an oil-in-water emulsion but which, on application to the skin, rapidly loses water and inverts to a water-in-oil system. Thus a repellent oil film would be deposited on the skin surface. This can be achieved by a fine balance of surfactant ingredients or by the use of quick-breaking carbomer emulsifiers. The choice of sunscreen can also influence water resistance. It is claimed that PABA-type sunfilters are more resistant to wash-off than other organic sunscreens because they can penetrate deeper into the skin's layers.

As far as actual ingredients which impose water resistance are concerned, the most well known are the silicone oils. These materials are extremely resistant to water penetration, are eminently spreadable and form a continuous thin water-repellent film on the skin surface which is highly acceptable. The most widely used materials are dimethicone 350, cyclomethicone and

dimethicone/trimethylsiloxysilicate which are all excellent waterproofing agents. More recently other polymeric film-formers have gained favour as waterproofing agents. Alkylated polyvinylpyrrolidones, which are closely related to the film-formers found in hairsprays, are also excellent for imparting water resistance to a formulation. As little as 1–2% will produce a repellent film which readily satisfies the legislatory tests, but these compounds require high levels of other suitable materials such as the emollient esters to ensure spreading and continuity of the film.

16.3.3 Emollients and diluents

The choice of oil and water phase diluents and oil-soluble emollients is very much that of the formulator. The types of material available are too numerous to mention here, but a few points concerning their choice are worth considering. One must avoid heavy, greasy materials if the intention is to formulate with elegance. Materials which impart a tacky feel should be avoided. On the other hand, the formulation must not be too thin and insubstantive, otherwise it is possible that settling will occur within the troughs of the undulating skin surface leaving the peaks exposed and unprotected. A uniform and continuous film is desirable to ensure complete protection. Branched-chain esters, because of their spreadability, are more likely to produce a more even protective film. They also improve the skin feel and acceptability of a product. However, they too have their drawbacks: they can sometimes disrupt a water-repellent barrier at the molecular level because of their branching, if the concentrations of other ingredients are not in balance.

The most serious effect of the choice of emollients and diluents is that of hypochromic and bathochromic shift [9]. The peak absorbence wavelength (λ_{max}) of sunscreen agents can be shifted to either longer or shorter wavelengths depending on the polarity of the sunscreen and that of the diluent. Thus an *in vivo* SPF measurement carried out on a product containing a sunscreen material plus solvent A, might give a markedly different value from an SPF obtained on the same material plus solvent B. This is because the sunscreen agent no longer has maximum absorption at its designated wavelength. It can be seen that this may have both beneficial and detrimental effects on a formulation, so the formulator must be aware of what may happen under certain conditions. As an example, octyldimethyl PABA has a λ_{max} at 315 nm in propylene glycol. In the non-polar solvent, mineral oil, the λ_{max} is shifted to the lower wavelength of 300 nm. This would suggest a drop in efficacy of the product if protection is required at the peak erythemogenic wavelength of around 310 nm. Similarly dioxybenzone has a λ_{max} at 326 nm in propylene glycol and at 352 nm in mineral oil. Thus its UVA screening properties are enhanced by the decrease in polarity of the solvent. Iso-arachidyl neopentanoate is a branched-chain ester which is claimed commercially to have remarkable SPF-enhancing properties. This may

be because of a spectral shift rather than because of any superior spreading and emollient properties it may possess.

16.3.4 Other ingredients

The waterproofing agents, emollients and diluents used in a formulation will all affect its aesthetics, rheology and overall performance in terms of SPF efficiency. These affect the way the product is perceived by the consumer on application; particularly important is the relative amount of time taken to apply and rub in, and the ultimate feel of the skin after application. Other ingredients can also affect these parameters. Some emulsifiers, for example, are specifically designed to 'break' from their original oil-in-water environment to rub in very quickly, leaving a layer on the skin which is effective in imparting a waterproof nature. Rheology modifiers are also important since they affect not only the ease with which the product is applied, but also the efficiency of both inorganic and physical sunscreens. Careful choice of emulsifiers can promote the formation of liquid crystals within the emulsion and this again can improve both aesthetics and sunscreen efficiency.

As a protective mechanism against sunburn the skin thickens. Overlong exposure results in wrinkling, loss of elasticity and dryness. This is the ultimate legacy of the accelerated ageing process. There are materials which help to combat such effects which may be included in product formulations.

It is important that any product should counteract loss of moisture. Moisturization should be achieved by humectant materials rather than by occlusion, in order to be more acceptable to the consumer. Humectants such as sorbitol, glycerol or propylene glycol are essential to skin-care products unless some of the more sophisticated materials are to be used. In such cases liposomes or natural moisturizing factor ingredients preclude the use of the simpler traditional moisturizers.

It is known that much of the damage attributed to UVA radiation is caused by the generation of free radicals within the deeper skin layers. These chemical agents attack the collagen and elastin structure of the underlying dermal matter by oxidative reactions. These lead to wrinkling by a breakdown in the elastic properties of the connective tissue. To prevent this damage, and allow the skin to retain or revert to its normal state, it is necessary somehow to 'trap' or inactivate the free radicals. Melanin itself is thought to be a free radical trap, albeit not a very efficient one. Those most likely to be found in modern formulations are the antioxidant vitamins such as vitamins E and C. These act as free radical scavengers, thus inhibiting the peroxidation of unsaturated lipids found in animal cell membranes. Vitamin E also has anti-inflammatory properties. It has been used to prevent oxidation of product ingredients and prolong shelf-life. For this purpose a concentration of 0.05–0.2% of the free vitamin is recommended. To have claim to free radical scavenging properties, an acetate concentration of

0.5–5.0% is likely to be required. Such levels of free vitamin tend to promote rather than depress oxidative reactions. The penetrative properties of these vitamins can be enhanced by liposome formation.

16.3.5 Artificial tanning agents

For those people unfortunate enough to find it necessary to wear very high protection products, either because of an allergic response to sunlight or due to severe erythemal reactions, or for those who simply require a tanned appearance and for whom the prospect of a holiday in the tropics is out of reach, there exist several ways of achieving a tan without radiation. The best-known method is to use products containing dihydroxyacetone. This material reacts with certain free amino groups in proteins near the skin surface to form products which condense and polymerize to form dark-coloured melanoidins. The effect appears within a few hours of application and persists for the life of the epidermis. Artificial tanning agents have also appeared in the form of tablets containing β-carotene or psoralens which claim to produce a systemic stimulation of a pigmentary reaction. Oil-soluble pigments which are resistant to wash-off or heavily pigmented face powders may be applied topically to imitate the tanned appearance of the skin.

Some products contain melanin precursors which are claimed to accelerate the tanning process. A commercial mixture of tyrosine and riboflavin is available, riboflavin to aid the oxidation of tyrosine and tyrosine to intensify the formation of melanin. Such products are not truly artificial tans, there still being a requirement for exposure to radiation.

It is now possible to formulate products which contain both sunscreens and dihydroxyacetone, so that the consumer can be protected from the sun and develop an artificial tan at the same time. Such products require very clear and careful labelling to avoid confusion, but are useful where a consumer requires a high level of protection from the sun and yet still desires a tan.

16.3.6 After-sun preparations

Despite all the precautions there will still be occasions when individuals suffer the pain of sunburn. Even if this is not the case, after exposure to UV radiation the skin will require palliative treatment to sooth, smooth and moisturize in order to maintain its condition. Often a cooling effect is beneficial and menthol provides just such a feeling. After-sun preparations usually take the form of low-viscosity lotions or milks. They must be non-irritant. Soothing and healing ingredients include aloe vera, allantoin and calamine. Mild anaesthetics such as xylocaine reduce pain. Vitamin E reduces the erythemal effect and reduces the time taken to heal by promoting enzyme activity. D-Panthenol, being a

precursor of vitamin B_5, acts to replace this vitamin which is found only at low levels in skin which has undergone sun damage. Vitamin A has a soothing effect and hastens wound healing and epithelization. Also, as we have seen, it is important to improve elasticity and dryness by maintaining moisture levels. The use of suitable moisturizing agents also prevents, or at least postpones, the unsightly features of skin flaking and peeling. After-sun shower gels are a more modern approach but their effect is largely transitory, little benefit being obtained from ingredients designed to penetrate the skin in products designed to be washed off. Their best effect is one of cooling, obtained from agents such as menthol, or of skin feel obtained by the use of skin-substantive cationic conditioners.

Finally, although antimicrobial agents can also be present to reduce the risk of infection, it is important to stress that after-sun materials and products containing them are not indicated where the skin is broken or severely blistered. In extreme cases of sunburn there is no substitute for medical consultation.

16.3.7 The millennium and beyond

The sunscreen market is a very fast-changing arena and technological advances are continually being made which affect the formulations. As an example, titanium dioxide is now available both as a dispersion in a variety of oils, and as a dispersion in an aqueous system. This has greatly improved its handling on the large scale by overcoming the need to handle large volumes of powder. Use of titanium dioxide has hence become much more widespread in recent years, particularly with products containing both organic filters and titanium dioxide in combination.

This increase in the use of titanium dioxide has led to questions over its photostability and potential to introduce free radicals into formulations. It has been shown that these problems are minimized by coating the surface of the titanium dioxide with such materials as silica, metal oxides and organic acids. There are many different coatings now available and each imparts different characteristics to the material which determines the emulsion type, the phase into which the titanium dioxide is dispersed, and the type of oils used in the product. Free radical scavengers, such as vitamin E or antioxidants, are now generally used to protect both the user and the product.

Zinc oxide is now used routinely as an alternative to titanium dioxide, or indeed in combination with it in products either with or without organic filters. Its main advantages are its minimal skin-whitening effect, good skin feel and very broad-spectrum protection. It is often used to boost the UVA protection in products containing either titanium dioxide or organic filters.

Some organic sunscreens have recently been questioned from a photostability viewpoint, with concerns of a reduction in level of protection as the product is

exposed to UV rays. The potential breakdown products of such instability must be carefully considered and products must be tested for photostability in use. Some combinations of organic filters are more photostable than others, with certain filters aiding the photostability of those less inherently stable. It is generally observed that popularity of individual sunfilters changes in any case, even though the majority of them remain on the approved positive listings.

Along with most other cosmetic and toiletry products, sun-care products are increasingly utilizing natural ingredients and materials with natural preserving properties. The latter include natural plant oils which possess antimicrobial properties, and a sun-care product with no artificial or chemical preservatives is now possible.

As in other areas, emulsion technology has moved forward most significantly in the area of water-in-oil emulsifiers which can now give non-greasy and cosmetically elegant products. Some of these are silicone copolymers which also aid water resistance. Modified carbomer copolymers are now available which are self-emulsifying as well as thickening. These produce products which have interesting rheology and useful emulsion-breaking qualities, leading to improved water resistance and skin moisturization.

In the past few years broad-spectrum protection has become increasingly important, as the effects of UVA exposure have become more apparent. As consumers have become more aware of the damaging effect of sunlight, they have generally used more sun protection and chosen products affording higher levels of protection. This should continue into the twenty-first century and beyond, encouraging further developments in both products and their claims. One area in which attention will be focused is the development of novel presentations with unique properties.

Finally, as research reveals more information concerning the adverse effects of sunlight other than sunburn, products may need to be adapted to ensure protection against all harmful effects, not just sunburn.

16.4 FORMULATIONS

Sunscreen products can take a number of forms such as gels, sticks, oils or emulsions. Each has its appeal to a particular consumer and each has its typical ingredient type and method of manufacture. The major formulation types will now be examined, looking at their benefits and drawbacks.

16.4.1 Gels

These are an extremely attractive and elegant formulation type. Their main drawbacks lie in their potential irritancy where alcohol is part of the formula, and their relatively low SPF and water-resistant properties.

1. Non-aqueous system	% w/w
Phase A	
Octyl methoxycinnamate	7.5
Octyl salicylate	5.0
Menthyl anthranilate	3.5
Phenyl trimethicone	1.5
Dimethicone copolyol	3.0
Isopropyl myristate	5.0
Phase B	
Hydroxypropylcellulose	1.0
Ethanol 95%	73.5

The gel structure is imparted by the cellulose which can also be added to a solution of all ingredients in the ethanol with stirring until gelled.

2. Aqueous alcohol system (Courtesy of Haarmann and Reimer)	% w/w
Phase A	
Ethanol 96% denatured	5.0
Demineralized water	60.4
1,2 Propylene glycol	5.0
Preservative	1.0
Allantoin	0.1
D-Panthenol	0.5
Carbomer (CARBOPOL 940)	1.1
Phase B	
Demineralized water	5.0
Triethanolamine	2.2
Phase C	
Demineralized water	15.0
Phenylbenzimidazole sulfonic acid (NEO HELIOPAN HYDRO)	2.0
Triethanolamine	1.2
Phase D	
Preservative	1.2
Fragrance	0.3

Here triethanolamine is used as a neutralizing agent to gel the carbomer, Phase B is added to Phase A, followed by Phase C. After gelling, fragrance and preservative are added.

3. Aqueous system	% w/w
Phase A	
2-Phenylbenzimidazole-5-sulfonic acid	4.00
Tris (hydroxymenthyl) amino methane	1.75

Sorbitol liquid	5.00
Demineralized water	38.25
Phase B	
Carbomer 950 (CARBOPOL 950)	1.50
Tris (hydroxymenthyl) amino methane	2.50
Demineralized water	47.00

Here the sunscreen (2-phenylbenzimidazole-5-sulfonic acid) is neutralized in sorbitol and water with Tris to solubilize. The carbomer is dispersed in water and is neutralized with Tris. The two phases are then mixed gently to gel.
Note: preservatives must be added to any water-based system and may require gentle heating to solubilize, as may any perfume.

All the above gel formulations can easily become aerated during manufacture. Often this is used to add a visual feature to the final product, but if this is not desired, great care must be taken when mixing.

16.4.2 Sticks

These are useful for direct application of sunscreens to a specific small area such as the nose, lips, forehead or nipples. They are often formulated to carry opaque sunscreens but give only mediocre performance with organic screens. They are usually good water-repellents due to the presence of oils and waxes, but are often expensive to prepare, for this reason. The choice of waxes determines the melting point of the stick and its performance on the skin. The melting point is reduced by the level and type of the emollients although firmness must be maintained in hot weather conditions.

	% w/w
4-Isopropyl-di-benzoylmethane (EUSOLEX 8020)	1.25
3-(4-methylbenzylidene)-camphor (EUSOLEX 6300)	2.00
Beeswax	10.00
Carnauba wax	6.00
Lanolin, anhydrous	4.00
Isopropyl myristate	6.40
High-viscosity paraffin oil	2.40
Castor oil	67.83
Propylparaben	0.08
Antioxidant	0.04

The waxes are heated to about 85°C to melt and the oils and sunscreens are added and dispersed. Pour into moulds at a temperature just above the cloud point and cool to room temperature. (Formula courtesy of Merck.)

16.4.3 Oils

These were very popular a few years ago when many people used low-SPF products and wanted a deep-coloured tan. They are convenient to use and have a good level of water resistance due to their oily nature. However, only low SPFs can be achieved due to the limitation of sunscreen solubility and the production of a very thin transparent film on the skin. Other disadvantages are that they are relatively expensive since no water is present, and are inherently sticky and greasy. These disadvantages, and the trend towards higher-SPF products, has meant that oils have become much less popular of late and now account for only a small proportion of sun-care sales. Oil formulations are as numerous as combinations of sunscreens and emollients. Depending on the solubility of the sunfilters in the oil base they can often be made without heating.

Formula 1 (Courtesy of Merck)	*% w/w*
3-(4-methylbenzylidene)-camphor (EUSOLEX 6300)	8.00
Isopropyl myristate	10.00
Low-viscosity paraffin oil	82.00

The components can simply be blended together at room temperature. The paraffin oil can be substituted by any suitable vegetable oil.

Formula 2	*% w/w*
Octylmethoxycinnamate	5.00
Butylmethoxydibenzoylmethane	2.00
Isopropyl myristate	22.00
Perfume/preservative	9.50
Light mineral oil	to 100.00

This mixture needs to be heated to 85°C to dissolve the butylmethoxy-dibenzoylmethane.

Oils can also be sold in packaging which allows the oil to be sprayed directly onto the skin, thus improving ease of application and consumer appeal. Care must be taken, however, to ensure that no areas are missed and that a sufficiently thick layer of product is applied to achieve the stated SPF. These spray oils have revived oil formulations to some extent but use is still limited by the low maximum SPF attainable.

16.4.4 Emulsions

By far the most popular formulation type for sunscreen products is the emulsion. These are highly convenient and cosmetically acceptable, can be found in a variety of packages and have a vast array of physical appearances from thick creams to light milks. They may be oil-in-water, water-in-oil or more complex

in nature. They are able to achieve the highest SPF of all formulation types because they deposit a uniform non-transparent film on the skin. They also have the ability to penetrate the skin's horny layer to some degree, thus increasing their efficacy and durability.

Much has been written about the formulation of emulsions, and the student is referred to Chapter 19 for information on ingredients and choice of surfactants. Looking back to the Ingredients section of this chapter will also help the formulator decide which materials to use. To obtain a satisfactory emulsion we can therefore make some general comments.

The oil phase can contain:

- Oil-soluble sunscreen materials.
- Oil-soluble antioxidant vitamins, for example vitamin E.
- Water-resistant agents, silicones, polymers.
- Emollients, esters or oils such as mineral or vegetable oil.
- Primary oil-soluble emulsifiers.
- Secondary emulsifiers.
- Lipid materials as skin conditioners or for skin feel.
- Oil phase thickeners.

The water phase can contain:

- Water-soluble sunscreen agents.
- Humectants, glycerol, sorbitol.
- Primary and secondary water-soluble emulsifiers.
- Water phase thickeners.
- Neutralizing agents.

Either phase may contain the preservative system, though these are normally added according to solubility. They can be dissolved in any propylene glycol or glycerol in the formulation and added after emulsification. Partition coefficients ensure that they are distributed between the phases and microbiological tests will ensure their efficiency.

The normal method of manufacture of an emulsion involves heating the oil phase components to such a temperature as to dissolve, melt or disperse them satisfactorily into a uniform liquid mass. The water phase is heated similarly and the two phases are then combined with colloid mixing to form the emulsion. Usually an oil-in-water emulsion is produced by adding the oil phase to the water phase with suitable mixing. The combined phases are then force-cooled and ingredients which are sensitive to heat added at the relevant temperatures. Oil-in-water emulsions can also be made by adding the water phase to the oil phase using a method known as phase inversion. In such cases the emulsion is first made as water-in-oil but then reverts to the required oil-in-water nature at a critical temperature during the cooling process. Using this technique the emulsion is often of a superior quality since the oil droplets in the final product are

considerably smaller than may be produced using the conventional method. Care must be taken, however, to ensure that the final emulsion is not inherently unstable by being a mixed emulsion containing both oil-in-water and water-in-oil portions. For a water-in-oil emulsion the two phases are heated in the same way and the water phase added to the oil phase with suitable mixing, followed again by forced cooling and addition of heat-sensitive ingredients.

The neutralizer may be added after the phases are combined. Neutralizing compounds such as triethanolamine are normally dissolved in a small volume of water prior to their addition. Where a neutralizer is added to gel a water phase thickener this is best done after phase mixing, otherwise the water phase may become too thick to handle efficiently. High-shear mixing may then be employed to reduce the particle size of the dispersed phase and thus improve the appearance of the final product. This is not always necessary however and in some cases can lead to irreversible shear-thinning of the emulsion with a corresponding loss of viscosity.

Special care must be taken when water phase thickeners are employed. Polymeric materials such as hydroxyethylcellulose or carbomers, or mineral thickeners such as veegum, require very careful addition and their complete dissolution must be ensured before proceeding with the manufacturing process. They are normally added to between one-third and one-half of the water and diluted with the remainder of the water phase after complete solution is achieved. The process involves slow addition of the powder to cold water into the vortex created by a high-speed stirrer. In this way the probability of producing gel-like lumps is reduced. Lengthy stirring then follows to hydrate completely the materials which, if well dispersed on addition, will eventually solubilize. Heating may then follow. If the thickeners are added too quickly, or if they are added into the vapour above heated water, surface gelling will occur, which prevents the hydration of the powder within the larger lumps. Dissolution then becomes difficult to achieve, although the lumps can be broken down by using a high-shear mixer; however, this might destroy the thickening capacity of the polymer. Any lumps present could be sieved out before proceeding with the method, but this will almost certainly lead to an unsatisfactory concentration of thickener and a consequent reduction in expected performance.

Perfume is added slowly once the emulsion has cooled to a temperature below the usual vaporization point of its constituents, and this is blended in by slow mixing. A vacuum may be applied during the cooling and prior to perfume addition to ensure de-aeration of the product.

Products formulated specifically for babies and toddlers are worth mentioning at this point. These are normally similar to adult formulations but are usually perfume-free to reduce the chance of irritation and sensitization. Irritation and sensitization potential is also minimized by baby products being formulated ideally with only physical sunscreens, that is zinc oxide and titanium dioxide. If organic filters are used then this should be in combination with these physical sunscreens

so that their use level is as low as possible. Babies and toddlers should ideally not be exposed to the sun, and products designed for their use should consequently have high SPF. In addition, a child's skin is more susceptible to moisture loss and so suitable products are highly moisturizing as well as highly protective.

There now follows a series of emulsion formulations which embrace most of the features and ingredients we have discussed in this chapter. The basic manufacturing method for emulsions applies to all these, and good results can be obtained on small-scale laboratory bench equipment. With a little experience, and a lot of ingenuity, the student will soon learn how to expand basic formulae and produce unique, elegant and highly protective and desirable products. The only limitations are the list of currently acceptable raw materials, which is vast, and the imagination and skills of the formulator, which should be constantly open to innovation.

1. **Oil-in-water lotion used as the high SPF standard in the COLIPA SPF test method**	% w/w
Phase A	
Lanolin	4.5
Cocoa butter	2.0
Glyceryl monostearate	3.0
Stearic acid	2.0
Octyl dimethyl PABA	7.0
Oxybenzone	3.0
Phase B	
Deionized water	71.6
Sorbitol liquid	5.0
Triethanolamine	1.0
Methylparaben	0.3
Propylparaben	0.1
Phase C	
Benzyl alcohol	0.5

Heat phases (A) and (B) and homogenize together. Cool to below 50°C and add benzyl alcohol, which is heat-sensitive.

2. **Water-in-oil waterproof sun lotion** (Courtesy of Haarmann and Reimer)	% w/w
Phase A	
Cetyl dimethicone copolyol (ABIL EM90)	2.00
Polyglyceryl-4-isostearate (TEGIN T4753)	1.00
Dioctylcyclohexane (CETIOL S)	17.00
Paraffin oil	8.50

Phase B	
Deionized water	65.75
Phenylbenzimidazole sulfonic acid (NEO HELIOPAN HYDRO)	3.00
Triethanolamine	0.35
1,2-propylene glycol	2.00
Preservative	0.40

This lotion is inherently waterproof, aided by the w/o formulation. The formula provides UVB protection only from the water-soluble sunscreen. Phase B is adjusted to pH 7.5 with triethanolamine with the correct pH being critical. It is then added cold to Phase A previously heated to 70°C, and after cooling is homogenized with a colloid mixer to establish the emulsion.

3. O/W cream containing inorganic sunscreen	*% w/w*
Phase A	
Titanium dioxide	6.0
Synthetic spermaceti (CRODAMOL SS)	1.0
Dimethicone/trimethylsiloxysilicate	9.5
PVP/eicosene copolymer (ANTARON V220)	2.0
Light liquid paraffin	4.8
Stearic acid	3.5
Glyceryl monostearate NE	1.5
Phase B	
Sorbitol liquid	5.0
Triethanolamine	1.0
Deionized water	65.7
Phase C	
Preservative/fragrance	q.s.

4. Sunscreen with rheology modifiers (Courtesy of Stepan)	*% w/w*
Phase A	
Deionized water	q.s. to 100.0
Xanthan gum	0.2
Magnesium aluminium silicate	0.5
Sodium stearyl amido benzoic acid (STEPAN MILD RM1)	2.0
Phase B	
Octyl dodecyl neopentanoate (ELEFAC I-205)	14.0
Octylmethoxycinnamate	3.5
Cetyl alcohol	1.0
Oxybenzone	1.5
Titanium dioxide	4.0
Citric acid	q.s.
Preservative	q.s.

Xanthan gum, magnesium aluminium silicate and sodium stearyl amido benzoic acid are used to create the correct rheological properties to enable even coverage of product on the skin.

5. High SPF, water-resistant, O/W Cream	*% w/w*
Phase A	
Octylmethoxycinnamate	7.50
Oxybenzone	4.00
Butyl methoxydibenzoylmethane	2.00
PVP/eicosene co-polymer (ANTARON V220)	2.00
Isoarachidyl neopentanoate	10.00
Glyceryl monostearate NE	4.00
Cetyl alcohol	0.40
Coco-caprylate/caprate (CETIOL LC)	6.00
Dimethicone	0.50
Vitamin E acetate	0.50
Butylated hydroxytoluene	0.05
Potassium cetyl phosphate	2.00
Preservative	0.05
Phase B	
Preservative	0.20
Disodium edetate	0.10
1-2, Propylene glycol	5.00
Potassium hydroxide	0.03
Demineralized water	33.62
Phase C	
Carbomer 950 (CARBOPOL 950)	0.05
D-Panthenol	2.00
Demineralized water	20.00

Procedure

Add Phase C to mixed Phases A and B below 60°C. Gives very broad-spectrum protection with expected SPF 20+. Contains UVB and UVA screens together with vitamins to assist free radical capture and to help prevent solar damage.

6. Artificial tanning milk	*% w/w*
Phase A	
POE fatty acid ester	1.50
POE-(5)-stearyl stearate (ARLATONE 985)	2.20
POE-(10)-stearyl alcohol (BRIJ 76)	1.50
Liquid paraffin	5.00
Caprylic/capric triglyceride (MIGLYOL 812)	5.00
Phase B	
Glycerol	5.00
Preservative	0.15
Demineralized water	69.65

Phase C	
Dihydroxyacetone	5.00
Demineralized water	5.00

Dihydroxyacetone is heat-sensitive and must be added below 40°C.

7. Aftersun lotion: a cooling, soothing lotion containing aloe vera	*% w/w*
Phase A	
Myristyl myristate	1.0
Glyceryl monostearate SE	3.5
PVP/eicosene copolymer (ANTARON V220)	3.5
Mineral oil	1.0
Shea butter	0.5
Dimethicone	1.0
Isodecyl oleate	1.0
Phase B	
Aloe vera gel 1:1	5.0
Carbomer 950 (CARBOPOL 950)	0.1
Triethanolamine 99%	0.1
Distilled Water	83.3
Phase C	
Preservative, fragrance	q.s.

16.5 MATERIALS AND SUPPLIERS

Material	*INCI name*	*Supplier*
Sunscreens		
Butyl methoxydibenzoylmethane	Butyl methoxydibenzoylmethane	Givaudan
Isopropyl dibenzoylmethane	Isopropyl dibenzoylmethane	Merck†
Menthyl anthranilate	Menthyl anthranilate	Felton
3-(4-Methylbenzylidene) camphor	4-Methylbenzylidene Camphor	Merck†, H&R
Octyl dimethyl PABA	Octyl dimethyl PABA	Felton, Merck, Van Dyk
Octyl methoxycinnamate	Octyl methoxycinnamate	Givaudan
Octyl salicylate	Octyl salicylate	Felton
Oxybenzone	Benzophenone-3	Merck, H&R, Van Dyk
2-Phenylbenzimidazole-5-sulfonic acid	Phenylbenzimidazole Sulfonic acid	Merck, H&R†
Titanium dioxide	Titanium Dioxide	Tayca, Degussa, Tioxide

(*Continued*)

Material	*INCI name*	*Supplier*
Thickeners		
Carbomer 940	Carbomer	BF Goodrich†
Carbomer 950	Carbomer	BF Goodrich†
Carnauba wax	Carnauba (Copernicia Cerifera) Wax	Astor Wax
Hydroxypropylcellulose	Hydroxypropylcellulose	Aqualon
Rheology additives/modifiers		
Magnesium aluminum silicate	Magnesium Aluminum Silicate	Vanderbilt
Sodium stearyl amido benzoic acid	Sodium Stearyl Amido Benzoic Acid	Stepan†
Xanthan gum	Xanthan Gum	Calgon
Humectants (moisturizers)		
Glycerol	Glycerin	Croda
1-2, Propylene glycol	Propylene Glycol	BASF
Sorbitol liquid	Sorbitol	Roquette
Neutralizers		
Citric acid	Citric Acid	H&R, Roche
Potassium hydroxide	Potassium Hydroxide	BDH/Merck
Triethanolamine 99%	Triethanolamine	Merck, ICI
Tris (hydroxymethyl)amino methane	Tromethamine	Merck, ICI
Preservatives/antioxidants		
Benzyl alcohol	Benzyl Alcohol	Nipa
Butylated hydroxytoluene	BHT	Nipa
Disodium edetate (chelating agent)	Disodium EDTA	Merck
Imidazolidinyl urea	Imidazolidinyl Urea	Sutton†
Methylparaben	Methylparaben	Nipa
Propylparaben	Propylparaben	Nipa
Speciality ingredients		
Allantoin	Allantoin	Hoechst, Rona, 3V Inc.
Aloe Vera Gel/Oil	Aloe Barbadensis Gel/Oil	Honeywill & Stein
Dihydroxyacetone	Dihydroxyacetone	Merck
D-Panthenol	Panthenol	Roche
Vitamin E acetate	Tocopheryl Acetate	Roche
Silicones and waterproofing agents		
Dimethicone	Dimethicone	Dow
Dimethicone copolyol	Dimethicone Copolyol	Dow

(*Continued*)

Material	*INCI name*	*Supplier*
Dimethicone/ trimethylsiloxysilicate	Dimethicone	Dow
Phenyl trimethicone	Phenyl Trimethicone	Dow
PVP/eicosene copolymer	PVP/Eicosene Copolymer	GAF†
Emulsifiers		
Arlatone 983	Proprietary Composition	ICI†
Beeswax	Beeswax (Cera Alba)	Astor Wax
Cetyl alcohol	Cetyl Alcohol	Henkel, Croda
Cetyl dimethicone copolyol	Cetyl Dimethicone Copolyol	Goldschmidt†
Glyceryl monostearate NE/SE	Glyceryl Stearate	Croda, ICI
POE-(5)-stearyl stearate	Steareth-5 Stearate	ICI†, Croda
POE-(10)-stearyl alcohol	Steareth-10	ICI†, Croda
Polyglyceryl-4-isostearate	Polyglyceryl-4 Stearate	Goldschmidt†
Potassium cetyl phosphate	Potassium Cetyl Phosphate	Givaudan
Stearic acid	Stearic Acid	Croda
Oils and emollients		
Caprylic/capric triglyceride	Caprylic/Capric Triglyceride	Dynamit Nobel†
Castor oil	Castor (Ricinus Communis) Oil	CasChem, Lipo
Coco-caprylate/caprate	Coco-Caprylate/Caprate	Henkel†
Cocoa butter	Theobroma Cocoa	Fanning
Dioctylcyclohexane	Dioctylcyclohexane	Henkel†
Isoarachidyl neopentanoate	Refer to supplier	Bernel
Isodecyl oleate	Isodecyl Oleate	Van Dyk
Isopropyl myristate	Isopropyl Myristate	Croda
Lanolin	Lanolin	Westbrook, Croda, Amerchol
Liquid paraffin/paraffin oil	Mineral Oil (Paraffin Liquidum)	Fina Chemicals
Mineral oil	Mineral Oil (Paraffin Liquidum)	Exxon Witco
Myristyl myristate	Myristyl Myristate	Croda
Octyldodecyl neopentanoate	Octyldodecyl Neopentanoate	Bernel†
Shea butter	Shea Butter (Butyrospermum Parkii)	Henkel
Synthetic spermaceti	Cetyl Esters	Croda†

† – Indicates the suppliers proprietary name is mentioned in the text.
INCI – International Nomenclature Cosmetic Ingredient.

The student is also referred to the numerous trade journals available, and to the wealth of information from raw-material suppliers.

16.6 ACKNOWLEDGEMENTS

The authors thank Haarman and Reimer, Stepan and Merck for allowing their formulae to be reproduced in this chapter.

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PART 3
QUALITY, STABILITY AND SAFETY ASSURANCE

17

Analytical methods

Ken Spears

17.1 INTRODUCTION

Analytical chemistry has traditionally been associated with basic research but in the past few years it has become a key support area in many industries. In the cosmetic and personal-care product industries it is used to support the commercial development and application of new ingredients, to ensure that specifications are met, to confirm the quality of manufactured products and to ensure that processes are operating correctly. Outside of the industrial environment analytical methods are regularly employed by enforcement and regulatory authorities to ensure that products conform to legal standards, and are safe and accurately described. Increasing demand for the determination of analytes at very low levels and more rapid results to match production levels has led to the development of a wide range of sensitive techniques, many capable of automation and multicomponent analysis. Despite the ease with which many of these techniques can be applied, the analytical chemist continues to play a key role in selecting the most appropriate method, managing the data, interpreting the results and commenting on their significance to other staff.

It is not possible to present in one chapter comprehensive methods to cover the analyses of all cosmetic and personal-care products. Nor is it intended to provide a detailed description of instrumental methods of analysis; there are many excellent texts available in that subject area. Examples of classical, sometimes called traditional, analytical techniques have been retained in this edition because such methods still provide appropriate information and results with minimum resources. Emphasis has been given to chromatographic and spectroscopic instrumental techniques because they represent the biggest areas of application and the instrumentation involved has become much more accessible in terms of cost, reliability and the expertise needed to analyse samples. Only the highly resourced laboratories or research institutes can routinely call on techniques such

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 507–554

as mass spectrometry (MS), nuclear magnetic resonance (NMR) or multi-component techniques for trace elements such as inductively coupled plasma–atomic emission spectroscopy (ICP-AES).

17.2 CLASSICAL OR INSTRUMENTAL METHODS

This classification of analytical techniques is largely for convenience rather than acknowledging rigid definitions. Classical techniques are based on observing and measuring the chemical reactivity of analytes in solution. Examples include complex formation, preparation of derivatives, precipitation, volumetric analysis and monitoring electrochemical changes. Many of these techniques may be linked to instrumental methods or used as pre-treatments of samples before more specific analytical methods are applied.

17.2.1 Examples of classical methods

(a) Gravimetric analysis

This is a direct analytical method in which the analyte is determined by change in weight. The most simple and direct method involves moisture determination by oven drying. More complex analyses involve converting the analyte into an insoluble form (precipitate) which can be filtered, dried and weighed.

(b) Electrochemical techniques

This range of techniques is based on electrical properties of solutions and may involve measurement of current, voltage, resistance or conductance of solutions. pH is perhaps the best known here.

(c) Volumetric analysis

This involves the use of standard solutions (known volumes of known concentrations) to react with the analyte to a defined 'end-point', e.g. a colour change or a pH value. These are convenient methods for determining the quality of fats and oils, and acids and bases, and can be carried out with great accuracy and reproducibility.

17.2.2 General notes on volumetric analyses

(a) Glassware

Incorrect selection, use and care of glassware, which represent the most basic tools to the analytical chemist, can lead to considerable errors in the determination of analytes. Even the most sophisticated instrument will not compensate for poor practice in preparing samples for analysis. Glassware for laboratory use and liquid

handling is graded as 'A' or 'B'. Class A glassware is calibrated to a higher level of precision and accuracy and should be used for quantitative work. Generally, Class A glassware can be used directly without further calibration but independent surveys have shown that samples of equipment purchased from reputable suppliers may be outside the tolerances required for compliance with the appropriate British Standard. When measuring trace amounts of components it is recommended that graduated flasks should be calibrated 'in house' by determining the weight of water held by the flask when it is filled to the mark at 20°C. Pipettes are usually graded as 'D' (for delivers) or 'Ex' (for expels). D-type pipettes should be allowed to drain for a specified time, usually 15 seconds. A pipette will not deliver constant volumes of liquid if it is discharged too rapidly; time of outflow for a 25 cm^3 pipette is about 30 seconds. Hence it is important that care is taken not to damage the tip and to keep the inner stem of the glass scrupulously clean.

(b) Calculations

In this chapter, concentrations of standard solutions have been expressed as follows:

$$c\ (H_2SO_4) \qquad c\ (NaOH)$$

where the symbol c (concentration) is followed by a formula in parentheses describing the molecular or ionic species to which the concentration refers. Units of concentration are mol dm^{-3}, although the non-SI term, mol/l, is used for convenience.

All the volumetric calculations in this chapter are derived from the same fundamental equation:

$$X = V \times \frac{M}{1000N} \times C \times \frac{100}{W_1}$$

where: $\%X$ is the percentage in the sample of the analyte X
V is the volume of titrant
M is the molecular weight of X
N is the number of molecules of titrant that react with each molecule of X
C is the concentration of the titrant in mol/l
and W_1 is the weight of sample titrated (g).

$M/1000N$ is the mass in g of X that would be titrated by 1 ml of titrant of concentration 1 mol/l. $C \times M/1000N$ is the mass in g titrated by 1 ml of the actual titrant. $V \times C \times M/1000N$ is the weight in g present in the titration vessel.
W_1 is given by:

$$W_0 = \frac{\text{Product of all aliquots taken}}{\text{Product of all dilution volumes}}$$

where W_0 is the weight of sample actually weighed out.

17.2.3 Examples of instrumental methods

Instrumental methods are based upon detailed examination of the physical or physicochemical properties of analytes related to their molecular or atomic structures. The methods are capable of providing qualitative information, that is the chemical nature of the sample or the presence or absence of certain compounds, as well as quantitative data, which involves determining the amount of a specific compound. Before instrumental methods are used it may be necessary to use classical methods to convert the analyte into a suitable chemical form or to remove substances which would otherwise interfere and give false readings. Volumetric techniques are frequently used in the preparation of standards for quantitative analysis. Very few samples, except for perhaps pure raw materials, lend themselves to immediate instrumental analysis.

Examples of instrumental techniques include measurement of the amount of electromagnetic radiation absorbed or emitted at a particular wavelength (spectroscopy), measuring the rate at which analytes migrate through a column containing an insoluble material (chromatography), or observing the types of molecular fragments produced after bombarding the analyte with subatomic particles (mass spectroscopy). Monitoring endothermic and exothermic changes in materials can provide information about structural changes in compounds (differential scanning calorimetry) whilst modern sophisticated techniques such as nuclear magnetic resonance (NMR) monitor the amount of radio energy absorbed by an analyte when placed in a magnetic field. NMR is used in body scans for medical diagnosis, and in the cosmetic industry NMR can be used to indicate solid/liquid ratios in lotions. There are also increasing applications for near-infrared (NIR) analysis which is able to scan samples in the infrared region of the electromagnetic spectrum and by reference to standard mixtures give rapid data on fat, moisture and protein contents.

Separative and non-separative methods

Instrumental techniques may be divided into *separative* or *non-separative* methods. Separative methods require the analyte to be extracted or isolated from the sample. This may be because the sample contains other components which behave similarly to the analyte of interest. Separation may also be used as a pre-treatment before final analysis by another technique.

Non-separative methods usually rely on the fact that a particular property can be observed or measured regardless of whether other components are present in the sample. NMR is a good example of a non-separative method, as is absorptiometry. Table 17.1 summarizes other separative and non-separative methods.

17.3 CHROMATOGRAPHIC METHODS

Nearly all analytical laboratories use some form of chromatography, either as a qualitative technique to identify the presence or absence of components or as a

Table 17.1 Classification of instrumental techniques

Separative	*Non-separative*
Chromotography	Spectroscopy (e.g. absorptiometry)
Solvent extraction	Radio-isotope determination
Distillation	Electrochemical determination
Centrifugation	NMR
Electrophoresis (mainly limited to protein separation)	Immunoassay (use of antibodies to detect specific proteins)
Filtration	Thermal methods
	NIR

quantitative technique to determine the amount of analyte present in a sample. Although there are sophisticated instruments available which are able to carry out separations in the gas phase with levels of detection to a few parts per billion (ppb), many successful analyses are still carried out using a thin layer of an inert adsorbent coated onto a glass or metal plate (thin-layer chromatography, TLC). TLC has been successfully used to identify semipermanent and direct dyes used for hair colouring [1]. It is this wide mode of application that makes chromatography such a versatile technique.

Chromatography is a process in which the components in a sample are physically separated between two phases. One phase, retained completely by the chromatography equipment, is called the *stationary* phase, whilst the other phase, called the *mobile* phase, is directed through the stationary phase 'carrying' the sample components. As the mobile phase passes through the stationary phase, the solutes progress through at different rates depending upon the degree of interaction that the solutes have with the stationary phase. The stationary phase can be a solid or a liquid. To ensure that the liquid remains stationary it is chemically bonded to an inert support and behaves as a 'coating'. The mobile phase may be a liquid or a gas; in gas chromatography, nitrogen (N_2) is the most commonly used mobile phase.

17.3.1 Modes of separation

Separation occurs by one of four ways depending upon how the sample components interact with the stationary phase. In some applications more than one interaction occurs.

1. Sample components dissolve in the stationary phase and move through as if in solution. This is called **partition** (stationary phase must be a liquid) and can be compared to continuous solvent extraction.
2. Sample components are adsorbed onto the stationary phase as a result of surface effects such as polar interactions between functional groups or van der Waals

forces. The mobile phase moves the components at different rates depending upon the strength of the surface interaction. This is called **adsorption** chromatography and requires a solid stationary phase.

3. **Ion exchange** chromatography requires a coated solid as the stationary phase. This solid is normally a resin to which is covalently bonded either positively charged ionic groups or negatively charged groups. Ions of opposite charge are bound to the surface electrostatically. Sample components with ionic groups displace the ions associated with the stationary phase and will move through the stationary phase at different rates depending on the strength of the ionic interaction. Domestic water softeners work on the principle of ion exchange where calcium ions in hard water (the sample) are bound to a solid stationary phase simultaneously releasing sodium ions from the surface.

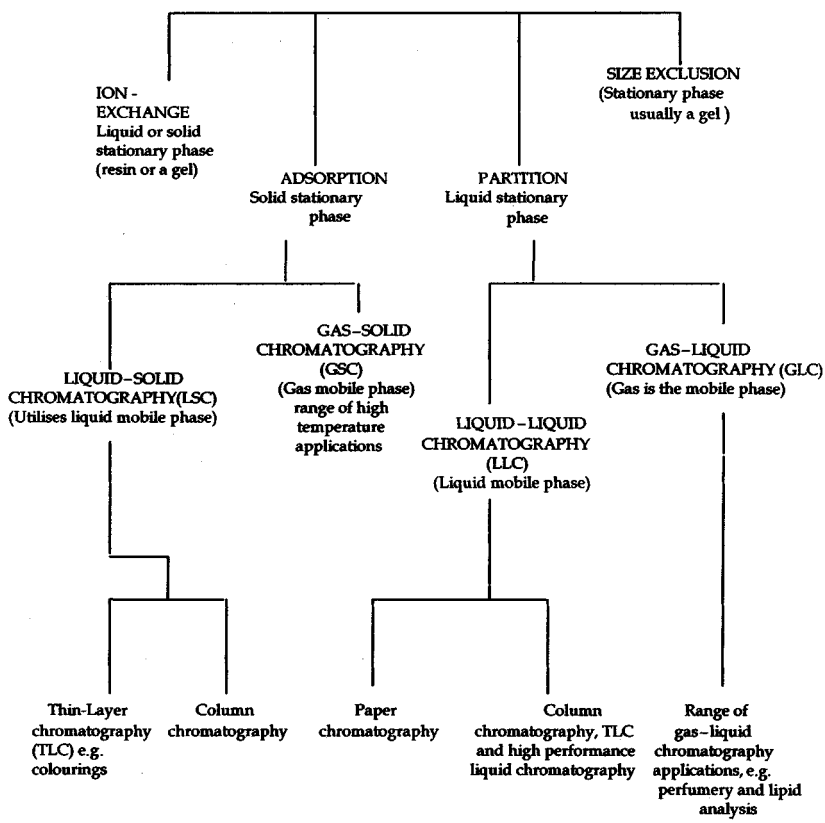

Fig. 17.1 Classification of chromatographic methods.

4. In **size exclusion** chromatography (sometimes called gel permeation) there is no chemical equilibrium established between the sample and the stationary phase. The stationary phase has a porous nature and only the smallest component molecules can enter the pores. Larger molecules will be washed through rapidly. Thus, during separation, the largest molecules will separate first and the smallest molecules will appear last. This has wide application in heterogeneous samples, e.g. to separate large molecular weight protein components from smaller salt components. Analysts describe chromatographic techniques by the mode of interaction and the type of application or method used (Fig. 17.1).

17.3.2 Gas chromatography

Gas chromatography is perhaps the most widely used of all instrumental techniques although the technique is limited to compounds which have appreciable vapour pressure and are thermally stable at the operating temperature of the gas chromatograph. Many separations are conducted between 100°C and 200°C, but separations at a temperature up to 350°C are not uncommon. The mobile phase gas used is usually nitrogen and separations can be carried out by gas–liquid chromatography (GLC) or gas–solid chromatography (GSC). For GLC the stationary phase is a high-boiling-point liquid chemically bonded to an inert support and the process of resolving (separating) sample components occurs predominantly by partition. In GSC the stationary phase is a solid and resolution occurs by adsorption. Samples are introduced into the gas flow at an injection port located at the top of the column. A continuous flow of gas elutes the separated components from the column and these then pass into a detector linked to a recording system. The components separate as a result of differences in boiling point, solubility or adsorption.

The development of capillary gas-chromatographic columns in which the stationary phase is coated onto the inner surface of a long glass or fused silica column has dramatically increased the range of applications, particularly of complex and high-boiling-point mixtures. The most common type of columns are referred to as wall-coated open tubular (WCOT) columns with typical column length of 80 m, 0.2 mm internal diameter with a stationary phase coating of 0.002 mm. These columns permit high gas flow rates for fast separation of complex mixtures and can withstand very high oven temperatures (*c.* 400°C) but tend to have short lifetimes because of oxidation effects and column 'bleed'.

17.3.3 High-performance liquid chromatography (HPLC)

Very efficient, or high-performance liquid chromatographic systems have developed at the same rate as gas chromatographs. In liquid chromatography the efficiency of a separation is enhanced by reducing the particle size of the stationary

phase to give a larger surface area for sample interaction. However, with very small particle sizes it is necessary to apply a high pressure to the mobile phase to force it through the column. With stationary phases of particle size 1–2 μm, separations are very efficient and short columns of length 20 cm with internal diameter of 4 mm are sufficient. HPLC can be carried out using any of the four modes described in Fig. 17.1, which makes it a very versatile technique. Consistent flow through the column is essential and most of the technology in developing HPLC has been directed to perfecting pump systems, tubing and fittings to withstand the high pressures involved, which are typically around 10 MNm^{-2} (100 atmospheres). The sample volumes used in HPLC are very small, *c.* 5–10 μl, and the separated components not easily collected from the column for identification. Therefore HPLC systems also include a detector system. Most organic materials show some absorbance in the UV/visible region so the eluant from the column with the separated components is directed through a small spectrophotometric cell linked to an amplifier and recorder. Other detector systems include conductivity cells, infrared detectors, refractometer and mass spectrometers.

The application of HPLC has been widened considerably by the development of non-polar stationary phases which permit separation by partition. Early liquid chromatography traditionally used adsorbents as the stationary phase and relied upon complex combinations of polar and non-polar solvents as the mobile phase to effect separation. With the development of hydrocarbons bonded to adsorbent supports, non-polar 'liquid' stationary phases are created which enable separations of polar and non-polar components with mobile phases of much simpler composition. For example, a methanol–water mixture will separate a range of polar and non-polar compounds on a bonded stationary phase of C-18 hydrocarbon known as octadecylsilica (ODS). This reversal of stationary phase from polar to non-polar form is called 'reversed-phase' chromatography.

17.3.4 Resolution

The desired outcome in chromatography is to effect separation of sample components followed by their identification. Separated components may be collected from some chromatographs for further analysis. The efficiency with which chromatography systems effect separation between components is measured by a quantitative term called resolution. Resolution is described as a ratio of the differences in retention of the components compared to the bandwidth of the components at the baseline. The equation used to calculate the resolution between two peaks X and Y is given by:

$$\text{Resolution} = \frac{\text{difference in retention between } X \text{ and } Y}{(\text{baseline width of peak } X + Y)/2}$$

For quantitative purposes, baseline resolution of at least 1.5 is desirable. A resolution of 1.0 will normally indicate the number of components in a mixed peak and may be suitable for qualitative purposes. A higher resolution, for example 5.0, may be required if components are to be collected for further analysis.

17.3.5 Quantitative analysis

An important attribute of chromatography is its quantitative capability. The size of every peak displayed on the chart is a measure of the amount of that particular component present in the sample. Strictly speaking, it is the area under the peak which is proportional to the quantity of the component present. Quantitative analysis is therefore directed to the methods of estimating the magnitude or size of the peak.

(a) Peak height

The height of a peak is a function of its area. For symmetrical peaks, peak height may be used directly for quantification. However, peak shape is likely to alter as a result of slight variations in operating conditions and injection technique.

(b) Triangulation

In this method the area under the peak (A) is approximated to a triangle enabling algebraic determination of area to be used (Fig. 17.2). Again it is important that peaks on the chromatogram are symmetrical.

In practice, modern GC instruments use recorders which measure and print the peak areas automatically – a process called integration.

17.4 SPECTROPHOTOMETRIC METHODS

Spectrophotometry is a term generally used to describe a range of similar techniques which all rely on the measurement of the amount of electromagnetic

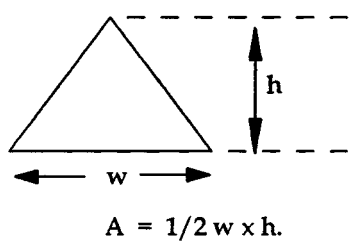

Fig. 17.2 Calculation of peak area by triangulation.

radiation absorbed or emitted by an analyte. Spectrophotometry provides both qualitative and quantitative data and, besides discrete analysis, spectrometric methods may be combined with other analytical methods, e.g. as detectors after chromatographic separation. Spectrophotometry is a non-separative method and therefore it may be necessary to 'clean up' the sample prior to analysis to remove compounds likely to interact in a similar way. The absorption or emission of electromagnetic radiation by the analyte is related to the atomic and/or molecular structure and may be caused by electron movements between energy levels, vibrations between atoms in molecular or functional groups, and even changes to the 'spin' of nuclei. Data are collected by scanning the sample in a spectrophotometer across a range of wavelengths or measuring the absorption or emission of electromagnetic radiation at a single wavelength. When used in chromatographic detectors the wavelength selected is usually a compromise value which will be absorbed by the sample components but not by the mobile phase.

17.4.1 Nature and characterization of EM radiation (the EM spectrum)

Electromagnetic radiation is defined mathematically by quite complex equations representing a combination of magnetic and electrical vectors. All EM radiation is transmitted at the same speed (3×10^8 m/s) and may be described in terms of wavelength (λ), wave number (the number of waves to a centimetre), or frequency (Hz). All of these terms are widely used in spectrophotometry.

17.4.2 Ultraviolet and visible spectrophotometry (UV/vis)

UV/vis spectrophotometry involves analysis of samples using EM radiation in the region which is detected by the human eye – the visible region (400–800 nm) – and also the ultraviolet region (100–400 nm). Generally a wide range of organic, metallic and biochemical compounds are able to *absorb* radiation of this energy, hence this area of spectrophotometry is frequently called *absorptiometry*. The specific wavelength where absorption is strongest gives the analyst information of a qualitative nature about the structure of molecules, whilst the amount of radiation absorbed gives a measurement of concentration or quantitative information. Absorptiometry is widely used for screening raw materials such as colourings and sunscreen preparations to check purity against manufacturers' specifications or to detect the presence of known contaminants.

17.4.3 Infrared spectrophotometry

The infrared region of the EM spectrum has wavelengths between 2.5×10^{-5} and 2.5×10^{-6} m, although absorption of radiation in this region is usually quoted as wavenumbers (400–4000 cm^{-1}). Absorption of infrared radiation is due to vibrations between bound atoms in molecules and therefore a scan of

samples in this region can give information about the presence of organic functional groups and in some cases the proximity of certain functional groups. Although infrared spectrophotometry is less sensitive than UV/vis, it can be used to analyse gases, liquids and solids provided they are suitably prepared, whereas absorptiometry tends to be limited to samples dissolved in suitable solvents. Infrared spectrophotometry has limited use in chromatographic detectors and its main application is in structural analysis of organic compounds, confirming the purity of raw materials and detecting trace amounts of contaminants. Analysts use infrared spectrophotometry to compile a library of characteristic spectra of pure raw materials which can then be used as standards for routine quality checks. The ratio of absorptions at characteristic wavenumbers gives a 'fingerprint' of the standard; this is the basis of near-infrared (NIR) spectrophotometry. A more familiar application of infrared spectrophotometers is in the use of hand-held devices used by police officers for checking breath samples of drivers for alcohol.

17.4.4 Nuclear magnetic resonance (NMR) spectrophotometry

NMR originally developed as a research tool for the structural identification of a wide range of compounds. This technique produces much more complex spectra than infrared techniques or UV/vis and requires sophisticated equipment, usually beyond the resources of most industrial laboratories. In low-resolution techniques, samples are exposed to radiofrequencies (60–100 MHz) in a sample chamber between the poles of a powerful magnet with field strength of between 10^4 and 3×10^4 gauss. High-resolution instruments permit operating frequencies

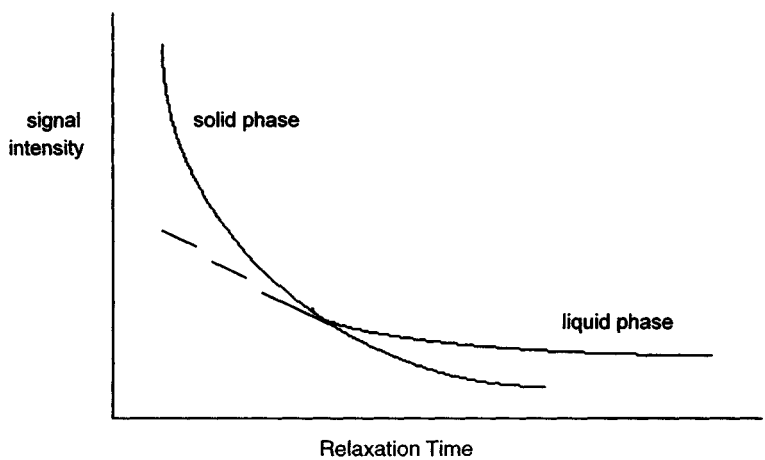

Fig.. 17.3 Use of NMR to indicate solid/liquid ratios in lipid-based samples.

up to 500 MHz and provide the ability to scan the radiofrequencies at a constant magnetic field or to maintain the radiofrequency constant and the magnetic field strength varied. When samples are exposed to these changes they absorb EM radiation at frequencies characteristic of the environment in which nuclei of certain atoms are contained in molecular structures. The spectrum, which requires analysis by experienced chemists, gives information about chemical structures and the physical nature of the sample. In low-resolution applications the resonance of protons in the scanned field over time can be interpreted as proportions of solid/liquid ratios in lipid-based samples. The differences in signal intensity are due to protons in the liquid phase having longer 'relaxation' times compared to the protons in the solid phase. Using standard mixtures and analysis at different temperatures, it is possible to use the technique to monitor the production of formulations and predict the melting behaviour of solid phases. A typical trace is given in Fig. 17.3. More sophisticated equipment using similar relaxation scans over time can be used to build 'whole-body images' of individuals and is finding regular use in medical diagnosis of cancer and hydrocephalus.

17.5 PLANNING AN ANALYTICAL SCHEME

17.5.1 General approach

Cosmetic and personal-care products can pose complex problems to the analyst because of their heterogeneous nature. Even so it is essential that the analyst is able to 'guarantee' results in terms of accuracy and precision. In an industrial situation there is pressure on the analyst to provide results quickly because of the high production speeds needed to meet customer demands; hence the continued application of instrumental and automated techniques. Many companies have submitted their analytical procedures for independent accreditation to assure customers of the quality of their products and in those situations analysts will need to demonstrate that the procedures they use give consistent results and that equipment is regularly calibrated. Increased legislation for consumer safety puts additional burdens on manufacturers and their analytical requirements because many statutory requirements specify the methodology that should be used for confirming certain product specifications. For example, regulations regarding the safety of cosmetic products specify the methods to be used for determining residual chemicals in hair-straightening preparations, toothpaste and nail cuticle solvents [2]. Local government laboratories and public analysts will use such methods in surveillance programmes to assure consumer safety. It is important, therefore, that if manufacturers use different methods for quality assurance purposes those methods must be equally rigorous in providing confident results. Generally, maintaining an analytical service requires considerable commitment of resources and the analyst should ensure that careful planning is carried out before investing time and materials in a procedure where the outcome

of results may prove to be largely meaningless. For example, there would be little point in developing a quantitative instrumental method for a potential contaminant in a raw material if a rapid, sensitive qualitative check could reveal its presence, thereby enabling the material to be rejected. Regular analytical services require considerable skill and experience and there are other factors that need to be considered in planning suitable procedures.

(a) Health and safety

Many analytical methods require the use of hazardous chemicals and/or hazardous procedures. In this context 'hazard' is defined as a substance, or instrument or procedure capable of causing harm. Analysts need to consider carefully the extent of hazard posed, by determining the level of 'risk' that the hazard could present. This is called 'risk assessment' and the assessment needs to take into account various factors such as concentrations of chemicals, work procedures, effect of temperatures, spillage and the possibility of unintentional reactions occurring. The same chemical used at different concentrations is likely to pose different levels of risk. Safety regulations regarding the use of chemicals in the workplace exist under statutory provision for consumer protection and require the application of risk-assessment procedures [3]. Suppliers of reagents and chemicals are required to comply with regulations which make provision for chemical hazard information and appropriate packaging [4]. The Health and Safety Executive (HSE) provide a useful free guide for employers describing their legal responsibilities with regard to risk assessment [5].

(b) Sampling

Obtaining a representative sample of a manufactured product or of a raw material from a bulk supply is a critical first part of the analytical process.

In an industrial environment, samples for analysis may well have been obtained from a very large batch of product. It is also important that the sample represents as near as possible the original nature of the bulk material and that no contamination is introduced or loss of volatile material allowed to occur. The type of sample obtained may very well also dictate the type of analytical method that can be used. It would be a waste of time carrying out quantitative analysis on a sample that was non-representative of the bulk supply.

Obtaining samples from bulk supplies often poses practical problems. It may be necessary to sample a bulk tank of liquid at different depths and combine these subsamples to obtain a representative portion. A consignment of powder packed in different sacks may require sampling of different sacks according to statistical tables to gain representation. With homogeneous liquids, simple mixing and shaking of the bulk material may be sufficient. With homogeneous solids, crushing and grinding may be sufficient. Semi-solid or waxy materials may need to be warmed before they can be sampled satisfactorily. Heterogeneous

materials such as cosmetic products pose particular problems because they may well be a mixture of solid, emulsified and liquid components which have a tendency to separate over time.

Even after sampling, the analyte may not be in a form suitable for analysis. Complex samples may need a 'clean-up' stage to remove interference from other constituents in the sample. General 'clean-ups' include filtration, precipitation, centrifugation and extracting the analyte of interest from the sample using an organic solvent. Other treatments may include removing moisture and volatiles by drying, ashing the sample by heating to 600°C to remove organic material and leaving inorganic residue, or dissolving the sample in an appropriate solvent.

In quantitative analysis the more steps involved in the analytical sequence, the greater the chance of losing some of the analyte. To ensure the analyst is able to interpret the results of the analysis it may be necessary to determine the 'recovery' of the analyte after a particular stage. This is carried out by subjecting samples with a known concentration of the analyte to the pretreatment, and then determining whether the pretreatment has affected the quantity of analyte originally present. If the pretreatment had no result on the content, the recovery should be 100%.

17.5.2 Screening tests

There is a tendency for analysts to resort to complex separation and instrumental methods before carrying out rapid checks that may indicate the need for more detailed examination. The term 'screening test' refers to analytical tests whose function is to confirm the nature of a sample – be it raw material or finished product – at a qualitative level.

(a) Visual examination

For dried or powdered material the most rapid test is visual examination followed by more detailed viewing using a low-power microscope. This examination can give information on the uniformity of particle sizes and, if carried out on a regular basis, indicate sudden changes in manufacturing processes. Visual examination will also reveal the presence of any physical contaminants in products – a frequent source of consumer complaints of products. A small sample of emulsified and lipid-based products can be smeared on to a microscope slide to which is added a light dusting of Sudan IV (a fat-soluble red dye). After gentle mixing with a capillary tube, the fat globules will take up the dye. The stained smear can then be examined under the microscope to give an indication of the uniformity of globule sizes and the relative distribution of phases within the product. It is possible to calibrate the microscopic field of view using an eyepiece graticule and a stage micrometer in order to measure the relative sizes of the globules. For water-in-oil emulsions, water globules can be examined similarly but using Methylene Blue instead of Sudan IV.

(b) Spot tests

Spot tests involve the addition of specific chemical reagents to small samples of material on a microscope slide or a white spotting tile. Specific reagents can be used to form coloured complexes to detect the presence (or absence) of a range of anions and cations which, from a quality point of view, confirm the presence of additives or indicate the presence of contaminants. For example, ammonium residues can be readily detected using Nessler's reagent, iron (III) reacts with thiocyanate in acid conditions to form intense red compounds and chloride is readily detected with mercury (II) thiocyanate in the presence of iron (III) ions. Although these methods are subject to a number of interferences and false results, they may give an indication that further investigation is warranted.

(c) Melting point

The determination of melting point – particularly for lipid-based materials – is a rapid, non-destructive and inexpensive test that can be used on many raw materials and manufactured products. Most lipid materials give a melting range rather than a sharp melting point but even the range will vary in the presence of mixed lipid components or the adulteration of usual raw materials by cheaper substitutes.

(d) Absorptiometry

Absorptiometry is an instrumental technique that is particularly suited to the screening of raw materials. The complex, heterogeneous nature of manufactured products is less easily screened in this way because of the potential number of interferences but, even so, an irregular peak in an absorption spectrum may indicate a contaminant or a change in the composition of a formulated product. Synthetic colourings used in a wide range of cosmetic products can readily be assessed in simple solution.

17.6 GENERAL METHODS

17.6.1 Determination of moisture, total volatile and non-volatile matter by drying

(a) Application

Raw materials and products with a high moisture or volatile content.

(b) Principle

A weighed sample is dried to constant mass at 105°C. The loss in mass is a measure of the total volatile matter and the mass of the dried residue is the non-volatile matter. For materials with a significant volatile content, a distillation

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technique is preferred in which the water is distilled from the sample with an immiscible solvent of high boiling point (toluene, b. pt. 110°C is suitable) and measured by collecting in a suitably calibrated receiver. Products likely to decompose at 100°C, or which are highly solvent-based, can be dried at a lower temperature at reduced pressure using a vacuum drying oven.

(c) Apparatus

Oven capable of maintaining 105°C or a vacuum oven programmed to dry materials at 70°C.
Weighing dishes; stainless-steel or aluminium.
Desiccator containing dried granular silica gel.

(d) Procedure

1. Samples should be analysed in duplicate. Dry the empty dish and lid in the oven for 15 minutes and transfer to the desiccator to cool. Weigh the empty dish and lid to the nearest mg.
2. Mix the prepared sample thoroughly and transfer about 5 g of sample to the dish. Cover with the lid and weigh dish and sample to the nearest mg. Mass of sample = W_1 g.
3. Remove the lid and place dish and lid in the oven. Dry sample for about 5 hours.
4. Remove the dish from the oven and quickly replace the lid. Cool the dish and dried sample in a desiccate. Re-weigh when cold. Return the dish and sample to the oven for a further hour followed by cooling in the desiccator until constant weight within 1 mg has been recorded. Mass of dried residue = W_2 g.

(e) Calculation

Moisture and total volatile matter (%) = $100\ (W_1 - W_2)/W_1$.
Total non-volatile matter (%) = $100\ W_2/W_1$.

17.6.2 Determination of water content by Dean and Stark distillation

(a) Application

Materials with a high water content, e.g. toothpastes, creams and lotions, some raw materials. Samples with a high water content may foam excessively.

(b) Principle

The water is removed from a weighed sample by azeotropic distillation and its volume measured.

(c) Apparatus

(i) Dean and Stark apparatus has a trap for use with a light entraining liquid. Traps are available with various capacities and for use with heavy entraining liquids. A 10 ml trap is suitable for general use.
(ii) Heating mantle with thermostatic control.

(d) Reagent

Toluene. CAUTION: FLAMMABLE. Other solvents, including some with boiling points less than 100°C, may be used for special purposes.

(e) Procedure

1. Accurately weigh into the distillation flask a sample containing 5–10 ml water. As a guide, take $800/X$ g, where X is the expected water content. Mass = W g.
2. Add about 400 ml toluene.
3. Place the flask in a thermostatically controlled heating mantle and assemble the apparatus.
4. Establish an adequate flow of water through the condenser. Check it at intervals during the distillation.
5. Switch on the heating mantle. When the toluene starts to boil, adjust the thermostat so that boiling is steady but not violent.
6. Read the volume of water in the trap after 30 minutes and then after 15-minute intervals until three successive readings are equal. Record all readings. Final reading = V ml.
7. Switch off the heating mantle, but do not turn off the water supply to the condenser until the apparatus has cooled to room temperature.

(f) Calculation

$$\% \text{ Water} = 100V/W$$

where V is final volume reading (step 7) and W is weight of sample (step 1).

17.6.3 Measurement of pH

(a) Application

Products and raw materials; aqueous liquids, pastes, gels, creams or water-based solids; water-insoluble-based solids dispersed in an aqueous base.

(b) Principle

Hydrogen ion concentration (H^+) is measured potentiometrically using a combined electrode. For general laboratory use the electrode must be regularly

replenished with a mixture of potassium chloride solution (3 M) and saturated potassium chloride solution.

(c) Apparatus

Besides bench-top, mains-powered pH meters there are a wide range of portable and hand-held meters available. Commercial electrodes available include those resistant to glass-fouling in protein solutions and gel-filled electrodes for robust use. For measurement of pH in solutions of low-ionic strength and non-aqueous phases, low conductivity combined electrodes are recommended. Modern pH meters contain circuitry for automatic temperature compensation permitting accurate measurement up to 50°C.

(d) Reagents

(i) Standard buffer solutions for calibrating meters and electrodes. Buffers are available as capsules for preparing 100 ml solutions of pH 4.0, 7.0 and 10.0 at 25°C. Alternatively, prepared solutions are available for more frequent use.
(ii) Electrode storage solution buffered to pH 7.0 and containing potassium chloride solution to minimize loss of electrode solution and a preservative to prevent glass surface fouling.
(iii) Electrode cleaning solutions suitable for removing protein or inorganic materials from the electrode surfaces. After cleaning, electrodes should be immersed in storage solution (see (ii)).

(e) Procedure

1. Calibrate the meter and electrode regularly according to the manufacturers' recommendations. When not in use, maintain the electrode immersed in the storage solution.
2. Most aqueous-based samples, solutions, pastes, gels and creams can be tested directly. Raw materials and other types of sample should be prepared by dilution as directed in the specification. For regular testing of specific products, the most appropriate electrode for that material should be used – commercial suppliers will be able to advise.
3. Place sufficient sample in a clean 100 ml beaker ensuring the end of the electrode is covered. Where possible, liquid samples should be stirred gently with a magnetic stirrer. Avoid prolonged or vigorous stirring because dissolved carbon dioxide will quickly affect the reading. Record the constant reading. Electrodes should be thoroughly cleaned after each measurement because 'carry-over' of sample may cause large errors.

17.6.4 Ash and metal ions by atomic absorption spectrophotometry

(i) Ash and acid-insoluble ash

(a) Application. Products and raw materials; dried products and powders, pastes, gels, creams or water-based solids; water-insoluble solids dispersed in an aqueous base. Not suitable for products with a lipid content in excess of 50%.

(b) Principle. Products are evaporated to dryness followed by charring of organic matter. The dried and charred residue is then heated at 550°C in an electric furnace and reduced to a fine ash of inorganic material which can be weighed. The ash can be dissolved in acid solution for further analysis. Metal ions can be determined by atomic absorption spectroscopy (AAS). Where an unexpected high ash content indicates a possible contaminant or adulterant, determine the acid-insoluble ash also.

(c) Apparatus

Vitreosil or porcelain crucibles.
Steam bath.
Electric hotplate with thermostatic control.
Electric furnace (muffle furnace) (maximum operating temp. 1100°C).
Long-handle tongs.
Desiccator.

(d) Reagents

(i) Deionized water.
(ii) Dilute hydrochloric acid.

(e) Procedure

1. Heat the crucibles without lids in the furnace at 550°C for 30 minutes.
2. Remove the crucibles (CARE!) from the oven and allow them to cool in the desiccator. When cool, weigh to the nearest mg.
3. Weigh the sample to the nearest mg into the crucible; use approximately 5 g for liquids, pastes or gels, or 2 g for solid materials. Mass of sample = W_1 g.
4. Heat liquid samples on a steam bath for about 45 minutes to remove most of the moisture and to prevent 'sputtering' and loss of sample.
5. Heat samples slowly on a hotplate in a fume cupboard or using an exhaust system. Continue to heat until smoking ceases and the sample is charred.
6. Place the crucibles in the furnace and ash overnight at 550°C.
7. Remove the crucibles from the furnace. Avoid strong draughts which may blow the fine ash out of the crucible. If black particles of carbon are still present in the sample, add a few drops of hot, deionized water and break up the particles with a strong platinum wire. Evaporate the water to dryness

(slowly) on the hotplate and return the sample to the furnace and continue to ash overnight at 550°C.

8. Remove the crucibles from the furnace and place them in the desiccator to cool.
9. After cooling, weigh the crucible and ash to the nearest mg. Mass of ash = W_2 g.
10. To determine the acid-insoluble ash content, boil the ash in the crucible with 10 ml of dilute hydrochloric acid for 5 minutes. Filter the solution through an ashless filter paper. Rinse inside the crucible with hot, deionized water and pass the washings through the filter paper. Rinse the filter paper thoroughly with hot water. After draining, carefully transfer the filter paper into the original crucible and evaporate to dryness on the hotplate. Return the crucible to the furnace and heat overnight at 550°C. After cooling, weigh the crucible and ash to the nearest mg. Mass of acid-insoluble ash = W_3 g.

(f) Calculation

Ash content (%) = 100 (W_2/W_1).
Acid-insoluble ash content (%) = 100 (W_3/W_1).

(ii) Metal ions by atomic absorption spectrophotometry

(a) Application. A wide range of metal ions in turn can be determined from an acid solution of the ash prepared from a sample. The method is suitable for the regular determination of a range of elements including calcium, copper, iron, strontium, lead, aluminium and zinc. Sodium and potassium are more effectively determined by atomic emission spectrophotometry (flame photometry) because of their high light-emission characteristics.

(b) Principle. An acid solution of the metal ion is sprayed into a flame. A cathode lamp of the element is used to produce an incident beam of wavelength characteristic for that element. Ions of the element will absorb the incident light in the flame. Radiation intensity is measured with and without the sample in the flame and the difference in intensity is calibrated by reference to a set of standards prepared from a solution of the element.

(c) Apparatus. Grade A volumetric glassware (thoroughly clean all glassware with dilute nitric acid before use; use dedicated glassware for trace metal analysis).
Atomic absorption spectrophotometer

(d) Reagents

Use analytical grade reagents (AR) for all trace element analysis.
Hydrochloric acid, 5M, 2M and 0.5M.

Lanthanum chloride (10% m/v).
Ashless filter papers for quantitative use (0.01% maximum ash).
Deionized water.
Stock standard solutions (1000 mg/l = 1000 ppm). Prepare as given in Table 17.2 from the metal or salt. Alternatively, pre-prepared aqueous acidic solutions (HCl or HNO_3) with elemental concentrations of 1000 ppm (0.5%) are available from commercial suppliers.
Working standard solutions. Dilute stock solutions with 0.5 M hydrochloric acid to concentrations that fall within the working range given in Table 17.3.

Table 17.2 Preparation of standard solutions of metal elements

Element	*Salt or metal*	*Preparation of 1000 ml of solution*
Al	Al metal	1.000 g Al in 1000 ml of 2M hydrochloric acid
Ca	$CaCO_3$	2.497 g $CaCO_3$ and 5 g of LaCl in 1000 ml of 2M hydrochloric acid
Cu	Cu metal	1.000 g Cu in 1000 ml of 2M hydrochloric acid
Fe	Fe metal	1.000 g Fe in 1000 ml of 2M hydrochloric acid
Zn	$Zn(NO_3)\cdot 6H_2O$	4.549 g $Zn(NO_3)\cdot 6H_2O$ in 1000 ml of 2M hydrochloric acid
Sr	$SrCO_3$	1.680 g $SrCO_3$ in 1000 ml of 2M hydrochloric acid
K	KCl	1.907 g KCl in 1000 ml of 2M hydrochloric acid

La = lanthanum = a metallic element in 3rd group of the periodic system.

Table 17.3 Wavelengths, working concentration range and normal detection limits for element analysis by AAS using air/acetylene flame source

Element	*Wavelength* (nm)	*Working concn.range* (μg/ml)	*Detection limit* (μg/ml)
Al	396	10–150	0.01
Ca	423	1–10	0.001
Cu	325	2–20	0.01
Fe	248	2–20	0.01
Zn	214	0.5–3	0.001
Sr	461	2–20	0.001
K	766	1–10	0.001

(e) Procedure

1. Prepare sample ash as described in 17.6.4 (i), steps 1–9.
2. Wet the ash with 5 ml of 5M hydrochloric acid and then evaporate to dryness slowly on a hotplate.

3. Add 15 ml of 2 M hydrochloric acid and heat the crucible on a hotplate to just boiling.
4. Cool the solution and then filter through a filter paper into a graduated flask. Select a flask size in accordance with the anticipated working range given in Table 17.3 and adjust acid volumes if necessary.
5. Add a further 15 ml of 2M hydrochloric acid to the crucible and heat to just boiling. Cool and filter into the flask.
6. Rinse the crucible with two 10 ml aliquots of water and transfer the washings through the filter into the flask.
7. If calcium is to be determined add 1 g of lanthanum chloride per 100 ml of solution to reduce interferences from other elements.
8. Cool the flask to the temperature of calibration and make up the volume with water.
9. Prepare a blank sample using the same reagents and following steps 1–9.

(f) Instrumental analysis

1. Set up the equipment according to the manufacturers' recommendations. For high-precision work ensure that set procedures are followed for calibration of the instrument. Many instruments are set to 'zero' using the reagent blank. Other instruments may require the standards and samples to be corrected for blank readings.
2. Measure the absorption of the standard solutions over the working range given in Table 17.3 and prepare a standard graph of concentration against absorption for the element of interest.

(g) Calculation

Measure the absorption of the prepared sample from the calibration graph.

Let weight of sample (g)	$= W$
Volume of acidified extract (ml)	$= V$
Concentration of sample solution determined from standard graph (μg/ml)	$= C_s$
Concentration of blank solution	$= C_b$
Element content (mg/g)	$= [(C_s - C_b) \times V]/1000W$
or, element content (ppm)	$= [(C_s - C_b) \times V]/W$

17.6.5 Determination of lipid material by solvent extraction

(a) Application

Lipid material refers to fats or oils of animal or vegetable origin, fatty acids, glycerol, lanolin, terpines, steroids and other raw materials soluble in organic solvents.

(b) Principle

Lipid material is extracted from a pre-dried sample by continuous refluxing with a suitable solvent. At the end of the extraction period the solvent is evaporated

and collected for re-use and the lipid residue remaining in the flask is dried and weighed. The method gives $\pm 1\%$ reproducibility. The solvent used for extraction depends upon the nature of the sample. The majority of extractions are carried out using diethyl ether but other suitable solvents include petroleum ether, chloroform/methanol or dichloromethane. Factors affecting solvent selection include dissolving properties, polarity, toxicity, inflammability and cost. The extracted lipid fraction can be subject to further analysis.

(c) Apparatus

Soxhlet extraction apparatus, reflux condenser and extraction flask (150–250 ml).
Soxhlet heating unit designed for good heat transfer.
A purpose-built extraction system (Soxtec ^{R}) is available from Foss UK Limited.
Extraction thimbles.
Heating oven.
Desiccator.

(d) Reagents

A 50:50 mixture of diethyl ether and petroleum ether (boiling range 40–60°C) makes an effective universal solvent.

(e) Procedure

1. Dry the sample as described in Section 17.6.1. Maximum weight of sample after drying should not be more than 10 g.
2. Transfer the dried residue to an extraction thimble. Avoid handling the thimbles and transferring fat residues from the skin.
3. Assemble the extraction unit and condenser with the thimble in the middle stage. Weigh a clean, dry extraction flask. Pour about 100 ml of solvent into the flask and connect it to the extraction unit.
4. Extract the sample for between 2 and 6 hours. Optimum time may need to be determined for individual samples.
5. Allow the flask to cool and then evaporate the solvent; the solvent can be collected for re-use.
6. Dry the flask in a ventilated oven at 100°C for 2–3 minutes. Place the flask in a desiccator to cool. Weigh the flask and lipid residue.

(f) Calculation

Weight of sample (g) before drying $= W_1$
Weight of flask (g) empty $= W_2$
Weight of flask (g) and lipid residue $= W_3$

Extractable lipid content (%) $= [(W_3 - W_2)/W_1] \times 100$
Note that lipid content may also be reported on a dry-weight basis.

17.6.6 Application of chromatographic methods

General

There are a bewildering array of stationary-phase materials available to the analytical chemist from a wide range of suppliers. The picture is made more confused because commercial suppliers use different trade names for similar chemical phases. Most suppliers will provide advice on suitable phases and separation conditions but will obviously recommend their own products. Many separations used in industrial situations for quality control purposes and those used for surveillance by public analysts have usually been developed 'in-house' and rarely become widely available through publications. For regular use and for accurate and precise work, it is important that the conditions for separation are always replicated and that sufficient time and resource is directed to checking results with standards and allowing instruments and columns to equilibrate and become conditioned before carrying out separations. Many analysts continue to use stationary phases which have been heated above their recommended operating temperatures or have been used for inappropriate applications. These conditions reduce the working life of a column, lead to loss of stationary phase and cause 'tailing' of sample peaks.

17.6.7 Gas chromatography

(a) Application

Qualitative and quantitative analysis by separation of a wide range of organic materials. Limited to volatile sample components and those which are stable at temperatures up to 450°C. More volatile derivatives may be formed from non-volatile components; e.g. fatty acids may be analysed after extraction and conversion to their methyl esters. Samples may also need 'clean-up' to remove non-volatile components such as proteins and inorganic salts.

(b) Principle

Samples dissolved in a suitable solvent are injected through a heated block onto a small-diameter column containing a chemical stationary phase. Sample size is usually 1–5 µl. Sample components are moved through the column by a gas stream (mobile phase) migrating at different rates depending upon their affinity for the stationary phase and differences in polarity, solubility and boiling point.

(c) Instrumentation

Gas chromatograph equipped with independently heated injection port and appropriate detector. A flame ionization detector (f.i.d.) is suitable for a wide range of organic compounds.
Packed or capillary column.
Compressed gas supply of nitrogen or helium for the mobile phase; air and hydrogen for the f.i.d. (health and safety requirements may require the cylinders to be sited away from the instruments and gases delivered through a regulated plumbed system).

(d) Operation and applications

Gas chromatography is carried out using a gas mobile phase and either a solid stationary phase or liquid stationary phase. In gas–solid chromatography (GSC), separation occurs because of the different rates of absorption of sample components to the stationary phase. In gas–liquid chromatography (GLC) the mobile phase is a high-boiling-point liquid coated onto an inert support. Separation occurs through differences in partition coefficient of the sample components between the mobile phase and the stationary phase. Although selection of the mobile phase is an important factor in the separation, the most important aspect is the selection of the stationary phase and the type of column used. Packed columns consist of coiled glass or stainless steel, 2–3 m in length with an internal diameter of 2–3 mm. To some extent they are considered as 'old technology' but still offer a number of advantages to the analyst. Packed columns can be emptied and refilled with different stationary phases, a much cheaper alternative to prepacked columns. They provide considerable opportunities for method development, are more robust and permit high sample capacity. The disadvantage is that they have a lower resolving power compared to capillary columns.

Capillary columns, or tubular columns, may be up to 80 m long and are made of a pure form of fused silica (quartz) which is very flexible and can be easily coiled to fit into the chromatograph oven. The physical nature of these columns restricts the stationary phase to a liquid which is coated as a thin film on the inner surface of the column. The bore of the column is up to 0.5 mm. These columns give a high level of resolution, rapid separations and very reproducible results because the mobile gas has very little restriction to flow. They are more expensive than packed columns and have a very low sample capacity which may require 'sample splitting' at the injection port. Not all chromatographs are equipped to take capillary columns.

(e) GSC applications

Packed columns are more suited to GSC than capillary columns. Adsorbents for GSC include silica (polymeric SiO_2), alumina (Al_2O_3), activated charcoal and

Table 17.4 Typical applications of solid adsorbents in GSC

Stationary phase	*Application*
Silica Gel (silica)	Light hydrocarbons
Alumina	Unsaturated and saturated light hydrocarbons
Diatomaceous earths	Pesticide residues; alkenes (C_{10}–C_{20}); steroids (cortisones); aromatic amines (aniline, methoxyanilines)
Activated carbon	Gases (air, carbon dioxide, carbon monoxide, methane, ethylene)
Porous polymers (made from styrene/ divinyl benzene; acrylic esters)	*n*- and iso-amines (C_1–C_7); low mol. wt esters and alcohols

porous inert polymers with good surface binding properties. They permit high operating temperatures (*c.* 500°C) and some are not affected by the presence of water in the sample whereas liquid stationary phases may be hydrolysed at high temperatures or become depolymerized. GSC gives a much better separation of low molecular weight hydrocarbons and geometric isomers than GLC. Table 17.4 shows some typical applications.

(e) GLC applications

GLC allows the use of packed and capillary columns and there are thousands of commercial stationary phases available. Desirable features of stationary phases

Table 17.5 Typical applications of liquid stationary phases in GLC

Stationary phase	*Application*
Non-polar	
High mol. wt hydrocarbons (e.g. squalene)	Hydrocarbons, petrochemicals, waxes
Dimethyl polysiloxane	Waxes, solvents, pharmaceuticals
Diphenyl dimethyl siloxane	Aromatic hydrocarbons, environmental samples, perfumes
Slightly polar	
Cyanopropylphenyl and dimethyl polysiloxane	Insecticides, solvent residues, alcohols
Intermediate polar	
50/50 phenyl/methyl polysiloxane	Triglycerides, steroids, phenols, phthalate esters
Polar	
Polyethylene glycol (PEG)	Fatty acid methyl esters (FAMEs), solvents, amines, organic acids
Diethylene glycol succinate (DEGS)	FAMEs, halogenated hydrocarbons

include stability at high operating temperatures, low column bleed, and their chemical inertness. Liquid stationary phases are prepared by chemically bonding a high-boiling-point liquid onto a solid support such as silica or diatomaceous earths. Following chemical bonding it is essential that any unreacted adsorption sites (e.g Si-O) are 'capped' by chemical derivatization to prevent irregular adsorption of sample components. Generally, liquid phases are characterized as polar and non-polar. Non-polar stationary phases separate mixtures of components on the basis of differences in boiling points. Introduction of phenyl groups, or cyanopropyl, or amino groups into the phase introduces selective polarity which influences separation by dipoles or functional groups. Polar phases effect partitioning through dipole–dipole interactions and hydrogen bonding. Where possible select the least polar phase to effect separation. Compounds with similar boiling points but differences in capacity for hydrogen bonding (e.g. alcohols and aldehydes) are readily separated using polyethylene glycol (PEG) phases. Table 17.5 shows some typical applications.

17.6.8 High performance liquid chromatography (HPLC)

(a) Application

Qualitative and quantitative analysis by separation of a wide range of organic materials and inorganic materials. Not limited to volatile compounds and many products can be analysed directly after dissolving a small sample in the mobile phase. Guard columns prevent fouling of the stationary phase by non-soluble components.

(b) Principle

Components separated on a wide range of stationary phases by partition, adsorption, size-exclusion or ion exchange mode. Sample is injected onto the column through a pressure loop valve and moved through the column by a high-pressure flow of mobile phase from a pumped delivery system. Careful selection of stationary and mobile phase and the pressurized flow effect rapid resolution of sample components. Separated components are detected in the eluent from the column by an appropriate detector (e.g. spectrophotometer, mass detector, refractive index detector) and displayed on a chart.

(c) Instrumentation

Chromatograph with pump able to give high flow constancy and low pulsation and compatible with a wide range of organic and inorganic solvents. There is a wide choice of equipment commercially available and an experienced analyst can develop a system suitable for a wide range of applications by further additional components.

Injection sample loops (1–25 μl) and Rheodyne-type high-presssure valve.
Guard columns.
Stainless-steel columns.
Stainless-steel tubing, unions, nuts and ferrules.
Flow-through detector.
Recorder or data management system.

(d) Operation and applications

In HPLC the mobile phase is pumped through a stationary phase of very small particle size, 5–25 μm in diameter. To achieve high flow rates and good resolution, the mobile phase is pumped at pressures up to 200 bar (3000 psi) giving typical flow rates of 1–5 ml/minute. Circulatory heating systems are available to maintain the stationary phase in the column at a precise temperature (10–100°C) to improve separation and reproducibility. Pumped delivery systems are usually microprocessor controlled delivering solvents from reservoirs into mixing chambers. The composition of the mobile phase may be maintained throughout the separation for *isocratic* elution or blended as a mixture of changing composition for *gradient* elution. Solvent systems must first be degassed by heating, applying vacuum or purging with helium before pumping. In-line filters are also used to remove particulate matter which could damage the pump seals. Columns are made from stainless steel tubing capable of withstanding high pressures with smooth internal finish and high chemical resistance. Typically they are 10–25 cm in length and 2–5 mm internal diameter. Columns are usually purchased pre-packed with the stationary phase retained by stainless-steel mesh discs of low porosity at each end.

Separations using HPLC can be carried out by adsorption, partition, ion exchange, size exclusion and even affinity mode using biologically selective stationary phases. There are also *chiral* phases suitable for the separation of optically active enantiomers. However, most applications are directed to adsorption and partition. As in gas chromatography, there are a limited number of suitable solid adsorbents but a wide range of liquid stationary phases which are made by chemically bonding high-boiling-point liquids to suitable supports. Unlike gas chromatography, however, the selection and composition of mobile phase is extremely important for successful resolution of components. The eluting power of a mobile phase is determined by its overall polarity, the nature of the sample components and the polarity of the stationary phase. Early HPLC applications were based on 'normal phase' chromatography. Here the stationary phase is silica or a polar liquid bonded onto the surface of a silica support. Normal phase chromatography requires a non-polar mobile phase such as hexane with the addition of slightly polar modifiers, e.g. IPA, ethyl acetate or methanol. Eluting power increases with increasing solvent polarity. Although normal phase conditions can usually effect good separation between non-polar and polar compounds, it is not able to separate compounds with similar functional groups or similar polarity. Developments in the preparation of stationary phases led to the

application of 'reversed-phase' liquid chromatography. Reversed-phase systems now represent the most widely used systems and consist of a non-polar hydrocarbon phase chemically bonded to the surface of very small silica particles. Suitable hydrocarbons include octasilyl (Si-C_8) and octadecylsilyl (Si-C_{18}; ODS). The mobile phase is polar and can be of simple composition such as water modified with methanol, acetonitrile or tetrahydrofuran (THF). Water can be replaced with an aqueous buffer to assist separation of ionic and biological components. In reversed-phase systems, eluting power *decreases* with increasing solvent polarity. Besides polarity other factors that influence solvent choice for mobile phase include viscosity, boiling point and compatibility with detectors. A low viscosity reduces band spreading of components and offers little back pressure to the flow rate. The most common detectors are based on UV absorption and therefore the solvent needs to have a UV 'cut-off' before that of the eluting component. Table 17.6 gives examples of solvents widely used in HPLC applications. Examples of the wide applications of HPLC in the fields of cosmetics, raw materials and pharmaceuticals are given in Table 17.7.

17.6.9 Determination of acid value, ester value and saponification value

(a) Application

Raw materials consisting wholly or largely of fatty esters; products containing such materials.

(b) Definitions

Acid value. The number of mg of potassium hydroxide (KOH, molecular weight = 56.1) required to neutralize the free acids in 1 g of sample. The acid

Table 17.6 Characteristics of common solvents used in HPLC

Solvent	*Organic group*	*Relative polarity*	*UV cut off (nm)*	*Viscosity (cP)*
Hexane	Alkane	0.0	200	0.33
Cyclohexane	Cycloalkane	0.2	200	1.00
Trichloroethylene	Halogenated HC	1.0	273	0.57
Diethyl ether	Ethoxy	2.8	220	0.32
Dichloromethane	Halogenated HC	3.1	235	0.44
Tetrahydrofuran	Cyclic ether	4.0	215	0.55
Acetonitrile	Cyano	5.8	190	0.37
Acetic acid	Carboxylic acid	6.2	230	1.26
Dimethyl sulfoxide	R_2SO	7.2	268	2.00
Water	–	9.0	200	0.90

Table 17.7 Applications of HPLC to analysis of raw materials, cosmetics and pharmaceuticals

Application	*Mode of chromotography*	*Stationary phase*	*Mobile phase and elution*
Parabens	Reversed phase	Octyl-	Water : acetonitrile (60% : 40%); isocratic
Phenols	Reversed phase	Octadecyl-	Water : acetonitrile (60% : 40%); isocratic
Antihistamines	Reversed phase	Octadecyl-	Solvent A: 0.05M NaH_2PO_4, pH4; solvent B: acetonitrile; gradient 85%A/15%B changing to 15%A/85%B in 12 min
Catecholamines	Reversed phase	Octadecyl-	0.5M NaH_2PO_4 buffer adjusted to pH 2.4 with H_3PO_4; isocratic
Thioglycolic acid [6]	Reversed phase	Octadecyl-	Acetonitrile (50%):0.07M triethyl ammonium phosphate pH 3.5 (50%); isocratic
Methyldibromo-glutaronitrile (preservative) [7]	Reversed phase	Octyl-	Water : acetone (60 : 40), Na_2SO_4 (0.02M) and NaCl (0.002M)
1,4-Dioxane [8]	Reversed phase	Octyl-	Solvent A: acetonitrile in water (5% v/v); solvent B: acetonitrile in water (50% v/v); isocratic elution solvent A (5%) and solvent B (95%) for 5 min, then 2-min linear gradient to 95% solvent B for 1 min.
Cortisones	Normal phase	Silica	Butyl chloride : water (satd with BuCl) : THF : methanol : glacial acetic acid (95 : 95; 14 : 7:6)
Nonionic surfactants	Normal phase	Silica	THF : water (90 : 10)
Anions in water (ppm)	Selective	Ion exchange	*p*-Hydroxybenzoic acid (2.5 mM)adjusted to pH 7.8
Flourine and monofluoro-phosphate (toothpaste)	Selective	Ion exchange	Succinic acid (20 mM) adjusted to pH 3.7

value gives information about the quality of a raw material or product. Rancidity and ageing of fatty materials is indicated by an increase in acid value.

Ester value. The number of mg of potassium hydroxide required to saponify, i.e. turn into soap, the fatty esters in 1 g of sample.

Saponification value. The number of mg of potassium hydroxide required to saponify the fatty acids and the fatty esters in 1 g of sample. Samples which contain esters of low molecular weight fatty acids will have higher saponification values. Generally, saponification value is inversely proportional to the mean of the molecular weights of the fatty acids in the glycerides present in the sample. The saponification value is of most use for detecting the presence of adulterants such as waxes or paraffin which have negligible values.

(c) Principle

Free fatty acids are titrated with alkali. The sample is then boiled with excess alkali to saponify fatty esters, and the excess alkali is titrated with acid. Soaps are partially hydrolysed in aqueous solution and so react alkaline. The titration must therefore be done in a largely alcoholic medium. The concentration of ethanol should not be less than 80% at any point in the analysis.

(d) Apparatus

Standard laboratory glassware.

(e) Reagents

(i) Alcoholic potassium hydroxide solution, c (KOH) = 0.5 mol/l. Dissolve 140 g potassium hydroxide (CAUTION: CAUSTIC) in 150 ml water with continuous stirring and cooling. Cool to room temperature, dilute to 250 ml and mix thoroughly. Dilute 50 ml of this solution to 1000 ml with ethanol and mix. Protect from exposure to the atmosphere. Allow any insoluble matter (potassium carbonate) to settle out before use.

(ii) Alcoholic hydrochloric acid solution, c (HCl) = 0.5 mol/l. Dilute 50 ml concentrated hydrochloric acid to 1000 ml with ethanol and mix. Standardize immediately before use by titrating a 50 ml aliquot with accurately standardized aqueous sodium hydroxide solution, c (NaOH) = 1.0 mol/l, using phenolphthalein indicator. Exact concentration of acid = $CV/50 = C_1$ mol/l, where C mol/l is the exact concentration of alkali and V ml is the volume required.

(iii) Ethanol (CAUTION: FLAMMABLE). Denatured ethanol may be used in countries where it is permitted. The water content must not exceed 5%.

(iv) Phenolphthalein indicator.

(f) Procedure

1. In a 150 ml flat-bottomed flask with a ground-glass neck, accurately weigh a sample containing 1.5–2.5 g saponifiable matter. Add 25 ml ethanol and

swirl to dissolve. Heat if necessary, but cool before titrating. Mass of sample = W_1 g.
2. Add about 1 ml phenolphthalein indicator and titrate with 0.5 mol/l alcoholic potassium hydroxide solution. Volume required = V_1 ml.
3. Add by pipette or burette 50 ml of 0.5 mol/l potassium hydroxide solution. Attach a reflux condenser to the flask, lightly lubricating the glass joint with petroleum jelly.
4. Boil under reflux for 1 h. Cool.
5. Titrate with 0.5 mol/l alcoholic hydrochloric acid solution. Volume required = V_2 ml.
6. Carry out a blank experiment by performing steps 3–5 in a second flask, without a sample. Volume of hydrochloric acid required = V_3 ml.

(g) Calculations

Exact concentration of alcoholic potassium hydroxide solution

$$= V_3C_1/50$$
$$= C_2 \text{ mol/l (so it contains } 56.1 \times C_2 \text{ mg/ml of KOH)}$$

where V_3 is the volume of 0.5 mol/l alcoholic hydrochloric acid solution (step 6), and C_1 is the exact concentration of this solution in mol/l.

$$\text{Acid value} = 56.1\ V_1C_2/W_1 \text{ mg KOH/g}$$

where V_1 is the volume of 0.5 mol/l alcoholic potassium hydroxide solution (step 2), C_2 is the exact concentration of this solution in mol/l (see above) and W_1 is the mass of sample (step 1).

$$\text{Ester value} = 56.1(V_3 - V_2)C_1/W_1 \text{ mg KOH/g}$$

where V_3 is the volume of 0.5 mol/l alcoholic hydrochloric acid solution (step 6), V_2 is the volume of the same solution (step 5), C_1 is the exact concentration of this solution in mol/l, and W_1 is the mass of sample (step 1).

$$\text{Saponification value} = \text{acid value} + \text{ester value.}$$

Where the saponification value of a raw material is known, the method may be used to determine that material in a product. The saponification value (*SV*) of the product is determined. Then % ingredient = SV of product × 100/SV of raw material.

A few fatty esters, e.g. those present in beeswax, require prolonged boiling to achieve complete saponification. If in doubt over a particular sample, carry out the determination on replicate samples, with 1, 2, 3, 4, etc. hours boiling. Saponification is complete and the SV found correct when two consecutive results are equal.

17.6.10 Determination of unsaponifiable matter

(a) Application

Unsaponifiable matter may form part of the specification of certain raw materials. The method is also useful for determining fatty alcohols sterols, etc. in products.

(b) Principle

The sample is saponified as described earlier. The matter remaining unsaponified is extracted with petroleum ether, dried and weighed.

(c) Apparatus

Separating funnels, 250 ml.
Standard laboratory glassware.

(d) Reagents

(i) As for determination of saponification value.
(ii) Petroleum ether (CAUTION: FLAMMABLE), boiling point 40–60°C.

(e) Procedure

1. Carry out the procedure described in the method entitled 'Determination of acid value, ester value and saponification value', steps 1, 3 and 4. Step 2 is optional. Mass of sample = W_1 g.
2. Quantitatively transfer the solution to a 250 ml separating funnel, using 75 ml water. Rinse the flask with 50 ml petroleum ether. Pour the petroleum ether into the separating funnel and insert the stopper.
3. Shake thoroughly, occasionally releasing the pressure by inverting the separating funnel and cautiously opening the stopcock. Allow the layers to separate.
4. Run the lower (aqueous) layer into another separating funnel. Add 50 ml petroleum ether and repeat the extraction. Allow the layers to separate. Repeat, this time discarding the aqueous layer.
5. Wash the three petroleum ether extracts in turn with 50 ml water. If an emulsion forms, add a few ml of ethanol.
6. Transfer the petroleum extracts in turn to a tared 250 ml beaker and evaporate to dryness on a steam bath. Rinse the separating funnels with two 25 ml portions of petroleum ether, add this to the beaker and evaporate to dryness.
7. Add a few ml ethanol to the beaker and evaporate to dryness.
8. Dry in an oven at 100°C for 20 min, cool to room temperature and weigh. Mass of dry residue = W_2 g.

(f) Calculation

$$\% \text{ Unsaponifiable matter} = 100\ W_2/W_1$$

where W_1 is the mass of sample (step 1),
and W_2 is the mass of dry residue (step 8).

17.6.11 Determination of acids and bases, free and combined with weak bases and acids

(a) Application

Shampoos, creams, lotions and other products containing acids or bases either free or combined with weak bases or acids.

(b) Principle

The sample is titrated in a largely non-aqueous medium, to prevent errors due to hydrolysis of salts of weak acids and bases. Titration with acid measures free bases, or bases combined with weak acids. Titration with alkali measures free acids, or acids combined with weak bases. The method as described uses indicators, but if an autotitrator is available it is better done potentiometrically.

$$\begin{gathered}
R.COOH + OH^- \rightarrow R.COO^- + H_2O \\
R.OSO3^-.HN^+ (C_2H_4OH)_3 + OH^- \rightarrow R.OSO_3^- + N(C_2H_4OH)_3 + H_2O \\
N(C_2H_4OH)_3 + H^+ \rightarrow HN^+(C_2H_4OH)_3 \\
R.COONa + H^+ \rightarrow R.COOH + Na^+
\end{gathered}$$

(c) Apparatus

Standard laboratory glassware.

(d) Reagents

(i) Alcoholic sodium hydroxide solution, c (NaOH) = 0.1 mol/l. Pipette 50 ml accurately standardized sodium hydroxide solution, c (NaOH) = 1.0 mol/l, into a 500 ml volumetric flask, dilute to volume with ethanol and mix. Exact concentration = C_1 mol/l.

(ii) Alcoholic hydrochloric acid solution, c (HCl) = 0.1 mol/l. Pipette 50 ml accurately standardized hydrochloric acid solution, c (HCl) = 1.0 mol/l, into a 500 ml volumetric flask, dilute to volume with ethanol and mix. Exact concentration = C_2 mol/l. Prepare fresh solution daily.

(iii) Phenolphthalein indicator.

(iv) Bromophenol blue indicator.

(v) Ethanol (CAUTION: FLAMMABLE). Denatured ethanol may be used in countries where it is permitted. The water content must not exceed 5%.

(e) Procedure

1. In a conical flask, accurately weigh a sample containing 1–3 mmol of the acid(s) or base(s) to be determined. Add 50 ml ethanol and swirl to dissolve, heating if necessary. Cool. Mass of sample = W g.
2. To measure acids, add a few drops of phenolphthalein indicator and titrate with 0.1 mol/l alcoholic sodium hydroxide solution to the first permanent pale pink colour. Volume of alkali required = V_1 ml.
3. To measure bases, add a few drops of bromophenol blue indicator and titrate with 0.1 mol/l alcoholic hydrochloric acid solution to a clear green colour. Volume of acid required = V_2 ml.

(f) Calculation

% Free acid, or acid combined with a weak base

$$= V_1 \times \frac{M_a}{1000N_a} \times C_1 \times \frac{100}{W},$$

where V_1 is the volume of 0.1 mol/l sodium hydroxide solution (step 2);
C_1 is the exact concentration of this solution in mol/l;
M_a is the molecular weight of the acid titrated;
N_a is the number of titratable hydrogen ions per molecule;
and W is the mass of sample (step 1).

% Free base, or base combined with a weak acid

$$= V_2 \times \frac{M_b}{1000N_b} \times C_2 \times \frac{100}{W},$$

where V_2 is the volume of 0.1 mol/l hydrochloric acid solution (step 3);
C_2 is the exact concentration of this solution in mol/l;
M_b is the molecular weight of the acid titrated;
N_b is the number of hydrogen ions absorbed per molecule of base;
W is the mass of sample (step 1).

17.7 ANALYSIS OF CREAMS AND LOTIONS

17.7.1 Determination of neutral fatty matter and total fatty acids

(a) Application

Creams, lotions and other products containing soap and/or fatty acid and other fatty matter.

(b) Principle

An alkaline solution of the sample is extracted with petroleum ether to extract mineral oil, silicones, fatty alcohols, fatty esters, lanolin and most waxes. The

aqueous layer is acidified and extracted again with the same solvent to extract the fatty acids. If the sample contains neutral fatty matter not extractable by petroleum ether, a final extraction is done with chloroform.

(c) Apparatus

(i) Separating funnels, 500 ml.
(ii) General laboratory glassware.

(d) Reagents

(i) Sodium hydroxide solution, c (NaOH) = 1 mol/l. Dissolve 40 g sodium hydroxide pellets (CAUTION: CAUSTIC) in water, cool. Dilute to 1000 ml and mix.
(ii) Hydrochloric acid solution, c (HCl) = 1 mol/l. Cautiously pour 100 ml concentrated acid (CAUTION: CORROSIVE; IRRITANT VAPOUR) into 500 ml water, dilute to 1000 ml and mix.
(iii) Ethanol (CAUTION: FLAMMABLE). Denatured ethanol may be used in countries where it is permitted. The water content must not exceed 5%.
(iv) Petroleum ether (CAUTION: FLAMMABLE), boiling point 40–60°C.
(v) Chloroform (CAUTION: TOXIC VAPOUR).

(e) Procedure

1. In a 250 ml beaker, accurately weigh a sample containing 0.4–0.6 g of either neutral fatty matter or total fatty acid, whichever is less. Mass of sample = W_1 g.
2. Add 25 ml ethanol and stir until the sample is completely dissolved, heating gently and adding more ethanol if necessary.
3. Transfer quantitatively to a 500 ml separating funnel, using several portions of ethanol.
4. Add a volume of water equal to the total volume of ethanol. Add 10 ml 1 mol/l sodium hydroxide.
5. Add 100 ml petroleum ether, stopper the funnel and shake thoroughly, releasing the excess pressure occasionally by inverting the funnel and cautiously opening the stopcock.
6. Allow the two liquid layers to separate and run the lower (aqueous) layer into a second separating funnel.
7. Repeat steps 5 and 6 twice more. Keep the aqueous layer.
8. Wash the three petroleum ether extracts in turn with a single 25 ml portion of 50% aqueous ethanol and add this to the main aqueous layer.
9. The petroleum ether extracts contain all or most of the neutral fatty matter. Transfer them in turn to a tared 250 ml beaker, evaporating each to dryness on a steam bath. Rinse each funnel with 10 ml petroleum ether, add the rinsings to the beaker and evaporate to dryness. Dry to constant weight. Weight of residue = W_2 g.

10. Acidify the aqueous layer by adding 20 ml 1 mol/l hydrochloric acid solution.
11. Repeat steps 5 and 6 three more times.
12. Repeat step 8.
13. The petroleum ether extracts contain the total fatty acid. Evaporate them to dryness and rinse the funnels as in step 9. Dry to constant weight. Mass of residue = W_3 g.
14. Some neutral fatty matter may remain unextracted, e.g. fatty alcohol ethoxylates. Add to the aqueous layer an equal volume of water and extract with three successive 100 ml portions of chloroform. Wash each chloroform extract in a second separating funnel with 50 ml water, then run it into a tared 250 ml beaker and evaporate to dryness. When all the chloroform has evaporated, dry to constant weight. Weight of residue = W_4 g.

The aqueous layer may be retained for further analysis if desired.

(f) Calculation

$$\% \text{ Neutral fatty matter} = 100\ (W_2 + W_4)/W_1$$
$$\% \text{ Total fatty acid} = 100\ W_3/W_1$$

where W_2 is the mass of dried residue (step 9);
W_3 is the mass of dried residue (step 13);
W_4 is the mass of dried residue (step 14);
W_1 is the mass of sample (step 1).

17.8 ANALYSIS OF HAIR TREATMENTS

17.8.1 Determination of thioglycollic acid

(a) Application

Permanent waving lotions containing thioglycollic acid or ammonium thioglycollate.

(b) Principle

Sulfite, if present, is removed by reaction with formaldehyde, and the thioglycollic acid (or thioglycollate) is titrated with potassium iodate in the presence of potassium iodide; 1 mol of iodate oxidizes 6 mol of thioglycollic acid.

$$6HSCH_2{\cdot}COOH + IO_3^- \rightarrow 3(SCH_2{\cdot}COOH)_2 + 3H_2O + I^-$$

When all the thioglycollic acid has been oxidized, further addition of iodate liberates iodine. This is made more obvious by its reaction with starch, with which it forms an intense blue colour.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

(c) Apparatus

Standard laboratory glassware.

(d) Reagents

(i) Acetic acid solution, 60 ml/l.
(ii) Potassium iodide solution, 100 g/l.
(iii) Formaldehyde, 40 g/l (CAUTION: IRRITANT VAPOUR).
(iv) Starch indicator. Stir 1 g potato starch to a smooth paste with a few ml of water. Pour into 100 ml boiling water, stir and cool. Prepare fresh weekly. Or use a proprietary iodine indicator.
(v) Potassium iodate solution, c (KIO_3) = 0.05 mol/l. Dissolve 10.5–11.0 g potassium iodate (Analar) in water, dilute to 1000 ml and mix. To standardize, pipette 10 ml into a 250 ml conical flask and add 25 ml of 60 ml/l acetic acid solution, 10 ml 100 g/l potassium iodide solution and a little starch indicator. Titrate with sodium thiosulfate solution, c ($Na_2S_2O_3$) = 0.1 mol/l, which may be purchased ready-standardized. Exact concentration of potassium iodate = $V_1/600 = C$ mol/l, where V_1 is the volume of sodium thiosulfate solution.

(e) Procedure

1. Accurately weigh a sample containing 2.0–3.0 g thioglycollic acid or ammonium thioglycollate, dissolve in water, transfer quantitatively to a 100 ml volumetric flask, dilute to volume and mix. Mass of sample = W g.
2. Pipette 20 ml into a 250 ml conical flask. Add 25 ml 60 ml/l acetic acid solution and 10 ml 10 g/l potassium iodide solution. If the product contains a sulfite, add 3 ml 40 g/l formaldehyde.
3. Titrate with 0.05 mol/l potassium iodate solution to the first permanent pale yellow colour, or add starch indicator and titrate to the first permanent pale blue. Volume required = V_2 ml.

(f) Calculation

$$\%\ \text{thioglycollic acid or ammonium thioglycollate} = \frac{V_2 \times 6 \times \text{mol.wt}}{1000} \times C \times \frac{100}{W} \times \frac{100}{20}$$

where V_2 is the volume of potassium iodate solution (step 3);
mol. wt is 92.1 for thioglycollic acid and 109.1 for ammonium thioglycollate (1 mol $KIO_3 \equiv 6$ mol thioglycollic acid);
C is the exact concentration of potassium iodate solution in mol/l;
and W is the mass of sample (step 1).

17.8.2 Determination of hydrogen peroxide or bromate

(a) Application

Neutralizers containing hydrogen peroxide or a bromate.

(b) Principle

The peroxide or bromate liberates iodine from potassium iodide. The iodine is titrated with thiosulfate.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2^- + 2H_2O$$
$$BrO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Br^- + 3H_2O$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

(c) Apparatus

Standard laboratory glassware.

(d) Reagents

(i) Acetic acid solution, 60 ml/l.
(ii) Potassium iodide solution, 100 g/l.
(iii) Starch indicator. Stir 1 g potato starch to a smooth paste with a few ml of water. Pour into 100 ml boiling water, stir and cool. Prepare fresh weekly. Or use a proprietary iodine indicator.
(iv) Sodium thiosulfate solution, $c\ (Na_2S_2O_3) = 0.1$ mol/l. Purchase ready standardized.

(e) Procedure

1. Accurately weigh a sample containing 0.8–1.0 g hydrogen peroxide or bromate ion. Dissolve in water, transfer quantitatively to a 250 ml volumetric flask, dilute to volume and mix. Mass of sample = W g.
2. Pipette 10 ml into a 250 ml stoppered conical flask. Add 25 ml of 60 ml/l acetic acid solution and 10 ml of 100 g/l potassium iodide solution. Stopper and allow to stand in a dark cupboard for 15 min.
3. Titrate with 0.1 mol/l sodium thiosulfate solution, adding 1–2 ml starch indicator near the end-point. The colour change is from blue to colourless. Volume required = V ml.

(f) Calculation

One mol hydrogen peroxide requires 2 mol sodium thiosulfate. One mol bromate ion requires 6 mol sodium thiosulfate.

$$\%\ \text{Hydrogen peroxide} = V \times \frac{34}{2000} \times C \times \frac{100}{W} \times \frac{250}{10}$$

$$\% \text{ Bromate } BrO_3^- = V \times \frac{128}{6000} \times C \times \frac{100}{W} \times \frac{250}{10}$$

where V is the volume of sodium thiosulfate solution (step 3);
C is the exact concentration of sodium thiosulfate solution (normally 0.10 mol/l);
and W is the mass of sample (step 1).

17.9 ANALYSIS OF TOOTHPASTES

17.9.1 Separation of water-soluble and water-insoluble components and determination of water-insoluble matter

(a) Application

All toothpastes. The insoluble matter consists of polishing agent. The water extract may be used for the determination of all soluble components except fluoride.

(b) Apparatus

(i) Centrifuge capable of 4000 r.p.m.
(ii) Plastic centrifuge tubes, 50 or 100 ml, with caps.

(c) Procedure

1. Accurately weigh about 10 g toothpaste in a 250 ml beaker. If sampling directly from a tube, discard the first few grams. Mass of sample = W_1 g.
2. Add 20 ml water and mix to a smooth paste with a glass rod, heating gently if necessary.
3. Add a further 30 ml water and stir until homogeneous.
4. Accurately weigh two 50 or 100 ml centrifuge tubes with caps. Mass of empty tube(s) = W_2 g.
5. Transfer the toothpaste suspension to either both 50 ml tubes or one of the 100 ml tubes, using several small volumes of water to effect the transfer. Do not allow the total volume to exceed 90 ml.
6. Balance the 50 ml tubes against each other, or the 100 ml tube against another full of water, to within 0.1 g.
7. Cap the tubes and place them in diametrically opposite positions in the centrifuge.
8. Centrifuge at 4000 r.p.m. for 5 min. Repeat if necessary until the supernatant liquid is completely clear.
9. Carefully decant the clear supernatant down a glass rod into a 250 ml volumetric flask.
10. Rinse the rod with a jet of water, catching the water in the flask.

11. Add 35 ml water to each of the 50 ml tubes or 70 ml to the 100 ml tube. Thoroughly resuspend the solids with a glass rod.
12. Balance the tubes, cap them and centrifuge again as in step 8.
13. Repeat steps 9–12, then repeat steps 9 and 10.
14. Dilute the solution in the 250 ml volumetric flask to volume and mix.
15. Uncap the centrifuge tubes, stand them in beakers and dry for 1 h at 100°C. Do not exceed this temperature, otherwise the wet solids may spatter. Cool to room temperature, re-cap and reweigh.
16. Repeat the heating, cooling and weighing until two successive weighings are equal. Final mass = W_3 g.

(d) Calculation

$$\% \text{ Insoluble matter} = 100\ (W_3 - W_2)/W_1 = \text{I}$$
$$\% \text{ Soluble matter} = 100 - \text{I}$$

where W_1 is the mass of sample (step 1);
W_2 is the mass of centrifuge tubes empty, with caps (step 4);
and W_3 is the mass of centrifuge tubes plus dried solids, with caps (step16).

17.9.2 Determination of glycerol or sorbitol

(a) Application

Determination of glycerol or sorbitol in products containing either but not both, and as raw materials.

(b) Principle

Polyols containing at least three adjacent –CHOH– groups are oxidized by periodate to produce formic acid from those –CHOH– groups that lie between two other –CHOH– groups, and aldehydes from those that do not. Terminal CH_2OH– groups yield formaldehyde. Thus glycerol ($CH_2OH \cdot CHOH \cdot CH_2OH$) yields one molecule of formic acid and two of formaldehyde, while sorbitol ($CH_2OH \cdot (CHOH)_4 \cdot CH_2OH$) yields four molecules of formic acid and two of formaldehyde. Either humectant may be determined by titration of the formic acid with standard alkali.

(c) Apparatus

Stoppered conical flasks, 500 ml.
General laboratory glassware.

(d) Reagents

(i) Hydrochloric acid solution, c (HCl) = c. 0.1 mol/l.
(ii) Sodium periodate solution, 50 g/l. Dissolve 12.5 g sodium periodate ($NaIO_4$) (Analar) in water, dilute to 250 ml and mix. Prepare fresh solution daily.

(iii) Ethane-1,2-diol (ethylene glycol) (Analar).
(iv) Sodium hydroxide solution, c (NaOH) = 0.1 mol/l, accurately standardized. Exact concentration = C mol/l.
(v) Phenol red indicator.

(e) Procedure

1. For products, use the solution prepared in the determination of water-insoluble matter, step 14. For raw materials, accurately weigh 1.20–1.30 g, dissolve in water, dilute to 250 ml and mix: Mass of sample = W g.
2. Pipette into a 500 ml stoppered conical flask an aliquot (V_1 ml) containing 0.10–0.25 g glycerol or 0.050–0.125 g sorbitol.
3. Add 5 ml 0.1 mol/l hydrochloric acid solution, and water to give a total volume of about 50 ml.
4. Heat to boiling and boil gently for 1 min. Cool.
5. Add a few drops of phenol red indicator and carefully neutralize with 0.1 mol/l sodium hydroxide solution.
6. Add 25 ml 50 g/l sodium periodate solution, stopper, swirl to mix and allow to stand in a dark cupboard for 30 min.
7. Add 5 ml ethane-1,2-diol, stopper, swirl to mix and replace in the cupboard for a further 20 min.
8. Titrate with 0.1 mol/l sodium hydroxide solution. Volume required = V_2 ml.

(f) Calculation

One mol of glycerol (92.1 g) gives 1 mol of formic acid and requires 1 mol of sodium hydroxide. One mol of sorbitol (182.2 g) gives 4 mol formic acid and requires 4 mol sodium hydroxide.

Mass of sample in aliquot taken at step 2 = $W \times V_1/250$ g.

$$\textit{Either } \%\ \text{glycerol} = V_2 \times C \times \frac{92.1}{1000} \times \frac{100}{W} \times \frac{250}{V_1}$$

$$\textit{or } \%\ \text{sorbitol} = V_2 \times C \times \frac{182.2}{4000} \times \frac{100}{W} \times \frac{250}{V_1}$$

where V_2 is the volume of 0.1 mol/l sodium hydroxide solution (step 8):
C is the exact concentration of this solution in mol/l;
V_1 is the volume of aliquot (step 2);
and W is the weight of sample (step 1). For products, this is W_1 from step 1 of the method for separating water-soluble and water-insoluble matter.

17.9.3 Determination of sorbitol by HPLC

Sorbitol, other sugar alcohols and saccharides are readily determined by HPLC. An effective stationary phase is a sulfonated styrene–divinylbenzene

cross-linked resin available in a number of ionic formats including calcium, sodium, hydrogen, potassium and silver. The ionic forms of the stationary phase are readily regenerated following separation. The elution is run in an isocratic manner using deionized water as the mobile phase at a temperature between 75°C and 85°C. Separated components are detected using a refractive index detector. Phenomenex make a suitable range of columns and stationary phases based on Rezex™.

17.9.4 Determination of pyrophosphate

(a) Application

Determination of pyrophosphate in tartar-control toothpastes. Other phosphate species, apart from monofluorophosphate, must be absent. Surfactants interfere and must be removed.

(b) Principle

The pH of an aqueous extract from which the foaming agent has been substantially removed is adjusted so that the pyrophosphate is present as $H_2P_2O_7^{2-}$. Excess silver ions are added, setting up the equilibrium

$$H_2P_2O_7^{2-} + 4Ag^+ \rightleftharpoons Ag_4P_2O_7 + 2H^+$$

The liberated hydrogen ions are titrated with alkali. As the titration proceeds the equilibrium shifts continually to the right. At the end-point the silver pyrophosphate is completely precipitated and the acidity quantitatively titrated. The titration is done in the presence of ammonium ions to minimize the effect of any weak acids or bases that may be present. The method is based on that described by Cullum and Thomas [9].

(c) Apparatus

(i) Centrifuge capable of 4000 r.p.m.
(ii) Plastic centrifuge tubes, with caps.
(iii) pH meter, calibrated before use.
(iv) Glass electrode and calomel reference electrode of the wick or sleeve type, or combined electrode.
(v) Magnetic stirrer and stirrer bar.

(d) Reagents

(i) Ethanol. Denaturated ethanol may be used in those countries in which it is permitted. The water content must not exceed 2%.
(ii) Nitric acid solution, $c\ (HNO_3) = 1.0$ mol/l.
(iii) Ammonium nitrate solution, 50 g/l.

(iv) Silver nitrate solution, 50 g/l.
(v) Sodium hydroxide solution, c (NaOH) = 0.1 mol/l, accurately standardized. Exact concentration = C mol/l.

(e) Procedure

1. In a 250 ml beaker accurately weigh a sample of toothpaste (W g) containing 0.10–0.15 g pyrophosphate, expressed as $P_2O_7^{4-}$. Add a few ml ethanol and, using a glass rod with a rubber 'policeman', work the sample to a smooth cream. This requires persistence as toothpastes are not normally readily dispersible in ethanol. Add more ethanol a few ml at a time, with thorough homogenization after each addition, until a total of 100 ml has been added.
2. Cover the beaker with a watch glass and stand it on a magnetic stirrer. Add a stirrer bar and stir for 1 h. Allow to settle, then decant and discard the clear supernatant. Avoid losing any of the insoluble matter.
3. Add 25 ml ethanol, stir thoroughly, allow to settle and decant and discard the clear supernatant. Avoid losing any of the insoluble matter.
4. Add a few ml water to the residue in the beaker and work the mixture to a smooth cream. Add more water to give a total volume of about 25 ml and stir until homogeneous, heating on a steam bath if necessary. Dilute to about 100 ml with water.
5. Place the beaker on a magnetic stirrer and add a stirrer bar. Insert pH electrodes and commence stirring.
6. Add 1.0 mol/l nitric acid solution until the pH drops to about 4.0, then add 0.1 mol/l sodium hydroxide solution dropwise until the pH is exactly 4.2.
7. Add 5 ml 50 g/l ammonium nitrate solution and 5 ml 50 g/l silver nitrate solution.
8. Titrate with 0.1 mol/l sodium hydroxide solution, allowing the pH to become constant after each addition, until the pH is 4.8. Titrate dropwise as the endpoint is approached. If the titration exceeds 20.0 ml, repeat the analysis on a smaller sample. Volume required = V ml.

(f) Calculation

The formula weight of the $P_2O_7^{4-}$ ion is 174. Each ion yields two hydrogen ions and reacts with 2 mol of sodium hydroxide:

$$\%\ \text{pyrophosphate as } P_2O_7^{4-} = V \times C \times \frac{174}{2000} \times \frac{100}{W}$$

where V is the volume of 0.1 mol/l sodium hydroxide solution (step 8);
C is the exact concentration of this solution in mol/l;
and W is the weight of sample (step 1).

Note: 1 g $P_2O_7^{4-}$ is equivalent to 1.528 g $Na_4P_2O_7$ or 1.897 g $K_4P_2O_7$.

17.9.5 Determination of available free fluoride and total available fluorine

(a) Application

Toothpastes containing fluoride or monofluorophosphate.

(b) Principle

Fluoride ion is determined in an extract of the product by direct potentiometry with a fluoride ion-selective electrode. The electrode shows an approximately Nernstian response, i.e. the electrode potential changes by approximately 59 mV for a ten-fold change in fluoride ion concentration. The electrode responds only to fluoride ions, but monofluorophosphate can be measured after acid hydrolysis to fluoride and orthophosphate.

(c) Apparatus

(i) Centrifuge capable of 4000 r.p.m.
(ii) Plastic centrifuge tubes, 50 ml, with caps.
(iii) Polypropylene 10 ml and 20 ml pipettes, 100 ml volumetric flasks and 100 ml beakers.
(iv) Potentiometer, or pH meter with millivolt scale.
(v) Fluoride ion-selective electrode. The Whatman selective electrode system is suitable. Use in accordance with the manufacturer's instructions.
(vi) Magnetic stirrer and plastic-coated stirrer bar.

(d) Reagents

(i) Standard fluoride solutions, 1000, 100, 10, 1 and 0.1 mg/l. Dry a little sodium fluoride (Analar) at 105°C for 1 h and cool to room temperature. Accurately weigh about 2.2 g, dissolve in water, transfer quantitatively to a 1000 ml volumetric flask, dilute to volume and mix. The exact concentration of fluoride is 452.4 W mg/l (NaF contains 45.24 % F^-), where W is the mass in grams. Using polypropylene pipettes and volumetric flasks, make successive ten-fold dilutions of this solution to obtain solutions containing 100, 10, 1 and 0.1 mg/l fluoride ion. Record their exact concentrations.
(ii) Total Ionic Strength Adjusting Buffer (TISAB). Dissolve 294 g trisodium citrate dihydrate (Analar), 68 g sodium acetate trihydrate (Analar) and 29 g sodium chloride (Analar) in about 600 ml hot water. Cool, adjust the pH to 6.4 with glacial acetic acid (Analar), dilute to 1000 ml and mix. The function of the TISAB is to ensure that all readings are made on solutions of the same ionic strength and at the same pH, and to sequester metal ions, particularly Al^{3+}, that form stable covalent complexes with F^- ions.

(iii) Sulfuric acid solution, c (H_2SO_4) = 1.0 mol/l. Slowly and with continuous cooling, pour 55 ml concentrated sulfuric acid (CAUTION: CORROSIVE) into about 500 ml water. Cool, dilute to 1000 ml and mix.
(iv) Sodium hydroxide solution, c (NaOH) = 1.0 mol/l. Dissolve 40 g sodium hydroxide pellets (CAUTION: CAUSTIC) in water, cool, dilute to 1000 ml and mix.
(v) Phenolphthalein indicator.

(e) Procedure

Part A: Preparation of calibration curve

1. Using polypropylene pipettes, transfer 20 ml of each of the 100, 10, 1 and 0.1 mg/l fluoride solutions into 100 ml polypropylene beakers.
2. Add to each by pipette 20 ml TISAB.
3. Add a stirrer bar to the beaker containing the 100 mg/l solution, place it on a magnetic stirrer, insert the electrodes and commence stirring.
4. Record the millivolt reading at 1-min intervals until two consecutive readings are equal.
5. Repeat steps 3 and 4 with each of the other three fluoride standards.
6. Let the four readings be A, B, C and D. Confirm that A–B, B–C and C–D are equal within 1 mV and that all three differences lie between 56 and 59 mV. If this is not so, or if the millivolt readings take an excessive time to become constant, carefully clean the sensing surface of the fluoride electrode and repeat the measurements.
7. On semi-log graph paper, plot millivolts (vertical axis) against concentration (logarithmic scale), or plot millivolts against the logarithm of the concentration on ordinary graph paper. Use actual, not nominal, concentrations. There is no need to divide by two to correct for the dilution with TISAB, because the test solutions will be diluted in the same ratio. Draw the best straight line through the points. The curve has a negative slope, i.e. higher concentrations give lower readings.

Part B: Preparation of aqueous extract of toothpaste

Fluoride ions react with some toothpaste abrasives, and high temperatures may accelerate this reaction. Heating during extraction is therefore to be avoided. Calcium fluoride is appreciably water-soluble (about 76 mg/l), and if fluoride has been lost by reaction with a calcium-containing abrasive, more will be brought back into solution by repeated extraction. A single cold extraction is therefore recommended. The error due to the volume of the insoluble matter is only about 1% and can reasonably be ignored.

1. Accurately weigh about 5 g (W g) toothpaste in a 100 ml beaker. If weighing directly from a tube, discard the first few grams.

2. Add 10 ml cold water and work to a smooth cream with a glass rod.
3. Add a further 20 ml cold water and stir until homogeneous.
4. Transfer quantitatively to a 100 ml polypropylene volumetric flask, dilute to volume and mix.
5. Transfer about 40 ml of the suspension to each of two 50 ml plastic centrifuge tubes and counterbalance them, with caps, to within 0.1 g.
6. Cap the tubes, place them in diametrically opposed positions in the centrifuge and spin at 4000 r.p.m. until the supernatant liquid is completely clear.
7. Decant the supernatant liquid into a clean, dry, stoppered polypropylene flask (solution A). Do not dilute to volume; this has already been done (step 4). Pipette 20 ml into a 100 ml polypropylene volumetric flask, dilute to volume and mix (solution B).

Part C: Hydrolysis of monofluorophosphate

1. Pipette 20 ml solution A (step B.7) into a 100 ml beaker, add 5 ml 1.0 mol/l sulfuric acid solution, cover with a watch glass and boil very gently for 5 min. Cool to room temperature.
2. Rinse the watch glass with a jet of water, collecting the rinsings in the beaker. Neutralize to phenolphthalein with 0.1 mol/l sodium hydroxide solution.
3. Quantitatively transfer to a 100 ml polypropylene volumetric flask, dilute to volume and mix thoroughly (solution C).

Part D: Determination of fluoride

1. For determination of free fluoride, use solution B (step B.7). For determination of monofluorophosphate use solution C (step C.3). Pipette 20 ml of the appropriate solution into a 100 ml polypropylene beaker.
2. Add by pipette 20 ml TISAB.
3. Add a stirrer bar, insert the electrodes and commence stirring.
4. Record the millivolt reading at 1-min intervals until two consecutive readings are equal. Final reading = E mV.

(f) Calculation

1. Read from the calibration curve (step A.7) the logarithm of the fluoride concentration corresponding to E mV (step D.4).
2. Take its antilog to find the fluoride concentration in the solution measured. Let this be C_1 mg/l for solution B (step B.7) and C_2 mg/l for solution C (step C.3).
3. Free fluoride concentration in solution A = $5C_1 = F_1$ mg/l. Total fluorine concentration in solution A = $5C_2 = F_2$ mg/l.
4. Free (f) fluoride in toothpaste = 100 $F_1/W = F_f$ mg/kg (ppm). Total (t) available fluorine in toothpaste = 100 $F_2/W = F_t$ mg/kg (ppm).

5. Percentage available Na_2P0_3F in toothpaste $= 0.0001\ (F_t - F_f) \times 144/19 = 0.000758\ (F_t - F_f)\ \%$.

17.9.6 Determination of fluoride and monofluorophosphate by HPLC

Fluoride and monofluorophosphate in toothpaste are readily determined by HPLC. An aqueous extract of the toothpaste is first prepared and 'cleaned up' to remove abrasive material. An effective stationary phase is a styrene–divinylbenzene cross-linked resin in an anion exchange form. This type of stationary phase has good pH stability and can tolerate a wide range of mobile phases. Fluoride and monofluorophosphate are quickly resolved using a dilute solution of succinic acid (20–40 mM at pH 3.7). The separated components can be determined quantitatively using a conductivity detector calibrated with known standards.

SUPPLIERS

The following suppliers are all mentioned in the text.

Phenomenex UK Ltd, Melville House, Queens Avenue, Hurdsfield Industrial Estate, Macclesfield, Cheshire, SK10 2YF.

Whatman International Ltd, St Leonard's Road, 20/20 Maidstone, Kent ME16 OLS.

Foss UK Ltd, Parkway House, Station Road, Didcot, Oxon OX11 7NN.

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18

Efficacy testing of cosmetics and toiletries

Marion Roberts

18.1 INTRODUCTION

The objective of this chapter is to discuss specifically the use of human volunteer panels in assessing the efficacy, or performance, of cosmetics and toiletries.

The human 'guinea pig' is clearly the most relevant species in which to evaluate consumer products. In functional terms human skin, hair, teeth or nails will be the ultimate substrates on which a novel product will have to prove its performance, while psychologically the human user, however unpredictable, will be the ultimate judge of how well a product works. Studies in humans must, therefore, furnish the best predictive estimate of potential success of a new product when it finally emerges in the marketplace to impress the world at large.

Successful products make money, and this provides inspiration and motivation from product concept, through formulation and packaging, to advertising and point of sale. It is critical to have the earliest possible indicator of a new product's potential worth, not only to avoid waste of resources on mediocre formulations, but to justify the very considerable expense involved in the production and promotion of potential winners.

It is now more important than ever to evaluate the performance of new products as the recently implemented 6th Amendment to the EU Cosmetics Directive requires that we must be able to provide 'proof of the effect claimed for the cosmetic product, where justified by the nature of the effect or product'. This means that, by law, we must have scientific data to justify product claims.

18.2 ESTABLISHMENT AND MAINTENANCE OF THE HUMAN VOLUNTEER PANEL

The first step in human volunteer testing is to set up a panel of test subjects and obtain information on various parameters of skin and hair type and routine

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 555–599

product use to allow subsequent selection of suitable volunteers for specific studies. Initial recruitment is usually achieved by advertising through local media, but once a panel has been established and has reached an adequate size, it may well be that the local 'grapevine' will maintain a steady flow of new recruits. In general this will be balanced by loss of panellists due to geographical moves, ageing and other factors.

The ideal size of panel will depend on the nature and volume of the workload. Large panels of several thousand volunteers can be handled using computerized databases to facilitate processing and retrieval of information but it is important to limit the panel to a level which permits a realistic frequency of participation in studies and encourages a degree of rapport between the test unit and the volunteers. This can have quite important implications in ensuring good compliance with test conditions.

Unless the panel is set up in a high-density population, the distance involved in travelling to attend studies is likely to impose its own restriction on panel size. The age range of the panel may also be subject to certain constraints. Below the age of 18, the written consent of a parent or guardian will be required before a 'volunteer' can participate in a study. In the case of infants, who cannot really be termed 'volunteers', this becomes a particularly sensitive issue and, although parental consent should be obtained, it is not legally robust. At the upper end of the scale the age limit may be set by the panel insurance cover, which generally excludes panellists over 65 on the grounds that they present an elevated level of risk. Our growing, healthy, retired population is increasingly being targeted by manufacturers, however, so special arrangements may be required to cover testing in more mature panels.

The type of information which should be obtained from new recruits includes: name, address and telephone/fax number, date of birth, physical characteristics (e.g. hair and skin type), types of products used on a regular basis, and medical history including known allergies (no volunteer reporting a confirmed allergy to cosmetics or toiletries should be permitted to take part in testing). This information is fed into a confidential database for future reference when specific types of test panel are required. For some types of testing it may also be advisable for subjects to undergo a formal medical examination prior to recruitment.

18.3 ETHICAL CONSIDERATIONS IN HUMAN TESTING

In all forms of human testing ethical standards must be carefully observed. Although most testing of consumer products does not involve a significant risk compared, for example, to new drug testing, the same ethical principles apply. The Declaration of Helsinki, although directed primarily at pharmaceutical testing, clearly implicates both therapeutic and non-therapeutic testing in many of its recommendations.

In all tests involving humans it is essential that volunteers fully understand the objectives of the test and what is required of them before they agree to take part. For this reason it may be convenient to recruit volunteers by means of a letter fully describing the test procedure. Panellists should then give their informed consent in writing when they enrol for the study. At this time they may also be reminded that they should not take part if they are allergic to cosmetics or toiletries, that any medical treatment being received should be reported and that female subjects who are pregnant or lactating are advised against taking part.

It is also important that any payment made in return for services rendered should not be sufficient to be construed as constituting 'undue enticement' to take part in something they would otherwise be unwilling to do. It would be naive, however, to expect volunteers to flock to the cause purely in the interests of science and a sensible level of remuneration is normally made in recognition of their cooperation.

The adoption of an independent ethical committee is recommended. Scientific, legal and lay representatives should be included and their function is to make an independent evaluation of new test protocols. In this respect the members of the committee should not be connected in any way with the research organization conducting the study. In addition, payment for their services should be limited to direct expenses, as financial reward could be viewed as a means of influencing their judgement.

The ethics committee does not, however, relieve the scientist in charge of a study of his or her ultimate responsibility for the outcome. It is up to the study director to decide what preliminary safety data, if any, are required before proceeding. This may vary considerably, depending on the nature of the test protocol and the degree of innovation represented by the product. For example, a short-term user trial on a variant of a hand cream might require, at most, preliminary skin irritation and sensitization data, but a long-term efficacy trial on a shampoo containing a novel antidandruff agent would require data from a full battery of toxicity tests.

A discussion of risk analysis is outside the scope of this chapter, but it is the responsibility of the study director to weigh up each test situation and ensure that human volunteers are not exposed to any undue or avoidable hazard.

Product safety is covered in Chapter 22.

18.4 STUDY DESIGN

Efficacy tests are essentially designed to show that a product performs the function for which it is intended, for example that a moisturizer 'moisturizes', a deodorant reduces or masks detectable body malodour, an antidandruff shampoo reduces visible dandruff scale, and so on.

In order to establish a frame of reference for the evaluation of product efficacy it is usual to include both positive and negative controls in a study.

The positive control is often a leading marketed product with an established history of effective performance. The negative control, in the simplest case, would be the test formulation minus the active ingredient, i.e. a placebo.

Alternatively, the test may be a simple comparison of new versus old, such as the comparison of novel and conventional moisturizing agents in a standard moisture lotion base, or comparing the effects of new and standard resins on the durability of a nail-polish formulation.

Whenever possible, tests should be run on a double-blind basis to avoid the risk of bias in the evaluation procedure. This involves providing test and control products in identical plain containers distinguished by coding so that test subjects and assessors are not aware which sample is which. The code is broken only on completion of the study or, in the case of contract testing, may be retained by the test sponsor who will receive the final report relating to the products by their codes. This has the advantage of ensuring a totally independent and unbiased result.

Before proceeding to discuss specific examples of efficacy tests it may be useful to examine some common features. Most tests are designed around all or part of a basic 'core structure' so I shall describe this structure in some depth initially and its application to various test procedures.

18.4.1 The core structure

(a) Selection of a suitable test panel

Volunteers must demonstrate characteristics which render them suitable for a specific study. For example, if a moisturizer is to be evaluated it is necessary to select subjects with visibly dry skin. Age, sex and sociodemographic distribution are other criteria which may be specified according to the particular target population of the test product.

The number of volunteers in each treatment cell must be sufficient to allow meaningful interpretation of the test results. Statisticians perform power calculations to provide this information and should be involved in protocol design. Most in-use studies include at least 25–30 subjects in each treatment group. Long-term studies require larger initial numbers of volunteers than short-term studies to allow for wastage due to illness or other factors which were not foreseeable at the start of the test. Many evaluation procedures involve subjective assessments which, by definition, introduce their own factor of variation. These tests often require greater numbers of test subjects than objective tests involving 'measured' assessments which are less subject to variance.

(b) Preconditioning period

It is usually desirable to standardize conditions to some degree at the start of the test. This involves a period of use of standard bland products before

commencement of the main phase of product testing and also ensures that there is no lingering influence of other 'active' products used prior to the trial. This procedure is commonly used in the evaluation of antidandruff preparations where a bland inactive shampoo is used for up to 4 weeks prior to testing.

Alternatively, the preconditioning period may require a period of total abstinence from using the product type to be tested, as in the evaluation of antiperspirants. The mechanism of antiperspirant agents such as aluminium chlorhydrate has not yet been fully elucidated but there is known to be a significant carry-over of effect following the final application of product.

(c) Baseline assessment

This is the first assessment of the main trial and will serve to select the most suitable volunteers, for example, those with the driest skin or greasiest hair, etc. It is also the point at which the panel, as a whole, is split into test and control groups, either randomly or according to preselected criteria. For example, the test cells in a dandruff trial may be selected to have the same mean and range of dandruff scores and may also be balanced for secondary criteria, such as hair type.

(d) Period of use of products

The duration of use may vary considerably from only a single application monitored over a few days in the case of a nail-polish durability test, to several weeks' use in the evaluation of antidandruff products. The number and nature of test assessments depend on the particular evaluation required but should be frequent enough to keep volunteers interested in the study. When a test protocol requires a fairly lengthy period of use, it is often advisable to ask volunteers to record something, such as dates when they shampoo their hair in a dandruff trial or details of diet in a toothpaste evaluation. This keeps them on their toes and helps to prevent boredom setting in once the novelty of the trial begins to wear off. Another ploy is to request return of the test products for weighing at the end of the trial as this might detect failure to use them as instructed.

(e) Questionnaire

A carefully designed product questionnaire is an important part of all consumer trials as it provides the opportunity to record feedback from the volunteers themselves. The questionnaire is normally completed after the panellists have finished using the products, although sometimes there is advantage in asking them to fill in at least part of it while they are actually using the test samples, if one is interested in immediate effects.

In designing a product questionnaire it is important that not too much emphasis is placed on any one aspect of product use, albeit the most important

criterion for evaluation. Human subjects are susceptible to pressure and may try to give the 'right' answer if they feel this is the desired result. It is advisable, therefore, to include a few 'red herring' questions which may not furnish much useful information but will serve to camouflage the more vital issues and encourage candid responses.

Whenever possible, questions should be posed with a range of responses between two extremes, e.g. from 'excellent' to 'very poor', requiring the volunteer only to choose the appropriate response. This saves time by sparing panellists the task of wording their answers and makes subsequent analysis of the questionnaire much simpler. If you want to force subjects to respond either positively or negatively to a question, it is better to avoid offering them a 'middle of the road' option.

Another convenient form in which to set questions is to ask panellists to mark a point on a line corresponding to their opinion between the two extremes, which lie at its opposite ends. This is more complex, however, and can be difficult for untrained or inexperienced volunteers to comprehend fully without supervision. It is important to keep the questionnaire as straightforward and unambiguous as possible as panellists may become frustrated if they do not fully understand the questions or feel their task is taking too long to perform.

Finally, panellists should be encouraged to make any additional comments they consider relevant, as this may raise points of interest which have been missed in the preparation of the questionnaire and also gives the volunteer a chance to make a personal contribution.

(f) Post-treatment period

At the end of the treatment period it is sometimes of interest to compare the test and control products for the duration of any effects observed during the treatment period. This involves a period of abstinence from using active product while monitoring any changes. It is a phase often included in the evaluation of antidandruff products, as there is a demand for products which are effective for longer. Many consumers find that antidandruff shampoos promote hair greasiness and would prefer to use a more cosmetic shampoo between active treatments.

(g) Product crossover

As the name implies, this involves a second treatment period in which the test and control groups reverse roles. The product crossover provides a means of demonstrating the reproducibility of a test result. It is often employed in the evaluation of deodorants which involves applying the test sample to one axilla and the control sample to the other. During the first treatment period half the panel use the test product on the left and the other half use the test product on the right. In the crossover the two volunteer groups exchange application

patterns. Each treatment period is preceded by a preconditioning period as described above.

18.5 EVALUATION OF SKIN-CARE PRODUCTS

This is one of the largest areas of cosmetic research and development, both in terms of effort and potential reward. The promise of a soft, smooth, youthful complexion persuades many a female consumer to invest substantial sums on skin creams and lotions. In efforts to substantiate this promise, every conceivable property of the skin has been studied minutely with a view to correlating a variation in that property with a change in skin condition. Skin impedance, friction, transepidermal water loss and numerous other factors have been implicated. In the final analysis, of course, the deciding factor will be whether the consumer herself can perceive a beneficial effect under conditions of normal use and within a reasonable time of purchasing and starting to use the product.

The various methods developed for evaluating skin moisturizing effects include:

1. Study of skin morphology – evaluation of gross or microscopic changes in the physical appearance of the skin. This includes both the subjective assessment (visual and tactile) of intact skin and objective methods such as topographical measurements made on intact skin or surface replicas, skin photography and image analysis.
2. Study of mechanical properties of skin – evaluation of skin smoothness and softness through measurement of parameters such as skin friction and elasticity.
3. Study of electrical properties of skin – correlation between changes in skin impedance or capacitance and varying skin moisture content.
4. Transepidermal water loss (TEWL) – measurements of the rate of evaporative water loss from the skin surface before and after various treatments.

18.5.1 Skin morphology

It is perhaps appropriate to begin with the subjective assessment of skin condition, as most objective methods have been developed to substantiate the results of clinical assessment by providing more tangible evidence of a beneficial effect in support of advertising claims.

When looking for a 'moisturizing' effect it is important to start with dry skin as a substrate; so the first step is to select a test panel who exhibit dry skin in the area of interest, usually the hands or the face. Bearing this in mind, the ideal time to perform a test of this nature is in winter when dry skin is most prevalent. Secondly, it should be remembered that most people, particularly females, treat their dry skin with at least one of the huge variety of products already on the market. A preconditioning period is therefore required, during which use of

moisturizers is restricted or prohibited. This also serves to standardize conditions at the start of the test.

An initial baseline assessment of the skin condition at the end of the preconditioning period selects the subjects with the driest skin and the panel is divided into the required number of test and control cells, having approximately the same mean and range of dryness scores. Following the baseline assessment, the test products are issued for a period of use which is usually at least 3 weeks, spanning an epidermal cell cycle. Further assessments of skin condition are made at intervals during this period and skin photographs may be taken to provide a visual record of any changes observed. At the end of the study, test subjects will normally be asked to complete a product questionnaire in order to obtain information on their own opinions of the test products. The results of the clinical assessments are subjected to appropriate nonparametric statistical analysis.

For the purpose of assessment it is routine practice to divide the hands or face into several areas, as some regions are more prone to dryness and skin flaking than others, making it difficult to award an 'average' score for the entire face or hand. Scores for the individual areas are then added together to provide total scores. As the hands tend to exhibit a wider range of symptoms than the face, the scoring systems for the two skin sites will not, in general, be the same (Table 18.1).

In addition, the hands may be scored for skin roughness by stroking the back of the hand with the fingertips and awarding roughness scores on a typical scale of 0, no detectable skin roughness to 5, severe roughness.

Assessments are performed under standard lighting conditions by independent trained assessors who are not aware which subjects are using test and control products. Because the severity of dryness symptoms observed on the hands is generally greater than on the face, any moisturizing effect demonstrated by a test material is more easily detected, so the hands are sometimes used as a

Table 18.1 Examples of numerical scales for rating skin dryness on hands and face

Facial assessment		*Hand assessment*	
Score	*Description*	*Score*	*Description*
1	Slight dryness	1	Slight dryness
2	Moderate dryness with visible skin flaking	2	Moderate dryness and/or slight flaking
3	Severe dryness and skin flaking	3	Severe dryness and/or moderate flaking
		4	Severe flaking and/or slight cracking
		5	Moderate cracking
		6	Severe cracking through stratum corneum

secondary treatment site, even if the product is intended primarily for use on the face. The elbows, knees, heels and shins are other skin sites which have been selected because of their high tendency to dryness [1].

In certain facial evaluations it may be preferable to employ the half-face test [2–4] in which the test and control products are applied to opposite sides of the face and each volunteer acts as his/her own control, improving the accuracy of the test. This is feasible, of course, only when a direct comparison between two treatments is required. Supervised application of the product is advisable in this situation to ensure correct use and avoid side-to-side contamination. The method cannot be applied to hand evaluation as cross-contamination between hands is difficult to prevent.

Skin photography may be used in conjunction with clinical assessment and can help reinforce the clinical data, particularly the latest video inspection systems which can store and analyse images using advanced image-processing software. The skin is a very difficult photographic substrate, however, and slight variations in angle or lighting can produce marked differences in photographs of the same skin site. There is always doubt that a result based purely on photographic evidence may have been optimized.

Another application of photography is the photographic standardization of dry skin. Standard reference photographs are prepared to quantify visually varying degrees of scaling, fissuring and other dry skin symptoms [5]. This is helpful in training clinical assessors and can aid consistent evaluation over a long-term study.

Scanning electron microscopy (SEM) [6,7] has been widely used in the study of skin surface effects. The technique involves first taking negative skin impressions in high-resolution silicone material then casting in epoxy resin or polythene to produce positive skin replicas. These are examined by SEM, and photomicrographs show clearly the curling edges of uplifting cell layers and areas of fissuring in comparison with the plump 'cushioned' appearance of hydrated skin. In practical terms the method is subject to the same limitations as normal photography in that closely adjacent areas of skin can appear quite different so, unless exactly the same site can be located before and after treatment, there may be suspicion that a result has been engineered. There is also a possibility that taking the silicone impressions will itself initiate changes by encouraging sloughing of loose cell layers.

Skin surface replicas may also be examined by surface contour analysis. The technique involves use of a surfometer which traces the surface of the skin cast with a stylus and gives an accurate representation of the surface profile of the specimen. This profile can be analysed in various ways to indicate the relative roughness or smoothness of the skin [8–10]. The method is very sensitive to the presence of artefacts in the replicas, the exact orientation of the trace and deposition of material in the skin furrows. A more recent advance using laser technology [11] allows measurements to be made on intact skin, therefore eliminating some of the problems of using replicas. Surfometry has been used

extensively in the evaluation of so-called 'anti-ageing' or 'anti-wrinkle' products.

18.5.2 Mechanical properties

Measurement of the mechanical properties of skin is not an easy task due to the physical heterogeneity of the substrate. Methods which have been developed with some success include the following:

1. Measurement of skin friction, to evaluate the degree of smoothness or greasiness of the skin.
2. Measurement of skin elasticity, to evaluate suppleness or firmness of the skin.
3. Point indentation, to measure skin softness.

(a) Skin friction measurement

This is a well-documented technique. Several good review articles [12,13] discuss the theory of skin friction in relation to Amonton's Law, which states:

$$\mu = F/L$$

where F is the frictional force;
L is the load or force normal to the surfaces;
μ is the coefficient of friction, a constant for a given pair of surfaces.

The friction of human skin appears to exhibit non-linearity, the coefficient of friction increasing as the load decreases. This non-linearity of the force/load relationship is attributed to other mechanical parameters such as skin elasticity and stratum corneum adhesion.

Several types of instrument have been used in the measurement of skin friction. Some methods have examined frictional forces generated during the linear motion of a sled over the skin surface [14,15]. This sled is driven by a constant-speed motor, and the force required to move the sled measured by a force transducer. Other methods have looked at the friction forces generated by a rotating deglazed stainless-steel probe under normal load [12]. The measured torque is converted to an electrical signal.

Skin treatment with water results in an immediate sharp increase in the coefficient of friction which lasts for only a few minutes before returning to the normal value as water evaporates from the skin surface. Treatment with various types of skin-care products produces a range of effects lasting several hours, as follows:

1. non-greasy skin hydrating lotions produce an immediate increase in coefficient of friction which is less than that following water treatment but persists for longer;

2. moderately greasy creams produce a moderate increase in coefficient of friction which continues to rise over a period of hours;
3. very greasy creams produce an immediate decrease in coefficient of friction followed by a subsequent steady increase.

In conjunction with subjectively perceived effects, these results can be interpreted in terms of surface residue effects. Heavier creams leave an oily residue on the skin surface which masks any hydrating effect by imparting a 'slippery' feel. Gradually this effect decreases as the product is absorbed, and is replaced by an increase in coefficient of friction over and above the initial value due to the skin-hydrating effects of the occlusive film. Similarly, areas of skin which are prone to oiliness, such as the nasal fold and forehead, may give half the friction values of those recorded on the cheek. In contrast, however, clinically dry skin also exhibits decreased values of skin friction coefficient compared with normal skin, so it is important to remember that a valid interpretation of skin friction data can be made only in conjunction with subjective skin assessment.

(b) Skin elasticity measurement

One type of skin elasticity measurement involves a torsion method [16]. Torque is transmitted by a disc glued to the skin with double-sided adhesive tape and a rotational sensor linked to the torque motor axis feeds information to a microprocessor. The resulting deformation curves indicate:

1. the instantaneous deviation angle = skin extensibility;
2. the ability of the skin to recover equilibrium state;
3. (2/1) the degree of firmness or elasticity of the skin.

Using this apparatus it was found that a single treatment of the inner forearm skin with a moisturizing product increased the skin extensibility for up to 5 hours, while long-term treatment increased the skin firmness significantly following 7 days' treatment, reaching a maximum at 24 days. The modern commercial equivalent of this instrument is the Dia-Stron Dermal Torque Meter [17,18].

Another instrument featured in the literature is the gas-bearing electrodynamometer (GBE) [19,20]. This instrument measures the displacement of, and force acting upon, a moving armature. The force is produced by a coil moving in a uniform magnetic field and is therefore directly proportional to the intensity of current circulating in the coil. The coil is activated by a low-frequency function generator and displacement of the armature is measured by a linear differential transformer mounted coaxially with the force coil. Attachment to the skin is made by a stiff wire probe having a small stub at the free end which is fixed to the skin with double-sided adhesive tape. The force (stress) and displacement (strain) signals are displayed on a screen in the form of a hysteresis loop with force on the vertical axis and displacement on the horizontal axis. The inverse of

the slope of the stress/strain curve (i.e. the strain/stress slope) is said to be a measure of the skin's softness: a high value corresponding to soft skin. Skin softness values obtained varied from subject to subject, site to site and with the direction of movement of the probe on the skin.

In one set of experiments the back of the hands was selected as the test site, the hands being immobilized by insertion of the fingers into a plaster cast. It was found that treatment with water had an immediate effect on increasing skin softness but this effect lasted only a few minutes. The majority of water-based emollients tested induced a long-lasting softening effect. A typical curve showed a rapid immediate softening due to the water component, levelling off later when the composition of the oil phase appeared to dictate the degree and duration of skin softening.

Other commercially available instruments are the Courage & Khazaka Cutometer and Cortex Technology Dermalab which utilize a different approach to skin elasticity measurement, involving the force of suction. A partial vacuum is applied to a small circular area of skin and the deformation into the aperture and subsequent recovery on removal of the vacuum are recorded. Recent studies have indicated, however, that this method may be less sensitive in the testing of moisturizers [21].

(c) Point indentation

This method of evaluating skin softness has also been approached in different ways. One method [22] involves an apparatus in which a needle of variable diameter tip is driven rapidly into the skin and immediately withdrawn, the rapidity of the cycle (4 ms) ensuring that only the stratum corneum responds. Resisting forces decrease after skin hydration and transiently increase following delipidization with ether [23].

In a second method [24] low-pressure indentation is used to study the softness, 'yield' and elastic recovery of forehead skin in female subjects of varying ages. The apparatus consists of a light rod with a circular plate, surface area $0.2\,cm^2$, at the end, representing the contact area. The rod is counterbalanced to give a net pressure of less than $1\,g/cm^2$ and is connected to a linear variable differential transformer whose output is recorded graphically. Baseline readings are taken for 10–15 s then a weight is applied suddenly to the rod, increasing the pressure to $10\,g/cm^2$. Indentation is recorded for 10 s then the weight is removed and elastic recovery is followed for a further 10 s. In this instance measurements involve behaviour of the dermis.

It was found that both indentation and elastic recovery are highly correlated with age, the 'young' age group (20–39 years) showing a deeper indentation (softer skin) and more complete elastic recovery. It was proposed that it may be possible to produce a 'desired range' of skin parameters representative of the 'young' skin condition and that this information could be of value in the

development of skin-care products with scientifically proven efficacy in countering age-related skin changes.

The Dia-Stron Ballistometer combines elements of point indentation and elasticity measurement with the flexibility of being hand-held. A spring-loaded ball-bearing is effectively fired at the skin and the resulting impact and rebound pattern is followed.

As the stratum corneum is a hygroscopic medium, all the above measurements should be performed under controlled conditions of temperature and humidity. It is also important to consider the effects of perspiration and sebaceous secretions and to standardize methods of cleansing and drying the skin. There are, as yet, no published standard methods for studying the mechanical properties of skin *in vivo*. This is not a satisfactory situation and means that valid interpretation of test data is still very much reliant on correlation with the results of simultaneous subjective skin assessments.

18.5.3 Electrical properties

Keratin is a dielectric medium, making it a weak electrical conductor, especially when dry. When skin is moisturized this conductivity increases, as water molecules are strongly dipolar and combine very readily with the keratin chains. Measurement of skin electrical properties, such as impedance, conductance and capacitance, may therefore provide information on the degree of hydration of the skin. There are several technical difficulties involved in making these measurements:

1. Generation of contact impedance between the electrode and the skin surface means that applied pressure has a strong influence on the results.
2. Application of the electrode to the skin prevents gaseous exchange between the skin surface and surrounding atmosphere and this modifies the degree of hydration in the surface layers of the stratum corneum.
3. In the case of direct-current or low-frequency measurements, polarization of the electrodes may occur and this will interfere with measurement.

Apart from these experimental points there is also a relative lack of knowledge concerning the nature and influence of anatomical structures involved in the measurement, due to the physical heterogeneity of the skin. Also the mechanisms of electrical conductivity in skin are not precisely known, so interpretation of results in terms of moisturizing efficacy is complicated by the effects of materials such as urea, which are active on proteins and can alter the interaction of water molecules with keratin.

All methods for making *in vivo* skin electrical measurements require careful control over the test subjects and environmental conditions. A detailed discussion of the various methods used is outside the scope of this chapter but the

reader is referred to an excellent review article by Leveque and De Rigal [25] and papers by Serban *et al.* [26–28] which describe several applications of the method.

There are four commercially available instruments which are used to make skin measurements: Courage & Khazaka's Corneometer [29–31], the Skicon-200 Hygrometer, the Nova DPM9003 and the Dermalab system from Cortex Technology. The first of these measures capacitance and the others measure impedance.

Increased skin hydration is indicated by an increase in electrical conductance and capacitance or a decrease in skin impedance. Thus electrical measurements provide information on variations in the water content of the stratum corneum but caution must be exercised in interpreting results in terms of total product performance, as the perceived effectiveness of a cosmetic results from combined effects of many different ingredients contributing to the overall quality of the formula. Furthermore, although a decrease in skin impedance can be indicative of a moisturizing effect, inflammation of the skin causes a similar decrease but one which is clearly not indicative of a cosmetic benefit.

In summary, studies performed to date using measurement of skin electrical properties to demonstrate relative degrees of skin moisturization or dryness indicate that these methods provide a potentially useful tool for objective evaluation. It is important, however, to have knowledge of the limitations and to avoid basing judgements on electrical data in isolation, without supporting evidence from other objective or subjective techniques.

18.5.4 Transepidermal water loss (TEWL)

While the electrical measurements discussed in the previous section were concerned with water within the skin, TEWL involves measurement of the rate of water loss from the skin surface.

The original instrument used for measuring TEWL is the ServoMed Evaporimeter, which was first developed in the Department of Biomedical Engineering at the University of Linkoping by Dr Gert Nilsson [32] and was used initially to measure the rate of TEWL in burn tissue. Subsequently TEWL has been used in a wide number of situations where information is required on the barrier function of the stratum corneum. It has been used clinically in dermatology and to measure water loss in pre-term infants, as this can be a critical factor in temperature control. It has also gained wide use in cosmetic skin evaluation [33–35]. The European Society of Contact Dermatitis have issued guidelines for the measurement of TEWL and these are the recommended methods [36]. The instrument employs a sensor arrangement. A small area of skin is defined and separated from the surroundings by a Teflon head shaped as an open cylinder. The head helps to protect the measurement area from disturbing draught. At each of two distances from the surface to be measured there is a pair

of transducers; one for relative humidity, the other a thermistor. From the signals derived from these transducers the instrument computes first the partial pressure of water vapour at the two distances from the surface, then the partial pressure gradient and, finally, the evaporation rate in g/m^2 h. The measurement depends on the physical law of water diffusion into the air from a surface. Close to the surface the water transportation is determined by the formula:

$$1/A \times dm/dt = -D\ dp/dx$$

where A is the area of the surface;
m is the mass of the transported water;
t is time;
D is a constant related to the diffusion coefficient;
p is the partial pressure of water vapour in the air;
and x is the distance from the surface.

The formula indicates that the evaporation rate dm/dt is proportional to the partial pressure gradient dp/dx and can therefore be determined by measuring the latter. Since the Nilsson patent on the measurement method has expired there are two alternative instruments available for TEWL measurement, namely the Tewameter of Courage & Khazaka and Dermalab from Cortex Technology.

These instruments can be used in the evaluation of cosmetic skin-care products, as the rate of water loss from clinically dry or damaged skin is greater than that from normal skin. The immediate effects of applying skin-care products on rate of TEWL vary according to the nature of the formulation. Highly occlusive materials, such as heavy emollient creams, cause a decrease in TEWL due to the occlusive effect of the oily film on the surface. This is followed by a gradual increase over a period of several hours as the occlusive film disappears. These products, therefore, moisturize the skin by retarding the escape of moisture from within.

Light moisture lotions containing large quantities of water cause an immediate increase in TEWL due to (a) evaporation of moisture from the applied product film and (b) increased evaporation from the skin surface as more water has been added to the skin from the product. The extent and duration of these effects will depend on the nature of humectant and lipophilic materials present in the formulation.

As TEWL measurements are a sensitive and reliable monitor of skin damage, they may also be used in conjunction with a soap chamber test, arm immersion test or exaggerated wash procedure to evaluate the mildness of surfactant-based products used in skin cleansing [9]. Once again, TEWL results should not be taken in isolation and should be substantiated by subjective observation of the clinical condition or by other objective methods such as those previously described.

Other high-technology methods have been developed for use in medicine, including magnetic resonance imaging microscopy [37] which actually allows one to visualize directly the moisture in the stratum corneum and still images can be linked together into a time-lapse video to show changes over time.

Opto-thermal transient radiometry (OTTER) [38] is a spectroscopic technique which uses low-energy laser probing to cause a rise in surface temperature and measures the decay curve of the resulting infrared radiation, the opto-thermal lifetime decreasing with increasing hydration. This technique is reported to be superior to other spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR) [39], which is based on the attenuated total reflectance (ATR) phenomenon, because the latter method is occlusive and less sensitive, requiring a large area of skin to be in close contact with the ATR crystal.

18.5.5 Evaluation of sunscreen products

The labelling of sunscreen formulations with sun protection factors (SPF) has become universal in recent years. The original demand for sunscreens stemmed from an increase in foreign holidays and winter sports, which exposed people to much more intense UV radiation than their skins were conditioned to withstand and resulted in painful sunburn. More recently, the important chronic implications of prolonged or intense UV exposure, such as premature skin ageing and skin cancer, have intensified the search for more effective sunscreens and, thanks to widespread education programmes, have also become more important considerations in the minds of the majority of consumers, who previously merely wished to tan without burning.

The SPF is a number arrived at by taking the ratio of the threshold UV exposure time which produces visible erythema at a sunscreen-treated skin site, to the corresponding exposure time taken to produce visible erythema at an untreated control site under the same experimental conditions. SPFs range from a minimal protection value of 2, to over 30, although some argue that, above SPF 15, any additional protection afforded by attaining higher SPF values may be compromised by the increased likelihood of adverse reactions to such high levels of sunscreens, many of which have associated problems in terms of skin sensitization or photosensitization.

There are various standard protocols for the determination of SPF values in human volunteers, depending on geographical location. The COLIPA method was recently introduced as the European standard [40] and America, Australia, Japan and South Africa all have standard protocols, although all follow much the same procedures and produce similar results. The source of UV light is a xenon arc solar simulator and test subjects with skin susceptible to sunburn are selected. An untreated skin site on the back is divided into five or six subsites, each of which receives one of a series of UV exposures of increasing duration. The sites are read approximately 20 hours later and the shortest time exposure

resulting in visible erythema is designated the minimal erythemal dose (MED) for the untreated site. Sunscreen is then applied to an identical adjacent site and a second series of UV exposures, appropriate to the theoretical SPF value, is performed. The MED is again determined approximately 20 hours later and the ratio of treated to untreated MED is calculated. The mean value for the test panel is the determined SPF and the result is validated by inclusion of a standard sunscreen in each test series. Additional protocols exist for water resistance or waterproof claims and involve redetermining the SPF value following defined periods of water activity in a swimming pool or spa bath.

Global harmonization of methodologies is the objective but is likely to remain elusive for some time. It might be appropriate at the same time to consider simplifying SPF labelling to take into account the way sunscreens are actually used by the consumer. Controlled application of large measured doses of product to delineated areas of skin in the laboratory is a far cry from a general slapping on of product on the beach or in the back garden, prior to engaging in various physical activities, including bathing and water sports. Quantity, quality and frequency of application are probably, in real terms, among the most important criteria dictating effectiveness, so perhaps we should limit SPF labelling to low, moderate and high protection, and concentrate on getting consumers to use sunscreens properly. SPF values are generated under highly artificial and contrived conditions and are misleading if customers assume they can achieve comparable performance under normal, uncontrolled conditions of use.

The SPF value relates to protection in the UVB, or normal sunburning range of terrestrial UV light. UVA, the longer wavelength range of UV light once thought to promote tanning without causing skin damage, has now also been implicated in skin ageing and cancer. UVB is thought to affect mainly the epidermis while UVA acts more at the level of the dermis. There was justifiable concern that commercial UVB sunscreens, by preventing or delaying burning, actually encouraged consumers to sustain much larger does of UVA. The need for effective UVA sunscreens became obvious and was actively campaigned by Boots who introduced a compulsory star rating system for sunscreens sold through their branches, to indicate the relative UVA/UVB protection they afforded. The UVA/UVB protection ratio was determined using an *in vitro* method developed by Professor Brian Diffey. The quantity of UV light transmitted through a strip of transparent tape is determined at 5 nm intervals throughout the UVA and UVB ranges (290–400 nm). Sunscreen is then applied and the measurement is repeated. The transmission values are converted into absorbance values to give a series of monochromatic protection factors from which the UVA/UVB protection ratio can be calculated. These values were used by Boots to award star ratings from 1* with a UVA/UVB ratio of 0.2–0.4 (moderate protection) to 4* with a UVA/UVB ratio of 0.8+ (maximum protection). Instruments for *in vitro* SPF testing are supplied by companies such as Optometrics and Labsphere. As technology improves, it is to be hoped

that *in vitro* testing will ultimately replace all sunscreen testing in human volunteers.

In vivo tests for UVA protection have also been developed. Massive doses of UVA are required to produce sunburn so a different action spectrum was required and it was found that some people with slightly darker skin types develop a purplish skin colouration following UVA irradiation which was termed IPD (immediate pigment darkening) or PPD (persistent pigment darkening). UVA protection factors could then be determined *in vivo* in the same way as UVB protection factors.

However UVA is measured, the important point is that sunscreens should afford broad-spectrum protection. There has been great debate as to how to label products with UVA protection indices and it is to be hoped that we do not overcomplicate matters as we did with UVB protection. Broad-spectrum protection should be defined and should be mandatory.

A further more recent concern is that not all sunscreens which protect effectively against sunburn may be effective in protecting against skin cancer. Suppression of the immune system by UV is suspected to be a major factor in skin cancer, and protocols have been developed to evaluate protection against UV-induced immune suppression and damage to DNA. This has indicated that UVB sunscreens which are highly effective in preventing sunburn may not be effective in protecting against immune suppression and this could have serious implications by allowing greater exposure.

The demands made of sunscreens are constantly increasing. They should be photostable, substantive to the skin, water-resistant or even waterproof, as well as being aesthetically attractive and skin-compatible. In view of the apparent importance of the protective effect of sunscreens in the prevention of UV-related skin cancers, these borderline products are clearly becoming more pharmaceutical than cosmetic in character and are already classed as OTC products in the USA and Canada. As an industry we seem to have encouraged this by using the threat of premature skin ageing and cancer to justify selling higher and higher factor products. Should sunscreens be generally classed as medicines, the fear is that the price will escalate and distribution outlets will be much more restricted, just at a time when we are trying to encourage people to use more sunscreen, more often. As the ozone layer of the Earth's atmosphere becomes more fragile, and the incidence of skin cancer continues to grow, sunscreens will be in focus for some time to come.

18.5.6 Other skin evaluations

As fashions and lifestyles change, there are demands for different types of products.

Exfoliators encourage the sloughing off of dead cells, thus leaving the skin looking more youthful and radiant. These products may be either physical exfoliators which gently abrade the skin to encourage the sloughing off of dead cells,

or chemical exfoliators, like the alpha and beta hydroxy acids and retinoic acid. It is thought that the acid pH these materials induce in the outer stratum corneum may dissolve the desmosome linkages between cells, resulting in shedding of the outer layers. This is accompanied by increased cell renewal, either as a reaction to this mild stratum corneum damage and/or by a direct effect of the acidic pH on certain skin enzymes. These products can be evaluated visually or by superficial sampling of the skin with image analysis of the cells thus removed.

Free radical scavengers counteract the damaging effects of pollution and UV light on the skin and many cosmetics are now being formulated with vitamins E and C as well as other 'actives'. Laboratoire Dermscan offer an evaluation method using their Fluoroscan II system to determine the concentration of cutaneous peroxides. Another method [41] uses as a model the inhibition of UVB-induced skin erythema by topically applied free radical scavengers as measured by skin reflectance spectrophotometry. Anti-inflammatory effects can also be evaluated by laser Doppler perfusion imaging (LPDI) [42] which records microvascular blood flow.

Skin tanning agents are increasingly popular to produce a healthy-looking skin without risking the acute and chronic ill-effects of prolonged UV exposure. On the other hand there is a demand for products which will lighten the appearance of hyperpigmented age spots, and sophisticated skin lightening and refining products are also in demand from growing Asian markets such as Japan, where a pale skin is a sign of prosperity and much coveted. These products can be evaluated subjectively by inspection or instrumentally using the Minolta Chromameter or Dia-Stron Erythema/Melanin Meter to monitor the development or reduction of colour.

Gabriel *et al.* [43] have reviewed some of the technologies for the evaluation of skin changes.

18.6 EVALUATION OF HAIR-CARE PRODUCTS

Over several years the field of hair care has become much more sophisticated. Effective cleansing is no longer the end of the story and consumers today expect additional benefits, such as conditioning properties, protection against UV damage and chlorine, strengthening, low static effects, more shine and increased manageability in general. In modern lifestyles, daily washing of the hair is common practice and there is, therefore, a demand for increasingly mild shampoos which allow high frequency of use without concomitant drying or damaging effects. It is important to be able to evaluate the cleaning and cosmetic properties of shampoos in a rapid and meaningful way to aid development of products with specific activities, such as shampoos for greasy hair or low-tangle conditioners.

18.6.1 Factors influencing cleaning of hair [44]

Although human hair is similar in terms of chemical composition, physical properties and histological structure, to the keratin fibres used in textile materials such as wool, the cleaning of hair presents an entirely different problem from the laundering of fabrics. There are several constraints to be considered in the formulation of shampoos, which do not apply to household products. For example, cleaning must be carried out at physiologically acceptable temperatures (40–45°C) and the time available for the cleaning operation is relatively short, in the region of 5–10 minutes. In addition, detergents must comply with stringent safety standards and the criteria for judging product efficacy are significantly different.

There are three types of materials which soil the hair: (a) oily substances such as sebum lipids; (b) proteinaceous matter – cell debris from the stratum corneum and proteins from sweat; (c) particulate soil – from environmental pollution and residues of hair-grooming products.

Rate of sebum production is influenced by a number of factors. It is affected by hormone levels which cause seasonal and daily variations and is also subject to age-related changes. The quality as well as the quantity of sebum varies with age, sex, season and nutritional status. Even after sebum has been secreted its chemical composition and physical properties change with time. Extracellular lipases abundant on the skin surface gradually hydrolyse the triglycerides of sebum and thereby increase the free fatty acid content.

The re-oiling of newly washed hair is governed by two rate processes: sebum production which is a constant rate process, and sebum removal which occurs at a rate directly proportional to the quantity present. The rate of sebum production is about 6–9 ng per gland per minute, assuming an average scalp surface area of 775 cm^2 and that an average head of hair contains 1.6×10^5–1.74×10^5 hair follicles or sebaceous glands. In a 4-day period some 60–70% of sebum produced may be lost due to brushing, combing and other mechanical effects. Methods of washing and drying the hair may also have an effect on the subsequent rate of sebum loss. For example, hair dried naturally in air apparently loses sebum more slowly than hair dried with hot air. Whether hair is perceived as clean depends on highly subjective judgements based on visual and tactile evaluations. Hair is perceived as clean when it is not oily, and the criteria commonly used for judging oiliness are lack of lustre and clumping of fibres into 'rat-tails'. Test methods for the subjective evaluation of oiliness are described later in this section. Shampooing can affect the perception of hair cleanliness by: (a) removing the bulk of the sebum; (b) modifying both the hair surface and consistency of the sebum, possibly by the selective removal of certain components.

It has been reported that sebum from oily-haired individuals differs from that of dry-haired subjects in its C18 unsaturated fatty acid content. That from the former contains predominantly 8-octadecanoic acid whereas the sebum from dry

hair contains more 9-octadecanoic acid. The significance of this difference has not been fully clarified but it would suggest that minor chemical differences may be important in determining the consistency of sebum and consequent perception of hair condition.

18.6.2 Evaluation of cosmetic effects in general [45,46]

It is difficult to evaluate quantitatively the aesthetic effects of a shampoo. In the absence of objective techniques to measure performance, evaluation usually relies on direct sensorial methods which may provide a very generalized picture. Sensory assessment can be made more discriminating if the overall appearance is divided into the various basic cosmetic parameters. This approach is used in the Profile method which aims to analyse aesthetic performance by assessing nine basic cosmetic parameters related to physical or mechanical properties of the hair.

The parameters examined are as follows: (a) comb-out on wet hair; (b) comb-out on dry hair; (c) shine; (d) silkiness; (e) absence of static electricity; (f) individualization; (g) bounce; (h) springback; (i) body. Assessment is carried out by trained observers. In general, successive evaluation of two or more shampoos is performed by a single assessor, while the comparison of a test product to a theoretical profile is made by a panel of judges.

As an example, two shampoo formulations for greasy hair were tested on a panel of six young women with fine, greasy hair. As a pretreatment to standardize conditions, the whole head was washed for 3 weeks with a different shampoo for greasy hair. During the test period the two experimental formulations were applied by skilled operators to left and right sides of the head, twice weekly for 4 weeks. The shampoos were coded and the test run on a double-blind basis. Assessments were made immediately after shampooing and on each week-day following shampooing. A total of 336 assessments based on 3456 observations of individual parameters resulted from the study. The evaluation was based on the following contributions:

1. evaluation of the nine parameters by the trained assessor;
2. the trained assessor's overall judgement;
3. the subject's overall judgement;
4. statistical evaluation of the data based on the paired sign test.

Results indicated that the positive effects of these greasy hair shampoos were of short duration (less than 2 days). The profiles of the two products became similar while the cosmetic ratings and overall aesthetic impressions were still relatively high and disappearance of the perceived cosmetic benefits preceded visible soiling of the hair.

This rationalized sensory technique is judged to be useful in the study of regreasing and soiling of the hair following shampooing, as well as in the investigation of physical and mechanical properties which are responsible for the aesthetic appearance of the hair.

In a second study, comparison was drawn between a salon evaluation using the half-head technique as above, and the consumer's own evaluation in a whole-head crossover study using the products at home. Results indicated that the overall judgement of an effective shampoo, both by the trained observer and the subjects themselves, was associated mainly with the mechanical properties of hair such as bounce, springback and suppleness, but the test subjects were additionally influenced in their overall judgement of product performance by apparently superfluous parameters, such as perfume and colour.

18.6.3 Evaluation of hair greasiness

Greasy hair is cosmetically unattractive. It appears lank, lacking in lustre, unable to retain style and generally neglected. Many individuals who have greasy hair are committed to frequent, often daily shampooing to maintain their hair in an aesthetically acceptable condition. The aim in developing 'antigrease' shampoo formulations is to extend the maximum interval between shampoos without loss of hair condition or, in other words, to transform a greasy hair condition into a 'normal' or acceptable state. Several methods have been developed to evaluate the efficacy of potential antigrease shampoos.

In one reported method, two protocols are compared, the first a highly supervised test, the second more representative of normal use [47]. Both protocols use the same subjective scale of assessment and involve three test cells: (a) an experimental antigrease formulation; (b) a placebo group; and (c) a positive control group using a shampoo containing the antidandruff agent, zinc pyrithione (ZPT), which is reported to increase hair and scalp greasiness. Both protocols utilize groups of 130–140 males over 18 years of age and having greasy hair. To qualify the greasiness rating was greater than 20 on the scale below. The scalp was divided into quadrants which were assessed independently before adding up the scores.

Greasiness was assessed on a numerical scale of 1–9, as follows:

1	3	5	7	9
Not greasy	Slightly	Moderately	Very	Extremely greasy

The supervised study spanned a period of 8 weeks. Panellists reported twice weekly for assessment and supervised washing as it was found that maximum regreasing occurred in 4 days. For the first 3 weeks the placebo shampoo was used and the scores recorded at the end of this phase were used to split the panel into three groups of approximately 40 subjects with balanced mean greasiness scores. On the following visit baseline scores were recorded and one of the three

test shampoos was used on each subject. Twice-weekly assessment and supervised washing continued for the next 5 weeks.

The results indicated that the greatest reduction in greasiness took place in the first 3 weeks, during the pretreatment period. This decrease continued, at a reduced rate, during the treatment period for both the placebo and 'active' groups, while the group using the ZPT shampoo showed an increase in hair greasiness which was statistically significant in comparison with the other groups.

The less supervised trial extended over 10 weeks, a longer period to allow for less controlled conditions. During a 2-week pretreatment period subjects were given a placebo shampoo to use at home at least twice a week. They then attended for a supervised wash with the placebo shampoo and were assessed for hair greasiness 4 days later. Scores recorded at this assessment were used to divide the panel into three balanced groups and to provide baseline scores. Sufficient test shampoo was provided for an 8-week treatment period of twice-weekly home washing, supervised washes were performed after 4 and 8 weeks and hair greasiness assessments were made 4 days after each supervised wash.

On this occasion there was no reduction in greasiness over the control period. During the treatment period both the placebo and 'active' shampoos demonstrated a decrease in greasiness, while the ZPT shampoo again showed an increase which was statistically significant in comparison with the other two products. These effects were more pronounced at the 4-week assessment than at the 8-week assessment, a phenomenon attributed to loss of interest in the study resulting in less strict adherence to test conditions.

Neither of the above protocols demonstrated efficacy of the 'active' products but, as a grease-promoting effect was demonstrated for the ZPT shampoo in both tests, it was concluded that the protocols were validated. The first protocol was considered more sensitive in that greater supervision was imposed. The second protocol, however, was more realistic and may better reflect any effect perceptible by the consumer.

Another approach to sensory assessment applicable to evaluation of greasiness involves use of panels of assessors who need not necessarily be highly experienced or trained [48]. Certain precautions should be taken in this situation, e.g. conditions of light, temperature and relative humidity should be kept constant; distractions should be minimized and all assessors in any panel should receive identical instructions. The number of assessors required depends on several factors, such as the required accuracy of the results, number of test 'items', magnitudes of difference between items, and the skill of the judges. As assessors gain experience and confidence their judgement becomes more consistent. No assessor should be allowed to observe the results of another judge's assessment or how the assessment was made.

An assessor can be asked either to estimate the magnitude of some property of a test sample or to rank two or more samples for that property. The former alternative, termed the Meter method, involves placing each sample on what has

been designated a meter for the test property. The meter which may be, for example, a length of horizontal rod, has no subdivisions and each assessor decides for himself what range it covers. Different assessors will, therefore, use different mental scales and do not, of course, necessarily agree on rank order.

All assessments can be put on the same scale by standardizing so that all assessors have the same mean and standard deviation. When this is done assessments can be averaged to give an overall evaluation in terms of mean scale values. The overall rank obtained is generally found to be consistent between different panels of assessors but, because different individuals use different mental scales, both the mean scale values and the differences between them are characteristic of the particular panel used. It is, therefore, difficult to compare the results of one test with another, even when a common standard is included. For an isolated experiment, however, the Meter method is more rapid and simpler in terms of analysis than the Ranking method described below.

In the Ranking method at least two test samples are considered together. The assessor indicates the order of the samples and will generally then go on to rank further sets of samples with a limit of about ten sets to avoid onset of fatigue. From the ranking data it is possible to generate scale values which can be compared directly with the results of another test provided some common standard is included. There are further advantages of the Ranking method over the Meter method; for example, assessors usually find it easier to select a rank order than to indicate relative magnitudes, especially where differences between items are small.

An experiment was devised to establish how people's sensory assessment of hair greasiness correlates with the rheological properties of the grease. Tactile and visual judgements were studied separately, since both modes were considered important in the self-assessment of hair greasiness. While the relevance of rheology to the feel of the hair is obvious, a connection with appearance is, perhaps, less clear. The most important visual clue, apart from changes in gloss, is the so-called 'rat-tails' effect resulting from a tendency for the individual hairs to clump together in strands.

Oily materials ranging in viscosity from low-viscosity liquid oils to hard waxes were applied to hair switches by spraying 1% w/w solutions in ether until the deposit equalled 1% of the weight of hair, then combing through to promote uniform distribution. The sensory assessments were carried out using the ranking procedure separately for tactile and visual assessments.

In the tactile test, samples were presented for ranking in pairs, hanging behind a screen so that judges could feel but not see them. Judges were asked to feel one switch in each hand and to wash their hands between each pair. Twelve judges assessed six pairs, in the course of which every switch was felt twice, once in the left hand and once in the right, to compensate for bias.

In the visual test, subjects could see, but were not allowed to touch, the samples. Lighting conditions were selected to avoid highlights on the hair so

that gloss variations were not obvious and the predominant clue to greasiness was the rat-tails effect. In this instance subjects ranked three switches at one time.

Results indicated that tactile greasiness, as might be expected, is low for the thinner oils, increasing to a maximum for the semi-solids and decreasing again with the harder waxes. The visual greasiness pattern is more complex, however, and the perceived greasiness continues to increase with increasing viscosity when the tactile greasiness has already taken a down-turn.

MacLennan *et al.* [49] used a similar study design to evaluate 'slip' in talc samples. Results obtained from this type of study imply that it is possible to obtain quantitative measurements by means of sensory assessment. While parameters such as gloss and individualization can be measured instrumentally by light reflection [50] and photographic techniques, the method is equally applicable to aesthetic parameters such as softness, body and condition of hair, which have no obvious physical correlation with any instrumental measurement.

Rigano *et al.* [51] have published a useful overview of sensory evaluation methods.

18.6.4 Evaluation of hair strength and ease of combing

Hair strength has been equated with health (or lack of damage) and much interest has been generated in hair-strengthening shampoos and conditioners since the advent of Panthenol (Provitamin B) in hair care and associated claims of strengthening properties. The force required to stretch and break individual hair fibres has been measured using the Instron tester, but a more specialized device, the Dia-Stron Miniature Tensile Tester (MTT), is now available and uses an automatic carousel arrangement to facilitate testing of multiple hair samples. An essential consideration in tensile testing is the hair fibre cross-sectional area and this can be measured by various means such as microscopy or weighing standard lengths of hair fibre. A commercially available solution is the Dia-Stron Fibre Dimensional Analysis System (FDAS), which employs a high-resolution laser scanner to measure cross-sections of the fibres.

Superior conditioning effects of shampoos and conditioners have been achieved using silicones and other materials. Wet and dry combing can be evaluated subjectively by trained assessors in the salon using hair switches, or in human volunteers, usually employing the half-head technique to obtain comparative results. Alternatively, switches can be evaluated instrumentally using a combing accessory attached to the MTT system described above.

The instrumental measurement of hair properties and how they are affected by hair-care products has developed rapidly over the past few years and protocols supported include curl retention, friction, resin adhesiveness and drying properties.

18.6.5 Evaluation of antidandruff formulations

Dandruff may be defined as excessive scaling of the scalp, readily seen with the unaided eye but not accompanied by any obvious inflammation. The difference between dandruff and non-dandruff states is merely a more intense desquamation in the former and is purely quantitative, as opposed to qualitative, so dandruff should not be regarded as a diseased state in this sense.

It is generally agreed that dandruff results from a low-grade underlying inflammatory process resulting in local 'hot-spots' of increased proliferative activity and the formation of parakeratotic foci which are, in fact, the visible flakes or squames when shed. Parakeratotic foci also occur in non-dandruff scalps but are fewer in number and do not result in flaking which is conspicuous enough in amount or diameter of scale to be recognized as visible dandruff.

There was originally controversy as to whether microorganisms play a part in the causation of dandruff. Kligman *et al.* [52], while noting that yeasts of the species *Pityrosporum* make up only about 45% of the total scalp population in non-dandruff subjects as opposed to 75% in subjects with dandruff, concluded that this was a consequence of dandruff, not a causative factor, the increased production of cells providing more surface and nutrients for growth. They claimed to have effectively eliminated all scalp microflora with antimicrobials without affecting levels of dandruff.

Van Abbé *et al.* [53,54] pointed out that a feature of all effective antidandruff agents is that they demonstrate good antimicrobial activity in the presence of sebum. They postulated that anaerobic species of *Pityrosporum,* deep within the hair follicles, may be inaccessible to antimicrobial treatment. These anaerobic yeasts may, through lipolysis of sebum triglycerides and production of fatty acids, cause threshold irritation which initiates the parakeratotic response and leads to the formation of dandruff scale. The stratum corneum has fewer layers in dandruff than in non-dandruff scalps, implying that it may be more permeable to potential irritants.

The opposing view was that antidandruff agents operate by a cytostatic effect, decreasing epidermal proliferation by inhibiting the multiplication of germinative cells. Advocates of this view [52,55] reported a scalp mitotic index of about a factor of two higher in dandruff as opposed to non-dandruff subjects and also demonstrated, by tritiated thymidine labelling of DNA synthesizing cells, that the number of actively dividing cells was about twice as great, indicating a much faster cell renewal. By measuring the transit time of radioactively labelled cells through the epidermis they concluded that this is much more rapid in dandruff, the viable epidermis turning over in about a week.

A faster generation of epidermal scale in dandruff indicates that more horny cells are being shed and can, therefore, be measured by corneocyte counting. Variations in corneocyte counts are great, both in dandruff and non-dandruff subjects and, while there is a tendency for heavy dandruff to parallel elevated

corneocyte counts, one cannot rely on the count as sole indicator of whether or not an individual has dandruff. It has also been pointed out by critics that corneocyte counting demonstrates the ease of removing both parakeratotic and normal cells from the scalp surface, which does not necessarily parallel the cell generation rate. Any treatment capable of improving intercellular cohesion in the horny layer would presumably lead to a decrease in corneocyte count without exerting any antimitotic influence.

It is now generally agreed that the *Pityrosporum* species *Malassezia ovalis* has a causal link with dandruff, since the introduction of effective antifungal drugs such as ketoconazole [56].

Before proceeding to examine specific protocols for evaluating anti-dandruff agents, it may be useful to look at some of the properties of one of the best known and most studied anti-dandruff agents, zinc pyrithione (ZPT), which may contribute to its efficacy:

1. It has good anti-microbial activity.
2. It is substantive to the skin.
3. It is soluble in sebum and has been shown to penetrate the hair follicles.
4. It has been reported to exert a cytostatic effect.
5. It has been shown to promote skin thickening in laboratory animals.

The effectiveness of formulations containing this agent may be due to one or any combination of these properties.

In the study of dandruff the experienced trained assessor is invaluable, as most protocols involve subjective assessment of the degree of scaling. In addition, there are several important points to bear in mind when designing a test protocol for evaluating an anti-dandruff agent if valid results are to be obtained. Firstly, most people who suffer from dandruff treat the condition with one of the many commercially available anti-dandruff formulations. An effective formula can suppress dandruff levels for up to a month so it is important that active agents are avoided for at least that length of time before commencing the treatment phase of the test. This is normally achieved by providing a bland shampoo for use by the entire panel during a 4-week pretreatment phase. Secondly, grading must be performed at a fixed interval after the final bland shampoo. The period selected is usually 4 days, as this is the approximate 'restoration' time for subjects with significant dandruff. This baseline assessment provides pretreatment dandruff scores and may be used to divide the panel into the required number of test and control groups having approximately the same mean and range of dandruff scores.

Various grading systems have been used in the quantification of dandruff. One commonly used involves a ten-point scale of assessment involving dandruff scale adherent or closely adjacent to the scalp but not accounting for loose scale in the hair (Table18.2). This scale is highly expanded to include all possible cases, but in practice the grades awarded are rarely greater than 7.

Table 18.2 Dandruff assessment scale

Score	*Description*
0	No visible dandruff
1, 2	Minimal diffuse scaling
3, 4	Slight scaling
5	Moderate scaling
6	Moderate-to-heavy scaling
7	Heavy scaling
8, 9, 10	Very severe scaling, not routinely observed

There is some controversy between study groups as to whether dandruff occurs in patches or is uniformly distributed over the scalp. Kligman *et al.* [55] considered that dandruff is evenly spread over the entire scalp and claimed that patchiness found by other groups was due to the counting of loose scale in the hair or to mistaking seborrhoeic dermatitis for dandruff. They therefore made scrapings at several points on the scalp and awarded a single global estimate of average dandruff grade for the whole head. Van Abbé *et al.* and other groups found that dandruff levels vary over different parts of the scalp; they therefore subdivided the head into a number of areas for the purposes of assessment. The number of subdivisions varies widely, from four to twenty-five in the literature. I have used twelve sections, making two or three scrapings in each and awarding a score for each section. The individual section scores are then added up to provide a total scalp score.

During the active treatment phase the objective may be to simulate the normal-use situation as closely as possible, in which case the subjects are permitted to wash their hair at home according to their normal pattern of use, provided that they use the product at least once a week. Because of the variability introduced by allowing unsupervised home use of the products, this protocol requires a fairly lengthy treatment period of about 8 weeks duration and relatively large numbers of subjects (30–50) in each treatment cell. Intermediate assessments are made at selected intervals during the treatment period, again 4 days after the final shampooing prior to each assessment. A final post-treatment period of use of the bland shampoo may follow the treatment phase in order to investigate the duration of any observed effects. It is normal to follow up for 2 weeks, at which time effective formulations still have a significant effect. The advantage of this design is that positive results are likely to reflect a benefit which will be perceptible by the consumer under normal home-use conditions.

The alternative objective may be to exaggerate and control conditions as much as possible in order to obtain results with the minimum number of subjects and in the most rapid and economical way possible. In this way it may be possible to demonstrate that a formulation has a positive effect on dandruff control under highly artificial and controlled conditions but there is no guarantee that this effect will be appreciated by the consumer.

One such method involves twice-weekly shampooing over a 3-week treatment schedule in a panel of ten subjects with grade 5 or greater dandruff severity. Two pretreatment hair washes with a bland product are used to achieve baseline dandruff levels. Test subjects are then shampooed twice weekly for 3 weeks with the test shampoo. Dandruff grades and corneocyte counts are obtained at the end of each week, always 4 days after the last shampoo. Bland shampoos are then resumed twice in the following week and a final assessment is made at the end of this period.

A second method, called the 'intensive shampoo schedule', and again involving ten subjects with minimum grade 5 dandruff severity, involves shampooing on 5 days a week for 2 weeks. Corneocyte counts and clinical grades are obtained on day 0 and then 4, 8 and 12 days after the last shampoo. The scalp is not shampooed at all during this 12-day observation period.

In examples of both these studies there were two test antidandruff shampoos containing either ZPT or selenium sulfide (SeS), another well-known effective antidandruff agent, plus a non-dandruff control shampoo. Results indicated that both actives were significantly more effective than the control and that the SeS shampoo was more effective and more lasting in its dandruff suppression than the ZPT formulation [57].

The corneocyte counting referred to in the above protocols is a means of measuring objectively the amount of scale loosely attached or adjacent to the scalp. The sampling technique removes corneocytes in the desquamating loose outer zone. This is accomplished by placing a small, 4 cm^2, glass cup on a clipped area of the scalp. One millilitre of buffered nonionic detergent is placed in the cup and the scalp surface is rubbed vigorously with a Teflon rod for 1 min. This procedure is repeated and the two resulting cell samples are pooled and mechanically agitated to disperse the cells. A few drops of crystal violet are then added and the cells are counted in a haemocytometer. The corneocyte count, like the clinical grading, is always performed 4 days after shampooing and is expressed as quantity of horny cells/cm^2/4 days. The count is reported to be remarkably consistent for a given individual, whether or not the scalp shows visible signs of dandruff. It is a useful method of providing objective back-up for subjective clinical grading but does not correlate sufficiently well with the observed dandruff condition to be relied on as the sole means of measurement.

Another type of dandruff protocol describes the so-called 'half-head' technique [58] in which test and control products are applied to opposite sides of the scalp. This calls for very carefully controlled application by skilled technicians.

While laudable in principle, being economic of volunteers and ensuring identical substrates for the action of test and control products, this technique does present a significant risk of side-to-side contamination, as compounds which are active in small amounts have been shown to be effective at sites removed from the area of application [59]. Moreover the scalp is a damp and greasy medium, ideally suited to the spreading of locally applied substances.

A final word on antidandruff evaluations is that testing is best performed between autumn and early spring as it is generally recognized that dandruff is heaviest in the winter months, a fact which is also appreciated by the consumer, as sales of anti-dandruff products are reported to decrease during the summer months.

18.7 DEODORANTS AND ANTIPERSPIRANTS: EVALUATION FOR AXILLARY ODOUR AND PERSPIRATION CONTROL

18.7.1 Deodorants

In some cultures, body odour seems to have positive correlations with degree of sexual attractiveness and, perhaps, heightened sexual potency. In modern western cultures, however, axillary odour is universally regarded as offensive and repulsive, to be suppressed at any cost.

The axillae are unique with respect to the nature and frequency of occurrence of odour which can arise there in some, but not all, individuals. When other body areas are occluded to produce similar conditions of temperature and relative humidity as in the axilla, any odour produced generally lacks axillary-type properties. The unique nature of axillary odour is attributed to bacterial degradation of the apocrine secretion which is claimed to be sterile and only faintly odiferous when initially secreted. Apocrine glands are larger and more numerous in the axilla than anywhere else on the body. Indeed they are mere vestiges in humans except in the axillae, pubic area and ear canal. Study of axillary odours involves characterization of responsible bacteria and understanding their interaction with apocrine secretion.

Two bacterial populations are recognized as responsible for differences in odour profiles between individuals. The Gram-positive diphtheroids are associated with selective generation of the pungent axillary odours while micrococci are implicated in production of sweaty acid odours. Control measures are directed at either masking odorous substances or interfering with their production by the bacteria.

A variety of materials have been reported to aid in axillary odour control and/or reduce malodour perception [60].

1. Topical antiperspirant substances, such as aluminium chlorhydrate, produce a localized reduction in sweat gland activity.

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A variety of materials have been reported to aid in axillary odour control and/or reduce malodour perception [60].

1. Topical antiperspirant substances, such as aluminium chlorhydrate, produce a localized reduction in sweat gland activity.

2. Bacteriocidal or bacteriostatic agents reduce or eliminate the formation of the volatile malodorous products of bacterial action. This is the most widely adopted form of odour control in commercial deodorant products.
3. Odour suppressors, such as zinc ricinoleate, have marked affinity for low molecular weight organic compounds and may actually help quench axillary odour after its formation.
4. Antioxidants, such as vitamin E, butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), have been used to complement the action of antibacterial agents.
5. Mild alkalis, such as sodium bicarbonate, may produce some measure of control by neutralization of volatile fatty acids.
6. Claims have been made for specific enzyme inhibitors, capable of deactivating the degradative enzyme system of the bacteria without, apparently, influencing cell viability. These have not, however, gained widespread application.
7. Odour modifiers, especially perfumes, may 'blend' with axillary odours producing an overall perceived odour which is acceptable, and antimicrobial perfume oils may enhance this effect. This area of treatment has received considerable attention in recent times.

Both *in vivo* and *in vitro* methods have been employed for screening potential deodorant systems. *In vitro* techniques do not, however, provide a reliable indicator of clinical effectiveness. The well-designed clinical trial must therefore be regarded as the most valid approach to deodorant evaluation. The two principal methods for the *in vivo* evaluation of deodorant efficacy are:

1. determination of the effect of treatment on the skin microflora; and
2. olfactory assessment of the effects on skin odours.

Techniques used to quantify microflora include tape stripping, contact plates, velvet replicate pads, swabbing, scrubbing and pressurized spray methods. A few of these procedures will be described in detail as they have become well documented in recent years.

The velvet replipad technique [61,62] lends itself to axillary examination. It is simple and rapid enough to allow large panels of test subjects to be sampled in a relatively short time and is also unlikely to interfere with sensory odour assessment when this is to be performed simultaneously. The technique samples the surface only, deeper-seated bacteria remaining untouched. The apparatus comprises an anodized tapered holder and ring which hold the velvet pad, and the entire assembly can be sterilized by autoclaving before use. For sampling, the pad is moistened on the surface of an agar plate, pressed firmly into the axilla, then applied to the centre of a suitable culture plate. Brain–heart infusion agar supplemented with 0.5% Tween 80 has proved successful for the isolation of axillary bacteria. Incorporation of Tween 80 promotes the growth of lipophilic diphtheroids and inactivates any carried-over antimicrobial agent. After 24–48 h aerobic

incubation at 37°C, the common resident microflora – staphylococci, pigmented micrococci and diphtheroids – are readily seen and identified. Plates are assessed by panels of at least five assessors using a 0–6 scale for density of colonies.

The mechanical scrub (MS) technique [63] involves a standardized scrub on an area of skin delineated by a small glass cup containing a nonionic detergent sampling fluid. The glass cylinder is placed firmly onto the exposed skin of the axilla, isolating an area of 3.8 cm^2. Three millilitres of phosphate buffer, pH 7.9 containing 0.1% Triton X-100, is added and the skin surface is rubbed with moderate pressure for 1 min using a blunted Teflon scraper. Sampling fluid is then removed by aspiration and the procedure is repeated. The two samples containing extracted bacteria are pooled and stored on ice prior to serial dilution. Recoveries for the sampling fluid are reported to average 90%. Situations in which repeated sampling from an axillary skin site is required can result in localized oedema and irritation, caused by the mechanical scrubbing.

A more recent refinement of the MS technique involves the use of a pressurized spray method to evaluate quantitatively, total axillary aerobic microbial populations. Use of the Thran Spray Gun (TSG), has been documented [60,64]. In principle the technique involves use of air pressure to aspirate a sampling solution over an isolated region of the axilla surface. A jar containing a 100 ml aliquot of sampling fluid is attached to the spray gun along with an empty sterile collection jar. The tip of the spray gun is firmly pressed against the axillary vault and the sampling fluid is simultaneously sprayed onto and aspirated from an area of 1.77 cm^2. Sampling fluid recovery for the 100 ml sample is reported to average 98% with an aspiration time of 65 s when the compressed air pressure is 1–8 bars (100–800 Pa). The collection jars are removed from the gun and stored on ice prior to serial dilution. The spray gun is sterilized by rinsing with sterilized water and alcohol between extractions. The total aerobic bacterial count is determined by serially diluting aliquots from each sample. The diluted samples are plated in soy agar supplemented to provide diphtheroid growth and incubated for 48 h at 37°C. Plates are counted under a dissecting microscope and colony-forming units (CFU) are converted to CFU/cm^2 of axilla sampled. Statistical tests (paired *t*-tests) may be used where appropriate to test the significance of differences in axillary bacterial populations.

Comparing the MS and TSG techniques, the TSG offers the advantage of ease of sampling, increased sampling volume with high recovery rates and reproducibility of sampling pressure. For operation the only outside source required is an electrically operated compressor capable of delivering compressed air at controlled pressure. This method also allows collection of several samples from one site without generating localized erythema. The MS technique removes larger numbers of bacteria in a smaller sampling volume and is therefore to be recommended for studies requiring concentrated bacterial samples.

As the apocrine fluid is reported to be sterile when it is first secreted onto the skin surface, it would appear that it is the action of skin-surface bacteria which

is relevant to the generation of odour. Extensive agitation of the skin surface, resulting in removal of much greater amounts of desquamating stratum corneum, may therefore be superfluous to requirement in the evaluation of deodorant products, particularly if it results in significant skin irritation. The ideal sampling procedure should be readily standardized, rapid without producing discomfort, reproducible with a high efficiency of recovery of bacteria, and adaptable to the variety of skin surfaces and contours encountered in the axillae.

It must be stressed, however, that none of the above techniques is of use in the evaluation of actives such as odour suppressors, modifiers or neutralizers which take effect after the formation of odorous substances by bacteria. They are also of little value in evaluating deodorant formulations based on bacteriostatic agents as, once the bacterial population has been sampled and the organisms removed from the axilla, the inhibitory effects of the antimicrobial are lost and the bacteria flourish normally. In these cases we must again resort to subjective sensory techniques for the evaluation of product efficacy.

Olfactory assessment of the effect of deodorants on body odours may be performed by direct armpit sniffing or by indirect sniffing of pads or other sampling vehicles. The sensory evaluation may be performed by panels of trained assessors, by the panellists themselves or by a combination of the two methods. These techniques are suitable for evaluating both materials which act by inhibiting formation of axillary odour and those which act by reducing perception of malodour once it has been produced.

The technique of Gee and Seidenberg [65] for evaluating deodorant soaps involves assessment of intensity of odour by sniffing the axillae directly and assigning a numerical value. The method has been widely used and lends itself to statistical analysis. A more recent adaptation of the method is described by Baxter and Reed [61]. The test panel involves 20–40 subjects, each panellist testing each product in crossover fashion. Potential subjects are screened for the amount of odour they produce following several days abstention from use of under-arm products except for daily washing with an unperfumed control soap. Male subjects are generally preferred since they object less to persevering with ineffective (placebo) products and tend to generate higher odour levels due to the presence of axillary hair. Whilst taking part in the trial, subjects are forbidden to use any products in the axillae, such as antiperspirants, talcs, perfumes, etc., other than those supplied by the tester. They are provided with two flannels, colour-coded for each axilla, and instructed to use separate volumes of water for washing each axilla to minimize the possible cross-transfer of actives.

The usual procedures of a double-blind clinical trial, balanced randomized order of product use and incorporation of positive and negative controls, are observed. If non-perfumed, specific actives are being evaluated the test products are formulated without perfume for the purpose of testing. Each crossover period lasts for 3 weeks. The first week constitutes a pretreatment phase when the panellist is instructed to wash the axillae once daily with control soap.

All subjects use placebo products during this week. During the second week subjects are given one of the following combinations of products to use, one on each axilla, once daily after washing:

Axilla A	Axilla B
Placebo	Placebo
Positive control	Vehicle
Test product	Vehicle

In the final week subjects do not wash or apply deodorant at home and washing is performed at the test centre, the same product combination being applied by personnel carrying out the study. Axillary odour is assessed each morning prior to washing and applying product and again in the afternoon, approximately 6 hours after the previous application. As subjects are then in their second week of treatment, these assessments are taken to represent the plateau for efficacy. Where appropriate, bacterial sampling may be carried out at the 24-h assessment and, occasionally, also at the 6-h assessment.

Odour assessment is performed by at least three assessors since even experienced judges have anosmias to particular elements. Selection of assessor panels is based on ability to rank graded dilutions of odiferous materials such as isovaleric or butyric acids. Sniffing is carried out with the nose less than 10 cm from the axilla and scores are assigned on a scale of 0–10 according to the strength of the perceived odour. The distribution of odour scores is usually skewed so that non-parametric statistical methods, such as the Wilcoxon signed-rank test, are used to analyse the results.

Direct panellist–judge interaction does have certain disadvantages in evaluating under-arm deodorants. For example, there is the risk of contamination of odour by the smell of clothing or other body odours. In addition the judge may be influenced by visual effects such as product residue in the axilla or recognition of the subject. As an alternative to direct axilla sniffing by the judges, odour may be collected on cotton pads or on some other suitable vehicle. The method discussed below uses the rounded end of 20×150 mm borosilicate glass test tubes which are placed in the axillary vault [66].

Panellists are pre-screened to ensure an ability to develop moderate axillary odour in both axillae when deodorants are not used. Conditions operating during and prior to testing are as follows. Panellists should:

1. abstain from use of all deodorants, antiperspirants, medicated or perfumed products for 7 days prior to testing and during the test period, with the exception of those products issued;

2. abstain from smoking, chewing gum and drinking alcohol for at least 15 min before each visit to the test location;
3. use control soap for all bathing and washing during pretreatment and test periods – during the test period only, all under-arm washing is performed at the test location under supervision;
4. refrain from washing for a full 24 h before assessment on the first day of the test period;
5. wear a clean shirt or blouse after each daily washing and application of product during the test period.

Judges are selected as described above on the basis of their ability to rank correctly increasing concentrations of isovaleric acid from 0 to 600 ppm. They are requested not to smoke or eat within 15 min of evaluations and to refrain from the use of fragrances throughout the study. Evaluations are made on a 10-point odour intensity scale, disregarding fragrance.

For evaluation a 20×150 mm borosilicate glass test tube is placed in each axillary vault and held in place by the subject keeping his arms by his sides. When directed the subject vigorously rotates the bottom portion of the tube in the axilla. The tube is then given to an operator who covers the bottom of each tube with a plastic closure. The two tubes from each pair of axillae are quickly passed to two judges who independently evaluate them for odour intensity. Judges evaluate pairs of samples from test subjects at intervals of approximately 1.0–1.5 min. Each evaluation is entered on a separate score sheet which does not record details of product assignments or previous scores.

A typical test design is as follows: on day 1 the final selection of subjects is made. Individuals achieving a pre-wash score of at least 4 in both axillae, as judged by at least half the assessors, are selected. This is the baseline score and is recorded. The axillae are washed, rinsed, dried and the designated product is applied to each axilla. Subjects return for evaluations, usually at intervals of 3, 6 and 24 h. On day 2 the first 24-h post-treatment assessment is made and the day 1 procedure is repeated. On day 3 the second 24-h post-treatment assessment is made and the test is then complete. The first-day scores, used to screen out subjects with low odour levels, are also examined to ascertain whether right/left side differences are sufficient to warrant using the day 1 scores as a covariate in the analysis of post-treatment data to adjust for left or right lateral bias. The data are analysed using a repeated-measures design. Odour scores for the two test materials are compared at each time point. Factors used in the analysis are panellists, treatment, test days and judges. Treatment differences are tested using the Wilcoxon signed-rank test.

Advantages of the indirect sniffing method over the direct sniffing method may be summarized as follows:

1. Subjects do not come into recognition proximity with judges, thus minimizing the effects of revulsion, embarrassment and bias.

2. Judges can perform their task in a relaxed position and may therefore concentrate more effectively on scoring.
3. The interference of extraneous smells from a subject's skin, hair or clothing is effectively eliminated.
4. The odour samples can be stored for several hours under refrigeration without quantitatively or qualitatively affecting the odour perceived. This can be most useful if one of the judges is temporarily incapacitated.

While these indirect methods of deodorant evaluation are admittedly less 'true to life' than the direct sniffing of axillary odour, which accurately mimics how we evaluate our own body odour, it would seem that the experimental practicalities are strongly in their favour.

18.7.2 Antiperspirants [67]

Thermoregulation in humans is a complex system which combines release of thermal energy, as a result of chemical and physical activities of the body, with central and local temperature control systems to maintain body and blood temperature at approximately 37°C. Sweating is a mechanism by which the body can involuntarily lose heat by evaporation and thus rapidly dissipate heat which would otherwise result in a rise in blood temperature.

The source of copious watery sweat is the eccrine glands. These are distributed generally over the surface of the body but are particularly dense on the palms and soles. Eccrine glands in the axillae can be activated by either thermal or emotional stimuli. Sweat produced in the axillae can be a problem as evaporation is limited in normal posture and liquid sweat can accumulate, wetting clothing and causing discomfort. Antiperspirants aim to bring about a temporary decrease in sweat production in the axillae to a level which is cosmetically acceptable but does not have any deleterious effect on normal regulatory function.

The most widely used procedure for efficacy testing of antiperspirants is a gravimetric method which involves the collection and weighing of axillary sweat under controlled conditions. A variety of different test methods have been cited in the literature. An example of the so-called ratio method involves panels of at least 20 volunteers who abstain from use of antiperspirants for a period of at least 2 weeks prior to testing, although the use of alcoholic deodorants is normally permitted. On 3–4 days following this pretreatment phase they enter a controlled environment chamber maintained at approximately 100°F and 35% RH, 'the hotroom', with absorbent pads (the 'A' pads) strapped to both axillae. After 40 min these pads are removed and discarded as sweating rates are highly variable over this initial period. A fresh pair of weighed pads (the 'B' pads) are substituted and remain in place for 20 min before being removed and reweighed. A second set of weighed pads (the 'C' pads) are placed in the axillae

for a further 20 min, then these in turn are removed and reweighed. This completes the control phase of the study.

Applications of product are made under supervision at least once a day over 5 days such that half the panel receive the test product on the right axilla and the left is untreated or treated with a control product. The other half of the panel receive the opposite pattern of application. Repeated applications are necessary to build up the maximum antiperspirant effect. On the fifth day, and at least an hour after the final application of product, panellists re-enter the hotroom and the series of A, B and C pads is repeated.

The percentage reduction in sweating is calculated according to the following formula:

$$1 - \frac{\text{(Post-treatment treated/untreated sweat ratio)}}{\text{Corresponding mean control sweat ratio}} \times 100$$

A product crossover may be employed to validate the reproducibility of the test result.

Panellists are selected on the criterion that they consistently yield at least 100 mg sweat from each axilla during control collections, which is reported to exclude only about 1% of a normal population. The only other reason for exclusion is a lack of reasonable uniformity in control sweating ratios. This appears to be due largely to poor compliance with test conditions and occurs infrequently. Most individuals produce slightly more sweat from the dominant axilla depending on right- or left-handedness.

Certain individuals exhibit pro-perspirancy, i.e. they fail to show the expected sweat reductions or actually yield increased sweat weights following treatment with known effective products. This is apparently not linked to product irritancy but is due to specific individual differences. Assuming a panel of reasonable size, such individuals should not be excluded as, in this way, it would be possible to achieve artificially much greater reduction values than those generated by non-selected random populations.

Close compliance with the test regime is crucial since axillary sweating is susceptible to many environmental influences. During hotroom sessions subjects should sit motionless and upright with both feet on the floor and their hands in their laps, and should avoid discussing emotive topics. It is best to use experienced panellists as emotional factors profoundly affect axillary sweating rates. Subjects familiar with the procedure are less likely to be apprehensive and therefore yield more reproducible results.

The question of application rate is another variable which can cause problems [68]. It seems implicit that we are interested in ranking products for efficacy under normal conditions of use. A seeming solution would be to determine by experiment the mean weight of products used over a huge number of subjects and use this as the test dose. This is hardly practicable, however, as it would

have to be repeated for each product, and is also scientifically wrong as the size and shape of the axillae may vary considerably and the appropriate dose rate will vary accordingly, particularly for roll-on products. Application of the mean amount is therefore no better than application of any other constant amount. The problem is obviated when comparing, say, a roll-on with an aerosol product. Such a comparison has no meaning unless the samples are applied under normal-use conditions, as the more effective product may otherwise be governed principally by the amount applied rather than its intrinsic efficacy. Even when products of the same type are considered, aerosols, for example, may differ in their non-volatile content, discharge rate, coldness etc., which would result in different application rates as a matter of personal preference. The most realistic procedure is to allow the subjects to apply the products themselves, but this risks greater scatter in the test results and a consequent need for larger panels. Any other procedure risks generating artificial ranking orders.

In this respect it is important to note that the result found in a particular test is not necessarily the same as would have been found under different test conditions, and percentage reductions should be qualified to read 'under the specific conditions of this test'.

One obvious drawback to the test protocol described above is that it takes a considerable time to obtain results. Allowing 2 weeks' preconditioning before testing and again before crossover, and 1 week each for determination of control and post-treatment sweat ratios, the complete test spans 8 weeks for one product comparison. Various protocols have been devised to shorten the required time by either omitting the necessity for control ratio determination or using an alternative skin site such as the back or forearm, for screening a larger number of samples before performing the extended axillary test on the final product selection.

The first of these alternatives is known as the 'sides, subjects, effects model' (SSEM) [69]. A larger panel of 36 subjects is used and the control phase of the test is omitted. The method features a randomization procedure appropriate to the crossover design and a system of data analysis which provides estimates of treatment effect and associated error uncontaminated by the influence of sides or subjects. The SSEM method is stated to produce different point estimates of percentage reduction in sweating from the conventional control ratio method but confidence intervals obtained by either method usually include both point estimates. The SSEM claims superiority as the method does not rely on the assumption that side-effects are eliminated by the control ratio adjustment and also reduces the time-scale by a period of 2 weeks. A further reduction of the SSEM [68] involves treatment over only 3 days followed by a hotroom sitting on the third day. Product crossover is not included but approximately 50 subjects are used in each test.

In order to screen a larger number of formulations a back-screening method was developed [67] involving ten 2 cm^2 skin sites in two columns running from the shoulder blade to the waist. Test products were applied in a randomized

pattern to six test sites leaving four sites as controls. One hour later a dried 2 cm^2 pad of gauze backed by a 5 cm square of occlusive tape was fixed over the collection site and subjects entered the hotroom for 45 min. Patches were then removed and weighed before and after drying in a desiccator for 24 h. The measured product efficacy is said to be greater on the back than in the axilla but six products can be compared directly, and potentially successful products are unlikely to be rejected during screening.

Another skin site which has been used for rapid screening prior to axillary measurement is the forearm [70]. This site was selected in preference to the back because the skin is less mobile, the density of sweat glands is higher and patches can be secured with wrap-round taping. Materials were applied via 15 mm Duhring chambers to the midvolar forearms of six subjects and fastened to the skin for 3 h. Up to eight chambers were glued to the skin of each forearm and further fixed by wrapping the limb with non-occlusive tape. Volunteers then entered the hotroom at 55°C and 30% RH until general sweating began, when they left the chamber and sat quietly in an air-conditioned room to complete the 3-h exposure. This pre-heating period fills the sweat ducts, promoting the inward diffusion of metallic salts. It was found to enhance product efficacy and reduce variability. It should be noted that 55°C is very hot indeed, but means that sweating starts earlier and is less variable under such strong thermal stress.

Sweat suppression was estimated by the silicone imprint technique 24 h after removing the chambers. Subjects were brought to profuse sweating in the hotroom as above, after which each test site was blotted dry. Immediately a 40-l mixture of silicone monomer and catalyst was evenly spread over the skin surface. Polymerization occurs in 4–5 min during which time bubbles of sweat are trapped in the hydrophobic film. The silicone sheet was pulled away from the skin and viewed under transmitted light when the bubbles were seen to form a discrete pattern which could be contrasted to the surrounding untreated skin. Sweat suppression was estimated to the nearest 25% in relation to the density of bubbles in a nearby untreated site. If higher precision is required the droplets can be counted in an image analyser as described by Sauermann *et al.* [71] who used the starch–iodine reaction to visualize sweat gland activity.

The silicone imprint technique is not suitable for use in the axilla because of the vaulted configuration of the armpit, so gravimetric procedures were used for further testing. The chamber test is viewed as a screening model for identifying effective agents or optimizing a formulation by vehicle manipulation. Although measured suppression of axillary sweating is always less than on the forearm the same rank ordering is obtained. Advantages of the forearm method are that 16 materials can be tested simultaneously, exposure conditions can be rigorously controlled, emotional influences have less effect and small panels are adequate. Axillary testing is, however, required to validate the test result.

Finally, two entirely different techniques, hygrometry and thermography, are worthy of mention [67]. Hygrometry involves measurement of the rate of

evaporation of moisture from the surface of the skin. The cooling effect of sweating is due to evaporative water loss at or below the skin surface. Thus, as ambient air flows over the skin its moisture content is increased. The product of (increased water content) × (air flow rate) is a measure of the rate at which sweat is evaporating. Provided that sweat droplets are not formed on the skin surface, the rate of evaporation is equal to the rate of emergence of sweat from the sweat ducts.

Cylindrical cells are fixed to test and control skin sites on the back of test subjects. Ambient air is drawn from the hotroom and pumped into the cells, which are held in close contact with the skin to prevent gross leakage. Outgoing air from each cell passes through a humidity sensor which records relative humidity. A modified version of the Servomed Evaporimeter equipped with dual probes is now available for this type of measurement.

Thermography is a process of recording variations in intensity of long-wavelength emissions from a surface, comparable to that of a visible-wavelength television system. Hot areas emit more energy in the sensitive range of the instrument than cold areas so are displayed on a TV screen as brighter areas in a monochrome system or as different colours in a colour system, displaying temperature variations over the skin surface as a map. The sensitivity is such that temperature differences as small as 0.1°C appear as distinct colour changes. Localized cooling of the skin contributes to thermoregulation. It is reasonable to assume, therefore, that there is less cooling of the skin when an effective antiperspirant has been applied to that area, i.e. the skin temperature is higher. Thermography requires only 1 s to map the surface temperature of the axilla. Hygrometry measurements can be made in less than 2 min while gravimetric measurements require at least 20 min collection period to achieve acceptable reproducibility. In addition both hygrometry and thermography allow antiperspirant activity measurements to be made under conditions which do not interfere with the normal operation of sweat glands or the cooling caused by sweat evaporation.

In summary, it is clear that methods for evaluating antiperspirant efficacy are many and varied. Almost any variation in experimental design can change the recorded antiperspirant effect. Whenever figures for percentage reductions in sweating are quoted, therefore, the method must be defined, the degree of thermal stress specified and the number, timing and dose rate of product applications must be detailed. It is also important to remember that none of the above measured parameters is necessarily used by the consumer to assess antiperspirant efficacy. Normally the consumer perceives inefficacy only through observing wet patches on clothing or sensory perceptions. Attempts have been made, via panellist questionnaires, to estimate the practical significance of sweating reductions as determined in controlled laboratory studies. These questionnaires seek to establish whether milligram amounts of sweat collected correlate with awareness of sweating by the panellist during normal activity, and at what level

of laboratory-demonstrated sweat reduction the effect becomes obvious to the consumer under normal conditions. Most panellists do not detect any noticeable sweating during their daily unstressed routine, but trends indicate that perceived sweating is less from treated axillae [72]. Perhaps this area of research deserves further investigation.

18.8 MISCELLANEOUS PRODUCT GROUPS

As the human population is the 'target organ' for action of all cosmetic and toiletry products, useful information on the efficacy and acceptability of almost any product can be gained through a well-designed study on selected groups of test subjects.

Historically, fluoride toothpastes were evaluated by conducting extensive clinical trials using populations not previously exposed to fluoride, to compare caries incidence in subjects using a fluoride toothpaste with those using a placebo formulation. This type of test would not be easy to perform today as the effectiveness of fluoride was validated so convincingly that most dentrifices now contain fluoride in one of its forms. It has also been introduced into many domestic water supplies, so populations not previously exposed to fluoride would be difficult to locate.

More recently antiplaque toothpaste formulations have also been evaluated in groups of volunteer subjects. Following a pretreatment period of brushing with a placebo formulation to establish baseline conditions, the accumulation of dental plaque is compared for test groups using the antiplaque formulation and control groups who continue to brush with the placebo. Plaque deposits are assessed by means of plaque-disclosing tablets which stain the plaque red, or by physically scraping off and weighing the accumulated plaque. The latter operation is performed by a qualified dental technician to ensure complete removal of plaque and minimize the risks of gingival damage. Other developments in dental care include tartar control and whitening formulae.

Nail polishes can be evaluated for wear properties by painting test and control colour-matched samples on alternate fingernails and assessing the degree of wear over the following 4 days on an arbitrary numerical scale of 0, representing no visible signs of wear, to 5, representing extreme wear necessitating removal of the remaining polish. Application is performed by trained technicians using a repeated randomized design and assessments are performed blind. Additional information on gloss, pay-off, ease of application and incidence of nail staining can also be recorded during the study.

Fragrance evaluation is highly subjective, although panels can be trained to differentiate accurately between different intensities and qualities of odour using standard batteries of scent samples. Some, probably most, people have specific anosmias, materials which they sense poorly and, of course, there is a high degree of variation among individuals in terms of preference for a particular

perfume or type of fragrance. It would also appear that our instantaneous impression of a fragrance may be misleading in terms of how we rate it over prolonged use [73] and this will have important implications in terms of the ultimate success of a product and brand loyalty. Although gas chromatography can identify many of the chemicals contained in essential oils, the effects of different essential oils on the brain are poorly understood. The psychological effects of essential oils form the basis for aromatherapy, and general associations are made between certain essential oils and relaxing, stimulating or other psychosomatic effects. This is a huge and complicated area of research which is waiting to be explored.

18.9 RESUMÉ

It is clear that there is no shortage of test methods available for evaluating products in human volunteers. All products can and should be tested under controlled conditions before being set loose on the population at large. Whether the evaluation aims to validate performance, to establish if the pack or pack copy works with the product, or merely to determine whether aesthetic aspects of the product appeal to the consumer, it is usually the culmination of many expensive hours of work. Even a small flaw in the total package of a new product can have disastrous results, and the human volunteer study offers a chance to put the product through its paces under conditions of relative anonymity, before putting all at stake.

In this respect it is essential that the product evaluation team is involved from an early stage of product development and has a clear picture of the marketing brief, the proposed packaging, pack copy and instructions for use. Effective study protocols can only be designed around clear objectives.

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19

Emulsion theory

John L. Knowlton

19.1 INTRODUCTION

The old adage 'oil and water don't mix' is something of a paradox in the context of emulsion theory for, in simplistic terms, emulsions are indeed mixtures of oily and aqueous materials.

Emulsions have been used for many centuries in a variety of ways, including that of cosmetic decoration. Modern-day emulsion technology provides massive scope for the design and production of a wide range of products in the cosmetics, toiletries and health-care markets. The reasons why emulsions have become so popular are manifold, the most obvious being that they allow incorporation of otherwise incompatible polar and non-polar materials in the same product. This, in turn, gives the opportunity for enormous flexibility in the choice of formulation design, and the possibility of incorporating topically applied 'active' materials is an added benefit for pharmaceutical and health-care products. Such flexibility offers scope for the creation of cosmetic elegance by modification of sensory attributes. Specifically, control of parameters such as product appearance, feel and viscosity, all have a significant impact on the consumer's perception of the finished product. Finally, but by no means least important, the level of water in many emulsion products provides a feasible route for marketing a cost-effective product.

The combination of the above factors has given rise to the enormous growth of emulsion products in the cosmetic and toiletries industry, with many hundreds of products on the market. Traditionally, emulsion technology has been associated with skin-care products, but over recent years the application of emulsions has been much broader. Hair conditioners, antiperspirants, colour cosmetics and even some personal-care cleansing products now take advantage of some of the latest emulsion technology available. Complex, multi-phase emulsion systems have made novel formulation designs possible and the development

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 601–623

of 'next-generation' manufacturing equipment has enabled the production of highly stable emulsions with low emulsifier levels.

19.2 DEFINITION AND TYPES OF EMULSION

An emulsion can be defined as 'A two-phase system, consisting of two immiscible or partially miscible liquids, one being dispersed in the other in the form of very fine droplets'.

The 'phases' described in the above definition are normally referred to as 'oil' and 'water', these terms being commonly used to describe non-polar **lipophilic** ('fat-loving') and polar **hydrophilic** ('water-loving') materials, respectively. In that every emulsion can be described as having an oil phase and a water phase, it is then obvious that two types of emulsion are possible. The first type is that in which discrete droplets of oil are dispersed in water, referred to as an oil-in-water emulsion, whilst the second contains discrete droplets of water in oil and is known as a water-in-oil emulsion. Irrespective of type, the discrete phase of an emulsion is known as the **internal** or **dispersed** phase whilst the continuum is referred to as the **external** or **continuous** phase.

In addition to these two types of simple emulsion, more complex systems also exist. So-called three-phase complex emulsions are classified into two distinct types, oil-in-water-in-oil (O/W/O) or water-in-oil-in-water (W/O/W). These complex emulsions are becoming much more prevalent in contemporary products, as they offer a greater degree of formulation flexibility which invariably delivers a much more efficacious and aesthetically pleasing product. A more detailed account of complex emulsion systems can be found later in this chapter.

19.3 THE FORMATION OF SIMPLE TWO-PHASE EMULSIONS

There are many approaches to the examination of emulsion formation but perhaps one of the most easily understood is to consider the energy of the system.

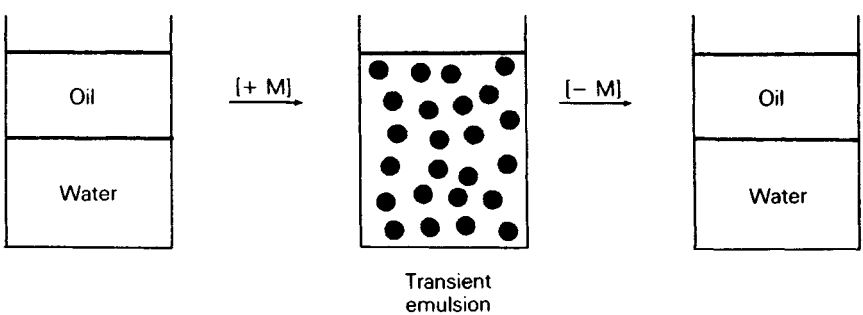

Fig. 19.1 The formation of an emulsion. M, Mechanical energy.

An emulsion can be formed by simply applying external mechanical energy (e.g. rapid stirring) to a system which contains immiscible or partially miscible oil and water phases. The mechanical energy will break down the phases, dispersing one in the other, in the form of very fine droplets. Once the mechanical energy is removed, the emulsion, in the absence of any other stabilizing force, will break down into its oil and water phases very quickly with time. This process is represented diagrammatically in Fig. 19.1.

The reasons for collapse of the emulsion can be explained in terms of the free surface energy of the system. This energy term will be directly proportional to the interfacial area between the oil and water phases as described by the following equation:

$$dS = K \cdot dA$$

where S is the surface energy,
and A is the surface area.

When the emulsion is formed, the interfacial surface energy of the system will rise enormously, due to the large increase in interfacial surface area.

However, fundamental laws of thermodynamics state that any system will, in the absence of external influences, occupy the lowest energy state. Removal of the mechanical energy from the system will therefore result in collapse of the emulsion, as it reverts to the lowest energy state by minimizing the interfacial surface area. This emulsion can only be considered as transient and not 'real', as it relies upon continuous input of mechanical energy for its existence.

In order to produce a stable emulsion system, it is necessary to reduce the surface energy at the oil–water interface, thus preventing collapse of the emulsion into its two component phases, when the mechanical energy is removed. This can be achieved by the addition of a special type of surface-active agent (or **surfactant**) to the system. Suitable surfactants exhibit the property of having an affinity for both 'oil' (non-polar materials) and 'water' (polar materials) in the same molecule and are referred to as **emulsifiers**. The part of the emulsifier molecule which exhibits an affinity for oily materials is referred to as lipophilic, whilst that part which has an affinity for the water is referred to as hydrophilic. When the emulsifier is added to the emulsion system it migrates to the oil–water interface, the lipophilic part of the emulsifier molecule being orientated in the oil phase and the hydrophilic part being orientated in the water phase. This orientation of the emulsifier molecule at the oil–water interface is represented diagrammatically in Fig. 19.2.

The migration of the emulsifier to the interface causes a large drop in the interfacial surface tension, thus reducing the interfacial energy and stabilizing the emulsion system. It is important to note that even so-called 'stable' emulsion systems are not entirely thermodynamically stable and, in theory at least, all emulsion systems will break down into their component phases, given sufficient time.

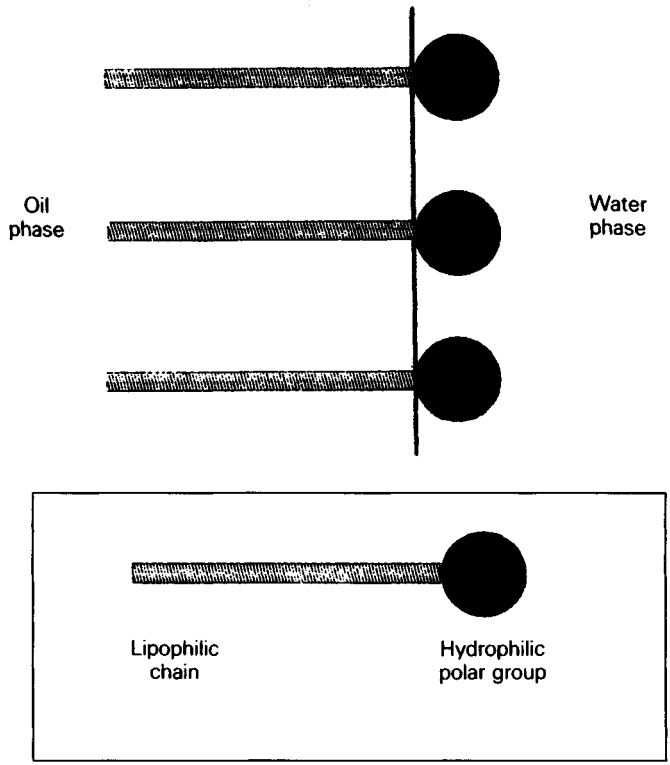

Fig. 19.2 Orientation of the emulsifier molecule at the oil–water interface.

19.4 EMULSION INSTABILITY

Emulsion instability occurs when dispersed-phase droplets of the emulsion collide and coalesce, thus producing correspondingly larger emulsion droplets, the presence of which begins to destabilize the system. These larger droplets may, in turn, collide and coalesce, and eventually complete emulsion destabilization, accompanied by phase separation, will result. There are many phenomena that contribute to emulsion instability to a greater or lesser extent. Consideration is given here to two significant contributory factors to the onset of emulsion instability.

19.4.1 London–van der Waals forces

These are short-range forces associated with the interaction of dispersed-phase droplets, in close proximity to each other. This phenomenon is analogous to the

London–van der Waals interactions between molecules and the same considerations apply throughout. A complex, mathematical treatment of this subject is beyond the scope of this text; in simple terms, however, the magnitude of the London–van der Waals forces of attraction between two dispersed-phase droplets is inversely proportional to the distance between them and directly proportional to their radius. In order to maximize emulsion stability it is therefore necessary to minimize droplet size, whilst maximizing the interdispersed-phase droplet distance.

19.4.2 Creaming and sedimentation

Irrespective of emulsion type, there will be an inevitable difference in density between the oil phase and water phase, the oil phase invariably being less dense than the water phase. This density difference will, over time, cause a migration of the dispersed-phase particles within the continuous phase, eventually resulting in partial phase separation.

In an oil-in-water emulsion the dispersed oil-phase droplets, being less dense than the continuous water phase, experience a resultant upward velocity, eventually producing an 'oil-rich' region towards the surface of the emulsion. This is known as **creaming**. Conversely, for a water-in-oil emulsion, the dispersed water-phase droplets exhibit a tendency to fall under gravity towards the bottom of the emulsion, a phenomenon normally referred to as **sedimentation**. It is important to note that both creaming and sedimentation describe the movement of the dispersed-phase particles within the continuous phase and not vice-versa. Creaming therefore is only relevant to oil-in-water systems, whilst sedimentation is a property confined to water-in-oil emulsions.

In order to examine the rate at which either creaming or sedimentation occurs, it is necessary to quantify the velocity of the dispersed-phase particle, in the continuous phase. This velocity, to a first approximation, is described by Stokes' Law, which was originally derived from a study of the velocity of a falling spherical body through a continuous medium of known viscosity. The Stokes' Law equation can be directly applied to emulsions as follows:

$$V = \frac{2r^2(\sigma - \rho)g}{9\eta}$$

where V is the falling velocity of dispersed phase droplet;
r is the radius of dispersed phase droplet;
σ is the density of the dispersed phase;
ρ is the density of the continuous phase;
g is gravitational force;
and η is the viscosity of the continuous phase.

If the value of the falling velocity, V, is calculated for an oil-in-water emulsion, a negative value will be obtained. This arises from the negative density difference in the top line of the equation. A negative velocity value should not give cause for concern as Stokes' Law describes the velocity of a falling droplet. The negative value obtained for oil-in-water systems merely indicates an upward velocity as the internal oil-phase droplet rises in the continuous water phase.

Examination of the Stokes' Law equation predicts maximum emulsion stability for the following conditions:

- minimization of the dispersed-phase particle size;
- reduction of the density difference between the two phases;
- maximization of the continuous-phase viscosity.

19.5 STABILIZATION OF EMULSIONS

Emulsion instability arises through collision of dispersed-phase droplets which, in turn, may cause coalescence leading to destabilization. There are two ways, therefore, in which the stability of any emulsion system can be increased:

1. Reduce the possibility of dispersed-phase droplet collisions. This method is referred to as **charge stabilization**.
2. Strengthen the dispersed phase–continuous phase interface, such that any dispersed-phase droplet collisions do not result in coalescence. This method is referred to as **interfacial strengthening**.

Both of these methods are important in the stabilization of emulsion systems and they are often used in combination.

19.5.1 Charge stabilization

This technique involves applying an electrical charge to the surface of the dispersed-phase droplets, so that when they approach each other, the chances of

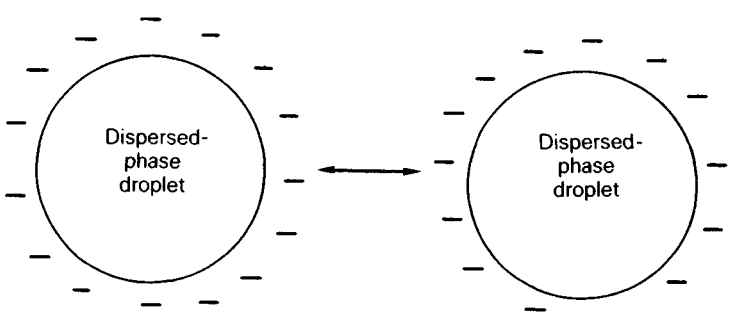

Fig. 19.3 Repulsion between negative charges associated with two approaching dispersed-phase particles.

$$CH_3(CH_2)_{16}COO^-Na^+$$

Fig. 19.4 Sodium stearate.

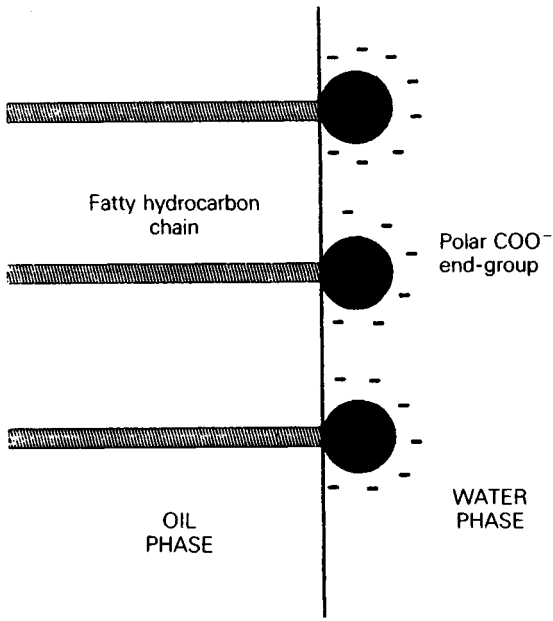

Fig. 19.5 Orientation of the emulsifier at the emulsion interface in charge stabilization.

collision are reduced by the effects of electrical charge repulsion. It is this phenomenon, represented diagrammatically in Fig. 19.3, which provides the theoretical basis for the stabilization of emulsions systems using anionic emulsifiers or, in rare cases, cationic emulsifiers. These emulsifiers contain a long, lipophilic, carbon chain attached to a small, highly charged, hydrophilic polar end-group.

A classic example of the anionic emulsifier type is sodium stearate (Fig. 19.4). When such a material is introduced into the emulsion system, the lipophilic carbon chain migrates to the oil phase, whilst the small, anionically charged, polar end-group (in the case of sodium stearate, the $-COO^-$ group) remains in the water phase. To satisfy this requirement the emulsifier resides at the emulsion interface (Fig. 19.5). This method relies solely on the effects of electrical charge repulsion. Only oil-in-water emulsions can be stabilized in this way; the continuous oil phase in a water-in-oil emulsion is unable to transmit electrical charge, thus rendering charge stabilization ineffective.

In an oil-in-water system, migration of the anionic emulsifier to the interface results in the dispersed oil-phase droplets carrying a net negative charge. This charge stabilizes the emulsion through the mechanism described above. When stabilizing emulsions by this method it is important to remember that each of the anionic charges present on the emulsifier molecules will have associated with them a corresponding positive charge (in the case of sodium stearate, Na^+). When the emulsifier is added to the emulsion system, these positive charges will be dispersed randomly in the continuous (water) phase, thus acting as an electrolyte. Some of these positively charged species will be drawn towards the negative charges on the dispersed- phase droplets by electrical charge attraction, resulting in a positive-charge density increase around the dispersed-phase droplet. This twin layer of negative and positive charges, distributed around the dispersed-phase droplet, is known as the **electrical double layer**. These positive charges will, to some extent, reduce the stabilizing effects of the negative charges that already reside on the dispersed-phase droplets, a phenomenon known as charge shielding, and will be associated with each of the dispersed-phase droplets in the emulsion system as shown in Fig. 19.6.

Emulsions that are stabilized with electrical charge can also be destabilized by the addition of electrolytes. Even small quantities of electrolyte of opposite

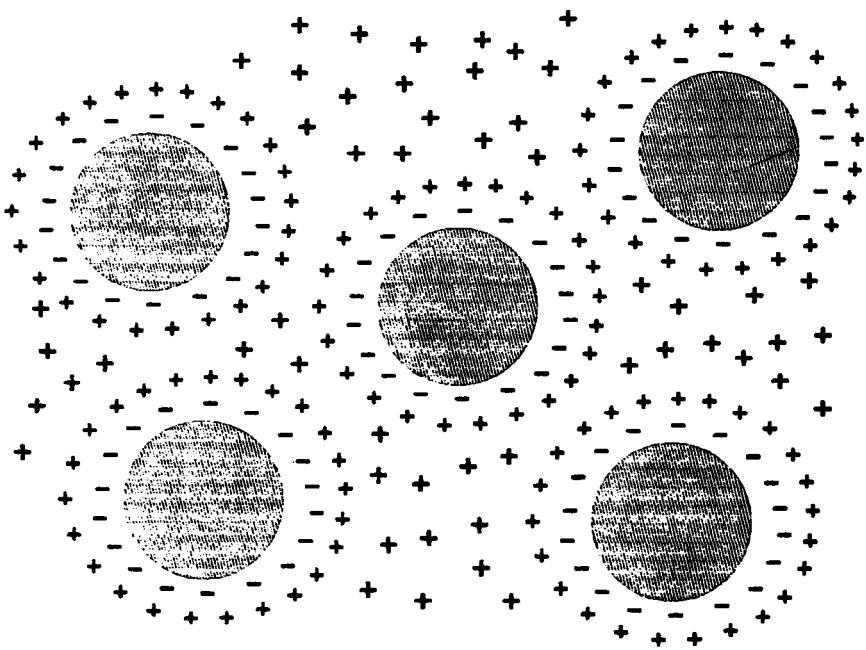

Fig. 19.6 Charge shielding effect of positive ions on dispersed-phase droplets.

charge to the net charge on the dispersed-phase droplets in the emulsion, will significantly destabilize the system. The quantity of electrolyte required to destabilize an emulsion is highly dependent on its ion valency: increasing the ion valency significantly reduces the quantity of electrolyte required.

A second disadvantage, from a practical viewpoint, is that anionic emulsifiers themselves cannot simply be added to a system containing an oil phase and a water phase to produce a stable emulsion. Emulsifiers of this type must be produced *in situ* by adding the non-polar precursor of the emulsifier system to the oil phase (stearic acid in the case of sodium stearate) and the polar precursor to the water phase (sodium hydroxide in the case of sodium stearate). When the water phase and oil phase are mixed, the emulsifier is instantly formed and migrates to the interface, producing a stable emulsion.

19.5.2 Interfacial film strengthening

The second, and perhaps most important, method of stabilizing emulsion systems is by strengthening the interface between the dispersed and continuous phases. This is a physical method which, unlike charge stabilization, does not lessen the chances of dispersed-phase droplet collisions but relies upon reducing the probability of coalescence when such collisions take place. If the process of coalescence can be reduced in this way, then the stability of the emulsion will be increased.

Interfacial strengthening is the theoretical basis for the use of nonionic emulsifiers as emulsion stabilizers. In addition, the incorporation of some types of polymer to the emulsion system can result in a stabilizing effect by the same mechanism. The use of polymers in this way is covered later in this chapter.

Nonionic emulsifiers are a special type of uncharged surfactant, with both lipophilic and hydrophilic properties in the same molecule. These emulsifiers will, when added to the emulsion system, migrate to the oil-water interface (Fig. 19.2), reducing interfacial tension. The presence of nonionic surfactant molecules at the interface will also provide a strengthening effect, the magnitude of which will be dependent upon the number of molecules present per unit area. The concentration of emulsifier molecules at the interface is often referred to as the **interfacial packing density**, which is related to emulsion stability.

This method of emulsion stabilization has many practical advantages over charge stabilization:

1. The mechanism of stabilization does not rely upon electrical charge and therefore both oil-in-water and water-in-oil emulsions may be stabilized.
2. Nonionic emulsifiers carry no charge and produce emulsions that are resistant to destabilization by electrolytes.
3. Nonionic emulsifiers, in contrast to anionic systems, are 'pre-formed', and can simply be added to the emulsion.

4. Nonionic emulsifiers exhibit excellent versatility, enabling the production of a wide variety of emulsion systems.
5. Nonionic emulsifiers are compatible with other emulsifier types and can therefore be used to increase the stability of emulsions stabilized in other ways.

A more detailed account of the use of nonionic emulsifiers is presented later in this chapter.

There are other, perhaps less important, ways of strengthening the emulsion interface to achieve stability. It is well known for example, that some forms of powder can be used to improve interfacial strength. A full review of this method is beyond the scope of this text but, in general, hydrophilic powders will stabilize oil-in-water emulsions, whilst lipophilic types will stabilize water-in-oil emulsions. This method of stabilization relies upon the powder's orientation at the emulsion interface, the fundamental requirement being that the powder should migrate to the interface, with its bulk in the continuous phase of the emulsion. This configuration provides a 'protective' layer of powder particles around the dispersed-phase droplet, thus reducing the chances of coalescence. Powders used in this way must, of course, have a particle size much smaller than that of the dispersed-phase droplet in the emulsion, otherwise no adsorption at the interface can take place. The stabilization of emulsions using powders is not particularly common in cosmetic products, although powders such as veegum and bentonite are sometimes used.

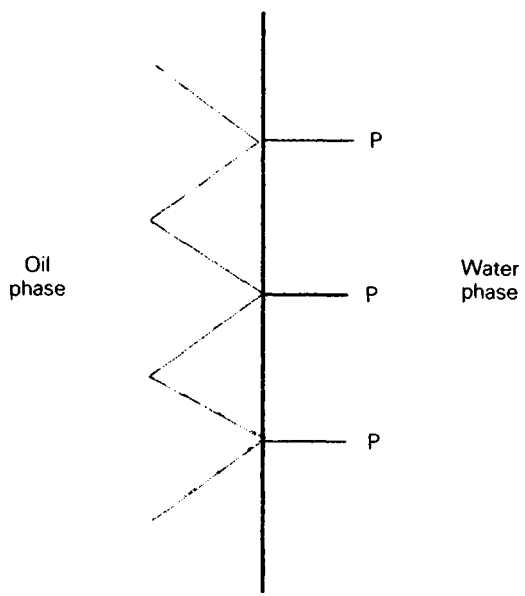

Fig. 19.7 Orientation of polymer in interfacial film strengthening. P, hydrophilic polar group; zigzag, polymeric backbone.

Polymers can also be used to stabilize emulsions through interfacial strengthening. They must be composed of a long lipophilic backbone, to which are attached side-chains containing hydrophilic polar groups. Polymers of this type will act as pseudo-emulsifiers and upon addition to the emulsion, migrate to the interface in the same way. The orientation at the interface is such that the hydrophilic side-chains reside in the aqueous phase, whilst the lipophilic polymeric backbone resides in the oil phase (Fig. 19.7).

Polymers are used mostly as stabilizers in oil-in-water emulsions where, apart from interfacial strengthening *per se*, the polymer produces an increase in the continuous-phase viscosity. This viscosity increase imparts a further stabilizing effect on the emulsion, by reducing the tendency for creaming or sedimentation. The stabilization of emulsions using polymers is common in cosmetic products, and materials such as hydroxyethyl cellulose, hydroxypropylmethyl cellulose and carboxyvinyl polymers are used extensively. They are invariably used in conjunction with nonionic emulsifiers to provide adequate emulsion stability.

19.6 NONIONIC EMULSIFIERS AND THE HLB SYSTEM

Many hundreds of nonionic emulsifiers have been developed and commercialized over recent years and the formulation flexibility provided by these is enormous. All nonionic emulsifiers stabilize emulsions in the same way, by migration to the interface where they impart a strengthening effect. To function as a nonionic emulsifier, a material must have some degree of solubility in both oil and water phases and should therefore possess both hydrophilic and lipophilic character. Indeed, it is the ratio of hydrophilic to lipophilic character, within the same molecule, that will determine the type of emulsion that will be formed and its inherent stability. It was out of an attempt to quantify this ratio that the **HLB (hydrophilic–lipophilic balance)** concept evolved.

The HLB system, as a qualitative concept, was first published in 1949 by Griffin, who showed that emulsifiers exhibiting greater solubility in water than in oil, would preferentially stabilize oil-in-water emulsions, while those with greater oil solubility would preferentially stabilize water-in-oil systems. As solubility in water and oil depends upon the extent of hydrophilic and lipophilic character within the emulsifier itself, it follows that the type of emulsion produced by any emulsifier can be correlated to its HLB. Figure 19.8 illustrates three different emulsifiers which, when added to an emulsion system, will reside at the oil–water interface in different ways.

Emulsifier A exhibits greater solubility in the oil phase than the water phase, indicating that it possesses more lipophilic character than hydrophilic character. It follows therefore that emulsifier A will have a low HLB value. Conversely, emulsifier C is far more soluble in the water phase and therefore has a high HLB value. Emulsifier B has approximately equal solubility in both phases and will therefore have an intermediate HLB value. Originally, the HLB concept was

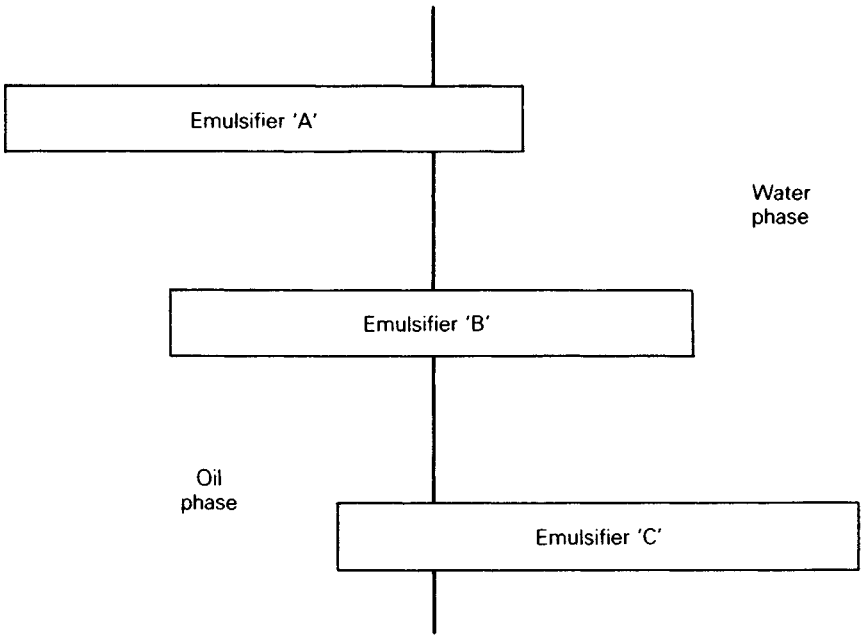

Fig. 19.8 Orientation of three different emulsifiers at the oil–water interface.

developed for ethoxylated nonionic surfactants and the HLB value was defined as follows:

$$\text{HLB} = \frac{(\%\ [\text{w/w}]\ \text{hydrophilic content of the emulsifier})}{5}$$

This gives a theoretical range of HLB values of 0–20. Further adaptations of this simple calculation were then developed for different types of nonionic emulsifier. For example, an approximate HLB value for the fatty acid esters of polyhydric alcohols, may be calculated from the following equation:

$$\text{HLB} = \frac{(E+P)}{5}$$

where E is the percentage by mass of ethylene oxide content,
and P is the percentage by mass of polyhydric alcohol content (glycerol, sorbitol, etc.).

For approximate calculation of HLB values these formulae still hold good today, although modern experimental techniques for determining actual HLB values for a wide variety of emulsifiers have rendered them unnecessary.

19.6.1 Emulsifier selection using the HLB system

The cosmetic formulator can choose from many thousands of nonionic emulsifiers to stabilize both oil-in-water and water-in-oil emulsion systems. Clearly many factors are implicated in this choice, such as toxicological profile, cost-effectiveness and ease of use. HLB values can help to rationalize emulsifier selection. In the same way that any emulsifier can be assigned an HLB value, the oil-phase components in any emulsion system can be assigned a **required HLB** value. This value is defined as being equivalent to the HLB value of the emulsifier which will optimally emulsify that particular oil-phase component, in either a water-in-oil or oil-in-water emulsion. Thus, each oil-phase component will have two required HLB values, one for each emulsion type. In the same way that HLB values for emulsifier mixtures are additive, so too are the required HLB values for mixtures of components in the oil phase of an emulsion. A simple calculation to determine the required HLB value of an oil-phase mixture, to be emulsified into an oil-in-water emulsion, is illustrated below.

Consider the following oil-phase mixture: 28% mineral oil (required HLB = 10.0) + 52% jojoba oil (required HLB = 6.5) + 20% isopropyl palmitate (required HLB = 11.5). The required HLB value of the oil phase, for an oil-in-water emulsion, is given by the following calculation:

$$\text{Required HLB} = \frac{(28 \times 10.0)}{100} + \frac{(52 \times 6.5)}{100} + \frac{(20 \times 11.5)}{100}$$

$$= 8.5 \text{ (approx.)}$$

Having determined the required HLB value for the oil phase, the emulsifier system can now be selected. The HLB of the selected emulsifier system should be chosen to match the required HLB of the oil phase, if optimum emulsion stability is to be achieved. Invariably, the emulsifier system will contain a mixture of two different emulsifiers, one of high HLB value and one of low HLB value. This produces a much more stable emulsion than a single emulsifier system because there is a higher packing density of emulsifier molecules, and hence superior interfacial strengthening at the emulsion interface. Higher packing density results from the relative lack of steric hindrance between adjacent emulsifier molecules; the bulk of the lower HLB emulsifier molecules resides in the oil phase, whilst the bulk of the higher HLB molecules reside in the water phase; this 'spreading' of the bulk means that a greater number of emulsifier molecules can be packed into unit interfacial area. In practice, when a blend of emulsifiers is used, it is usual to incorporate the lower HLB emulsifier into the oil phase, while adding the higher HLB emulsifier into the water phase. Irrespective of the HLB value, the chosen chemical type of the emulsifier system is a vitally important factor in producing an emulsion with an optimum stability profile (Fig. 19.9).

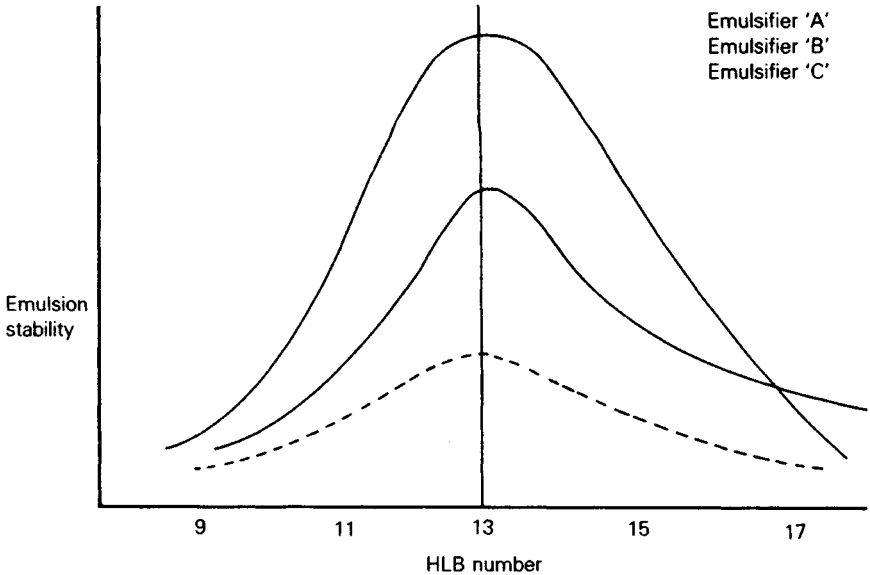

Fig. 19.9 Plot of emulsion stability against HLB value, for an oil-in-water emulsion with a required HLB value of 13, using three emulsifier systems (A, B, C) of different chemical types.

Each of the emulsifier systems in Fig. 19.9 has the same HLB value which, in turn, is equivalent to the required HLB value of the emulsion oil phase. It can be seen from the diagram, however, that emulsifier system A produces a more stable emulsion than system B which, in turn, produces a more stable emulsion than system C. This stability difference can be attributed to the chemical type of the emulsifier system used as, from consideration of the HLB value alone, all the emulsifier systems are equally suitable. It is very difficult to predict the chemical type of emulsifier necessary to produce optimum stability for any particular emulsion. Final selection of the most suitable emulsifier system is normally made through trial and error and, indeed, it is often the skill and experience of the individual formulator that is the deciding factor between an excellent emulsion product and one that is merely adequate.

Having selected an emulsifier system which produces an emulsion with a suitable stability profile, other attributes of the emulsion can be adjusted by slight formula modification. In the case of O/W systems, post-application skin feel and absorption characteristics can be changed by slight modification of the oil-phase composition, accompanied by a minor adjustment in the ratio of the selected emulsifiers, should this prove necessary. The viscosity of an O/W

emulsion can be increased by the addition of a low level of a hydrophilic gum which frequently confers added benefits to overall emulsion stability. In the case of W/O emulsions, viscosity can be increased by the addition of high-melting-point waxes to the oil phase, although over-zealous addition should be avoided if pleasing sensory attributes are to be retained. The addition of low levels of inorganic electrolytes to the water phase of a W/O emulsion will often improve emulsion stability. Magnesium sulphate is frequently chosen for this purpose because of its effective physiological compatibility with human skin.

Although the HLB system is undeniably useful in emulsifier selection, it does possess some rather severe limitations. Firstly, the HLB system is qualitative only and gives the formulator no information on the level of emulsifier needed to stabilize any particular emulsion system. Secondly, the HLB system is a function of the solubility of a given nonionic emulsifier in both oil and water phases. As the solubility in both phases will be temperature-dependent, it follows that the HLB value of any emulsifier system will change with temperature. Lastly, the required HLB for any given oil phase in an emulsion will change when other additives such as perfume and preservatives are added to the system.

Whilst the HLB system is still of some value in the selection of suitable emulsifier combinations, many formulators prefer to use the recommended systems offered by many of the major manufacturers of cosmetic emulsifiers. These systems invariably consist of high and low HLB emulsifiers combined in a certain ratio, depending upon the type and nature of emulsion to be stabilized. The selected emulsifier pair has a known high level of chemical compatibility, often as a result of their similar chemical structure, and may be used together in widely varying proportions, without problem. One such system is POE-(2)-stearyl alcohol (HLB = 4.9) used in combination with POE-(21)-stearyl alcohol (HLB = 15.5) to produce stable O/W emulsions with a wide variety of oils of varying required HLB value.

The resultant emulsions are characterized by excellent stability over a wide range of storage conditions, a good safety profile and uniform particle size distribution. The physical characteristics of these emulsifier systems are such that effective manufacture of high-quality emulsions can be carried out, even with relatively modest manufacturing equipment.

Recently, the concept of recommended emulsifier systems has been extended into the commercial availability of single emulsifier materials composed of a specially selected combination of emulsifier molecules. These 'one-stop' emulsifier solutions are often of proprietary composition and are unique to the particular commercial organization selling them. Irrespective of source, the aim is identical – to produce a single emulsifier which can easily be incorporated into a wide variety of formulations to produce aesthetically pleasing emulsions that are commercially attractive, safe in use and possess long shelf-life without significant degradation.

19.6.2 Polymeric emulsifier systems

While combinations of nonionic emulsifiers are still routinely used to produce contemporary cosmetic emulsions, more recent advances in emulsion technology allow complex polymeric emulsifiers to be available, which are capable of producing stable emulsions with high dispersed-phase volumes. These polymeric emulsifiers are frequently based on silicone copolyol chemistry. Whilst W/O emulsions have many advantages as cosmetic vehicles, including superior appearance and better delivery of lipophilic 'actives' into the epidermis, their exploitation has been avoided until recently because of their perceived oily nature when applied to the skin. Stabilization of W/O systems with polymeric silicone emulsifiers produces emulsions with all the traditional advantages mentioned above and, in addition, aesthetically pleasing characteristics when applied to the skin. Owing to the relatively high molecular weight of polymeric emulsifiers and their film-forming capabilities, emulsions stabilized in this manner frequently exhibit superior skin feel and improved product safety profiles because of reduced penetration into the epidermis.

Classic examples of polymeric emulsifiers are the silicone copolyols, normally composed of a polydimethylsiloxane lipophilic backbone attached to which are alkyl side-chains to improve oil solubility and polyether side-chains to confer hydrophilic character to the molecule. An example of this type of structure is shown in Fig. 19.10.

The siloxane molecular weight ($x+y+z$), alkyl/polyether ratio (y/z) and the molecular weights of the alkyl and polyether side-chains are variables that can be adjusted for optimized emulsifier performance.

In many ways silicone copolyol emulsifiers function in a similar manner to the conventional nonionic emulsifiers described earlier. The emulsifier is held at

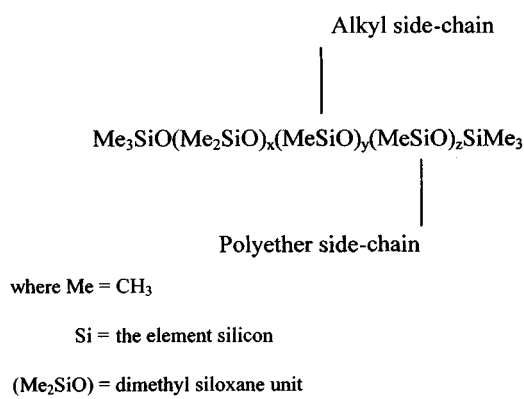

Fig. 19.10 Example diagram of a polymeric molecular arrangement.

the oil–water interface by the hydrophilic polyether fraction in the water phase and the lipophilic alkyl group in the oil phase. However, in contrast to conventional nonionic emulsifiers, the highly flexible siloxane backbone between these groups allows the emulsifier molecule to adapt to the interfacial geometry very easily, without steric hindrances. This results in the generation of a highly stable viscoelastic film at the oil–water interface allowing the development of W/O emulsions with excellent stability properties, using relatively low concentrations of emulsifier. The viscosity of these emulsions can also be increased by the addition of high-melting-point waxes to the continuous oil phase, albeit at the risk of negatively impacting sensory attributes on skin. A more elegant method for increasing viscosity is to modify the phase ratio by increasing the volume of the dispersed phase of the emulsion. Stability can be further improved by the addition of low levels of electrolytes such as magnesium sulfate, as in the case of W/O emulsions stabilized with conventional nonionic emulsifiers. In addition to their value in stabilizing W/O emulsions, polymeric emulsifiers such as silicone copolyols can also be exploited to formulate W/O/W multiple emulsions.

19.6.3 Multiple emulsions

Multiple emulsions, frequently referred to as complex emulsion systems, can be classified into two basic types, water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O). Even with modern emulsifiers it is difficult to formulate multiple emulsions with good aesthetics combined with commercially acceptable stability profiles. Despite this fact, formulation designs of this type are gradually finding their way into commercially available products, probably due to the following distinct advantages exhibited by this emulsion type:

1. Otherwise incompatible ingredients can be incorporated into the internal and external oil or water phases.
2. Highly sensitive actives can be protected more effectively in the internal phase of the primary emulsion.
3. Both immediate and longer-term moisturization benefits can be obtained using W/O/W emulsion systems.
4. The potential for controlled release of cosmetic 'actives' exists, enabling sustained efficacy after application.

Multiple, three-phase emulsions of this type require at least two emulsifiers with distinctly different HLB values for effective stabilization. A lipophilic emulsifier is required to stabilize the oil–water interface and the oil–droplet interface between the O/W emulsion and the external oil phase in O/W/O emulsions. Similarly, a hydrophilic emulsifier is required to stabilize the water–oil interface and the water–droplet interface between the W/O emulsion and the external water phase in W/O/W emulsions. It is no surprise that selecting a suitable emulsifier combination for a three-phase multiple emulsion is significantly more

difficult than selecting an emulsifier system for a simple two-phase emulsion, and both emulsifier HLB value and chemical structure are important factors to consider when making this choice.

Suitable lipophilic emulsifiers include multifunctional nonionic materials such as cetyl dimethicone copolyol or polymethacrylate polyalkyl polyether copolymers. These materials typically have molecular weights greater than 7000 with HLB values of less than 6 and are characterized by their comb-like structures. Strongly hydrophilic, multifunctional ionic emulsifiers with HLB values greater than 30 best stabilize the hydrophilic part of the system. In W/O/W emulsions these surfactants should have a molecular weight below 500 and must also exhibit a high potential to self-emulsify.

By contrast, for O/W/O multiple emulsions, suitable hydrophilic emulsifiers must form very finely dispersed O/W primary emulsions with droplet sizes of less than 1 micron, without significantly reducing the interfacial tension between the O/W droplets and the external oil phase of the multiple emulsion. Suitable candidates in this case include nonionic polyethylene glycol derivatives with molecular weights of greater than 1000 and HLB values of greater than 15.

19.6.4 Microemulsions

Microemulsion is the term used to describe an emulsion in which the dispersed-phase droplet is very small indeed, normally 0.1 micron or less. In practice, commercially important microemulsions are of O/W designation. The concept of microemulsions is not new – indeed, the solubilization of lipophilic fragrance oils in hydrophilic cosmetic systems relies upon the process of microemulsification. The dispersed phase of a microemulsion is normally stabilized by the micelle structure of strongly hydrophilic surfactants, typically with HLB values of 15 or greater. Microemulsions exhibit different properties from their conventional counterparts. Optical clarity or translucency frequently identifies the presence of a microemulsion and the aesthetic properties of these systems differ greatly from emulsions with a conventional particle size distribution. The stability profile of microemulsions is frequently excellent, the small droplet size virtually eliminating the conventional instabilities associated with Stokes' Law (refer to Section 19.4.2). The very small dispersed-phase droplets in microemulsions also enable cosmetic ingredients in the dispersed phase to penetrate more quickly into the epidermis, thus producing more efficacious products. Although this advantage may be used to good effect in cosmetic skin care, the higher propensity for allergic reaction on the skin must be carefully controlled before a new product can be released into the commercial market. Although the dispersed-phase droplet size of cosmetic microemulsions is very small, only a relatively low amount of mechanical energy is required for their manufacture, provided the correct quantities of an emulsifier with a sufficiently high HLB value are employed.

19.7 THE MANUFACTURE OF EMULSIONS

Manufacturing an emulsion consists of two basic stages: (a) the mixing of the two phases under low shear conditions, forming a 'pre-emulsion' and (b) subjecting the system to a high shearing force in order to create the emulsion proper. The 'pre-emulsion' as described here is sometimes a stable system in its own right and some commercially available products are manufactured using low-shear conditions only. The initial mixing of the two phases is referred to as the phasing process. It is common to add the phase which will ultimately become the dispersed phase to the phase which will ultimately become the continuous phase. For example, in the preparation of an oil-in-water emulsion, with a 30/70% phase ratio, phasing would be carried out by adding the oil phase to the water phase.

Most emulsions are subjected to the high-shear mixing process, following the initial phasing. This reduces the particle size of the dispersed phase which, in turn, will normally increase emulsion stability. There are many devices available for the high-shear mixing of emulsion systems: rotor-stator homogenizers, valve homogenizers, ultrasonic homogenizers, and colloid mills. All these instruments force the emulsion through a very narrow gap or orifice to reduce the emulsion particle size.

19.7.1 Phase inversion

In certain circumstances it is preferable to add the phase which will become the continuous phase of the emulsion to the phase which will become the dispersed phase of the emulsion, when carrying out the initial phasing process. Consider, for example, the production of the same oil-in-water emulsion system referred to earlier (30/70% phase ratio), by this method. In the initial preparation the water phase would be added to oil phase under low-shear conditions, producing a temporary water-in-oil emulsion. As further water phase is added, a point is reached where the water-in-oil emulsion initially formed becomes unstable and undergoes a phase rearrangement, in which the emulsion 'flips' and reverts to an oil-in-water system. The remaining water phase simply serves to dilute the continuous phase of the emulsion, as the addition is completed. The point at which emulsion rearrangement takes place is referred to as **phase inversion** and is often accompanied by an increase in emulsion stability. The manufacture of emulsions using the method of phase inversion is compared with the standard method of manufacture in Fig. 19.11. The reasons for the increase in emulsion stability when using the phase inversion method are complex, but the use of two emulsification stages is significant.

19.7.2 Advanced emulsification techniques

Over recent years a number of novel manufacturing techniques have been developed, enabling more rapid production of advanced emulsion systems. Low-temperature emulsification using specially formulated oil phases which are entirely liquid at room temperature, in combination with specially selected

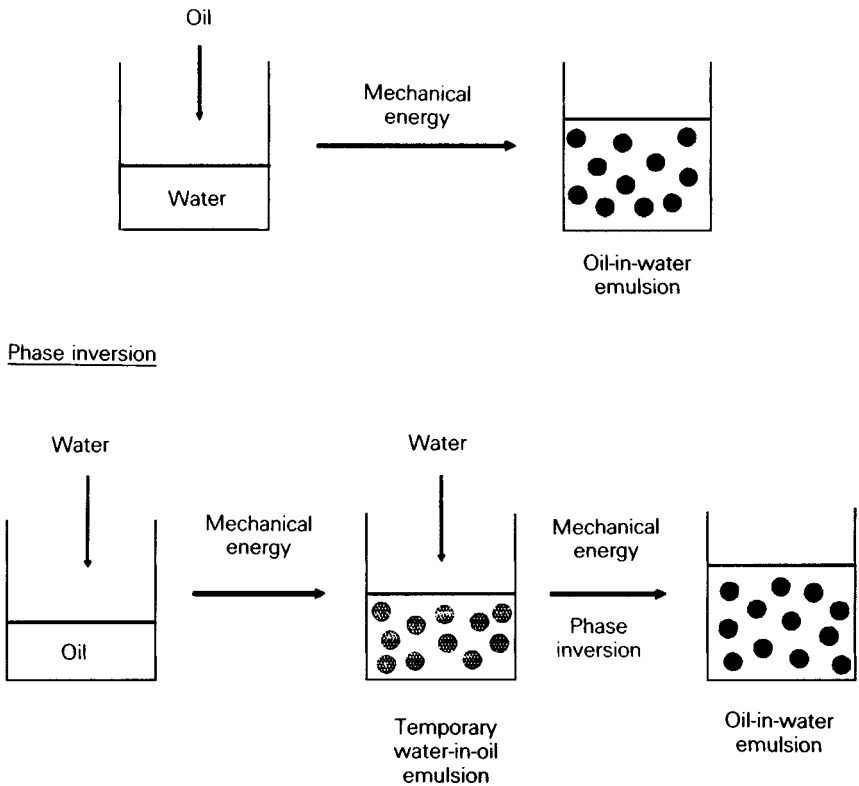

Fig. 19.11 Comparison of phase inversion method with standard method of manufacture.

emulsifier systems, is now becoming commonplace. Processing of this type negates the requirement for heat, and stable, aesthetically pleasing emulsions can be produced rapidly at lower cost using relatively modest mixing equipment.

More sophisticated manufacturing techniques are being developed to produce emulsion systems with unique properties. Of particular interest is the manufacture of stable emulsions with little or no presence of conventional emulsifiers, using sophisticated high-pressure mixing techniques. This technique involves bringing the oil and water phases of the emulsion together under ultra-high pressure (>1000 kg cm^{-2}), whereupon the forces of fluid velocity, shear and cavitation form the emulsion *in situ*. The resultant emulsion exhibits a dispersed phase with a very small droplet size, typically 0.5 microns or less. This manufacturing technique offers the cosmetic formulator the ability to produce stable, aesthetically pleasing emulsions which rapidly absorb into the epidermis upon application to the skin, with a significantly reduced potential for adverse skin reaction.

19.8 PROPERTIES OF EMULSIONS

A comprehensive review of the properties of emulsions is beyond the scope of this chapter, but their viscosity and appearance will be examined. These factors are the most important ones in cosmetic formulation because they determine how aesthetically pleasing the finished product will be.

19.8.1 Appearance

Emulsion appearance can vary widely, from a visible coarse dispersion of one phase in the other, to a completely transparent microemulsion. The two main factors influencing the appearance of emulsions are the particle size of the dispersed phase and the refractive index differences between the two phases in the system.

The opacity observed when viewing an emulsion is caused by refraction and reflection at the emulsion interface, as transmitted light passes from the continuous phase into the dispersed-phase droplets. If the refractive indices of the oil phase and the water phase are identical, then the system can be considered to be optically homogeneous and a totally transparent appearance will be observed. In practice this phenomenon is very rare in the cosmetics and toiletries industry and, assuming refractive index differences between the two phases are present, the particle size of the dispersed phase becomes the most significant factor in determining emulsion appearance. Whilst it is foolish to generalize on the correlation of emulsion appearance with the size of the dispersed-phase particles, Table 19.1 provides a guideline for this relationship.

Most emulsions encountered in the cosmetic and toiletries industry possess dispersed phases with particle sizes between 1 and 20 μm. They have the familiar milky-white appearance due to the reflection and refraction of composite white light. As the dispersed-phase particle size becomes smaller, it approaches the wavelength of light and the reflected and refracted light becomes increasingly blue. When the particle size falls below 0.1 μm a large proportion of the transmitted light passes through the body of the emulsion without hindrance, thus resulting in a translucent appearance. Finally, when the size of the dispersed-phase particle falls to below 0.05 μm, the particles themselves are too small to

Table 19.1 Guidelines for size/appearance relationship of dispersed-phase particles

Dispersed-phase particle	*Appearance*
> 0.5 mm	Visible macroglobules
0.5 mm–1.0 μm	Milky-white emulsion
1.0 μm–0.1 μm	Blue-grey emulsion
0.1 μm–0.05 μm	Translucent
< 0.05 μm	Transparent

produce any light interaction. At this point the system becomes transparent and is normally referred to as a **microemulsion.**

19.8.2 Emulsion rheology

The viscosity and feel of an emulsion can be a significant determinant in its commercial success or failure. Both of these parameters are functions of emulsion rheology, which describes the flow behaviour of the system when it is subjected to applied external forces. Rheological behaviour for emulsions can be described in terms of classical viscosity/shear curves as shown in Fig. 19.12.

If the viscosity of the product is constant when subjected to different rates of shear, then its rheology can be described as Newtonian. A good example of a material exhibiting Newtonian behaviour is water. The vast majority of emulsions, however, are non-Newtonian and exhibit a change in viscosity, or perceived 'thickness', as the rate of shear is varied. Many emulsions exhibit a drop in viscosity as the shear rate applied to the system is increased. This behaviour is referred to as **pseudoplastic** or 'shear-thinning'. The viscosity of the emulsion system will be restored when the shear is removed from the system, although full recovery to its initial viscosity after the application of shear is rare. Another rheological characteristic often observed in cosmetic emulsions is **thixotropic** behaviour. This also

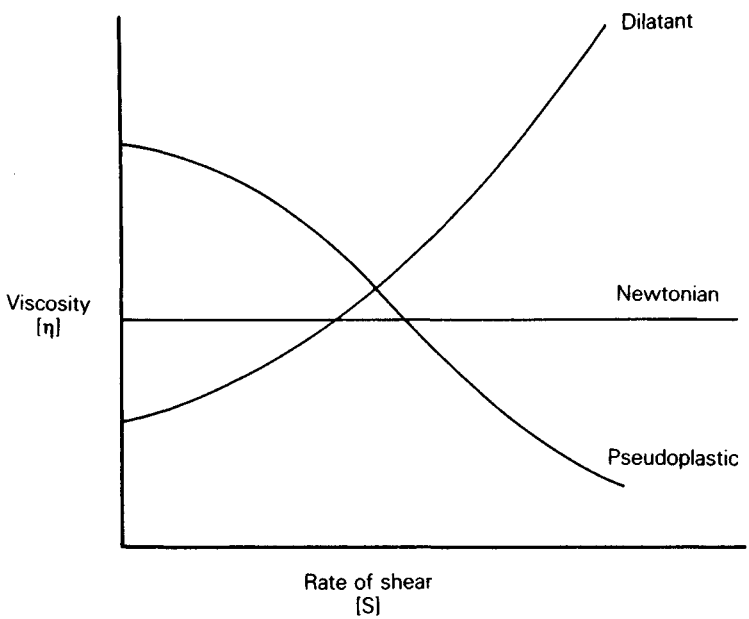

Fig. 19.12 Viscosity/shear curves for emulsions.

describes a loss in apparent viscosity with increase shear rate, but differs from pseudoplastic behaviour in that it is time-dependent. Thus, thixotropic systems exhibit a loss in apparent viscosity over time, even under conditions of constant shear. The other form of rheological behaviour illustrated in Fig. 19.12 is referred to as **dilatant** or 'shear-thickening'. This type of behaviour is rarely found in cosmetic emulsions.

The rheology of an emulsion is normally a function of the rheology of the continuous phase and the phase ratio. If the continuous phase is the major phase, then the rheology of the resultant emulsion will be largely dictated by the rheology of the continuous phase itself. If, however, the dispersed-phase is the major phase then emulsion rheology will be a function of the dispersed phase particle–particle interactions. In the latter case the viscosity of the emulsion at rest will rise sharply and its rheological behaviour will often be thixotropic in nature. In some cases little or no rheological flow will be observed when shear is initially applied to the system, due to the emulsion structure. Eventually, as the shear is increased, the emulsion will begin to flow. The point at which flow begins, as the shear is applied, is referred to as the yield point. Pseudoplastic behaviour with a yield point is often found in cosmetic emulsions.

The rheological properties of any emulsion system are extremely important both from a manufacturing point of view and in terms of use of the product by the consumer. In manufacturing, a knowledge of emulsion rheology will determine the optimum methods for mixing of the product on the plant, ensuring that its aesthetic properties are consistent from batch to batch. Emulsion rheology is also a significant factor in determining product appeal to the user. For example, a cosmetic formulator may purposely design his or her product, such that it exhibits pseudoplastic behaviour with a yield point. A product of this type may have a thick, creamy feel in its container but, when rubbed onto the face and hence subjected to a degree of shear, a viscosity decrease occurs, allowing easy absorption into the skin.

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20

Legislation and safety regulations for cosmetics in the United States, the European Union and Japan

Paul D. Wilkes

20.1 INTRODUCTION

The manufacture and sale of cosmetic products are regulated in most countries of the world. In the industrialized countries these regulations have evolved to the point where they are rather extensive and, largely because the United States (US), the European Union (EU) and Japan are the three largest markets in the world for cosmetic products, the regulations in these territories are used as a model for the developing world. It is therefore important for a cosmetic manufacturer to understand the difference in the regulatory systems that are in place in these three markets if it is to market products on a global basis. The regulatory authorities have continued to develop and refine the legislation governing the manufacture and sale of cosmetic products to the extent that the regulatory maze is now large and complex.

Another very important factor to take into account when considering entry into a new market is the relationship between legislation governing the manufacture and sale of cosmetic and medicinal products (drugs). To ensure that a product falls into the definition of a cosmetic, close attention has to be paid to the claims for the product, the ingredients in the formulation and the presentation of the product. Certain products are categorized differently in the US, EU and Japan. Examples include sunscreens, antidandruff shampoos and toothpastes containing fluoride. From a European perspective it is usually the case that products classified as cosmetics in the EU may be classified in the US and Japan as medicinal products, whereas the reverse is rarely the case. Such products merit special attention and care, because the fact that a product falls into the category of a medicinal product (usually an Over-The-Counter drug – OTC) will bring into play aspects of medicines legislation that will impact on labelling and manufacturing.

To avoid delays and disappointment, the wise product developer will consult his or her colleagues in Regulatory Affairs at a very early stage in the development

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 625–645

process with a clear idea about the countries where it is intended to market a product, the proposed product claims and the main ingredients of the formulation.

Regulations which impact directly on the manufacture and sale of cosmetic products include the following: legal authority, cosmetic definition, labelling, ingredient listing, registration of cosmetic establishments, registration of raw materials and formulations, collation and reporting of adverse events, restrictions on ingredients, safety substantiation, efficacy substantiation, product information packages, inspection authority, good manufacturing practices and poison centre notification. Aspects of these regulations affecting the manufacture and sale of cosmetic products in the US, EU and Japan are discussed below.

20.2 THE UNITED STATES

(a) Summary of legal authority

The regulation of cosmetics is governed by the Federal Food, Drug and Cosmetic Act and the Fair Packaging and Labeling Act. The authority responsible for regulating cosmetics is the Food and Drug Administration (FDA). The current regulatory framework centres on the prohibition of 'adulterated' and/or 'misbranded' cosmetics. It is intended to ensure that cosmetics are safe, properly labelled and that the packaging and label statements are truthful and informative.

(b) Definition

There is one definition for drugs and another for cosmetics; a product that can be considered as both a drug and a cosmetic will have to follow the regulatory requirements of both product categories. In addition to adhering to the cosmetic labelling requirements, such a product will have to comply with the labelling requirements for drugs along with additional requirements not applicable to cosmetics, including pre-market notification, monographs, good manufacturing practice regulations and registration. For example, sunscreen preparations that claim to offer protection against sunburn are considered to be both drugs and cosmetics.

Cosmetics are defined by the Federal Food, Drug and Cosmetic Act as 'articles intended to be rubbed, poured, sprinkled, or sprayed on or introduced into, or otherwise applied to the human body or any part thereof for cleansing, beautifying, promoting attractiveness or altering the appearance, and articles intended for use as a component of any such articles; except that such a term shall not include soap'. The exception for soaps is limited and applies only to products consisting only of alkali salt of a fatty acid and making no labelling claim other than cleansing.

In order to determine whether a product is a drug or a cosmetic, or both, the 'intended' use of the product has to be determined by reference to the claims

or representations made for the product in its labelling or advertisements. Categorization of the product will largely depend on the labelling claims. However, the FDA considers some products to be categorized as drugs simply because they contain certain ingredients. For example, the inclusion of a source of fluoride in a toothpaste (dentifrice) product even without an anticaries claim will cause that product to be categorized as a drug and make it subject to the requirements of the OTC drug monograph for such products. The reasoning for this is that fluoride is widely known to the consumer as an active anticaries agent, and its mere inclusion in an ingredient list on a label is sufficient notice to declare to the consumer that a product has anticaries activity (and hence is an 'OTC monograph' product).

(c) Cosmetic labelling

In US legislation there exists the concept of the Principal Display Panel (PDP), whereas this does not appear in EU legislation.

The PDP is the part of the label that the consumer will see first and examine. Certain key labelling items must appear on the PDP which must be large enough to accommodate this mandatory information in a clear, conspicuous manner without being obscured or crowded by other printing. The principal difference between the US and EU labelling requirements with regard to the PDP lies in the US requirement for the weight or volume declaration to appear on this panel. In the EU the positioning of this declaration is not specified, and hence may appear elsewhere on the container.

There are a number of items of information which must appear on either the outer or inner container (or both) of a cosmetic product. This section will discuss labelling requirements for information other than ingredients, which will be dealt with in the next section.

The following information in sections (i), (ii), (iii) and (iv) is required to appear on both the inner and outer container in indelible, easily legible and visible lettering:

(i) A statement of the net quantity of contents. In addition, there are a number of mandatory requirements for type size and label location, and methods for designating weights, volumes or measures.
(ii) A statement of the name and place of business of the manufacturer, packer or distributor.
(iii) If a specific warning is required for the safe use of a cosmetic product, this must appear on the inner and outer container. Some warnings are mandatory for certain categories of cosmetic product and there are warnings that are required on labels of cosmetics sold in the US which are not required in the EU (and vice-versa).
(iv) Imported cosmetic products require a statement indicating the country of origin, which is defined as the country of manufacture, production or growth

of the article. Products manufactured in bulk in the EU and shipped into the US for filling into containers and labelling for retail sale are regarded as being manufactured in the EU and will require labelling with the country of origin.

The following information in (v) and (vi) is required to appear on the label of the outer container only:

(v) A statement of the identity of the product. Most manufacturers choose to put this information on the inner container also. The terms that may be used include, but are not limited to, the common or usual name or a descriptive name.
(vi) Ingredient listing (see next section).

There are certain limited exemptions from some of the requirements for small packages, samples and decorative containers.

Expiry dating is not required. Batch identification is not required, but the industry has developed guidelines for batch number identification and these are widely followed.

All required information must be in the English language, although other languages may also appear on the label.

(d) Ingredient labelling

All ingredients must be listed on the outer container, the principle being that the consumer should be able to make an informed purchasing decision. If it is not possible or practical to list the ingredients on the label, there are a number of other permitted ways of providing the consumer with this list, depending upon the design of a particular product (for example, there are allowances for small and/or decorative containers).

Ingredients are listed in descending order using the nomenclature defined in the *International Cosmetic Ingredient Dictionary* [1] which is officially accepted by the FDA. Fragrances and flavours are listed by their generic descriptions as 'fragrance' and 'flavor' and in addition the FDA can grant trade secret status to other ingredients rendering them exempt from listing. In the EU, the recent 6th Amendment to the Cosmetics Directive requires ingredient labelling for the first time. Unfortunately, because of the problems of the existence of common words in the *International Cosmetic Ingredient Dictionary* in the English language, some non-English-speaking EU countries were unable to accept certain aspects of this nomenclature, so although ingredient listing is required now in both the US and the EU, there are differences in nomenclature, which means that manufacturers cannot simply use one system for products in both markets.

In the US, ingredient listing is required on products for retail sale to the consumer, whereas products given away as free samples, professional products used

in salons and cosmetology schools or used as make-up in the theatre are exempt from this requirement. In the EU these exemptions do not apply and ingredient listing is effectively required on all products in all circumstances.

Cosmetic–drug products, such as sunscreens, are required to list the active ingredients separately first, followed by the excipients (non-active ingredients) in descending order.

The International Cosmetic Ingredient Dictionary is recognized worldwide as the primary source for identifying cosmetic ingredients. The latest edition contains the nomenclature recognized in both the US and the EU [1].

(e) Registration of manufacturers

Cosmetic manufacturers are not required to register manufacturing premises with the FDA. However, the CTFA has set up a voluntary registration scheme in co-operation with the FDA using an approved form. Acknowledgement of receipt of registration by the FDA does not signify approval of manufacturing premises.

(f) Registration of raw materials and formulations

As with registration of manufacturing premises, the FDA does not require notification of ingredients or formulations for cosmetic products. The industry has set up a voluntary registration programme for reporting to the FDA raw materials used in finished products and the formulations of these products. The manufacturer or supplier of the raw materials furnishes the information on raw materials and the manufacturer, packer or distributor furnishes the information on the formulation. Information that is agreed by supplier and FDA to be a trade secret is not divulged.

(g) Reporting of adverse reactions

There is no compulsory reporting of adverse reactions to the FDA. However, a voluntary scheme exists (the 'Voluntary Cosmetics Product Experience program') under which companies send to the FDA annually any adverse reactions reported by consumers during the preceding year. In addition, under the 'Voluntary Cosmetic Registration Program' companies submit information listing all cosmetic products distributed by the company during the preceding year. Both manufacturers of finished cosmetic products and raw materials report ingredient information to the FDA.

(h) Restrictions on ingredients

There is no positive list of raw materials allowed in cosmetics, nor is there a negative list of those not allowed. A manufacturer is generally free to use any raw material as a cosmetic ingredient, with the exception of colour additives and a few materials which are prohibited or whose use is restricted (these number

only approximately 10). Colour additives are closely regulated and have to be approved by the FDA for their intended use. Note that the list of approved colours is similar, but not identical, to that of the EU, and furthermore the specifications for a small number of colours differ, so a manufacturer formulating one product for the US and EU needs to pay attention to this.

(i) Safety substantiation

A product is required by the Food, Drug and Cosmetic Act to be safe in order for it to be placed on the market. Although the law does not explicitly require that animal or human tests be conducted on the product or its ingredients, FDA regulations require that a manufacturer substantiate the safety of the ingredients and the product. If it is not substantiated prior to placing on the market, then the product must bear a statement that 'the safety of this product has not been determined'. For obvious commercial reasons products do not appear on the US market with this statement.

To ensure the safety of cosmetic products, the industry has set up an industry-funded programme entitled the Cosmetic Ingredient Review Program (CIR). The CIR brings together all available scientific data on the safety of cosmetic ingredients for review and evaluation by an independent panel of leading academic scientists and physicians. The panel prioritizes ingredients for review. After completion of a review of a particular material or group of materials, the panel determines that an ingredient is safe for use in cosmetics with or without limitations; that the ingredient is unsafe for such use; or that there are insufficient data currently available to determine whether the ingredient is safe or unsafe. The panel findings are made public.

(j) Inspection authority

The FDA is authorized to inspect any establishment where cosmetic products are manufactured or stored for distribution. Inspectors may examine any equipment, finished product, raw material, container or labelling pertaining to cosmetic products and may take samples. Non-US manufacturers are not subject to inspection.

(k) Good Manufacturing Practice

There are no regulatory requirements with regard to Good Manufacturing Practice (GMP). However, the CTFA has adopted a set of GMP Guidelines which are widely followed.

(l) Advertising

The Federal Trade Commission and not the FDA regulates advertising of cosmetics. The standard for compliance with the FTC requirements is whether an advertisement is misleading or deceptive. Comparative advertising is permitted.

However, the FDA is responsible for the enforcement of the regulations concerning drug products and will take action against companies which make medicinal (drug) claims for cosmetic products which in the view of the FDA cause such products to fall outside the definition of a cosmetic and into the definition of a drug. The FDA will issue warning letters to companies making drug claims for cosmetic products and such letters are made public.

(m) Packaging standards

There are no requirements for cosmetic products to be packaged in standard quantities in pre-packaged sizes.

(n) Other issues

The US is a federation of states, which operates in practice in a similar way to which the EU is developing. Issues of concern in one or several states are legislated on initially at state level, which creates difficulties for manufacturers who want to be able to market one product across the whole of the territory. A familiar pattern develops – one lead state develops a new piece of legislation, which is picked up by like-minded states, and then the Federal authority has to step in to harmonize the situation. In the meantime manufacturers have to deal with a situation of diverging legislation. In recent years manifestations of this phenomenon have been seen in the regulation of products containing volatile organic compounds (VOCs), where the state of California took the lead in the US, and the Packaging Waste Directive in the EU which arose from a regulation in Germany concerning the recycling of packaging waste.

20.3 THE EUROPEAN UNION

(a) Summary of legal authority

The European Union (EU) was formerly known as the European Community (EC), but following its recent expansion to admit Austria, Finland and Sweden the term EU is used. Legislation is still referred to by the abbreviation 'EC'. The European Union currently comprises the following fifteen Member States: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, The Netherlands, Portugal, Spain, Sweden and the United Kingdom. In addition there are countries which have close economic ties to the EU such as Iceland, Norway and Switzerland that, while not members, have aligned their cosmetic regulations to match closely that of the EU. Furthermore, other countries in Europe who intend to seek membership at some time in the future are also changing their cosmetic regulations to bring them more into line with the EU.

The legislation governing the sale of cosmetic products in the EU is the 1976 EC Cosmetics Directive. This has undergone many changes but in 1993

underwent the most substantial revision, known as the 6th Amendment. This revision was necessary because of the still-divergent requirements governing the sale of cosmetics in the Member States.

In order for an EC Directive of this type to take effect in the Member States, the legislation must first be incorporated into the law of each separate state and this takes time. The original date anticipated for the 6th Amendment to take effect throughout the EU was 1 January 1997. The majority of the Member States did not meet this date and enforcement practices with regard to the revised legislation did not become apparent until the end of 1998.

The 6th Amendment introduced a number of new features into the legislation: a revised definition of a cosmetic product, requirements for ingredient labelling, product information packages containing comprehensive details of the product composition, data to support product safety and, where justified by the nature of the claims, data to support efficacy. Furthermore, manufacturers now have to notify the relevant authorities of all manufacturing sites and the safety assessment has to be signed by a 'qualified person'.

The Cosmetics Directive consists of the legislation governing the sale of cosmetic products and, attached to it, a series of annexes which contain in tabular form an illustrative list of cosmetic products, and lists of details of banned substances, restricted substances, permitted colours, preservatives and UV filters.

(b) Definition

There are separate definitions for a medicinal product and a cosmetic. Unlike the US, it is not possible for a product to be both a cosmetic and a drug; it is one or the other. Whether a product is considered a medicinal or cosmetic product depends upon a number of things, of which, perhaps, the label claims are the most important. Ensuring that product claims do not cause a cosmetic product to be reclassified as a medicine is an ongoing feature of the work of the regulatory professional in the EU. The situation is not helped by the different ways in which the Member States draw the line between medicines and cosmetics. It is possible to make claims on cosmetic products in some Member States, which would be regarded as medicinal claims in others. A detailed discussion of this aspect of cosmetic regulation in the EU is beyond the scope of this chapter, but is a factor which merits serious attention. The definition of a cosmetic is: 'any substance or preparation intended to be placed in contact with the various external parts of the human body (epidermis, hair system, nails, lips and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance and/or correcting body odours and/or protecting them or keeping them in good condition.' This definition appears to leave open the possibility that a cosmetic product may have a cosmetic function as its main feature, but may have a subsidiary function as a medicine.

(c) Cosmetic labelling

The following information is required to appear on both the inner and outer container in indelible, easily legible and visible lettering:

(i) The name or style and the address or registered office of the manufacturer or the person responsible for marketing the cosmetic product who is established within the EU. This information may be abbreviated if the abbreviation makes it possible to identify the undertaking. Member States may require that the country of origin be specified for goods manufactured outside the Community; there is currently no EU legislation governing this aspect of product labelling, this is left to the Member States.

(ii) The nominal content at the time of packaging, given by weight or volume, using the metric system of measurement. The following are exceptions when this declaration does not need to appear: packages containing less than five grams or five millilitres and free samples and single-application packs. For pre-packages normally sold as a number of items, for which details of weight or volume are not significant, the content need not be given provided the number of items appears on the packaging. This information need not be given if the number of items is easy to see from the outside or if the product is normally only sold individually.

(iii) The date of 'minimum durability' (expiry date), except that this is not mandatory for cosmetic products which have a minimum durability of greater than 30 months. The date of minimum durability of a cosmetic product is defined as 'the date until which a product, stored under appropriate conditions, continues to fulfil its initial function and, in particular, remains in conformity with Article 2 of the Directive' which is concerned with product safety (i.e. does not cause damage to human health when applied under normal or reasonably foreseeable conditions of use, taking into account, in particular, the product's presentation, its labelling, any instructions for its use and disposal, as well as any other indication or information provided by the manufacturer).

The date of minimum durability is required to be indicated by the words: 'Best used before the end of...', followed by either the date itself, or details of where the date appears on the packaging. The date must consist of the month and the year in that order and, if necessary, this information can be supplemented by an indication of the storage conditions which must be satisfied to guarantee the stated durability.

(iv) Particular precautions to be observed in use, especially those listed in the column 'Conditions of use and warnings which must be printed on the label' in Annexes III, IV, VI and VII (these Annexes contain warnings related to specific ingredients when included in cosmetic formulations) as well as any special precautionary information on cosmetic products for professional use, in particular in hairdressing. Where this is impossible

for practical reasons, an enclosed leaflet, label, tape or card must contain that information to which the consumer is referred either by abbreviated information or the symbol given in Annex VIII (the 'Hand and Book' symbol), which must appear on the inner container and the packaging (outer container).

(v) The batch number. Where this is impossible for practical reasons because the cosmetic products are too small, this information need appear on the packaging only.

(vi) The function of the product, unless it is clear from the presentation of the product.

The following information is required to appear on the outer container only.

(vii) A list of ingredients in descending order of weight at the time they are added, preceded by the word 'INGREDIENTS'. Where that is impossible for practical reasons, an enclosed leaflet, label, tape or card must contain the ingredients to which the consumer is referred either by abbreviated information (e.g. 'See leaflet for ingredients') or the symbol given in Annex VIII (the 'Hand and Book' symbol), which must appear on the packaging.

For decorative cosmetic products marketed in several colour shades, all colouring agents used in the range may be listed, provided that the term 'may contain' is added. Industry has adopted the symbol +/− preceding the colours, all enclosed in square parentheses [+/− *colours*] to denote 'may contain'.

Where it is impracticable, for reasons of size or shape, for the particulars referred to in points (iv) and (vii) to appear in an enclosed leaflet, then they must appear on a label, tape or card which is enclosed or attached to the cosmetic product.

In the case of soap, bath balls and other small products where it is impracticable for the ingredients listing to appear on a label, tag, tape or card or in an enclosed leaflet, they must appear on a notice in immediate proximity to the container in which the cosmetic product is presented for sale.

Language

The 6th Amendment made provision for Member States to require certain of the labelling of cosmetic products to be in the official language(s) of the country of sale. All Member States have included this provision in their national implementing legislation. In practice, in the majority of countries where the Latin alphabet is used, the only parts which require translation are the function of the product (unless obvious), instructions for use and warnings.

(d) Ingredient labelling

The 6th Amendment introduced mandatory ingredient labelling in the EU for the first time. As mentioned earlier in this chapter, although the industry lobbied

strongly for the adoption of the established US system of nomenclature, that finally adopted for use in the EU is different in a number of respects.

Because English is the official language of only two of the Member States, some non-English-speaking countries would not accept the use of terms for 'common' ingredients in English (examples include water, liquid paraffin, honey and the common English names for plants). The solution to this problem was to adopt the use of Latin terminology and, for plant names, the Linnaean botanical nomenclature. Thus, water becomes *Aqua*, liquid paraffin is *Paraffinum liquidum* and honey, *Mel*. An example of a plant name is *lavender,* which appears in the ingredient lists as *Lavandula angustifolia*, or *Lavandula hybrida*, depending upon the species used. The system of naming materials derived from plants by using the botanical name of the plant only is a less specific system than that currently used in the *International Cosmetic Ingredient Dictionary*. All extracts from a specific plant species, regardless of the part of the plant or the extraction process used, are referred to in the ingredient list by the botanical name of the plant.

Industry was required to submit to the EC Commission a list of all cosmetic ingredients currently in use, and this formed the basis of the official ingredient nomenclature and which is an indicative list [2]. This is not a 'permitted' list, thus cosmetic raw materials which appear on this list are not officially recognized as safe, and ingredients which do not appear are also allowed for use in cosmetic products. Raw materials used in cosmetic products are listed in the indicative inventory of materials used in cosmetic products, as described above. This inventory will be updated regularly and manufacturers are expected to obtain official names for new ingredients by application to the CTFA International Nomenclature Committee. This Committee works closely with the COLIPA Liaison Committee on Labelling Nomenclature to ensure that as far as possible the International Nomenclature for Cosmetic Ingredients (INCI) names are harmonized.

Manufacturers, for reasons of trade secrecy, may apply not to include one or more ingredients on the above-mentioned list.

Perfume and aromatic compositions and their raw materials are referred to by the words 'perfume' or 'flavour', but in order to overcome the language difficulties mentioned above, the terms 'parfum' and 'aroma' are unofficially recognized. Ingredients in concentrations of less than 1% may be listed in any order after those in concentrations of more than 1%. Colouring agents may be listed in any order after the other ingredients, using the Colour Index number.

(e) Registration of manufacturers

Pre-marketing registration of the place of manufacture or initial importation of a cosmetic product into the EU is required. The registration procedure is not centralized and is the responsibility of the individual Member States. A manufacturer is required to register in the Member State in which he resides.

(f) Registration of raw materials and formulations

No positive registration of raw materials and formulations is required. For reasons other than conformance with the Cosmetics Directive, manufacturers of raw materials supplied in specified tonnages are required to register raw materials for the purposes of other legislation.

(g) The Product Information Package

The manufacturer or importer must keep accessible at the address shown on the label (which must be an address in an EU Member State) the following information, which is known as the Product Information Package (PIP). Where a number of addresses appear on the label, industry has adopted the convention of underlining the address where the PIP may be obtained.

1. The qualitative and quantitative composition of the product. In the case of perfume compositions and perfumes, the name and code number of the composition and the identity of the supplier.
2. The physicochemical and microbiological specifications of the raw materials and the finished product, and the purity and microbiological control criteria of the cosmetic product.
3. The method of manufacture complying with the Good Manufacturing Practice (GMP) laid down by Community law or, failing that, laid down by the law of the Member State concerned. COLIPA has issued guidelines for GMP [3]. COLIPA is the umbrella organization in the EU for the national cosmetic industry associations and is an acronym of 'Comité de liaison des associations européennes de l'industrie de la parfumerie, des produits cosmétiques et de toilette'; COLIPA is referred to in English as 'The European Cosmetic Toiletry and Perfumery Association'.
4. Assessment of the safety for human health of the finished product. 'To that end the manufacturer shall take into consideration the general toxicological profile of the ingredient, its chemical structure and its level of exposure.' In practice this means that a manufacturer has to have available for inspection on demand a toxicological profile of the finished product, including all its constituent ingredients and a signed safety statement by a 'Qualified Person' as described below.

The 'Qualified Person'

For the purpose of safety assessments, the 6th Amendment introduced the concept of the 'Qualified Person' into EU cosmetics legislation.

This person has to be qualified in the disciplines of pharmacy, toxicology, dermatology, medicine or similar. The 'Qualified Person' does not have to reside within the EU, but must meet the qualification requirements.

The assessment of the safety for human health must be carried out in accordance with the principle of Good Laboratory Practice. COLIPA has issued guidelines concerning safety assessments [4].

The Scientific Committee for Cosmetology (since 23 July 1997 re-established as the 'Cosmetic Products and Non-food Products intended for Consumers Scientific Committee', following the restructuring of the responsibilities of certain committees) was established in 1978 to assist the Commission in the application of the Cosmetics Directive, and in 1982 issued 'Guidelines for the Testing of Cosmetic Ingredients for their Safety'. These guidelines were revised in 1999 and set out the testing parameters that a company should follow in order to obtain approval for raw materials which appear in the Annexes to the Directive.

5. Proof of the effect claimed for the cosmetic product, where justified by the nature of the effect or product.

This is a significant new requirement. Products whose function is obvious and generic will not be required to provide efficacy data (for example, the inclusion and action of detergents in shampoos is well established). Cosmetic products which make strong and/or unique claims will be expected to be able to provide data to support such claims. COLIPA has issued guidelines concerning what test data may be required in particular circumstances [5].

The PIP information must be available in the national language or languages of the Member State where it is held, or in a language readily understood by the competent authorities.

(h) Inspection authority

The inspection of PIPs and manufacturing premises is the responsibility of each Member State. In the event of a problem with a particular cosmetic product in one Member State when it is manufactured in another, the inspection authority in the former Member State has to request inspection by the latter. How this will operate in practice remains to be seen.

(i) Good Manufacturing Practice

There is no specific Good Manufacturing Practice legislation or guidelines for cosmetic products. However COLIPA has issued guidelines [3].

The person responsible for manufacture or first importation into the EU of a cosmetic product must possess an appropriate level of professional qualification or experience in accordance with the legislation and practice of the Member State which is the place of manufacture or first importation. Some Member States have legislation in place which specifies what this qualification shall be, whereas others do not.

(j) Advertising

There is no pre-clearance requirement for cosmetic advertising. There is a Misleading Advertising Directive and comparative advertising is now permitted, subject to tight restrictions.

(k) Packaging standards

Certain products are required to be sold in standard sizes if the requirement for unit price marking is to be avoided. However, the Directive which contains this requirement is not mandatory and has been adopted rather patchily by the Member States. The Commission has recognized that this Directive has not achieved its objectives and intends instead to legislate for unit price marking across all products, with certain exceptions. At this time it is not anticipated that cosmetics will be allowed as an exception. When implemented (after the end of 1999), all cosmetics offered for sale will have to bear a price marking showing the price per pack and the price per unit (e.g. per 100 ml).

(l) Poison centre notification

Individual Member States can request that manufacturers supply details of the formulation of a cosmetic product to the Competent Authority. In some Member States this means a mandatory requirement to provide the national or regional poison centres with certain information on cosmetic products as they are launched on the market. In others, if a problem arises this information is required to be supplied.

(m) Animal testing

This aspect of the 6th Amendment is the one which has caused the most public interest and controversy.

The final text of the 6th Amendment contained a ban on the use of ingredients or combinations of ingredients tested on animals after 1 January 1998 in order to meet the requirements of the Cosmetics Directive. This recognizes that there are other Directives which might require the testing on animals of the same ingredients used in cosmetic products.

If there has been insufficient progress in developing satisfactory methods to replace animal testing, and particularly where alternative methods of testing have not been scientifically validated as offering an equivalent level of protection for the consumer, the Commission could postpone the date of implementation of this provision. This it duly did, until 30 June 2000.

If a manufacturer makes any reference to testing on animals on the product label or printed material associated with the product, it must state clearly whether the tests carried out involved the finished product and/or its ingredients.

(n) Other issues of concern

The environment is high on the agenda of both the consumers and the regulators in the EU. A Packaging Waste Directive is now in place, a particularly complicated piece of legislation in practice, obliging sectors of the manufacturing and supply chain to be accountable for the packaging they use, and to recover and recycle it. To assist this process, recycling symbols which identify the types of material(s) used have been included in EU legislation, although it is not currently mandatory to use these on packaging.

A Directive has recently been finalized which will regulate the use of biocides. Some aspects of this piece of legislation will impact on cosmetic products since several of the materials used as biocides are also used in cosmetic products as preservatives.

In conclusion, the 6th Amendment to the Cosmetics Directive has now come into operation. How industry will comply with the new requirements has been discussed at length over the past five years and the time has come to see how it will work in practice. It is to be hoped that the EU has moved a step closer to complete harmonization of cosmetics legislation.

20.4 JAPAN

To some, the Japanese system of cosmetic product regulation and the requirement for pre-marketing registration appears onerous. However, rather helpfully, the Japanese authorities publish the essential regulations and guidelines in English and make them readily available. The key to formulating a product for the Japanese market is to recognize very early in the development process that the formulation is subject to certain criteria that it does not have to meet if it is sold only in the US and the EU. If one formulation is to be sold in all three markets then Japanese regulatory considerations will predominate and the use of novel ingredients will be restricted.

(a) Summary of legal authority

Cosmetic products are regulated and subject to pre-marketing registration by the Ministry of Health and Welfare (MHW), under the Pharmaceutical Affairs Law No. 145 of 1960. This law and its accompanying Notifications are intended to guarantee the safety of each ingredient and combination of ingredients in all cosmetic products sold in Japan. To this end, the MHW has the responsibility to review each individual formulation prior to granting a manufacturing or importation licence. The granting of a licence, and the time it takes to obtain it, depends upon whether the formulation of a particular product contains ingredients which are recognized as safe in the product's particular category, whether the materials have been used in another cosmetic category in Japan, or have never been used in Japan.

(b) Definition

A cosmetic is defined under the Pharmaceutical Affairs Law as follows: 'The term "cosmetic" means any article intended to be used by means of rubbing, sprinkling or by similar application to the human body for cleaning, beautifying, promoting attractiveness and altering the appearance of the human body, and for keeping the skin and hair healthy, provided that the action of the article on the human body is mild.'

The 'mild' nature of a cosmetic product is one of the criteria used in Japan to distinguish a cosmetic from a drug product.

There is also a third classification for products, known as 'quasi-drugs'. Quasi-drugs by definition must have a mild effect on the body but, distinct from cosmetics, quasi-drugs have a 'definite purpose of use', such as:

(i) Prevention of nausea or discomfort, foul breath or body odour.
(ii) Prevention of prickly heat, sores and the like.
(iii) Prevention of hair loss, promotion of hair growth, or removal of hair.
(iv) Eradication or repellence of rats, flies, mosquitoes, fleas, etc. for the health of humans or other animals.

Within the above definitions the MHW has classified the following types of products as quasi-drugs:

(i) Mouth refreshers.
(ii) Body deodorants.
(iii) Talcum powder (agents to prevent prickly heat, sores, etc.).
(iv) Hair growers (external agents to prevent loss of hair and to grow hair).
(v) Depilatories.
(vi) Hair dyes.
(vii) Bath preparations (indicated for use against e.g. prickly heat, eczema, athlete's foot).
(viii) Medicated cosmetics (including medicated soaps).
(ix) Medicated dentifrices (including fluoride toothpastes).
(x) Insecticides (including repellents).
(xi) Rodenticides.
(xii) Permanent waving agents.
(xiii) Sanitary cotton (sanitary napkins etc.).

Under 'Medicated cosmetics', MHW has further clarified the type and the scope of claims and effects which are associated with this category of product. Thus, products which make claims such as prevention of dandruff, prevention of razorburn, prevention of acne, and a host of other claims would cause a product to be classified as a quasi-drug.

The regulatory system for quasi-drugs is more restrictive than that for cosmetics.

(c) Cosmetic labelling

Certain information has to appear on the inner and outer containers or wrappers of cosmetic products (in Japan cosmetic products often have a primary container, a secondary container (e.g. carton) and a final wrapper (shrink-wrap). The label must identify:

(i) Name and address of the licensed manufacturer or importer.
(ii) Full and precise trade name of the licensed cosmetic.
(iii) Batch code.
(iv) Shelf-life or expiry date (in specific cases).

A special provision exists for small containers, which allows the batch code and expiry date to be omitted if this information is given on the outside container or wrapper. The information on the label must be in the official Japanese language (Katakana) and must be accurately described and legible.

Cosmetic labelling is also regulated by fair competition codes under the Law for the Prevention of Unreasonable Premiums and Misrepresentation Concerning Products and Services.

(d) Ingredient labelling

A cosmetic product label must list the ingredients determined by the MHW. The Pharmaceutical Affairs Law requires ingredient labelling of approximately 100 'Shitei Seibun' ingredients plus coal-tar colours and fragrances (not required for perfume products). Products containing any of these 'Shitei Seibun' ingredients must list the ingredient according to the names designated by the MHW.

(e) Registration of manufacturers

A licence to manufacture or to import cosmetic products is required in Japan. Applicants must submit written applications to the relevant Prefectural government which will then conduct inspections of buildings and facilities of the manufacturing plant or business office. Following confirmation of authenticity, the Prefectural government forwards the application to the MHW for examination and subsequent licensing.

Licences are granted based on the suitability of the following factors:

(i) The actual physical facilities.
(ii) The personal qualifications of the applicant.
(iii) The designation of the qualified person as the technical supervisor.

Licences are granted for each manufacturing facility or business office (in the case of importers) for a period of three years.

(f) Registration of each cosmetic product

A specific licence is required for each cosmetic product sold in Japan. The licence is obtained from the MHW or via the Prefecture office depending upon

whether a product falls into a listed function category and all the ingredients have been used in this category previously (a 'Todokede' application), or whether an ingredient is completely new to Japan or if it has not been used in the specific category before (a 'Shonin' application). 'Todokede' applications are handled at Prefecture level, whereas 'Shonin' applications are handled centrally at MHW. There is a big difference in the time required. For a simple 'Todokede' application the manufacturer has to supply the formulation of the product on official documentation to a strict format. For a 'Shonin' application the same documentation is required, together with the safety data needed to support the intended new use of the ingredient. 'Todokede' applications can be approved in a day, whereas 'Shonin' applications will take at least three months.

An ingredient that has never been used in a cosmetic product in Japan before, and which is of a type which might be of especial concern because of its function (e.g. a preservative), may take several years to achieve approval.

The Enforcement Regulations specify the data requirements and also provide that certain data may be omitted if the contents of the application are well known and that omission has a scientific basis. For example, data concerning skin irritation will always be required and usually based on application to people with Asian (i.e. preferably Japanese) skin types. However, data on the reproductive or mutagenicity effects of a material are not routinely required, unless this is warranted by the formulation and its intended use.

In 1985 a system was established to provide for the Comprehensive Licensing Standards of Cosmetics by Category (CLS). Under this system the MHW publishes a list of ingredients previously allowed for use in certain categories of cosmetics, together with the upper limit on concentration if one is specified. A product formulation which complies with the CLS only requires a simple 'Todokede' application before the product can be sold in Japan. Up to 1997 there were a total of 24 categories of cosmetic products listed in the CLS and 2484 individual ingredients. In 1997 the MHW published a new edition of the CLS [6] and in this updated version the number of categories was consolidated to 11 with a total of 2628 ingredients. In order to achieve this, some of the ingredients were re-designated as approved or not approved for certain categories. Since then an updated version of the CLS has been published annually; the latest version, 1999, contains a total of 2779 ingredient entries. Companies registering new formulations in Japan should ensure they are using the latest version of the CLS. A complicating factor with regard to the CLS is that many raw materials are listed using a chemical name which is different from that used in the *International Cosmetic Ingredient Dictionary*. However, the CTFA has published a comparative guide to the chemical names used [7].

For products which are classified as quasi-drugs there are lists of permitted ingredients by category in which combinations of active ingredients and concentration ranges are laid down [8].

(g) Safety monitoring period

An ingredient used for the first time in a cosmetic product or a specific product category in Japan is subject to a post-marketing examination or 'safety-monitoring' period. For those products that contain raw materials or ingredients new to Japan and the rest of the world, the applicant must collect and submit post-marketing safety data to MHW for a period of two years. Ingredients considered new to Japan but not completely newly developed ingredients are subject to a safety monitoring period of one year. During this period the applicant who is granted the licence has exclusive use of that ingredient in that product category (although if a material is not subject to other protection, such as via a patent, another company may also make an application to use the material, but the application must be based on its own data via a separate submission). After the completion of the monitoring period, provided that the safety requirements have been satisfied, the new ingredient will be published in the *Japan Cosmetic Ingredients Codex* [9] and the CLS.

(h) Restrictions on ingredients

In Japan all ingredients used in cosmetic product formulations must be pre-approved by MHW. There are several published sources of ingredients approved for use in cosmetic products in Japan. The CLS lists all the materials permitted by name, unique reference number and maximum permitted level by cosmetic product category. The *Japanese Cosmetic Ingredients Codex* (JCIC) [9] includes the raw material specifications for raw materials most frequently used in cosmetic formulations. Materials which are used in cosmetic products and which have specifications listed in JCIC are expected to meet these specifications. For naturally derived materials such as plant extracts, the plant species, the part(s) of the plant used and extraction solvents are listed.

In addition, there is a list of coal-tar colours permitted for use in cosmetics and quasi-drugs, although from a practical point of view the *CTFA International Color Handbook* [10] provides the best comparative guide of permitted colours. MHW publishes lists of substances that may not be included in any cosmetic product or that are subject to certain restrictions [8].

(i) Safety substantiation

Applications for cosmetics containing ingredients new to Japan must contain information on the origin and details of discovery, use in foreign countries, characteristics and comparisons with other cosmetics, as well as data on physical and chemical properties, standards, test methods and other information. Extensive safety testing may also be required for new cosmetic ingredients not listed in the CLS or JCIC, nor previously approved in a cosmetic formulation. The safety data

to be included with an application for a cosmetic containing a new ingredient include: acute toxicity, primary skin irritation, continuous skin irritation, skin sensitivity, phototoxicity, ophthalmic irritation, mutagenicity and human patch test data on the raw material. For materials which show no absorbency in the ultraviolet (UV) region of the light spectrum, the phototoxicity and photosensitivity tests may be omitted. With some exceptions data on acute toxicity, ophthalmic irritation and human patch testing are also required for the finished product. Subacute toxicity, chronic toxicity, reproduction and ADME (Absorption, Distribution, Metabolism and Excretion) tests may also be required for new ingredients 'requiring more careful handling with respect to toxicity', such as preservatives, antioxidants, chelating agents, UV absorbers and coal-tar dyes.

The range of test data that are required depends very much on the nature of the material. For preservatives new to Japan extensive data are required and the registration process may take years to complete. On the other hand, an application to register a raw material, for use in cosmetics, that has previously been used in foodstuffs will not require such an extensive array of data and will attain registration more quickly.

Human patch data must be generated on Japanese subjects, and in the past MHW has required these tests to be carried out in Japan, although data from Japanese subjects outside of Japan may now be acceptable.

(j) Good Manufacturing Practice

Although there are no official or mandatory GMP regulations for Japan, the cosmetic industry has issued voluntary technical guidelines for manufacturing and quality control.

(k) Packaging standards

There are no prescribed quantities or standard sizes for cosmetic products.

(l) Other issues of concern

The Japanese market has in the past proved difficult for companies from Western countries to penetrate. The Japanese system of licensing cosmetic products and ingredients is the most restrictive of the industrialized world and has been the subject of bilateral trade negotiations between the US and Japanese governments. There are other structural business restrictions which also act as impediments to market entry. Gradually, the Japanese government is reviewing and revising the regulations and it is expected that, within the next few years, the system of licensing cosmetic products and ingredients will be completely revised to adopt a model based on the US or EU systems with positive and negative lists for only a small range of materials and/or types of materials.

20.5 SUMMARY

This chapter has attempted to summarize the main points to consider with regard to the manufacture and sale of cosmetic products in the three major markets of the world, the US, EU and Japan. Many other countries of the world regulate cosmetics differently from the methods described above, although there is a growing trend for uniformity and harmonization. With the advent of the 6th Amendment to the Cosmetics Directive in the EU the harmonization process in Europe is extending outwards, with many countries adopting similar legislation, especially those that aspire to EU membership in the future.

The potential changes to the Japanese regulations in the near future will be awaited with interest, and it is to be hoped that the countries of the Asia–Pacific rim will also start to relax and harmonize their cosmetic regulations.

Companies developing new products for sale outside their home country should be very clear about where they intend to sell such products. Research should be carried out at the formulation and development stage of a product to ensure that all the requirements of the target countries can be met in terms of permitted ingredients and safety and efficacy data. This will ensure that the data can be generated in a timely and cost-effective manner, avoiding delays to the product launch at a late stage.

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21

Microbiological control of cosmetics

Hilda Butler

Cosmetics. The word Cosmetics will be used to include toiletries, i.e. have the definition originally found in the EEC Cosmetic Directive (1976) which has been slightly modified in the 6th Amendment to it in 1993 [1].

21.1 INTRODUCTION

The main change compared with the corresponding chapter in the 9th edition of this book is that the voluntary microbial controls described there must now be practised and be controlled in law. An outline here has been added of the mandatory legal regulatory requirements in the extended European Union (EU) for microbial control of cosmetics; countries outside the union are also interested in applying them. The USA and Japan have recently added to their laws which include cosmetic safety. There is a need to harmonize standards globally, though this has not yet happened. This would assure a consumer that any cosmetic is within the set microbial limits and will remain so until the product is used up. That is, a marketed cosmetic will have been tested for its microbial status throughout its formulation development, manufacture, storage in the finished package and also under conditions of repeated in-use contamination during the consumer trials for safety and stability. These stages will be considered in order, after a general consideration of microbial growth.

21.1.1 General observations on unhindered microbial growth

Microorganisms will grow wherever conditions are favourable (suitable temperatures, nutrients in abundance, and a moist environment). In this ideal state the biomass is increased by division of cells exponentially. After 48 hours, with no lethal factors operating, the Gram-negative bacterium *Klebsiella aerogenes,*

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 647–684

1	2	4	8	16	32	64
2^0	2^1	2^2	2^3	2^4	2^5	2^6

(The exponent expresses the generations passed)
N_O initial number of cells;
N_T number after time T.
$N_T = N_O 2^n$
n is the number of generations
$= T/T_d$
where T_d is the time for cells to double.
$N_T = N_O\, 2^{T/Td}$
$N_O = 1$; $T_d = 20$ min; T = 48 h
$N_T = 1 \times 2^{48h/20\,min}$
$= 1 \times 2^{144}$
$= 2.2 \times 10^{43}$ cells
Each cell weighs 10^{-12} g
Biomass is therefore
2.2×10^{31} g
$= 2.2 \times 10^{28}$ k
4000 times the mass of Earth estimated as
5.97×10^{24} kg

Fig. 21.1 Calculation showing number of *Klebsiella aerogenes* generated after 48 h given no lethal factors.

whose viable cells double every 20 minutes, would form a biomass 4000 times the estimated mass of the Earth [2] (Fig. 21.1)! The reasons this does not happen are: (i) that there would be a depletion of nutrients in the immediate region of growth, (ii) the bacteria would be poisoned by the toxic substances they produce, and (iii) the mass of dead cells would inhibit growth.

Microorganisms constitute 'the third kingdom' (the other two being plants and animals), and occur everywhere in the environment. Fortunately, although they adapt more quickly than the other two kingdoms under stress conditions, with judicious care they can be controlled.

Originally the science of microbiology was concerned with the effects of microorganisms, for example in disease and decay, but in the twentieth century it was developed by research to give a vast increase in the knowledge of their occurrence, physiology, biochemistry and genetics; and there are today laboratories that specialize in the production of pure culture media and the supply of specific strains of organisms for research and routine testing.

Many cosmetics, particularly emulsion-type formulations, provide good media for the growth of bacteria and fungi (the latter group includes moulds and yeasts). Means of inhibiting their growth are therefore essential to prevent deterioration of the product and to ensure the safety of the consumer during its use. Spoilage of product in time by the formation of bad odours, changes of colour or texture and separation of phases quite often indicates contamination. On the other

hand, the presence of microorganisms is not always apparent but can be demonstrated by sampling and growing on enriched culture media. By counting the colonies so formed, the original numbers can be assessed.

Some of the organisms may be pathogenic or become pathogenic under certain conditions. A pathogen can give rise to disease, most often under the following circumstances [3]:

1. If broken or abraded, skin allows invasion through to the underlying tissue, as when *Staphylococcus aureus* gives rise to septicaemia.
2. During illness when general resistance may be lowered.
3. If the skin is delicate, as in the very young whose immunity is undeveloped, or in the elderly where it is impaired or weakened by age.
4. The eyes are especially vulnerable, mainly because they are so moist; *Pseudomonas aeruginosa* flourishes in moist conditions.
5. If the consumer is undergoing antibiotic or steroid therapy.

Numerous experiments have demonstrated that normal skin flora are the most important defence against infection by pathogenic organisms [4], and the skin itself is a major barrier to external organisms.

Although many species once thought to be harmless are now known to be potentially harmful in certain conditions, it has been difficult to link skin infections to the use of cosmetics, although there have been reports in both the USA and Europe of eye infections caused by contaminated eye products (mainly mascaras) [5].

The trend of modern public opinion is to believe that 'chemical additives' are harmful to humans, so ever more companies are marketing '**natural products**', '**naturally preserved**' or even '**preservative-free**'. In actual fact, if the products so labelled comply with the present microbial regulations which will be described in this chapter they must contain an operating preservation system. Although some '**natural ingredients**' can kill microbes others can definitely encourage their growth. Also some '**active**' ingredients are themselves microbiocidal. However, many consumers are unaware of the dermatological risks which could arise from insufficiently preserved cosmetics [6].

In order to comply with standard regulations for microbial safety it is necessary to know the efficacy of the antimicrobial system throughout the development and lifetime of a product.

In the 1960s and 1970s various surveys showed that some cosmetic creams and lotions supported large numbers of organisms. In 1970 the Society of Cosmetic Chemists of Great Britain (now the Society of Cosmetic Scientists) formed a working party headed by N.J. Van Abbé and issued a monograph entitled 'The hygienic manufacture and preservation of toiletries and cosmetics' [7]. Later Voluntary Microbiological Guidelines were published in the USA by the Cosmetics, Toiletries and Fragrance Association (CTFA), independently in the UK by the Cosmetics, Toiletries and Perfumery Association (CTPA) and in Europe

by the Comité de Liaison Des Syndicats Européens de l'Industries de la Parfumerie et des Cosmetiques (COLIPA). These industrial organizations, together with the societies forming the International Federation of Societies of Cosmetic Chemists (IFSCC), helped in this way to maintain the excellent safety image of the industry and increased the confidence of the governing bodies and the public. By publicity, education by workshops and increased awareness through symposia and scientific and trade literature, legislation was warded off by the almost universal microbiological control of products according to the Guidelines adopted by companies.

However, the Cosmetic Directive was passed by the European Commission in 1976 and finally became law in the Member States. Various amendments were made to its Annexes in the next two decades but in 1993 the 6th Amendment completely changed, by regulation, the marketing of cosmetics [1]. This amendment under Article 7a introduces a new requirement for a Product Information Package (PIP) which, when asked for, must be available to the Regulatory Authorities for inspection. The required information includes microbiological specifications and reports of test results for the raw materials, the finished product and the microbiological control systems in product development, manufacture, storage and checks for consumer safety-in-use [8].

Although many companies were voluntarily following Good Manufacturing Practices (GMP) and Microbial Quality Management (MQM), the statutory regulations were introduced to ensure harmonization and good standards throughout the enlarged community. Microbial control throughout the development of a product and its manufacture, to its safety in use by the consumer, is inherent in the emphasis on GMP, and this includes MQM.

COLIPA published amended Guidelines under the title 'Cosmetic Product Information for the European Union' on Article 7a of the 6th amendment to the Cosmetic Directive, 1995 [8]: CTPA, *New Microbial Quality Management (MQM): Limits and Guidelines*, 1996 [9]. COLIPA issued amended Guidelines on Microbial Quality Management (MQM) in 1997 [10].

All the Guidelines for MQM suggested maximum microbial limits (see Table 21.5). Although these limits are not mandatory they are a useful standard, and it is necessary to determine whether growth increases, stays the same or decreases; and because organisms can recover with time, and growth can restart, checks are carried out over months and a comprehensive dossier built up of the effectiveness of the preservation system.

The standard can be accomplished in the following ways; by:

(i) Challenge testing products with selected organisms at the formulation stage to assess the efficiency of the preservative system of the product in its final packaging; including consumer trials which will check the long-term efficacy of the preservation under repeated contamination by the consumer.
(ii) Buying guaranteed 'clean' raw materials, stored in sealed containers in clean warehouses.

(iii) Adopting good hygiene in manufacture, filling and storage.
(iv) Carrying out routine testing on all raw materials including water for processing and cleaning.
(v) Routine testing periodically at all stages of manufacture and storage of product, equipment and environment and in all factory areas; including applying the concept of Hazard Analysis Critical Control Point (HACCP) [11] (see Section 21.3).
(vi) Accumulating knowledge of the product's behaviour under repeated contamination in storage and during consumer use to assess the activity of the preservative system.

The results of all these tests should be assessed by a qualified microbiologist to be passed or rejected according to the limits set.

As part of the Product Information Package (PIP), the recorded results of the above tests for each product should form complete microbiological documents available when asked for by Regulatory Bodies. The PIP must be kept for inspection at the address of the company where the product was manufactured and which appears on the retail label of the product, underlined if there is more than one address (see Chapter 20).

'Companies may continue to apply their own internal control specifications and validated test methods, together with an appropriate level of MQM, to satisfy themselves that they produce products which comply with the criteria specified in this document when tested by the methods detailed' [10].

The report of the tests should cover:

(a) Identification of the samples: (i) product type, (ii) brand name, (iii) manufacturer, (iv) batch number, (v) date and place of sampling, (vi) identification methods and storage conditions.
(b) The test conditions: (i) date, (ii) technique, (iii) neutralization medium.
(c) The test results.

The report should have a conclusion and identify the person responsible for testing [10].

The worker in cosmetic research and development, quality control, and in factories or warehouses should have some knowledge of the basic principles of microbiological methods to be a useful member of a team which understands and maintains microbial control throughout all operations. The authority for maintaining standards should be in the hands of a qualified microbiologist with suitable technical staff operating in well-organized microbiological laboratories. Many companies undertake this as an in-house arrangement. Some find it convenient, and maybe safer, to use the services and experience of an outside consultant; others limit their microbiological work to routine monitoring of processing rooms, equipment, operations, and raw materials, including air and

water, and the testing of factory products, but have all challenge testing carried out by a consultant. In the latter case the company's staff do not need to handle live, virulent organisms, which could introduce contamination to susceptible products and the factory and be difficult to eradicate. This arrangement is allowed under the 6th amendment to the Directive.

Whichever arrangement is followed it must be stressed that the microbiologist's authority to pass or reject samples must be respected and management must realize that testing takes time. Accelerated tests are available and are useful as screening tests but they may have disadvantages. They need accurate calibration and must be validated by the standard plate count methods. Computerized electronic methods can measure impedance, conductance or capacity of low numbers of organisms and the time to detection is reduced to hours instead of days.

21.2 BASIC MICROBIOLOGY AND MICROBIOLOGICAL TECHNIQUES

Figure 21.2 shows the types of microorganisms in existence. The difference between these groups is mainly in cell structure. The eukaryotes are more evolved than the prokaryotes, with a complex cell structure including a nucleolus and a nuclear membrane. All cells have nuclei which carry the 1000 or more genes of the cell which duplicate before cell division, and all cell activity is catalysed by enzymes.

Organisms are classified, morphologically, by their size, shape and motility; their staining characteristics: flagella stain, (position, number); spore stain, (position, number); and their capsules, cell inclusions, and pigments. They are classified into orders, suborders, families, and subfamilies. The classification of

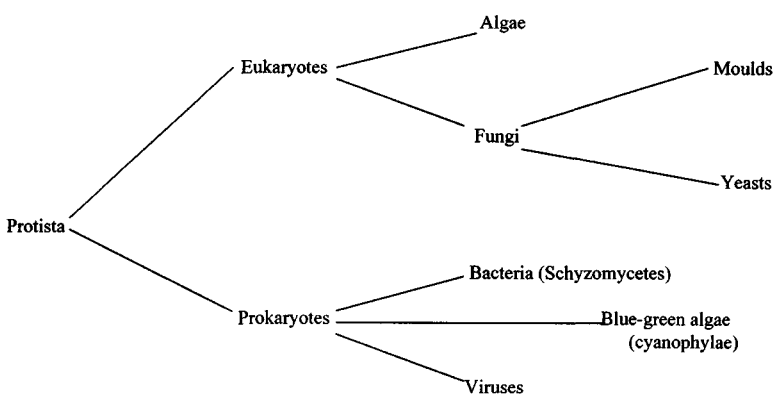

Fig. 21.2 Types of microorganisms.

bacteria is different from that of the higher organisms because, as there is no fossil evidence, no evolutionary system is possible and so the basic units are categorized into groups of similarity of the above properties. Of the two names given to known organisms the first denotes the genus (subfamily) and the second the species.

21.2.1 Viruses

Viruses propagate only inside living cells and are therefore obligate intracellular parasites. They were discovered in 1892 by Iwanowski because they could pass through filters used to retain bacteria. Progress on knowledge of their behaviour was slow because it was not realized that they were parasitic and it was impossible to grow them in microbiological media. They cannot grow in a cosmetic substrate but when bacteriophages (viruses which infect bacteria) are detected, contamination by bacteria is proved.

21.2.2 Bacteria

There are more than 1600 known species of bacteria and they are given the general name of schyzomycetes. They are very variable in shape and of a size between 1 and 3 μm (micrometres). They consist of single cells with cell walls of unique composition; they enable the bacteria, which are in a state of high osmotic pressure, to remain intact in water, where the osmotic pressure is low. Bacteria contain a nucleus which does not have a distinct membrane surrounding it and is known as the 'nuclear apparatus'. Useful tests used to classify bacteria are:

1. Gram's stain;
2. the classification of their differing requirements for oxygen;
3. their shape:
   (a) spherical – *coccus*
   (b) rodlike – *bacillus*
   (c) spiral – *spirillium, spirochaete*
   (d) comma-shaped – *vibrio*
   (e) filamentous – fungal-like.

Numerous variations can occur. Many are motile bearing flagellae, some possess an outer capsule, others a slimy covering to the cell wall, and some produce resistant spores.

(a) Gram's stain [12]

In 1884 a Dutchman named Christian Gram, while investigating methods of staining bacteria, discovered a method of differentiating some of them because of their different behaviour with certain dyes.

A dry bacterial smear is formed on a microscope slide. Gentian Violet in alkaline solution is used to stain the preparation for 1 min, then Gram's iodide (iodine in potassium iodide) is added as mordant for the colour. After a further 1 min the slide is washed with ethanol until the washings are a pale purple, and then washed with tap water. At this stage the Gram-positive bacteria retain violet dye and the Gram-negative bacteria are decolorized. Carbol fuchsin or Safranin is added and after 5–10 s the slide is washed gently with tap water and then gently blow-dried. When examined under a microscope using oil immersion, purple-blue cells denote Gram-positive bacteria; pink cells denote Gram-negative bacteria.

It is thought that the mucopeptides of the walls of Gram-positive cells occur in thick continuous sheets, retaining the dye, whereas they are present in thin layers in the walls of the Gram-negative organisms, allowing the dye to be washed out easily. The reaction is lost by old, mechanically damaged Gram-positive bacterial cells or those treated with lysozyme so that the test is of diagnostic value only with young cultures. The ability to retain the stain is confined almost entirely to yeasts and some bacteria (moulds stain irregularly).

(b) Differential use of oxygen

1. *Aerobic organisms* (aerobes) use and absorb atmospheric oxygen, and those that cannot do either are called anaerobes. *Mesophilic aerobes*, which grow best at 20–55°C, are the microorganisms assessed in the total plate count (TPC).
2. *Obligate aerobes* are strictly aerobic and cannot grow without oxygen.
3. *Microaerophilic organisms* require very little oxygen.
4. *Anaerobes*. Strict anaerobes cannot survive in the presence of oxygen, but some species can adapt and slowly survive and multiply in the presence of oxygen; these are known as:
5. *Facultative anaerobes*.

21.2.3 Fungi

(a) Moulds

Moulds are filamentous fungi widely distributed in soil and water. They can be white, yellow, green, blue, pink, lilac, brown or black, according to their spore colour; the mycelium itself is colourless. They reproduce either by budding, by sexual means or by spore formation. The long filaments, which can be branched or unbranched, are called hyphae. Some hyphae burrow into the substrate and others produce stalks bearing sporing heads. The heads drop their spores, which germinate if they fall on a moist surface and form a velvety mass. This effect can be seen on the surface of creams in pots or on the cardboard lining of lids,

where condensation can enable any spore present to grow. This occurs because of ineffective or insufficient preservative, contaminated raw materials or packaging, or bad hygiene in production. Some moulds can grow in slightly alkaline or neutral conditions but most prefer an acid environment of pH 4.5–5.5. The fungicide chosen for the product should be active in that region. Fungi grow best at 28–30°C and test samples should be maintained at this temperature and incubated for 7 days.

(b) Yeasts

Yeasts are unicellular fungi with yellow, pink, red, green or black pigments, averaging 5 μm in diameter. They reproduce by budding, fission or ascospore formation. They cannot manufacture their own food but obtain energy from oxidative dissimilation or anaerobic fermentation. They grow best on any medium containing fermentable sugar over a pH range of 2.2–8.0, although most flourish in acid conditions at temperatures of 17–20°C and need oxygen to grow.

21.2.4 Requirements for growth of microorganisms and type culture media

No organisms can grow without relatively high levels of available water but many have stages in their life cycle when spores or cysts are formed, which enable them to survive long periods of desiccation. The water requirements for survival or growth of microorganisms are expressed as water activity, a_w, i.e. equal to one-hundredth part of the corresponding relative humidity. The requirement can also be related to the osmotic pressure and absolute temperature. The minimum values of a_w of classes of microorganisms have been published and the characteristic optimum and range of values are known for different species. Reducing the available water below the optimum would cause stress; it also increases the lag phase and decreases the rate of growth [13].

All organisms require carbon for growth and those which can use carbon dioxide gas or the bicarbonate ion, solely, are called autotrophs; those which require organic carbon as a source are called heterotrophs. Recent research indicates that it is possible that carbon dioxide is required universally, even though in very small amounts.

Nitrogen is also an element in metabolism. Some bacteria can fix nitrogen gas. *Azobacter* spp. and *Clostridia* spp., together with the symbiotic organism *Rhyzobium* spp., are the best known, although this ability to fix the gas has been found to be more widespread than previously thought. Ammonium salts are most favoured, with nitrates less readily used. Some bacteria grow better in the presence of amino acids, proteins or protein hydrolysates, a point to be remembered when formulating products using nitrogen-rich organic compounds as cosmetic ingredients.

Phosphorus, potassium, sulfur, magnesium, calcium, iron and sodium are usually required at fairly high concentration (10^{-3}–10^{-8} M); manganese, copper, cobalt, zinc or molybdenum at 10^{-6}–10^{-8} M. Metal-sequestering agents are useful biocides.

In addition to an adequate supply of nutrients and the correct environment for any specific organism other factors influencing growth are pH, temperature, osmotic pressure, surface tension and oxygen tension. The reactions for growth in the cell are catalysed by enzymes. Vitamins act as coenzymes, and while some organisms can synthesize them, all thrive better if they are supplied externally. Inositol and folic acid are also growth factors required by some. Enriched media, both solid and liquid, prepared with the needs of specific organisms in mind, are used to develop growth of small numbers of microorganisms so that the colonies they form are visible to the naked eye and can be counted. **Type culture media** are formulated so that each element is present in the correct amount for specific organisms and is available in a form which can be taken up by them [14].

21.2.5 Preparation of an inoculum [15]

Type cultures can be bought from specialist laboratories to be used in research (Appendix A). They consist of single named pure species. Suspensions of organisms of known colony-forming units (c.f.u.) per gram or ml (c.f.u. g^{-1} or ml^{-1}) can be prepared from the pure cultures and used for inoculation. By the controlled inoculation of cosmetic samples the preservative system can be assessed. This is known as challenge testing and will be discussed below.

(a) Bacteria and yeasts

One colony of bacteria from each type culture is transferred to 10 ml of tryptone soya broth and one colony of yeast is transferred to 10 ml of Sabouraud dextrose broth and incubated at 28°C for 24 h in a shaking incubator; 2 ml of the resultant growth in each is then transferred to 200 ml of a similar broth and incubated for 24 h at 28°C. After incubation the broths are centrifuged at 4000 r.p.m. for 10 min, the supernatant liquid is decanted and 100 ml of sterile distilled water added to the pellet resuspended by mixing. The centrifugation and washing procedure is repeated and the final pellet is resuspended in 100 ml of sterile distilled water. This gives a final concentration of 10^8–10^9 c.f.u. ml^{-1}. These can be stored in a refrigerator and used for up to 1 week and then discarded. If not used promptly they can be monitored by the plate count method using serial dilution.

For each organism two agar slopes are made so that further inocula can be prepared. Here the organism is grown in an incubation tube using the same nutrient media in solid form set with the tube at an angle so that a 'slope' is formed.

Serial dilution [16] is used to facilitate the counting of colonies formed and can be used to determine the amount of inoculum to take to give the required number of organisms per g or ml of sample to be tested. One millilitre of the inoculum is added to 9 ml of diluent; 1 ml of this is further diluted in 9 ml of diluent. This serial dilution by a factor of 10 is repeated until a solution of 10^{-6} of the original concentration is achieved; 0.1 ml of the 10^{-6} solution is mixed thoroughly with 10–15 ml of a molten sterile agar medium corresponding to the broth used for the initial cultivation, and poured into a sterile Petri dish at 45°C, covered and incubated for a minimum of 24 h.

Each organism becomes separated and forms a colony, and the total colonies can be counted. Each plate count represents one-tenth of that of the previous dilution so that the initial c.f.u. ml^{-1} in the broth can be calculated. For challenge tests using bacteria a concentration of 10^6–10^7 c.f.u. ml^{-1} is added for each g or ml of sample under test; for yeasts and moulds a concentration of 10^5 c.f.u. g^{-1} or ml^{-1} is used.

(b) Moulds [15]

Using a sterile needle some of the spores from one colony are transferred into 0.1% peptone water + 20% Tween 80 and, after whirlymixing, 0.1 ml aliquots are spread onto the surface of prepared Sabouraud dextrose agar plates. These plates are incubated until good mould growth is observed. The spores are harvested by pouring 5 ml of 1% Tween solution onto the surface of the agar to wet the spores and aid in their removal by pipetting up the freed spores using the tip of the pipette to loosen spores from the surface of the colonies. Care is taken not to remove any agar into the inoculum. Counts of 10^8 can be obtained.

A Petri dish containing a solid medium is known as a 'plate'; and the resulting colony count as a **total plate count** (TPC). A pure culture in **peptone water** forms a suitable inoculum for fermentation tubes and other diagnostic tests. The peptone water can be used as a growth medium and also used as a diluent to prepare raw materials and cosmetic samples for microbial testing. Used in this connection it is mixed with suitable preservative inactivators (p. 676).

21.2.6 Sterilization

Sterilization is an absolute term indicating the complete destruction or removal of all microorganisms including the most resistant bacterial spores. It is imperative to practise these techniques in laboratories where the isolation, identification and use of virile test or contaminating organisms are studied, and wherever samples for routine testing are taken.

(a) Moist heat

Autoclaving is the application of steam heat for 15–20 min. It is useful for culture media, glassware, distilled water and instruments not affected by this

method. At a pressure of 10 Pa (15 lb in^{-2}) water boils at 121°C and both spores and vegetative organisms are destroyed. The temperature of 121°C will not be reached if air is mixed with the steam. A preliminary evacuation of the autoclave before the steam is passed in will achieve this, and evacuation after sterilization will dry the equipment which must *not* be left moist to allow for random contamination [7].

Media containing some carbohydrates or milk should be autoclaved at 3 Pa (5 lb in^{-2}) for 30 min.

For media containing gelatin or other materials which will not withstand normal autoclaving, steam heat at 100°C for 20 min on each of three successive days is necessary. Each day the samples must be incubated. The first day of treatment destroys the vegetative cells; any survivors and spores will remain and grow and germinate in the medium but will be killed on the second day. Any further spores will germinate and these vegetative spores will be killed on the third day.

(b) Dry heat

Some materials such as cotton wool and paper can be sterilized in a hot-air oven, thermostatically controlled, and maintained at 180°C for 1 h. All open-ended apparatus should be plugged with cotton wool to prevent aerial contamination before sterilization and plugged again immediately after use. Heating to 140°C for 3 h may be used in some cases. Dry heat kills by oxidation; a lower power of penetration necessitates the higher temperatures and longer duration than with moist heat.

In the past platinum loops, rods, glass pipettes or other metal or glass means of transferring cultures of organisms from one vessel to another were used and sterilized by passing through a Bunsen flame before and after use. Metal was heated to a dull red heat and glass until the flame just turned yellow. Such apparatus had to be allowed to cool before touching the organism, sample or media, otherwise residual heat would have destroyed the organisms present.

(c) Modern use of sterile disposable consumables

However, today, because of the danger of transmitting the pathogens responsible for new incurable diseases, which it is believed are not completely destroyed at very high temperatures, **sterile disposable consumables** are used (see 'Hygiene', below) and supplied by a number of companies who specialize in the production of sterilized plastic forms of equipment for microbiological laboratories (Appendix B).

Prepared sterilized agar 'plates' can be purchased which are useful for on-site routine testing of floors, benches and other equipment to identify aerial contamination, and for testing swab samples taken from odd corners and parts of process equipment.

(d) Membrane filtration

Vegetating organisms and spores may be physically removed from liquids by filtration. This is useful for culture media, enzyme preparations, water and solutions of antibiotics. Several types of filter are available and all are used over slight negative pressure achieved by means of a vacuum pump. They must be changed frequently or sanitized with water containing 200 ppm of chlorine, or 2% formalin with a final flushing with sterile water which should be tested for sterility.

(e) Hygiene in the microbiological laboratory

After contact with microorganisms every piece of disposable equipment, including used Petri dishes containing discarded media, must be disinfected, e.g. with 2% phenol, before being destroyed.

This is not only because some of those present might be pathogenic but because, if this is not a standard procedure, the laboratory environment will become contaminated.

Further aseptic precautions to take are as follows:

1. The external neck of the receiver, when samples are taken, should be wiped with ethanol; for example, batch samples.
2. Disposable plastic gloves should be used once only when testing samples.
3. Distilled, freshly sterilized water must be used in preparing media and whenever water is called for in a test.

Sterilization and sanitation during processing and in the factory will be discussed later.

21.3 PREVENTION OF MICROBIAL GROWTH IN COSMETICS

When the ubiquitous nature and vast variation of types of microorganisms are considered the task of preparing safe and stable cosmetics may seem daunting and impossible. It might be thought that, like many pharmaceuticals, they should be sterile; but this is costly and unnecessary since, once the cap is removed from a multidose pack, contamination can occur. However, with the knowledge gained from published research, specific to cosmetic microbiology, the help given by the Guidelines mentioned above, and the 6th Amendment to the EU Directive in 1993 ensuring that companies have available the complete microbial history of each cosmetic, products can be and are produced which, if not self-sterilizing, support the growth of very few organisms, even during normal consumer use. Table 21.1 and Sections 21.3.1–21.3.7 outline the steps required to formulate and manufacture a product which complies with the microbial limits set in the EU and the USA. The concept of 'Hurdle Technology' has been in use in the food industry since the 1970s to control microbial growth

in food and is now used in the cosmetic industry. Since the aim is to retard growth in products, remove organisms from the environment and sell products which are safe-in-use, these steps can be likened to this technology. As each *'hurdle'* is tackled there is more likelihood of marketing a mild product containing a minimum amount of preservative.

The recommended microbial limits at point of sale suggested in the CTPA MQM Guidelines are as follows (Table 21.5):

1. Products intended for general use: total viable count (aerobic bacteria, yeasts and moulds) less than 1000 c.f.u. g^{-1} or ml^{-1}.
2. Products intended for specific use in the eye area and those recommended for use on babies: total viable count (aerobic bacteria, yeasts and moulds) less than 100 c.f.u. g^{-1} or ml^{-1}.

In order to comply with these it is recommended that in-house warning limits at levels ten times lower should be set; i.e. 100 and 10 c.f.u. g^{-1} or ml^{-1}, respectively.

3. Harmful organisms should not be detected when testing with the requisite specialist techniques.

During manufacture for Good Manufacturing Practice it is suggested that vulnerable places for contamination should be considered as 'hazardous', marked as points for testing, and extra care taken to study the results; i.e. susceptible inlets in machinery, addition of deionized or distilled water or aqueous solutions of raw materials. This concept is known as the Hazards Analysis Critical Control Point (HACCP) [11].

21.3.1 Planning product formulation and development

Point number 1 in Table 21.1 outlines the steps required to plan the formulation and development of a product which complies with the microbial limits. The more that is known of the behaviour of the product at this stage when contaminated at any stage of its life-span (i.e. if it can be shown that the growth of organisms is slowed to the limits), the greater is the confidence in its safe development, production and marketing when supported by GMPs. This knowledge is gained by extensive microbial research at the development stage.

(a) Planning the formulation

(i) Type of product. The physical form of the product, from aqueous liquids to anhydrous compacts, is one of the first considerations, because every formulation offers a different environment for organisms. Formulations which limit the availability of water for microbes help to inhibit their growth, because the most vulnerable products for high levels of contamination are aqueous liquids, unless the pH approaches the upper limit, the osmotic pressure is high, there are solutes

Table 21.1 Outline of steps in formulating and manufacturing a product within safe microbial limits

1. Product formulation and development
   (a) Planning the formulation
      (i) product type
      (ii) raw materials
      (iii) choice of preservatives
      (iv) antimicrobial methods of manufacture during development
      (v) packaging
   (b) Challenge testing for long-term preservative efficacy
      (i) preliminary challenge tests for choice of preservatives
      (ii) repeat tests for changed formulations
      (iii) challenge tests on finished product
   (c) Preservative assessment in consumer panel trials
2. Prevention of contamination during manufacture
   (a) Raw material testing for purchase, in storage and use
   (b) Planned production area
   (c) Good factory hygiene
   (d) Good in-process hygiene/sanitization
3. Laboratory control methods
   (a) Ingredients, and water testing
   (b) Sampling with no enviromental contamination
   (c) Finished product testing
      (i) preparation of sample
      (ii) dilution methods
      (iii) preservative inactivation
      (iv) total viable counts
   (d) Assessment of TVCs
   (e) Tests for effective sanitization/'cleaning'
4. Responsibilities of the microbiological laboratory
5. Microbial records for the Product Information Package

such as salts, polyols, etc. or a substance with an inhibitory effect on growth is present. Ethanol is a good microbicide at concentrations above 20% so that alcoholic lotions packed in containers which do not allow evaporation are usually well preserved. Oil-in-water emulsions are more susceptible than water-in-oil emulsions, while compacts and powders rarely support growth. If the surface of a compact is slightly damp and uneven then fungi might be found growing in the hollows.

(ii) Choice of raw materials. If the raw materials are of natural origin there is a possibility that they will be heavily contaminated; suspect ingredients are talc [7], bentonite, kaolin, pigments and natural gums. Others supply abundant nutrients which will make the product more favourable for microbial growth and

their presence will add to the problems of preservation, particularly in aqueous formulations. Such substances include herbal extracts, egg, starches, animal and human derivatives, vitamins, enzymes and some synthetic organic compounds. Suppliers should be found who offer products well packed in protective containers with a specification of low or nil microbial content when delivered.

(iii) Choice of preservatives. Much research work has been published on the effectiveness, safety and stability of preservatives in different types of products. As of April 1997, there were 51 preservatives allowed on the Positive list with their acceptable levels of use and three on the Provisional list in Annex VI of the EC Cosmetics Directive. The *CTFA Ingredient Dictionary* includes preservatives and in Japan the Ministry of Health and Welfare (MHW) lists permitted ingredients and concentrations allowed for use. Most are widely used in cosmetics and are well researched for safety. Some of them cover a wide spectrum while others are more specific.

For example, hexachlorophane is active against the Gram-positive *Staphylococcus* spp. but less so against Gram-negative spp.; it is thought that its use alone in surgical scrubs suppressed *Staphylococcus* spp., and this allowed the spread of infections in hospitals caused by the pathogen *Pseudomonas aeruginosa*, which could flourish in the preparations [17]. Triclosan suffers the same *Pseudomonas* 'gap' [18]. Nevertheless it is used extensively in cosmetics because it also has anti-inflammatory properties. Research has shown that it reduces the redness of the skin in acne and other skin disorders. However, because of the 'gap' it must be combined with other preservatives.

A mixture of methyl, ethyl, propyl and butyl *p*-hydroxybenzoates is effective against a wide range of fungi and some bacteria since their different solubilities enable them to be well distributed between the various phases in an emulsion. Their different partition coefficients and solubilities prevent the methyl ester from diffusion from the water phase to the oil phase. The presence of propyl ester in the oil phase will tend to stabilize the distribution between the phases. They are, however, among those which suffer some inactivation in the presence of some nonionic surfactants, and can prove weak in some modern formulations. In certain conditions, i.e. concentration of preservative and minimum critical micelle formation, some can be effective.

Sorbic acid is a good fungicide and is not so affected by nonionic emulsifiers [19]. Dehydroacetic acid, although a good fungicide, is not very water-soluble; however, it exerts a synergistic effect if used with sorbic acid, i.e. each chemical can be used in a lower concentration to give an effect greater than if each were used alone. Thus 0.1% sorbic acid with 0.03% dehydroacetic acid dissolved in 2% propylene glycol can be an effective fungicide in a wide range of creams and lotions. The humectant propylene glycol also contributes to the effectiveness apart from its solubilizing property, so will increase the availability of the water present. Challenge tests might show that this combination would need

further specific preservatives against Gram-positive and Gram-negative bacteria. It is possible that, by using a combination covering the main groups of organisms rather than one wide-spectrum chemical, lower quantities of each preservative can be used. This might be especially helpful when an abundance of susceptible ingredients are included such as protein hydrolysates and vegetable oils.

Iodopropynyl butylcarbamate (IPBC) is a fungicide which has gained increasing use in personal-care products. Elder *et al.* [20] report that the Cosmetic Ingredient Review (CIR) accepted it as safe in cosmetics but not in aerosols, in concentrations up to 0.1%, on 20 September 1996, and it is included in the EU list of permissible preservatives and in Asia at the same concentration. They describe a patent consisting of a modern synergistic blend of diazolidinyl urea (DU) with IPBC in the ratio of 100:1 of DU to IPBC which can be used in concentrations ranging from 0.5% to 2.5%.

Gruening, in an article entitled 'As much as necessary, as little as possible', lists the minimum inhibitory concentration (MIC) in ppm of selected preservatives against specific organisms. For instance, the combination methylisothioazolinone and methylchlorisothioazolinone (MI/MCI) requires 9 ppm against *Aspergillus niger* whereas Bronopol requires 3200 ppm against the same organism but IBPC only needs 1ppm. However, the latter preservative alone is not so efficacious against *Pseudomonas aeruginosa* in comparison with MC/MCI at 250:1 ppm [21].

The preservative system should be safe in use, stable at the pH of the product, possess a partition coefficient to give an effective concentration in the aqueous phase of the product, and be compatible with the cosmetic's ingredients, i.e. have no deleterious chemical effect as long as the product lasts. The methods used to decide on the most efficient, safest, most long-lasting of preservatives in the best combination and minimum concentration needed in any product, will be outlined in Section 21.3.2.

(iv) Antimicrobial methods of manufacture during development. The method of manufacture should be exactly as is intended for the subsequent factory process. It should be monitored accurately for each formulation.

In processes designed to reduce contamination by heating the ingredients, the water phase can be boiled for 30 min and made up for evaporation before the rest of the ingredients for that phase are added; and the heat maintained for 10–15 min at 85–90°C on the oil phase in a steamjacketed, stainless-steel pan. Materials which are degraded at this heat can be added at the temperature of emulsification, or sterilized and added when the batch is cooler.

For products made without heat, all ingredients should be tested microbiologically before use and action taken before mixing if contamination is detected (see Table 21.1, item 2a). The process water should be boiled for 30 min, cooled and sterile water added to make up for evaporation. This prepared water should be used immediately; stored water easily becomes contaminated. Any process

which is likely to remove microorganisms or prevent their growth should be used; i.e. filtration through a fine filter, closed-circuit manufacture as far as possible in scrupulously clean machinery, refrigeration, centrifugation, etc.

(v) Packaging. Glass bottles, by reason of their manufacture, are usually sterile when delivered but can be tested by washing a number of them, depending on size (six 500 g bottles) with sterile water and plating out samples to recover any contamination. If a wide-necked plastic jar is used whose lid has a coated cardboard liner then an inner plastic or metal shield should be used to cover the surface of the cream. If this is not done the cardboard disc can allow mould to grow if condensation occurs with changes of temperature during the lifespan of the product.

Brannan [22] discusses the role of packaging in preservation and in preventing microbial contamination. He shows how improved closures for liquid containers can protect the product from contamination during consumer use and possibly allow the use of a lower concentration of preservative.

The pack should be used in all final challenge tests.

21.3.2 Methods of predicting long-term preservative efficacy (challenge testing)

Biocides act by interrupting the chemical pathways within the cell, and can be assessed by their effectiveness at preventing growth of a virile inoculum added to products under controlled conditions, i.e. challenge testing. These conditions can be varied to suit microbiologists but are carried out extensively at the development stage of a formulation and whenever an existing product is modified. By this means the capacity of the formulation to support microbial growth under ideal conditions for growth is determined, and thus the efficiency of the preservative system which causes the numbers of organisms to decline. If the initial inoculum increases or remains static then the product is inadequately preserved. If it decreases too quickly then the concentration of preservatives may be unnecessarily high; longer incubation might show whether any weak organisms can recover [23].

Initial microbiological challenge tests

These tests compare the type, and determine the minimum effective concentration, of a single antimicrobial or a combination of two or more needed for preservation. Such preliminary tests should be undertaken at an early stage in development to save time and effort should stability not be maintained with early formulations, and so that possible reaction between preservative and product can be detected. A change in pH or colour might occur if preservation is inadequate. There are many variations on the methods adopted and these are found in books and journals of the cosmetic industry.

The first step in any procedure is to choose the organisms for the preliminary challenge tests. The pure type cultures in Table 21.2 are considered

non-pathogenic, though it is as well to remember that microorganisms are unpredictable and strict hygiene principles should be followed at all times.

1. Quick challenge test (Fig. 21.3)

This is a quick challenge with bacteria and fungi for growth inhibition using the pure type cultures of Table 21.2. (It can be used for creams, gels and viscous lotions and similar aqueous products.)

(a) Preparation of product samples:
  (i) make up control products with no preservative;
  (ii) make up samples with different preservatives, different combinations and concentrations; such tests give early results for an indication of the most likely system;

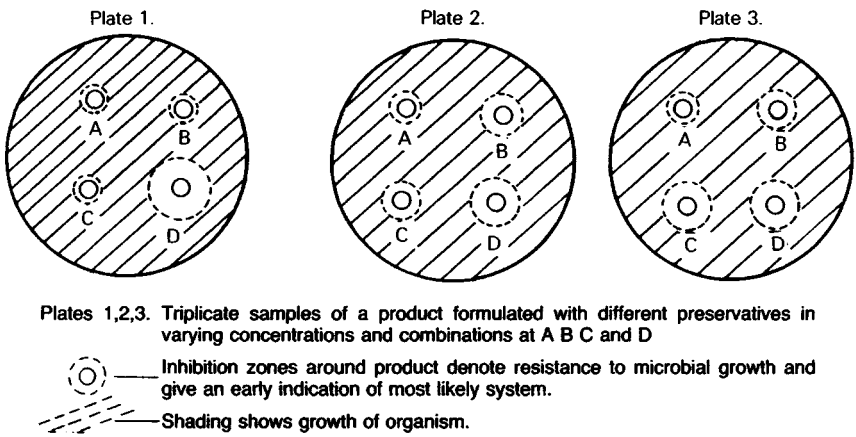

Fig. 21.3 Quick challenge test.

Table 21.2 Pure type cultures considered non-pathogenic

	Organism	*Plating media*
Gram-positive	*Staphylococcus albus*	Tryptone soya agar (TSA)
	Bacillus subtilis (spore-bearing)	Tryptone soya agar (TSA)
Gram-negative	*Pseudomonas fluorescens*	Tryptone soya agar (TSA)
	Escherichia coli	MacConkey agar no. 2
Mould	*Aspergillus niger*	Sabouraud agar
Yeast	*Saccharomyces cerevisiae*	Malt extract agar (MEA)
Organisms isolated from contaminated product		Suitable [7]

(iii) store all samples at 4°C for 48 h to allow the preservative to stabilize in the product; observation of any changes in appearance of these samples will give an indication of the chemical and physical compatibility of the preservative system (compare with (a.i) for any change and difference).

(b) Bacteria and yeasts – preparation of inocula:

(i) Prepare and sterilize three tubes of nutrient broth and one of MacConkey's broth. Inoculate each tube with a loopful of a single bacterial type culture, reserving the MacConkey's broth for the *Escherichia* coli. Incubate for 2 days at 35°C.

(ii) Prepare sterilized, cooled (45°C), but still molten solid media, TSA, MacConkey's and MEA.

(iii) Inoculate 25 ml of each molten agar with 0.25 ml of each broth culture of spore suspension from (b.i). Pour 25 ml plates in triplicate.

(iv) When set, cut wells in the agar on triplicate plates with a flamed No. 7 cork borer. Apply product to be challenged in the resultant holes.

(v) Store the plates at 4°C for 24 h to allow any preservatives to permeate the surrounding agar while inhibiting growth.

(vi) Incubate the bacterial plates at 35°C and the yeasts and moulds at 25°C for 1 week.

(vii) Inhibition zones around product denote resistance to microbial growth (Fig. 21.3). The disadvantage of this method is that it depends on the penetration of the preservatives into the agar and also a preservative such as formalin evaporates and is lost.

(c) Moulds – preparation of inocula. Harvest the spores in 5 ml Ringer's solution/Tween 80 and use this spore suspension immediately; 0.25 ml of the spore preparation is added to the surface of 25 g of cream in a jar and the lidded jar incubated at 25°C. After 1 week to 1 month, growth will be apparent if the preservatives are unsatisfactory.

The quick challenge test gives a rough indication of the physical and chemical compatibility of the added preservatives and the smallest quantity of the best combination for the subsequent challenge trials of the finished pack.

2. *Conventional plate count procedures for preliminary and final challenge tests on the finished product in its final pack*

During development the non-pathogenic organisms and specific media of Table 21.2 can be used in the pour plate procedures. When using the test organisms of Table 21.3 usually required by standardizing authorities, tests should be carried out by a qualified microbiologist.

Under specialist conditions and techniques a minimum of five pure culture organisms are used as inocula on samples of the product. Some companies also test with resistant strains found in the factory. In addition some microbiologists

Table 21.3 Species used in challenge tests

Gram-negative	– *Pseudomonas aeruginosa*[*]	ATCC 9027
	– *Escherichia coli*[†]	ATCC 8739
	– *Staphylococcus aureus*[*]	ATCC 6538
	– *Candida albicans*[*]	ATCC 10231
	– *Aspergillus niger*[*]	ATCC 16404

[*] Considered to be harmful to man, i.e. pathogens. Should be handled by a qualified microbiologist in specialist laboratories away from the factory producing products for marketing.
[†] An organism indicative of faecal contamination.

test with a 'cocktail' of organisms, the theory being that the 'fittest will survive', and show the one most difficult to suppress in the opinion that the extra tests are an additional safeguard; but others consider that the house organisms could become resistant to the product preservatives and it is better to consider stringent factory hygiene which should prevent their development anyway. These tests must be satisfactorily passed by the named qualified person and reported in the PIP before marketing takes place. The general procedures are as follows:

1. Bacteria
   (a) Prepare nutrient broth cultures of the challenge organisms, and from them suspensions in sterile distilled water (Section 21.2.5, Preparation of an inoculum).
   (b) Add aseptically in the proportions of 0.25 ml of each suspension in 25 g of product sample in its final pack (i.e. for a 100 ml shampoo pack, 1 ml in 100 ml of product). The original numbers being 10^{8-9} c.f.u. ml^{-1} or g^{-1}, now become 10^{6-7} c.f.u. ml^{-1} or g^{-1}. For each challenge organism inoculate samples including an unpreserved sample as control in triplicate. *Note*: not more than one type of organism per sample. Validation of the number of viable organisms is made immediately after inoculation, carried out by standard methods of counting (serial dilution and plate counts, Section 21.2.5).
   (c) Incubate for 24 h one set of inoculated samples for each challenge organism; one at 22°C, another at 32°C, and another at 36°C.
   (d) One millilitre or gram of each is aseptically transferred to 8 ml of nutrient broth and 1% Tween 80 and thoroughly mixed.
   (e) An immediate count of viable organisms is made by aseptically adding 1 ml aliquots of each sample to 9 ml plate count agar and 0.1% Tween 80, incubated, and colonies counted. The 1 ml aliquots are serially diluted, usually 1:10 and 1:100, plated and incubated to facilitate counting any organisms that may be present.
   (f) Estimations of viable counts are made on the samples from (c) and are repeated each week for 4 weeks or longer if time is available. Some

organisms originally fall in numbers and are undetected and then recover to large numbers. Tests concluded in too short a time give a false claim for the efficacy of the preservative system [23]. The broth from (d), especially when testing emulsions, may become cloudy, making it difficult to distinguish the colonies for counting when plating. One helpful method is to prepare duplicate samples and store in the refrigerator at 4°C to inhibit growth so that the number of colonies can be compared with the incubated samples. Another method is to flood the surface of the agar with a fresh 0.1% aqueous solution of resazurin, drain off the excess and allow 15 min for penetration into the agar. True colonies turn pink. The count must be made within 1 h. The use of a 0.45 μm membrane filter followed by measured amounts of sterilized wash fluid may be helpful for dilutions in some cases. These suggestions are given in CTPA's MQM publication [9].

(g) The number of times that inoculated samples are taken can be more frequent (24 h, 2 days, 7 days, 14 days, 21 days, 28 days) and plate counts recorded of surviving viable organisms, which give information on how effective the preservative is. The extension to 28 days ensures that weak or injured organisms are not recovering.

2. Yeasts. The inoculation and plate count procedure is the same as for bacteria except that yeast counts are made from malt extract agar plates.
3. Moulds. Using a sterilized 2 mm loop, scatter the spores obtained by the method of preparation of the mould inoculum over the surface of the emulsion and incubate in a moist atmosphere (95–100% RH) at 25–28°C. Examine visually at regular intervals for evidence of mould growth. If no growth is visible, subcultures on malt extract broth and agar can be made to establish whether the inoculum has been inhibited or killed.
4. Record any changes in appearance of the inoculated samples to give an indication of the chemical and physical compatibility of the preservatives with the product.
5. Results. The preservative system is apparently effective if the viable bacteria are reduced to not more than 10^3 after 14 days, the concentration of yeasts and moulds remains static or decreases, and there is no change in numbers for the remainder of the 28 days.
6. To assess the long-term viability of the preservatives, TVCs are repeated on the samples after 6 months' storage at 20°C and 37°C and again after 1 year. The samples must still be within the microbial limits.
7. Repeat inoculations on samples which are satisfactory after 1 month indicate whether the preservative system is still active, and also give a useful indication of the results of repeated contamination during consumer use.

Note: The challenge tests should be done on all new or changed formulations:

(a) even though the product is anhydrous or the ratio of solid/water is high or;

(b) it is to be manufactured in a continuous process with heat;
(c) it is packed in a tube and protected from air contamination;
(d) it contains therapeutic additives which are antimicrobial (many of the therapeutic agents may be specific in their activity and allow the growth of other types of organisms).

3. *Some rapid screening methods for preservative efficacy*

The standard methods recommended by the different Guidelines in the different countries and in their Pharmacopoeia use the same inoculating organisms and aerobic plate counts (APCs) to assess the results; but a disadvantage of them all is the length of time they take. If repeat formulations are necessary the tests could take months to complete.

Therefore over the past decade scientists have been working on speedier methods for preliminary investigations of preservative efficacy, though the standard plate count methods must be used to validate them and appear in the records.

Morris [15] has described the **repeat challenge test** which has been used successfully to predict the susceptibility of a number of product types to microbial contamination, and to test the activity of the preservatives under repeated contamination. The test samples are inoculated daily with selected strains of organisms which are then incubated at 28°C. Total viable counts (TVCs) are made on 1 ml/g of the samples each day. The end-point of the test on each sample is reached when a TVC greater than 10^2 c.f.u. ml^{-1} or g^{-1} occurs on two consecutive days. By this means different preservatives and different concentrations of the same preservative system can be compared. Morris gives details of a method for shampoos and also a procedure for emulsions where, in the latter case, the daily addition and mixing-in of the inoculum would disrupt the emulsion. However, it has been pointed out that repeated inoculations of 10^6 daily are equal to 10^7, once.

In 1979, Orth [24] described the **linear regression method**. Since that date he has reported many results from research by himself and others which show its usefulness.

This method can be used to determine the preservative efficacy of cosmetic products in 48 h for bacteria and yeasts and 7 days for moulds. The rate of inactivation of selected test organisms is given by the decimal reduction time (D-value) calculated from the plot of the log of the number of surviving organisms per gram as a function of the time after inoculation of the product; e.g. the D-value is the time for a reduction from 10^6 to 10^5 organisms.

The D-value can give the quantitative expression of the rate of death of a specific organism in a selected product and can be compared with the rate of death of that organism in different products. It can also be used to compare the rate for different organisms in one or more products. Knowledge of the D-value

enables the time for complete destruction of an organism to be calculated; for example, the time for 10^6 *Staphylococcus aureus* to be totally inactivated is given by the log of the number of organisms per ml times the D-value $(2.5\,h) = 6 \times 2.5\,h = 15\,h$.

In 1987 Mulberry *et al.* [25] reviewed three such rapid screening methods using the D-value. All use the same organisms, the same recovery methods and APC for assessment. A summary is given here.

1. The 'linear regression' method is used for preservative systems. They point out that the data must be verified by standard methods for the actual destruction time of the inoculum.
2. The 'presumptive challenge test', which is applicable only to water-soluble products, is based on the 'minimum inhibitory concentration test' and assessment is by a scale of activity to no activity. The minimum inhibitory time (MIT) determines the lowest concentration of preservative needed to retard microbial growth.
3. The 'rapid kill curve' determines the short-term rate of death by sampling and plating at frequent intervals between 0 and 3–4 h. The D-values are calculated from these results.

Methods 2 and 3 both determine efficacy in 48 h but Method 2 is a semiquantitative test which correlates well with the 'rapid kill curve' and USP test method; while Method 3 is a quantitative measurement of the death rate. The two can be combined to show preservative synergism.

4. The 'accelerated preservation test' or 'repeat challenge test' evaluates preservative systems early in development and predicts their success in the standard double-challenge test. It can be used to eliminate underpreserved products and to identify those that are overpreserved. The criteria for passing are a 2–3 log reduction in the bacterial inoculum at a Day 2 assessment and no recoveries by Day 7. No recoveries on Day 2 indicates over-preservation. Mould recoveries are evaluated on an individual product basis with significant die-off for product acceptance. The formulae for the minimal salts to buffer the product which with glucose added form the 'nutrified' system are listed by O'Neill *et al.* [26]. The disadvantage is that the buffer systems interfere with mould growth and so a remedy has been to compare results obtained with and without buffer addition to the nutrient.

Mulberry *et al.* also carried out challenge tests using a model Schobel emulsion vehicle inoculated with a panel of organisms. They compared the above rapid screening methods and a 'standard' 28-day test and prepared six tables showing their results. They concluded that though all the methods are time-saving they are conservative in their selectivity of adequately preserved formulations [25].

In 1997 Orth [27] reviewed the various methods for preservative efficacy testing and concluded that 'the likelihood of preservative system failure is lower in products which meet the acceptance criteria in the linear regression method than in those which do not because these products are more likely to kill contaminating organisms fast enough to prevent their adaptation and regrowth during testing and consumer use – and that's the bottom line'.

Further tests. As before, challenge tests should be made with each change in product formulation, during development and samples stored for stability checks.

The final formulation is validated by standard methods for inclusion in the PIP.

21.3.3 Preservative assessment in consumer panel trials

Preference trials by consumer panels afford not only means of assessing the acceptability of the preservatives, but also an opportunity to repeat the challenge tests at the end of the trials and re-assess their stability and efficacy. At the same time the effect of contamination by the consumer during normal use, by counting the organisms surviving, assesses the long-term efficacy of the preservatives.

21.3.4 Prevention of contamination during manufacture

In spite of very satisfactory results at the development stage of a product, a preservative-resistant organism might develop in a factory if good hygiene procedures are not followed during processing, filling and packing. Cleanliness is imperative and directions for its maintenance should be included in the processing instructions to all personnel.

(a) Raw material testing for purchase, in storage and use

Raw ingredients and packaging materials should be purchased from the same suppliers as those used during the development of the product and should be accompanied by certificates showing identical specifications and guaranteeing microbial safety, e.g. sterility in the case of talc to be used in face powders. Samples should be taken of each delivery and these should be tested for bacteria, yeasts and moulds. They should be stored in a clean, dust-free warehouse in clean, sealed sacks, bags or drums away from the manufacturing area, and taken in strict rotation when passed by the control laboratory as satisfactory for use. Arrangements can be made with suppliers to add acceptable preservatives to some ingredients to minimize contamination; for example, liquid surfactants susceptible to pseudomonads.

The raw materials for a production should not be taken to the processing area until all the items, including packaging, have been delivered and all the test results on the substances passed as satisfactory for use.

(b) Water [7, 28, 29] *(see Section 21.3.8)*

The water used in manufacture is one of the most likely sources of contamination, whether mains, demineralized or distilled. The microbial count may reach 10^6/ml or more and can include *Pseudomonas, Xanthomonas, Flavobacterium, Actinobacter* and *Aerobacter* spp. The presence of *Escherichia coli* can be a sign of recent contamination with sewage.

Storage tanks, pipework, joints, filters, ion-exchange resin beds and reverse osmosis equipment for demineralization must all be sanitized regularly. Small amounts of organic matter present are sources of nutrients for growth, and also render the chlorine used in the mains supply inactive. 0.25% formalin (37% formaldehyde solution) can be used to sterilize the microfilters and resin beds, care being taken to flush the solution out thoroughly with sterile water after treatment.

Microbial checks should be made periodically since the count may vary considerably from day to day.

(c) Planned production area

The weighing room. Where possible the bulk of the materials should be weighed and checked in a room set aside for this purpose and kept scrupulously clean. Part-used containers should be resealed and returned to the raw materials warehouse. They should be retested if there is a delay before they are next required for use.

The manufacturing floor. The processing area should be capable of being sealed off from adjacent activities and should not form a thoroughfare for other employees. Visitors should be discouraged.

(d) Factory hygiene

The floors and walls should be free from ledges, smooth and easily cleaned. Cleaning should be frequent with a sanitizing solution – sodium hypochlorite (Chloros), for preference. The floors should slope to the drains which can be covered when not in use.

The air should be as free from dust as possible. If air-conditioning is installed it should be at a slightly raised pressure and frequently tested for microbial contamination. Where there is no air-conditioning, and windows are required to be opened, muslin screens can be fitted over them which prevent the entry of dust and microbial spores which are prevalent in dry conditions.

Access to equipment should be made as simple as possible for the purpose of dismantling the parts for cleaning. Standard connections should be used,

care being taken to ensure that screw threads and valves are included in any scouring work.

(e) In-process hygiene/sanitization

Equipment should be constructed in non-corrosive material to withstand the effect of the sanitizing liquids; i.e. good-quality stainless steel or, where possible, food-quality plastic (capable of withstanding steam heat) (the HACCP principle should be applied [11] – see Section 21.3.8). The formula quantity of ingredients should be added to the batch with minimum exposure to the air, as a further prevention against contamination from the environment.

The pipework used to transport liquids within the manufacturing area should have as few joints as possible and no blind ends for trapped product which can act as food for microbial growth. It is at such sites that an organism specific to the product, but otherwise harmless, can multiply, leading to widespread contamination which is difficult to eradicate.

Mixing tanks should be cleaned thoroughly between batches, especially if there is to be a delay, such as over a weekend. A convenient way to sanitize a unit to save the labour of dismantling each time is to pump solutions round the processing delivery pipes and mixing tank. To do this a light pump can be installed at the outlet to the tank, and transparent plastic piping connected in turn to its outlet. The other end of the flexible piping is connected to the inlet of the delivery pipe to the tank, forming a closed circuit through the processing equipment. Firstly, detergent solution can be pumped round to wash out the remains of product; secondly, sanitizing solution should be circulated for 1 h. Finally, sterile water should be used to rinse the system until it runs away clear. This method is especially useful if a liquid is delivered from a tanker to a storage tank and then piped some way to the processing vessel.

(f) Processing

This should follow the method used in the development of the product or be even more rigorous; a factory procedure might be subject to unexpected contamination (p. 663 (iv)).

(g) Handling bulk production

It is a good plan to have the bulk manufacture on an upper floor with the filling machines directly underneath the processing tank, so that pipelines for delivery of product are as short as possible. If transported by containers these should be closely lidded. Part batches should not be left in them for more than a few hours. If a third of a batch of cream is left in the container overnight this can be covered with sterilized muslin, rung out in propylene glycol/glycerol which contains the solubilized preservatives used in the batch, and the lid replaced.

For warm liquid products stored similarly, the muslin is best tightly drawn across the top of the container and close to the lid, to prevent condensation (which does not contain non-volatile preservative) becoming contaminated.

(h) The filling and packing floor

Automatic filling and capping machinery is the obvious solution here but occasionally machinery has to stop, and exposure of product must not be allowed to occur. The slogan on the filling floor should be 'Cover everything as soon as possible', or 'dispose of material possibly contaminated, ***asap***', and that means not only recently filled pots and bottles but packaging materials next in line for use. It is an obvious maxim that the filling equipment is placed as far from entrance and exit doors as possible. For very vulnerable products the filling can be in a separate area behind a screen, through which the capped product passes on the conveyor belt.

(i) Personnel

Operators in both processing and packing rooms should be aware of the need for extreme cleanliness and good personal hygiene. A simple basic training in dealing with unwanted microbes is useful for all personnel, including management. Most people can accept the concept of 'epidemics' caused by 'infection' and although cleaning jobs are looked upon as menial, the cleaner's status can be raised when the aim is to eradicate or prevent microbial contamination. For example, pride in cleaning for MQM can be encouraged by the results of random spot checks taken around the factory. These are done by swabbing surfaces, or by leaving open agar plates on benches or ledges for a week and taking a count after appropriate incubation.

Caps and clean overalls should be worn at all times. Clean gloves should be supplied daily and worn by those handling empty bottles, jars or tubes, etc., or having any contact with them when filled but not capped.

A wash-basin and hot-air dryer should be sited just inside the doors of the processing and filling rooms. No smoking is to be allowed. No food must be consumed or even brought into these areas. All operators should be strictly supervised for their personal cleanliness. Wearing white overalls and caps etc., and disinfectant smells, are just 'window dressing' if procedures for thorough cleaning of equipment and prevention of contact contamination are not maintained [28].

21.3.5 Laboratory control methods

(a) Ingredients

The raw materials are tested before delivery and rejected if unsatisfactory. They are checked when delivered and placed in quarantine until the laboratory passes them as satisfactory for use. If storage is prolonged the testing is repeated.

The action to take if growth has developed will depend on the concentration of the raw material in the final product and subsequent treatment in the manufacturing process.

(b) Routine testing of water supply [7, 9, 29]

To test water routinely, a sample not less than 100 ml, and preferably 250 ml, is taken aseptically in a sterilized bottle. If the water contains chlorine, a 3% solution of sodium thiosulfite is added to the bottle before sterilization to give a concentration of 18 mg l^{-1}. This should neutralize up to 5 mg l^{-1} of chlorine, i.e. 0.01% in a 170 ml bottle [7].

Two sets of plates are prepared and incubated. Fewer than 100 c.f.u./ml at the point of use with no pseudomonads and a mean value usually below 100 are the general guidelines in MQM. Process water can be tested by filtration through a 0.22 μm membrane filter to retain pseudomonads and the membrane aseptically cut in half: one half plated using TSA and the other half using SDA, and incubated and assessed as above [9].

The Microbiology Committee of the Cosmetic, Toiletry, and Fragrance Association [29] has published an article on microbiological tests of process water which is an overview of conventional and rapid methods, and discusses some specific organisms found in water i.e. coliforms, faecal coliform and pseudomonads. A typical design for a water supply of constant quality which can be tailored to suit local conditions was designed for the Max Factor Company by N. Wheeler and J. Kilsheimer in the *Water Documentary of Cosmetic & Toiletries* in 1983.

(c) Sampling

It is necessary to take representative samples of known weight or volume of the product in the finished pack. The limits suggested in the MQM Guidelines are intended to cover the product at point of sale. If good formulation and manufacturing practices have been followed few samples will show evidence of contamination. When a product is first launched sampling should be frequent, to establish that the pattern set at the development stage is followed. This initial period should last at least 3 months; after this the sampling plan will depend on the product's susceptibility to microbial growth. In general, however, the finished pack should be sampled at the beginning of a new batch and three times daily: morning, noon and evening. As the testing takes time the batches are carefully labelled and removed to a quarantine area in a cool, dry warehouse until passed for sale.

(d) Finished product testing

Preparation of sample for testing. The weight of the sample in the pack to within ±5% should be recorded. Liquids, creams and powders are thoroughly

mixed in their containers. The exceptions are compressed powders, which may have to be ground before mixing; soaps, lipsticks, etc., are scraped with a sterile knife into a jar and to aid dispersion in the diluent samples may be warmed in a water-bath to 40°C for up to 3 min. Aerosols are sprayed directly into a sterile jar containing diluent whose weight is accurately recorded [7].

Method of dilution. The outside of the pack should be disinfected and, under aseptic conditions, 1 ml or 1 g samples added to 9 ml of a suitable diluting medium in sterile flasks, giving a 1:10 dilution. When thorough mixing is obtained a further dilution is made by taking 1 ml of the first dilution in 9 ml of diluent to give 1:100 and so on if required. A colony count on any dilution after plating and incubation is one-tenth of the preceding one.

Preservative inactivation. Although the dilution technique lessens the chance of preservatives still acting to prevent growth during incubation it is usual to add a preservative inactivator in the diluent. Singer [30], in a comprehensive paper listing preservative neutralizers, suggests a means for the validation of their effectiveness: If no growth is obtained on the 1:10 and 1:100 dilution plates after incubation, streak the agar surface with a single loopful (about 1000 units) of each culture used in the challenge tests. These organisms should be recoverable at the correct growth level. If again no growth is detected, or just a few colonies, the neutralization of the preservative system is ineffective and another neutralizer must be tried.

The two neutralizers suggested by the CTPA MQM [9] for use are:

No. 1. Peptone /Polysorbate 80 (Tween 80, ICI Speciality Chemicals Ltd)

No. 2. Universal Diluent...	Lecithin	3 g
	Polysorbate 80*	30 ml
	Sodium thiosulfate $5H_2O$	5 g
	L-Histidine	1 g
	Proteose peptone	1 g
	Sodium chloride	8.5 g
	Distilled water	to 1000 ml

The formula should be buffered to pH 7.0 $\pm$0.1 at 25°C. Once this is decided the diluent and inactivator can be made up for routine sampling of the product under test.

General method for total viable colony counts. One millilitre of each dilution is pipetted into each of two Petri dishes. To one dish, sterilized tryptone soya agar (TSA), prepared according to the manufacturer's instructions, is added at 45°C; Sabouraud dextrose agar is added to the other. Keeping each dish with the lid in place flat, it is rotated to mix the sample and, when the agar is set, inverted.

The TSA plates are incubated at 28–30°C and inspected daily and colonies formed counted if less than 300. If more than this they are labelled too numerous to count (TNTC) and the batch must be discarded.

The SDA plates are incubated at 25°C, inspected after 48 h and incubation continued for 5 days. The colony counts on these plates will usually be nil or very low if the development research on the product is successful and the subsequent hygiene in the processing is good.

21.3.6 Scheme for testing TVCs including for harmful organisms

The following is a suggested scheme for general microbial monitoring. For eye and baby products the initial sample testing establishes whether harmful organisms are present.

Preparation of product samples in media:

1. Prepare in triplicate plates/tubes for (a)–(f) in Table 21.4, by adding 1 ml of diluted sample from a sterile pipette and then 20 g of sterile media as required for the test.
2. Streak triplicate nutrient agar plates, (g), with undiluted product.

Procedure for steps (a)–(g) in Table 21.4:

(a) Tryptone soya agar/(TSA). The addition of 0.001% cycloheximide to the agar before sterilization inhibits the growth of yeasts and moulds but allows the growth of bacteria. 'Actidione' (cycloheximide) agar is a ready-prepared medium from Oxoid. At the end of the incubation of TSA plates, i.e. after

Table 21.4 General scheme for microbial monitoring

Medium	*Temperature of incubation (°C)*	*Observation and incubation time*
Bacteria		
(a) Tryptone soya agar (TSA)* or TSA + 0.001% cycloheximide	32	Every 24 h for 7 days
(b) Nutrient broth	32	Every 24 h for 7 days
(c) MacConkey agar	32	Every 24 h for 7 days
(d) *Pseudomonas* selective	37	24 h
(e) Cooked meat medium	37	3–4 days
Yeasts and moulds		
(f) Sabouraud dextrose agar adjusted to pH 5.0	25	48 h, and after 5 days
Undiluted product		
(g) Nutrient agar	32	48 h

*Actidione Agar, Oxoid Ltd.

†This medium should be freshly prepared and inoculated as soon as it has cooled to 37°C. Prepared tubes a day or two old should be placed in a bath of boiling water for 10 min to expel oxygen and then cooled without agitation, and inoculated immediately.

7 days, count all visible colonies. If more than 300, report as TNTC (too numerous to count), prepare fresh samples and repeat incubation.

(b) Nutrient broth. At the end of the incubation of the nutrient broth tubes any colonies formed are aerobic organisms. Test for *Staphylococcus aureus* by plating colonies on *Staphylococcus* medium consisting of dipotassium hydrogen phosphate, gelatin and a high salt content. Orange colonies give a positive reaction for acid production and gelatin liquefaction is positive for this pathogen.

(c) MacConkey agar. At the end of the incubation of these plates coliforms are selected. Sterilize MacConkey broth (purple) in tubes made up according to and fitted with Durham tubes, at 121°C for 15 min. Inoculate from the plates of coliform colonies and incubate for 48 h at 37°C. Acid formation is indicated when the broth turns yellow and gas filling the cavity at the top of the Durham tube indicates presumptive coliforms. Production of gas after 48 h by subculture into a fresh tube of broth and incubation at 44°C is almost specific for *Escherichia coli.*

(d) *Pseudomonas*-selective medium. For the identification of *Pseudomonas aeruginosa* antibiotic supplements are added to this medium. The supplement contains 0.1 g cetrimide equivalent to 200 mg/l of medium and 0.0075 g nalidixic acid equivalent to 5 mg/l.

(i) Preparation of medium. The agar base: suspend 24.2 g of the agar base (Oxoid code CM559) in 500 ml of distilled water. Add 5 ml glycerol, bring to the boil to dissolve completely, sterilize by autoclaving at 121°C for 15 min. Allow to cool to 50°C.

(ii) Addition of antibiotic supplement (C-N102). To 500 ml of agar base at 50°C add 0.1 g cetrimide and 0.0075 g nalidixic acid rehydrated in 2 ml of sterile distilled water. Mix well and pour into sterile Petri dishes.

(iii) Procedure. Dry the surface of the plates. Swab the sample over half the area of a plate and with a sterile loop streak it over the other half to obtain isolated colonies. Incubate at 37°C and examine after 18, 24 and 48 h with both white and UV light. Any growth indicates the presence of *Pseudomonas* spp. Blue-green brown colour or fluorescence indicates the presence of *Pseudomonas aeruginosa.* Further tests must be carried out to confirm the identity of the organism.

(e) Growth on cooked meat medium (CMM) at the end of incubation. Make up blood agar slopes in test tubes. Stab-inoculate slopes with colonies from the CMM. Anaerobic growth under the surface of the medium indicates *Clostridium* spp. Alternatively for anaerobic organisms using solid medium, plate as normal and allow to solidify, spread the inoculum from CMM on the surface and pour another layer of medium over the first [3].

(f) At the end of the incubation of the Sabouraud dextrose agar (SDA), examine microscopically for yeast/fungal identification. Test for *Candida albicans.*

Suspected colonies of this yeast growing on the SDA are plated onto BIGGY agar prepared as follows:

(i) Preparation of the medium, which must not be autoclaved: 42 g are suspended in 1 l of sterile distilled water and brought gently to the boil, then cooled to 50–55°C and mixed to disperse the flocculant precipitate; 20 ml of this reconstituted medium freshly prepared are poured into sterile Petri dishes. Slant tube cultures are unsatisfactory.

(ii) Incubation at 28–30°C with daily examination for sulfite reduction. After 48 h the presence of brown to black smooth circular colonies with a slight mycelial fringe indicates *Candida albicans*. A small inoculum from any black colony is added to 0.5 ml of serum (human or animal) in a small test tube and incubated at 37°C for 4 h. A drop of the incubated serum is then placed on a microscope slide and the yeast cells examined for germ tube production. If germ tubes have been produced the yeast may be presumed to be *Candida albicans*.

(g) At the end of the incubation of the nutrient agar containing undiluted product these plates may show microbial growth which is not detected by using dilute samples as prepared in (1) (above). If growth occurs on these plates (g), inoculate directly from them to freshly prepared triplicate plates from (a–f) and proceed as before.

21.3.7 Assessment of total viable counts (TVCs)

If the TVCs of the TSA and the SDA plates are >1000, i.e. TNTC, then the batch should be held, resampled and retested, and if the numbers have remained the same the batch should be rejected and investigations made to discover the cause of the contamination. If further batches show contamination extensive cleaning and sanitization programmes should be carried out and equipment and factory should be carefully monitored by the microbiological laboratory. Cries from staff of 'we've just done all this!' will cease and pride in the job increase when they realize that the despised 'cleaner' can affect the quality of production.

Those samples with 100–1000 TVCs/g and no harmful organisms present can be passed. The knowledge gained of the long-term stability and effectiveness of the preservatives at the development stage will help in deciding the fate of any batch. In MQM the CTPA [6] sets out a Sampling and Testing Scheme based on the Three-Class Attribute plan. The scheme uses five randomly selected samples per batch. A total viable count (TVC) is carried out on each sample unit and according to the result of this will have one of three 'attributes'. The TVC should not include any harmful organism. The classes are:

- Class I – Acceptable.
- Class II – Hold and retest.
- Class III – Unacceptable.

Table 21.5 Sampling and testing scheme

Product	*Upper limit M*	*Lower limit m**	*C*
General	1000 c.f.u./g	100 c.f.u./g	2
Baby/eye	100 c.f.u./g	10 c.f.u./g	0

C = Number of defective sample units allowed.
* *m* provides an early-warning system and should be 10 times smaller than *M*.

Specific tests are set out for *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Candida albicans*. Record test results in the test report as presence or absence of these organisms [9].

The scheme is expanded and explained in the Guidelines, and is summarized from the results of five samples for each of the two product categories in Table 21.5.

Results of tests on sanitization/cleaning

It may be necessary to carry out further sanitization programmes depending on the findings mentioned above, but if equipment has been properly cleaned and 'sterilized' the number of bacteria left will not exceed 1 cm^{-2} by a swab test or 1 ml^{-1} by a rinse test [28]. These tests are quite adequate in a general sense. If the swab test covers 1000 cm^2 and less than 1/ml c.f.u. are found then it can be assumed that no pathogens will survive.

21.3.8 Laboratory responsibility

All the microbiological testing by the laboratory is useless if unsatisfactory results are not taken as a warning and acted upon.

(a) Summary of responsibilities

1. Test raw materials before and after delivery. In the latter case hold in quarantine until passed for processing.
2. Test mains, demineralized, distilled, and sterile water routinely.
3. Carry out routine product tests according to production plan including bulk and filled products. Hold in quarantine until passed. Retest Class II and supervise the ultimate fate of any rejected product.
4. Monitor factory cleansing by swabs and exposed plates at varied times not expected by the staff; especially identified hazardous places (concept of Hazard Analysis Critical Control Point, HACCP) [11]. These should be tested before and after a point in the flow of product where it might become contaminated; e.g. a pump, or transfer of high-risk material necessitating opening the batch to the air. Report any contamination to the person concerned with factory hygiene and test after repeat sanitization.

5. Test swabs or rinses of equipment before and after sanitization.
6. Depending on the qualifications or experience carry out preliminary or final preservative efficiency tests on new or changed products.

21.3.9 Microbial records for the Product Information Package (PIP)

The records of the test results of formulation development and production of a cosmetic are a useful reference for a company, not only from aspects of safety and quality, but as a means of assessing the efficiency of the whole operation and for reference should a consumer need insurance.

21.4 EQUIPMENT DESIGNED FOR RAPID TESTING OF MULTIPLE SAMPLES

Using standard plate count methods the minimum time for release is 72 h to 1 week, and space must be found for raw materials and finished products during the quarantine time. All this means increased cost. However, they must be used for results presented in the PIP and when validating shorter methods.

Manufacturers are investing in automated systems so that, even though the initial costs may be high, routine sampling costs at least will be lower eventually and routine testing time will be reduced.

21.4.1 Accelerated electrical methods

Electrical methods use the fact that the metabolic results of microbial growth affect the impedance, conductance and capacitance of an electrical cell.

(a) Impedance method [31, 32]

As early as 1899 Stewart reported to the British Medical Association that microbial growth caused changes in electrical impedance [33]. The observation has been developed in the past decade into a rapid computerized method which is being installed by companies who need to process large numbers of samples daily.

Samples to be tested are added to selected nutrient media in cells across which there is an electrical potential. Viable organisms absorb nutrients from the medium and produce smaller charged molecules when growing, and this affects the impedance of the cell, which is measured by the instrument. For use for routine sampling the system must be calibrated and validated by standard methods. Muscatiello and Penicnak [34] tested 2580 cosmetic samples over a period of 8 months by this method and compared them with standard plate count methods. The impedance time for aerobic counts gave results in 20 h or less while the standard method took 72 h.

This scheme detects high numbers earlier than low numbers so that samples that are unsatisfactory can be rejected quickly. There can therefore be a more rapid turn-round of raw materials and finished stock, and early warnings of contamination in equipment and the environment can prevent spoilt stock and heavy factory contamination. The method is widely used for total counts, selective tests (such as coliforms and anaerobes), sterility testing and shelf-life predictions [35].

(b) Capacitance measurement [31]

This is useful with high-conductivity media and for detecting yeasts and moulds. These organisms produce little in the way of charged metabolites but produce large changes in capacitance. Test times for yeasts and moulds are shorter than by plate methods but because the growth rate of these organisms is slower the detection time may be up to 48 h or longer for very low initial numbers [35].

(c) The use of conductance [31, 35–37]

Unlike the impedance method this method can be used to identify organisms specifically.

21.4.2 ATP bioluminescence

This system uses the fact that all living matter uses adenosine triphosphate (ATP) in the transfer of free energy during growth. Instrumentation has been developed which measures the fact that one photon of light is produced when one molecule of ATP oxidizes the substrate firefly luciferase in the presence of the enzyme firefly luciferase. It has potential for use in testing cosmetics since it is possible to detect 10 c.f.u. ml^{-1} in under 24 h [38]. The capital outlay is high, however, and the reagents are costly; and although the process is automated highly trained staff are needed to handle it to avoid false-positive results. It is useful in the food industry but is of little use in the cosmetic industry where the number of organisms found is usually so small.

21.5 CONCLUSION

The one predictable thing about microorganisms is their unpredictability. They are living organisms, and can adapt quickly to their surroundings and to using the available nutrients for survival.

This chapter gives only a basic overview of the subject, and the references given should be read if possible, in order to gain further insight into modern research. New knowledge about specific organisms and new species is being

gained; improved methods for controlling them and faster methods of detecting their presence and destruction are constantly being written about in the modern literature.

Appendix A: Machines for Counting Organisms

Coulter Counter (UK) Ltd, Colony Counting Equipment Luton, UK.

Appendix B: Suppliers of sterile disposable consumables

Bibby Sterilin Ltd, Stone, Staffs., ST15 0SA, UK
LIP Equipment Services
Dookfield, Shipley, W. Yorks, BD17 7SJ, UK

Appendix C: Suppliers of culture media and laboratory services

Oxoid Ltd, Wade Road, Basingstoke, Hants, RG24 8PW, UK.
IDG UK Ltd, Topley House, 52 Wash Lane, Bury, Lancs, BL9 6AU, UK.

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22

Safety

John D. Middleton

22.1 INTRODUCTION

There are three main factors to be taken into account in considering the safety of a cosmetic product.

First and foremost is always the need for human safety, both for the consumer and for people who may handle cosmetic products or their ingredients in their daily work. It is the task of the safety evaluation scientist to consider and obtain the information necessary to arrive at a conclusion on the safety of a new product. This chapter will describe the information required and how conclusions on safety can be drawn from this information.

The second factor to be considered is the requirement of legislation, which may vary according to the country in which the product is to be sold. The subject of legislation is covered elsewhere in this book and all that need be said here is that the safety evaluation scientist must be aware of, and take account of, the requirements of legislation.

The third important factor to be taken into account in safety evaluation of cosmetic products is the increasing social pressure to avoid the use of animals in the process. The cosmetic industry has responded actively to this pressure and this chapter will consider the ways in which animal testing can be avoided without compromising the primary aim of consumer safety.

In principle the safety of a cosmetic product can be determined from a knowledge of the safety of its individual ingredients. The process of safety evaluation of a product consists of two distinct phases. In the first phase an estimate of the potential hazard of each ingredient must be made, drawing information from all sources. This phase can be termed hazard determination. In the second phase one must determine the likelihood or risk of any hazard identified in the first phase actually causing harm to the consumer. This phase can be termed risk assessment and the outcome depends on a number of factors, in particular

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 685–696

the degree of consumer exposure to the various ingredients. In the risk assessment phase one also has to consider the possibility of interactions between ingredients.

In practice of course safety evaluation of most new products does not involve a full hazard assessment of every ingredient, as in most cases the ingredients will have a long history of safe use and the new product will consist of recombinations of known ingredients. In these cases the risk assessment can use this accumulated information to arrive at a conclusion on product safety as described later.

The following sections describe the process of determining the potential hazard of a new hitherto unused ingredient, and describe how this information is used in risk assessment. The case of an existing ingredient being used in a new application is also considered.

22.2 HAZARD DETERMINATION OF INGREDIENTS

22.2.1 Types of hazard

In determining the possible hazard of a new ingredient one has to consider a number of possible adverse effects that could occur. For cosmetic ingredients it is convenient to divide these effects into two types. The first are those affecting the external parts of the body, skin, eyes or mucous membrane – so-called topical effects. The second are those which may occur should an ingredient enter the body through the skin, by swallowing, or by inhalation – so-called systemic effects.

It is beyond the scope of this chapter to describe all these effects in detail and give accounts of the numerous methods available to determine the hazard. However, a brief description of each effect serves to illustrate the complexity of a full hazard evaluation.

22.2.2 Topical effects

(a) Skin irritation

Irritation can be likened to a direct chemical attack on the skin. This may either be directly on the surface horny layer resulting in dry, flaky or rough skin or the material may penetrate into the skin and cause inflammation and reddening. A secondary process may result in a disturbance of keratinization so that the new horny layer is affected and becomes dry, flaky or rough.

Irritation is an effect to which everybody is susceptible, with some people reacting more strongly than others. Nearly all chemicals will irritate susceptible people at high concentration but irritation is concentration-dependent. There is normally a threshold concentration below which the great majority of consumers will not react. It is clearly important for an estimate of this threshold

concentration to be available for risk assessment, and it follows that more irritant materials may be acceptable as minor ingredients in a product, while the major ingredients must have a low irritation threshold.

Methods of determining skin irritation are in general comparative, with the objective being to show whether or not a new ingredient is more irritant than existing ingredients with the same degree of exposure to the skin. A conclusion that a new ingredient is of less or equal irritancy can be used directly in the risk assessment procedure.

(b) Eye irritation

Damage to the eye is of course a potentially greater hazard than skin irritation because of possible effects on vision. Great care must be taken particularly with cosmetics intended for use around the eyes. The principles of concentration effects and comparative data for risk assessment also apply to eye irritation.

Using animals to assess eye irritation is one of the areas attracting the most attention in attempts to eliminate animal testing and this will be referred to later. It must however always be remembered that a mistake in this area can lead to very serious consequences for the consumer.

(c) Mucous membrane irritation

The area around the eye and the ano-genital region have mucous membrane tissues which cosmetic products may contact either accidentally or by design. Mucous membranes do not have the protective horny layer of the skin and are therefore more susceptible to irritants. Some ingredients may be acceptable for use on skin but not for use in products which are likely to contact mucous membranes. Again the principles of concentration limits and comparison with existing ingredients are used in risk assessment procedures for mucous membrane contact.

(d) Skin sensitization

One of the adverse effects most commonly associated with cosmetics is that of skin sensitization or allergy. Allergy differs from irritation not in the reaction itself but in the mechanism that produces the reaction. The immune system is involved and only a limited number of people will become allergic to an ingredient which has the potential to cause problems. Chemicals differ in their allergenic potential and vary from materials such as poison ivy, which can sensitize most people, to chemicals for which only one or two cases worldwide have been reported.

It is frequently said that any chemical will sensitize someone somewhere, and the object of cosmetic safety evaluation is to reduce the number of sensitized people to a minimum. Zero reactions is an impossible target. The available test methods therefore aim to determine the relative potential to sensitize.

As with irritation, sensitization is concentration-dependent, although in sensitized people the concentrations that can elicit a reaction may be much lower than those which cause irritation. The risk assessment procedure uses the relative potential to sensitize together with the degree of exposure.

(e) The effect of ultraviolet light

Some chemicals cause skin irritation or allergy only in the presence of ultraviolet light. The terms photoirritation and photoallergy are used to describe these two distinct processes. The reactions are of course of concern only for products applied to skin exposed to sunlight. However it would be difficult to ensure that an ingredient is never on exposed skin, and it has become routine to consider all new ingredients for their potential to cause photoirritation or photoallergy. Ingredients which do not absorb ultraviolet light are not considered to present a problem and need be considered no further.

A particular problem with both photoirritant and photoallergic reactions is that they can be more severe to an individual than their non-light-mediated counterparts. Particular care is therefore required in the safety evaluation. Sunscreen agents are a potential problem and new ones are thoroughly evaluated before use.

(f) Miscellaneous skin reactions

Occasionally there are skin reactions which do not fit neatly into any of the categories outlined above. Some may be combinations of these effects but in recent years two further categories have been recognized and their importance and frequency is still under investigation at the time of writing.

The first is known as an urticarial response (nettle rash) and is characterized by a direct release of histamine, and possibly other mediators of inflammation, into the skin. The importance of these reactions for cosmetics is uncertain but some ingredients used in cosmetics, e.g. cinammic aldehyde, have been shown to have this effect.

The second phenomenon is that of skin stinging. A small (around 10%) proportion of people suffer a severe stinging sensation when some chemicals such as lactic acid are applied to the skin, while most people feel nothing. Again the significance of this reaction for cosmetics is uncertain and further investigations are required. Stinging is certainly a factor frequently mentioned in complaints by consumers to manufacturers.

22.2.3 Systemic effects

A harmful effect resulting from a cosmetic ingredient entering the body is not a possibility which many cosmetic chemists would take seriously in view of the similarity of many of the major cosmetic ingredients such as fatty alcohols or emulsifiers to their counterparts used in the food industry. There are however

potential problems if care is not taken to undertake a proper safety evaluation of speciality ingredients used in cosmetics, particularly those with known biological activity such as preservatives, or new chemicals which might for example be used as sunscreens, colours and dyes or perfume ingredients.

A cosmetic ingredient may enter the body through the skin or mucous membranes, by swallowing or by inhalation. Almost any chemical in contact with the skin will penetrate to some extent and enter the bloodstream so that effects anywhere in the body are possible. The extent of penetration may vary from a fraction of a per cent of the applied dose to almost all of it. The actual amount penetrating depends on a large number of factors including the nature of the chemical, its concentration, duration and amount of skin exposed, nature of vehicle, state of the skin and the skin site, as well as on variations between individuals. If there are doubts about the systemic toxicity of the ingredients, skin penetration clearly needs to be considered and determined, and plays an important part in the risk assessment to be described later.

The effects of swallowing cosmetics need consideration for products where significant quantities may be swallowed during normal use; for example with oral hygiene products or with lipsticks. One must also never forget the possibility of children obtaining and accidentally swallowing a cosmetic product. Some information on the effects of swallowing is therefore necessary.

The inhalation route of entering the body is of most significance for aerosol and other spray products but the possible inhalation of more volatile ingredients from other products should not be forgotten.

There are several types of systemic toxicity which need to be considered during safety evaluation, and information on each needs to be available. Specific effects such as cancer (carcinogenicity), birth defects (teratology) or toxic effects on the nervous system (neurotoxicity) are the most dramatic and cause the most concern, although it is extremely rare for such effects to be associated with cosmetics and their ingredients. More general effects, or effects confined to specific organs following a large single dose (acute toxicity), or smaller repeated doses over a prolonged period (subacute or chronic toxicity) also need consideration.

The ways in which information on systemic and topical effects can be obtained is described in the next section, and the section on risk assessment gives an account of the way in which the information is used to arrive at a final conclusion on the safety of a product.

22.2.4 Sources of information for hazard determination

(a) Databases

The first step in the process of hazard determination should always be to determine what is already known about the safety of an ingredient. The three main

sources of this information are a history of safe use of the ingredient in other products, suppliers' data and the scientific literature.

Before using a history of safe use as the basis for concluding that there is no problem one should always check that the exposure to the new ingredient will be no greater than that in existing products. Clearly an increased exposure will require further consideration. Care should also be taken to ensure that there is a true history of safe use by keeping comprehensive files on all reported complaints to existing products as described later. Indeed such records are necessary for inclusion in the Product Information Package (PIP) required to be kept under the 6th Amendment to the Cosmetic Directives (see Chapter 20).

If no history of safe use to the anticipated exposure can be established, the suppliers' data may be a useful source of information. In many countries safety data on cosmetic ingredients are required by chemical legislation in order to provide adequate warnings and protection for workers handling the concentrated materials. These data on the concentrated material, e.g. irritation, sensitization, acute toxicity, can be extrapolated to consumer exposure during risk assessment. Many suppliers may also have data directly relevant to the projected use in cosmetic products, and such data will normally be available to assist their customers in risk assessment of final products.

The scientific literature is, of course, an important source of information, particularly for chemicals which are new to the cosmetic industry. The use of modern computerized literature-searching systems makes the task of finding relevant articles much easier than it once was. The literature should also be continually reviewed for new publications on existing ingredients so that any new findings of adverse effects can be considered and remedial action taken if necessary.

(b) Structure–activity relationships

If no existing data can be found on a new cosmetic ingredient, it may be possible to arrive at a conclusion of likely hazard by considering what is known about hazards of chemicals with related structures. With the present state of knowledge these considerations are rarely likely to produce sufficient confidence for a full safety clearance without further data, but can certainly alert the investigator to likely problems.

The science of quantitative structure–activity relationships (QSAR) is a new one, but with rapidly developing computerized databases and predictive systems, significant advances can be expected in future.

(c) Toxicological test data

If the procedures outlined above are followed a very large proportion of the ingredients used should have adequate hazard data to allow a satisfactory risk assessment of the final product. In fact it is only for the most unusual or innovative formulations that any extra data will be required.

There is an increasing pressure on the cosmetic industry to avoid testing on animals. An increasing number of alternative testing methods are under development and coming into use within the industry. These methods include a large variety of tests on cell or tissue cultures and studies in human volunteers.

It is beyond the scope of this chapter to review in detail the *in vitro* methods available or to recommend any specific methods. The most important principle in selecting a method is that it should have been validated against consumer responses, or if this is not possible against historical animal data whose results have been used to clear products subsequently found to be safe.

It must always be remembered that the human body is an incredibly complex system with innumerable interactions which are by no means completely understood. In addition different chemicals react in totally different ways and again a simple cell or tissue culture system cannot be expected to respond in all these ways. It is therefore perhaps asking too much for a simple system to mimic the reactions of the human body.

It is not, however, necessary for a single *in vitro* system to be a panacea for all testing. The members of many classes of chemicals act *in vivo* by similar mechanisms and if an *in vitro* system is capable of responding by a similar mechanism, then a valid system for evaluating a specific class of chemicals may be developed. This principle is being used, for example, in evaluating surfactants in shampoos for eye irritation using *in vitro* techniques, but extreme care would be needed in extending such a method to testing, for example, hair dyes.

Amongst the toxicological effects which now have promising *in vitro* predictive techniques are skin and eye irritation, phototoxicity and carcinogenicity. Other effects involving complex interactions in the body are still a long way from being replaced. Examples are general systemic toxicity, teratology, allergy and photoallergy. However, even in these areas advances are being made and ideas being tested which may eventually lead to solutions of the very difficult and complex problems.

As an alternative to *in vitro* studies much safety evaluation is now being carried out in human volunteers. The toxicological effects which can be studied are obviously limited for ethical reasons but, particularly in the area of skin irritation, human studies are now routinely performed by many companies.

Patch tests for irritation can give valuable information on hazards of both ingredients and final products. It is important to remember that these tests are comparative in nature and that control ingredients or products with a history of safe use should always be used.

There are also routine tests available for determining allergenic potential in human volunteers. These tests have considerable ethical problems as there is a risk of sensitizing volunteers to chemicals which they may subsequently contact in their daily lives. For this reason the tests tend to be used only to confirm the absence of reactions as predicted from other information. In cases of doubt many investigators refuse to carry out these tests without satisfactory data from

animal tests. Because of the ethical problems human sensitization studies are not widely carried out in Europe but can be performed with appropriate safeguards for the volunteers. Human testing, again with appropriate safeguards, is more common in the USA.

22.3 RISK ASSESSMENT

The hazard of an ingredient or product is its potential to cause harm. Toxicological data define the hazard and the purpose of risk assessment is to come to a conclusion about the likelihood of hazard manifesting itself during use of a cosmetic product.

All ingredients have some potential hazard, however slight, and therefore any product has a finite risk. Zero risk or absolute safety does not exist. Risk assessment defines whether a risk is acceptable or not.

In the process of risk assessment of a cosmetic product the first stage is to evaluate the risk of each ingredient and the second stage to consider whether the combination of the ingredients into the final product poses any additional risk.

22.3.1 Risks of ingredients

The risk of an ingredient with a known hazard depends upon the degree of consumer exposure. In order to determine exposure one must consider the following factors:

1. concentration of ingredient in a product;
2. frequency and quantity of product used;
3. total area of skin contact;
4. method of product use – left on skin, rinsed off, sprayed, etc.;
5. number of products containing the ingredients.

After making a quantitative estimate of all these factors the total dose to which a consumer is likely to be exposed can be calculated. It must always be remembered that consumers will vary widely in their habits: risk assessors must consider the maximum, as well as the average, likely exposure.

In making a risk assessment from the calculated exposure the nature of the potential hazard is important. For topical effects on the skin such as irritation the dose per unit area of skin is important, whereas for systemic effects the total dose applied to the skin, regardless of area involved, may be more significant.

For irritancy, be it to skin, eyes or mucous membranes, the test data from validated methods indicating the degree of hazard should be compared with similar data on ingredients currently in use and showing no safety problems. If the new ingredient is no more irritant than the existing ingredient under the test conditions, then it can reasonably be assumed that the risk to consumers will also be no greater.

Skin penetration may result in systemic toxicity. Here the total dose applied to the skin is important. As the hazard data will not normally be determined in humans, it is traditional to employ a safety factor of 100, or even 1000 if the hazard is carcinogenicity or teratology, when relating a maximum non-toxic dose in the experimental situation to the exposure experienced during use of products containing the ingredient. The degree of skin penetration is obviously relevant and should be determined if the hazard data indicate a potential problem assuming 100% penetration. If skin penetration is less than 100% the calculated dose can be reduced proportionately.

Some products such as lipsticks and toothpastes may be partly swallowed during normal use and estimates of the amount swallowed should be made and compared with no-effect doses using appropriate safety factors. Similarly estimates of the quantity of ingredients inhaled while using aerosol and other spray products can be used for risk assessment via the inhalation route.

After taking into account the hazard of an ingredient, its exposure and appropriate safety factors, the risk assessment may indicate a risk at high levels of exposure but not at lower levels where the ingredient may still be useful. In such cases the exposure of an ingredient can be limited either by restricting the product concentration at which it is used or by restricting the type of product in which it may be used (e.g. to rinse off products or products with no mucous membrane contact). This approach is used in the EC Cosmetics Directive in the annexes, and in self-regulation by individual cosmetic companies and organizations such as the International Fragrance Association (IFRA).

22.3.2 Risks of products

The risk presented by a product depends primarily upon the risks of the individual ingredients under the exposure conditions associated with the product. However, there always remains the possibility that combining ingredients in the product may change the risk by some form of interaction. There are three main types of interaction which should be considered:

1. Chemical reactions between ingredients producing a new chemical whose safety must be considered.
2. Some ingredients such as surfactants can cause damage to the skin which, although in itself not sufficient to be a problem, may allow a greater penetration of other ingredients into or through the skin. Also, the degree of skin penetration of an ingredient depends on the solvent, so that the nature of the product can affect penetration of ingredients. In designing studies on skin penetration of ingredients it is always useful to consider carefully the likely nature of the final product so that relevant solvent systems can be used.
3. Biological interactions in which two or more ingredients react with a biological system producing a different effect from that of a single ingredient.

In all the above cases the interaction may produce either a smaller or greater adverse effect than that of a single ingredient alone. For example combinations of some surfactants result in less skin irritation than either alone.

It will be apparent from reading the above that changes in risk caused by interaction of ingredients are very difficult to predict. This difficulty can usually be overcome by consulting databases containing formulations of products which have been shown to have no safety problems in use. A comparison of ingredient combinations in a product with a similar exposure and low risk can allow a satisfactory risk assessment of a new product. Only if a new product contains totally new combinations of a potentially hazardous ingredient with other ingredients such as solvents or surfactants, should obtaining data on the product itself be considered.

In practice there are very few occasions when data on the product itself are required. The careful compilation of databases of low-risk product formulations almost removes the need for testing. The most frequent area of doubt is that of skin irritation and here a simple human patch test can provide the necessary data.

22.4 MONITORING HUMAN USAGE

22.4.1 Objectives

The process of safety evaluation of cosmetics does not stop once a product has been placed on the market. It is important to monitor any adverse reactions it may produce in consumers. There are two main reasons for this. The first is, of course, to ensure consumer safety and to confirm that the predictions made from hazard determination and risk assessment were correct. Careful monitoring of consumer response to a new product ensures that any problems are quickly recognized and appropriate action taken to identify and remove offending ingredients or to reformulate products. In the longer term investigation into what went wrong with the predictive safety evaluation procedures may allow changes to the procedure so that the same cannot happen again.

The second reason for monitoring human usage relates to the importance of establishing known low-risk products as benchmarks with which new product formulations can be compared. Several examples of when this can be useful have been given in this chapter (Sections 22.2.1, 22.2.2 and 22.2.3). It is important to have documented evidence that a product has a low risk and not just to assume it is satisfactory because it has been on the market for several years.

There are several ways of monitoring the safety of a product in use, and attention should be paid to all of these.

22.4.2 Consumer tests

With a new product a consumer test may provide the first opportunity to monitor human exposure. Panellists' comments can provide a first indication of any

adverse effects. In all consumer tests records should be kept of the number of panellists commenting on adverse effects. One or two such comments on relatively trivial effects, such as itching or stinging, are normal, but anything above the normal level should be investigated, as should any individual comment about a severe or persistent adverse effect. The number of comments may vary according to the type of product or composition of the panel. Careful records of these comments should be kept so that a normal level for each type of consumer test can be established. It is then much easier to recognize any unusual occurrence.

An important aspect of consumer tests is the design of the questionnaire. A questionnaire with specific questions about adverse effects will elicit many more comments than one without. Such questions may make it difficult to determine what is a real effect and may also affect the answers to other questions on product performance. On the other hand the absence of any question relevant to adverse effects may result in a problem remaining undiscovered. A reasonable compromise is to include questions such as 'was there anything (else) you particularly liked/disliked about the product?'. This question provides the opportunity for anyone with a genuine effect to record it, without drawing the attention of everyone else to the possibility and producing imaginary effects.

22.4.3 Consumer complaints

Consumer complaint files are an important source of information for confirming product safety or identifying adverse effects. Records of the number of complaints of adverse biological effects related to the number of units sold provide a complaint index for each product. The normal level of the complaint index can then be used to assess the performance of a new product.

There are however a number of difficulties with this procedure which must be recognized before using the complaint index as a yardstick for product safety. Almost every new product produces an initial burst of complaints, which settles to a steady level after a few months. It is the steady level which should be used in comparing products. The initial burst cannot be ignored and experience will show if anything unusual is occurring. However, this burst is often a consequence of people not liking the performance or appearance of the new product in comparison to their old one, and in their complaint they include what may or may not be imaginary adverse biological effects. There may be, and probably are, a few allergic reactions in this burst in which people with pre-existing allergies have problems with ingredients they have learned to avoid elsewhere.

The complaint rate may also be affected by a number of other factors and care should always be taken to compare like with like. Complaint rates differ with different product types with, for example, antiperspirants normally giving higher rates than skin creams. Social habits in different countries result in greatly differing rates across national boundaries with, for example, the UK and Scandinavia having higher than normal rates. Ease of access of the consumer to

the manufacturer is important, and consumers are much more likely to complain about a store's own brand, in which case they have direct access, than they are to write to a distant manufacturer.

22.4.4 Medical reports of dermatologists and others

Historically dermatologists have been the first to recognize a number of problems with consumer products, including cosmetics, as patients arrive at their clinics with skin reactions. Other areas of the medical profession, particularly poison centres, may also recognize a problem. In some countries poison centres act as a clearing centre for skin effects while in others they are restricted to the effects of swallowing. It is important for the cosmetic industry to have good contact with the medical profession, particularly dermatologists, so that it becomes aware of any potential problems at as early a stage as possible.

22.4.5 Investigating adverse effects

Once a true adverse effect of a product has been recognized the first step must be to find the cause as quickly as possible, so that an early decision can be made on whether to reformulate or withdraw the product completely. Historically adverse effects have almost always been topical effects, with allergy and occasionally photoallergy predominating. Skin irritation and other effects such as stinging and urticaria also occur, and in fact may be more common than was previously realized.

The dermatologist can be of great assistance in identifying an offending ingredient. Many companies do their best to arrange for people with genuine complaints to see a dermatologist so that diagnostic patch tests or other investigations can be carried out. The results of these tests are often successful in identifying the problem so that remedial action can be taken on the product and investigations made into the reasons why the safety evaluation procedures failed to predict the problem.

There is therefore a full circle between the hazard determination of ingredients, the risk assessment of ingredients and products, monitoring the effects of consumer exposure, identifying any adverse consumer effects, and modifying the hazard determination and risk assessment procedures to prevent the reoccurrence of the problem.

23

Stability testing

John S. Cannell

23.1 INTRODUCTION

It is axiomatic that, before any product is placed on the market, there must exist convincing evidence that during the time between its manufacture and its use by the consumer it will not undergo any change that will adversely affect its performance, render it less acceptable to the consumer or cause it to represent a risk to the user. That is, it must be known to have an adequate shelf-life.

Although these requirements are self-evident and the establishment of the stability of the product is an integral part of its development, it is nevertheless likely to be that part of development that is executed least thoroughly. Stability testing is sometimes seen as a process to be conducted when other stages of development have been completed. In fact, considerations of stability should be borne in mind at all stages of the development of a product. The importance of stability testing of medicinal products is well recognized. Applications to regulatory authorities for marketing authorization for medicinal products must include detailed data on which the proposed shelf-life is based. While cosmetic products may not require pre-marketing authorization, it is important that their stability be tested and established in equally systematic and rigorous ways.

There is no official or legal definition of shelf-life as applied to a cosmetic product. It is required by the Cosmetics Directives of the European Community that cosmetic products having a stability of less than 3 years shall be labelled with an expiry date. In the United Kingdom the Cosmetic Products (Safety) Regulations 1996 require that any cosmetic product that within 30 months from the date of manufacture either no longer fulfils the purpose for which it is intended, or becomes liable to cause damage to human health when applied under normal or reasonably foreseeable conditions of use, shall be labelled with a 'Best Before' date, that being the earliest date on which it is likely no longer to comply with the above requirement of efficacy and safety.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 697–713

Cosmetic products that are neither ineffective nor hazardous may nevertheless be considered unsuitable or unsaleable and to have come to the end of their shelf-lives. A product may be regarded as having reached the end of its shelf-life when it no longer complies with its specification. It follows that the shelf-life is that period of time between the date of manufacture and the date on which it ceases to comply with its specification. Every product undergoes change with the passage of time; therefore, if the product is close to the limit of its specification in respect of any parameter when it is released for sale, it is likely that it will cease to comply with its specification in a relatively short time; that is, it will have a short shelf-life. This fact can be addressed by setting two specifications, namely a release specification with which the product must comply at the time of its manufacture and release for sale and a check specification or shelf-life specification having wider limits with which it must comply throughout its shelf-life. The shelf-life of the product is therefore that period of time required for the least stable parameter of the product to change from the limit value of the release specification to the limit value of the shelf-life specification. This is illustrated in Fig. 23.1.

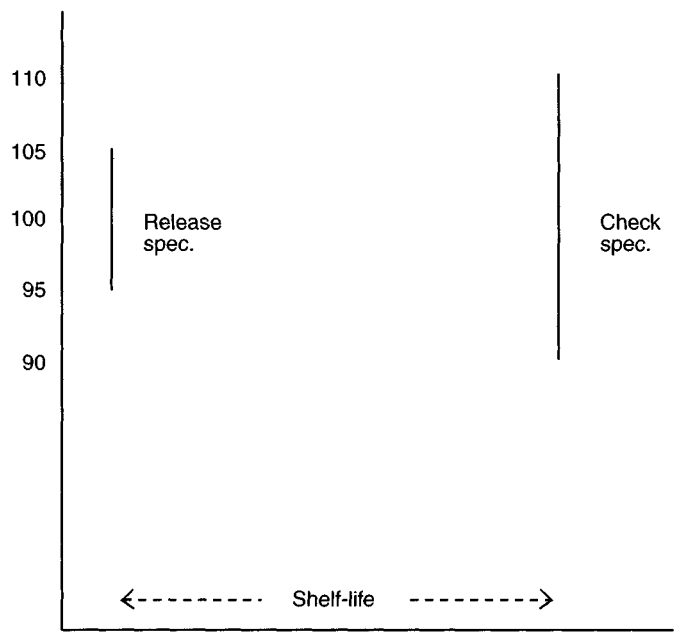

Fig. 23.1 Release and check (shelf-life) specifications determine shelf-life.

The limits of the check specification need not necessarily be extended beyond those of the release specification at both the upper and lower limits. Parameters with values which tend to fall need only the lower limit extending; those which tend to rise, e.g. viscosity, hardness and water content, require only the upper limit of the release specification to be raised.

The stability of a product is made up of two distinct components:

1. The inherent stability of the contents of the immediate container. This refers to the stability of the contents when stored in an inert, impermeable container with which it does not interact and which protects it completely from the ambient atmosphere.
2. The compatibility between the contents and the immediate container. This includes all interactions between the contents and the container. Such interactions may be any or all of the following:
   (a) sorption of constituents of the contents by the container,
   (b) leaching of constituents of the container into the contents,
   (c) adverse effects on the container such as corrosion.

Contents–container compatibility also includes the effectiveness of the container in protecting the contents from atmospheric oxygen and/or water vapour and in retaining water and other volatile constituents of the product.

Since 'product' is often used to refer to the contents and 'product–container compatibility' is often used to refer to compatibility between contents and container, in the following 'product' will be used to refer only to the combination of contents and container.

It is important that it be borne in mind, in designing and interpreting the results of any stability study, that total product stability consists of these two components. The significance of changes observed when samples are stored can be assessed only if it is known whether they indicate instability of the contents or incompatibility between contents and the immediate container. Stability tests should be designed in such a way as to show to which of these any observed changes are due.

The types of change that can occur on storage include the following:

1. Contents
   (a) Physical
      (i) viscosity
      (ii) texture
      (iii) colour
      (iv) odour
      (v) pH
      (vi) loss of volatile constituents
      (vii) uptake of water, oxygen or carbon dioxide.

(b) Chemical
  (i) degradation of (active) constituents
  (ii) interaction between constituents
  (iii) loss of constituents by sorption by container.
(c) Microbiological
  (i) loss of antimicrobial preservative efficacy
  (ii) microbial spoilage.

2. Container
   (a) Leakage
   (b) Corrosion
   (c) Stress cracking.

23.2 SPECIFIC OBJECTIVES OF STABILITY TESTS

While it is true that the overall purpose of any stability test is to determine whether the contents of a pack are stable and the contents and the immediate container are compatible, the specific purpose of a particular test can often be more specifically defined. If the product under test is a new product, then it is necessary to carry out a full programme of stability and compatibility testing. In many instances, however, stability tests are conducted on modifications of products, the stability and container compatibility of which are already known. Thus, tests may be required to investigate the effect on product stability of, for example:

1. a modification of the formula,
2. a modification of the manufacturing process,
3. a change in the specification of a raw material,
4. a raw material from a new source of supply,
5. a change to the immediate container,
6. an immediate container from a new manufacturer.

When any such change has been made, it is necessary to conduct stability and compatibility tests on the modified product. But since much is already known about the stability of the original product, the test programme on the modified product can normally be shortened and simplified in comparison with the test programme necessary for a completely new product. It is already known which parameters of the product are most likely to be affected by the modification to the product or the immediate container. Therefore, much time and effort can be saved by designing the test to concentrate on those aspects of the product and/or the immediate container.

It is important, therefore, before planning any stability–compatibility test, to define clearly the specific objectives of the test and to design the test to yield the information necessary to meet those objectives in the most efficient way. It is inefficient to submit all stability test samples to a standard battery of tests.

23.3 ACCELERATION OF CHANGES

Products are normally required to have shelf-lives that are measured in years. Therefore, in addition to real-time studies (storage at ambient conditions) tests must also be conducted under conditions which accelerate any changes occurring at ambient temperature and humidity. Among the storage conditions which accelerate change are the following:

23.3.1 Elevated temperatures

Raising the temperature at which samples are stored normally accelerates the rate at which changes occur and, as a general approximation, a rise of 10°C doubles the rate of reaction. The extent to which this can be applied in practice is limited, however, because reactions at temperatures far removed from those to which the product will be exposed in practice may not occur at all under 'normal' conditions. Hence a product that is unstable at very high temperatures may not necessarily be unstable under the conditions of the market. On the other hand, a product that is stable when stored for a short time at high temperatures is very likely to be stable on long-term storage at lower temperatures.

23.3.2 Elevated humidity

Since many products are adversely affected by moisture, storage at elevated humidity normally forms part of a stability test. It is to be noted, however, that storage at such conditions almost always represents a test of the effectiveness of the pack in protecting the contents from atmospheric humidity rather than a test of the contents. If the contents are liable to lose water and the container does not adequately protect them, then storage at elevated humidity will retard rather than accelerate changes liable to occur under normal conditions.

23.3.3 Cycling tests

Storage conditions which undergo cyclic change often stress the product more severely than does storage in constant conditions. This can be particularly true in relation to contents–container compatibility, where cycling temperature and humidity often reveal inadequacies that constant storage conditions do not.

23.3.4 Freeze–thaw tests

Subjecting a product to alternate freezing and thawing can be of value in indicating the tendency of liquid products to cloud or crystallize and the physical stability of creams or other liquid emulsions.

23.3.5 Exposure to light

Where products are likely to be exposed to light in the market or in use, it is necessary to investigate the effect of such exposure. Accelerating the effect of light on products is not always easy, and since it is often difficult to assess the duration and intensity of exposure to light that products receive in the market, interpretation of test results is often difficult.

23.3.6 Mechanical tests

Vibration of samples can be useful in indicating whether demixing is likely to occur in powder or granular products; it can also serve as an indicator of emulsion stability.

23.4 TEST CONDITIONS

23.4.1 Temperature

In order to be able to extrapolate from the results of storage under conditions designed to accelerate change, it is necessary to store samples at several (that is not less than three) different temperatures. A range of temperatures such as the following is suggested:

- 4°C/ambient humidity
- 25°C ± 2°C/60% ± 5% relative humidity
- 37°C ± 2°C/60% ± 5% relative humidity
- 45°C ± 2°C/70% ± 5% relative humidity.

The temperatures need not be, and frequently are not, exactly those listed above. What is important is that there should be several temperatures reasonably widely spaced.

Samples stored at 4°C are unlikely to undergo much change and therefore they serve as control samples against which changes occurring in samples stored at higher temperatures can be assessed. 25°C approximates to room temperature. It is important that samples be stored at defined conditions of temperature and humidity which are constant within narrow limits. Only then is it possible to assess the significance of changes occurring in samples stored at higher temperatures and/or humidities. While 25°C approximates to room temperature, the storage of stability test samples at ambient conditions is to be avoided. 'Room temperature' or 'ambient conditions' fluctuate and can vary over a very wide range, making interpretation of test results difficult or impossible.

Storage at the higher temperatures produces significant acceleration of the changes taking place at normal storage conditions. Still higher temperatures can sometimes yield useful information. For example, short-term storage at 60°C,

70°C or 80°C can give convincing evidence of stability but, as has already been stated, instability at such high temperatures does not necessarily indicate instability at 'normal' temperatures.

23.4.2 Humidity

As storage at excessively high temperatures can yield misleading information, so also can storage at excessively high humidities. It is suggested that test samples be stored at humidities not higher than 80% relative humidity (r.h.). At relative humidities higher than this, moulds may grow – something which very rarely happens even in markets having very high humidities. The test conditions suggested in Section 23.4.1, and particularly storage at 45°C/70% relative humidity, normally provide adequate evidence of the ability of the pack to protect the contents from high external humidities; but if the goods are intended for markets where they may be subjected to extremes of temperature and humidity, tests at other conditions may be helpful.

The climatic conditions in any region are available in published data [1]. It is suggested that samples be stored at the mean maximum temperature and the mean maximum humidity. Such storage will give some exaggeration of the actual conditions in the market in question, the extent of which will depend on the daily and seasonal variations in that market.

It is possible to reproduce any desired conditions of humidity in a closed vessel, the atmosphere of which is in equilibrium with a saturated solution of a salt. Table 23.1 gives examples of the range of humidities that can readily be achieved in this way.

Where goods have to be transported by sea or by air to distant markets, they may be exposed to severe conditions. The temperatures in the holds of ships in tropical regions can be very high and in the cargo holds of aircraft they can be very low. The conditions such goods may encounter cannot be accurately

Table 23.1 Constant humidity solutions

Saturated solution	*Temperature (°C)*				
	10	*20*	*30*	*40*	*50*
Potassium nitrate (KNO_3)	95	93	91	88	85
Potassium chloride (KCl)	88	86	84	82	80
Ammonium sulfate $(NH_4)_2SO_4$	82	81	80	79	78
Sodium chloride (Nacl)	76	76	76	75	75
Ammonium nitrate (NH_4NO_3)	72	65	59	53	47
Magnesium nitrate ($Mg(NO_3)_2,6H_2O$)	57	55	52	49	46
Potassium carbonate (K_2CO_3)	47	44	43	42	–
Magnesium chloride ($MgCl_2,6H_2O$)	34	33	33	32	31

known. Therefore it is always desirable to despatch test goods to tropical markets by the normal means used for full consignments and arrange for samples to be returned for examination at specified intervals.

23.4.3 Cycling tests

As has already been stated, tests under conditions that are periodically changed can impose greater stress on samples than storage under constant conditions. The most appropriate conditions in any given case will depend on the conditions that the product will encounter in the market.

The following are suggested as generally useful cycling conditions:

- 37°C/80% r.h. alternating 24-hourly with 20°C/ambient humidity.
- Mean maximum temperature/mean maximum humidity alternating 24-hourly with 20°C/ambient humidity.

23.4.4 Freeze–thaw tests

Freeze–thaw, that is −30°C alternating 24-hourly with ambient temperature, tests are desirable for all solutions, emulsions, creams and other liquid or semi-solid products.

23.4.5 Exposure to light

Products that are likely to be exposed to light should always be tested for their photosensitivity. While it is on the colour of a product that the effects of exposure to light are most readily apparent, other less obvious effects may occur.

The amount and nature of light exposure that products receive is difficult to quantify. Natural light varies in intensity and duration with the location and the season. This alone makes it difficult to accelerate quantitatively the effects of light exposure in the market. This difficulty is compounded by the fact that most artificial light sources do not have the same spectral distribution as daylight. Xenon lamps do have a spectral distribution similar to daylight and are used for assessing the effects of daylight on products of various kinds. In conducting tests to assess the effects of light on cosmetic products, the following storage conditions are suggested as being more convenient and practicable:

1. North-facing daylight. Exposure to direct sunlight is not recommended since even relatively short exposure to strong sunlight can produce changes that rarely, if ever, occur in practice.
2. Continuous exposure in a light-testing cabinet. Daylight-type fluorescent tubes, having outputs in the visible and ultraviolet spectra, provide a suitable source of illumination. Samples may be held about 1 ft (30 cm) away from a battery of several such tubes, the samples being supported on a wire mesh or

perforated tray to allow the free circulation of air and so minimize the heating effect of the light source. A few samples wrapped in foil should be stored with the samples. These serve as dark controls and enable changes due to light to be distinguished from any effects of heat from the light source.

Because it is difficult to quantify the amount of light that products are exposed to in the market, it is also difficult to assess the significance in relation to shelf-life of changes observed in test samples. This difficulty may be overcome, at least in part, by the use of control or reference samples. The interpretation of test results can be simplified if products known to have adequate light stability are exposed to the same test conditions at the same time. If the light stability of the test samples is comparable with that of the control samples, then it is very likely to be satisfactory in practice. Light exposure may be quantified more accurately by a method developed for assessing the colour-fastness of textiles. This is described in detail in British Standard 1006 (1978), 'Methods of test for colour-fastness of textiles and leather'. In this test, quantification of the light exposure is achieved by the use of standardized strips of woollen cloth coloured with dyes which differ in their light-fastness. There are eight such standards of which No. 2 requires twice as much exposure to fade to a given extent as does No. 1; No. 3 requires twice as much as No. 2 and so on. While designed for use with textiles, this test can be adapted to cosmetic products. For the latter, which do not have to have the same degree of light-fastness as textiles, it is usually more convenient to rely on comparison with other similar products known to have adequate light stability in the market.

23.4.6 Mechanical tests

Tests for a period of some hours in a suitable vibration apparatus are useful in assessing the behaviour during transport and storage of powders and granular preparations. It is desirable to use different frequencies and amplitudes of vibration. Centrifuging emulsions can also give useful information on their tendency to cream or separate. The results of such tests should, however, be interpreted with caution. While an emulsion that does not separate when centrifuged is very likely to be stable on prolonged storage under normal conditions, an emulsion that does tend to separate on centrifuging may nevertheless exhibit quite adequate stability under normal conditions.

23.5 TEST SAMPLES

Stability testing is liable to be regarded as the final stage in the development of a product to be carried out on the finished product. In fact, considerations of stability should be taken into account at all stages of the development of a product. It is recommended that stability should be investigated not only on pilot batches

and production-scale batches but also on products prepared on the laboratory scale at an earlier stage of development.

While full formal stability/compatibility testing on every formulation produced during development is quite impracticable, useful information can be gained at an early stage, if the formulation chemist carries out some *ad hoc* tests to evaluate those aspects of the formulation that are recognized as those most likely to limit the stability of the product. In this way stability problems can be recognized at an early stage and corrective action taken, so saving much development time and effort. Even formulae that are superseded by other formulations can yield useful stability information if they are kept on test and examined periodically.

23.5.1 Pilot batches

Stability tests should always be carried out on pilot batches. At least two pilot batches should be tested, and if these are to yield the results of maximum value they should be manufactured from different batches of raw materials. The test samples should be stored either in the containers in which the product will be marketed or at least in containers that approximate closely to them. Stability tests on pilot batches are important in that they yield information on the stability, or instability, of the product earlier than tests on production-scale batches. They are never a substitute for the latter.

23.5.2 Production batches

Since the scale of manufacture can influence the characteristics of the product, it is essential to study the stability of the product made by the full-scale production procedure and with the equipment used for routine production. At least two such batches should be studied. These test samples must be stored in the containers to be used for marketing. If the product is to be marketed in more than one size of container, all sizes should be included in the stability/compatibility test. The samples should be placed on accelerated stability test; that is, they should be stored at elevated temperatures, elevated humidity and, where appropriate, submitted to cycling tests, freeze–thaw tests, exposure to light and mechanical tests. Samples should also be stored at normal room temperature or the normal market conditions and these samples should be kept on test for the whole of the proposed shelf-life of the product.

Even when a product is established and is in regular production, its stability should continue to be monitored. With the passage of time unsuspected and undetected changes may take place in raw materials, method or scale of processing, in the material or method of manufacture of the container or in some other way which may affect the stability of the product. For these reasons, the stability of all products in regular production should be regularly and continuously monitored. It is desirable that samples of all products in regular production should be periodically withdrawn and placed on long-term stability test. Such samples

need be stored only at room temperature and examined at relatively infrequent intervals. Normally only those aspects of the contents or the container that are recognized as being those most likely to undergo change need be examined.

Stability tests on pilot and production batches should be conducted not only on new products, but also wherever there has been any change in the formulation, the container, the sources of starting materials or container, the method or scale of manufacture or any other change that could influence the stability of the product.

23.6 PLANNING OF TESTS

The first action in setting up a stability/compatibility test must be to define the objectives of the test. This will enable the numbers of samples to be put on test and the frequency of examination to be calculated. An examination schedule should then be drawn up. This shows the time intervals at which samples stored at the different conditions are to be tested and the tests to be applied at each examination. An outline test schedule for an imaginary product is shown in Table 23.2.

Table 23.2 Stability test schedule

Product Name:
Formula No.:
Analytical Spec. No.:
Packaging Component Spec.:
(immediate container)

Storage condition

Time (months)	*4°C*	*25°C/60% r.h.*	*37°C/60% r.h.*	*45°C/70% r.h.*
0.5	–	–	–	P
1	–	P	P	PA
2	–	P	PA	PA
3	–	PAC	PAC	PAC
6	–	PACX	PAC	–
9	–	PACX	–	–
12	–	PACX	–	–
18	–	PACX	–	–
24	–	PACX	–	–
36	–	PACX	–	–
48	–	PACX	–	–
60	–	PACX	–	–

P = Appearance, odour, texture, viscosity, pH, weight loss.
A = Assay of any active constituents.
C = Preservative challenge tests.
X = Assay of preservatives.

Examinations are most frequent in the early stages of the test and on the samples stored at elevated temperature and humidities. No single test schedule is applicable to every test. A stability test on a new product about which little is known will require more detailed and more frequent examinations than one on an established product to which a minor modification of the formula or the manufacturing process has been made.

The examination schedule having been drawn up, the numbers of samples to be put on test at each condition can then be calculated. The number put on test must exceed that calculated from the schedule in order to allow for tests to be repeated when unexpected results are obtained or for the frequency of examination to be increased if changes are found to occur more rapidly than anticipated. An examination schedule is not to be regarded as inflexible but as a best estimate made at the start of the test.

When samples are removed for examination, the remaining product in the opened container should be destroyed and a fresh unopened container used for each subsequent examination. Where products are supplied as bulk containers the contents of which are removed at intervals over a period of time, additional tests should be conducted on partly filled containers.

When the container is closed by a screw cap, the caps should be applied with a standard torque and when each sample is opened the release torque should be measured and recorded.

23.7 CONTROLS

In any stability/compatibility test, control products can often greatly facilitate evaluation of the data yielded by the test. They can be either container controls or product controls.

When the product under test is packed in an immediate container with which there is any possibility of interaction, samples of the contents contained in inert, impermeable packs should always be submitted to the same test conditions. Only if this is done will it be possible to attribute any observed change to instability of the contents, or interaction between the contents and the immediate container, or inadequate protection of the contents from the atmosphere afforded by the container. Appropriate remedial action can then be taken.

It is also very helpful to include a reference product in the test. If the test product is a variant of an established product which is known to have an adequate shelf-life, then the original product should always be used as a control. In such instances the objective of the test is not to determine the stability and compatibility of the product, but to determine the extent to which the variation in formula, method of manufacture and so on, has affected its stability and shelf-life. This can enable the nature and extent of the testing carried out at each examination to be directed specifically to those aspects of the product most

likely to have been affected by the change, thus saving much time and effort. This situation exemplifies the importance of defining the specific objectives of a stability test before starting to plan it and draw up examination schedules.

23.8 EXAMINATION SCHEDULES AND TEST METHODS

Those samples most likely to undergo change, that is, those stored under the most severe conditions, are those which are examined most frequently in the early stage of a stability test. These samples are also those which are left on storage for the shortest time since, as has already been mentioned, storage at conditions far removed from those to which the product will be exposed in the market, can bring about changes which do not occur on even very prolonged storage under market conditions. The following are suggested as periods of storage under the different test conditions. These are offered as indications only and should be varied depending on the nature of the test and in the light of the findings as the test progresses.

• 4°C/ambient humidity • 25°C ± 2°C/60% ± 5% r.h.	for the projected shelf-life of the product
• 37°C ± 2°C/60% ± 5% r.h.	6 months
• 45°C ± 2°C/70% ± 5% r.h.	1–3 months
• Light exposure	1 month maximum

In the case of tests of the stability of products under tropical conditions, since storage at the mean maximum temperature and the mean maximum humidity in the markets in question may give only slight acceleration of actual conditions in the market, samples should be stored for the projected shelf-life of the product.

Many of the important properties of products – for example, appearance, colour, odour, taste and texture – are assessed subjectively and cannot readily be recorded in numerical terms. Record keeping and the evaluation of the results of tests are facilitated if, rather than attempting to record a subjective description, results are recorded in terms of the extent of change from the original on a scale such as: 1, none detectable; 2, barely discernible; 3, slight; 4, distinct; 5, marked; 6, very marked. Where freshly manufactured product is not available for comparison, the samples stored at 4°C serve as useful comparators since they are normally less likely to have undergone any marked change in these properties.

Before a stability test is started a specification will normally have been developed and test methods defined for use in the routine quality control of the product. In examining stability test samples the tests applied are not always those used for quality control purposes. While the product put on test must have been

tested fully against the specification before it is put on stability test, it may be appropriate to omit certain of the quality control tests in the examination of stability test samples; examples are identification tests for specific constituents. On the other hand, it is often necessary to apply to samples tests that are not included in the quality control specification; these may include tests for specific degradation products.

Where the product contains an active ingredient which is determined quantitatively, it is imperative that the analytical method by which it is determined in the stability test samples differentiates between the compound and its decomposition or degradation products; in other words, that it is stability-indicating. High-pressure liquid chromatographic (HPLC) methods are to be preferred. They enable degradation products to be detected and measured well before their identities have been established. Furthermore, the increase in the area of a degradation product peak may give a clearer picture of the degradation process than the proportionately much smaller decrease in the area of the main peak.

It need hardly be said that all analytical methods applied to cosmetic products, whether for quality control or stability test purposes, must be fully validated in respect of precision, accuracy and linearity. Methods applied to stability test samples need additional validation as stability-indicating methods. Those used to detect and quantify degradation products must also be validated in respect of the limit of detection and the limit of quantification; absence of detectable degradation products is meaningful only if the limit of detection of the method used is known and stated.

The most obvious effect of exposure to light is a change in colour, but it is not necessarily the only one. Some compounds are photo-labile and therefore samples that have been exposed to light should be examined fully and not only in terms of their colour. Emulsions should be examined microscopically and the droplet sizes of the disperse phase measured and noted, even where this is not included in the quality control specification.

Many cosmetic products contain antimicrobial preservatives, the efficacy of which will have been proved at the time of formulation by means of challenge tests. That the efficacy of the preservative system in stability test samples is unimpaired must also be confirmed by challenge tests. The method of the European Pharmacopoeia, 3rd Edn., is a standard method that is equally applicable to cosmetic products. The efficacy of the preservative system is challenged against *Aspergillus niger, Candida albicans, Pseudomonas aeruginosa* and *Escherichia coli*. It is essential that tests be conducted to confirm that the product continues to be adequately preserved throughout its shelf-life. In addition, chemical analyses should be carried out to confirm that the preservative system is unchanged. In this way any instability of the preservative(s) may become apparent before it is shown by microbiological challenge tests.

In examining stability test samples attention should also be given to the pack. Where the contents contain volatile constituents or are hygroscopic, measurements

of weight loss or gain, particularly in samples stored at high temperatures and high humidities, should always be carried out. The immediate container should also be carefully examined for evidence of change during storage; such changes may include locking (that is, the cap or other closure having become so firmly held in place that it is difficult to remove) or backing-off (that is, a reduction in the release torque during storage, which may ultimately result in leakage) of screw caps, delamination of laminates, stress-cracking of plastic tubes, detachment of internal lacquers, blockage of spray valves and so on.

23.9 RECORDING RESULTS

In any stability test a considerable quantity of data is accumulated over a relatively long period of time; it may also be necessary to produce stability test reports at intervals throughout the duration of the test. While results can be recorded manually on cards, the recording of stability test data lends itself particularly well to storage and recall on a computer. Data can be input by the chemist or technician as results are produced. If the examination schedule is also held in the computer, a weekly printout can be produced showing the examinations due each week, so making it unnecessary to keep a manual diary. Such a system also greatly facilitates the production of the stability reports that may be required at intervals throughout the test.

It need hardly be said that every test result must be recorded and any anomalous or unexpected results thoroughly investigated at the time. It is important that stability test data be periodically critically reviewed. If this is done, trends can be detected and possible instability in respect of a particular parameter recognized long before that parameter has reached the limit of the shelf-life specification.

23.10 INTERPRETATION

The assignment of shelf-lives on the basis of accelerated stability studies is a predictive process, the accuracy of which increases the longer the test continues. It also depends on the type of test concerned and its objectives. Interpretation is also greatly facilitated if suitable controls are included. Tests, which are essentially comparisons, are relatively easy to assess. For example, if the purpose of the test is to determine the effect of a modification of the manufacturing process or of a new immediate container, product made by the original method or in the original container is available as a control against which the modified product can be assessed. It is often possible to perform such tests under severe conditions to produce great acceleration of any changes since it is only necessary to determine whether the modified product is superior to, equal to, or inferior to the original products.

The evaluation of stability test data on completely new products and/or immediate containers is more difficult. In some cases it is possible to find a comparable

product that can be used as a control; if such a product is included, interpretation of the test data is facilitated. In evaluating test data it is necessary to distinguish between the stability of the contents and incompatibility between contents and container or inadequacy of the container to protect the contents. That is, it is necessary to know the cause(s) of any changes for remedial action to be taken.

The true indication of the stability of the contents is that obtained from the control samples contained in inert, usually glass, tightly closed containers. The degree of acceleration can be estimated by comparing the extent of the changes occurring at 37°C and 45°C or other elevated temperatures, with those occurring at 25°C.

Assessment of samples stored at elevated temperatures can be made very approximately on the assumption of a doubling of rate of change for each 10°C rise in temperature; but this is, at best, a rather crude approximation. A more accurate method of predicting the rate of change at a lower temperature from data produced at higher temperatures is the Arrhenius equation

$$K = Ae^{-Ea/RT}$$

or

$$\log k = \log A - \frac{Ea}{2.303} \cdot \frac{1}{RT}$$

where k is the specific reaction rate, A is the frequency factor, Ea is the energy of activation, R is the gas constant and T is the absolute temperature.

This is, however, applicable only to liquid homogeneous systems, which excludes almost all cosmetic products. In any case, the critical properties of cosmetics are frequently subjective and not capable of being expressed numerically. There may be instances, however, where it can be applied in determining the stability of isolated cosmetic ingredients.

An estimate of the degree of acceleration of change over market conditions can be made only if the mean temperature, or more precisely the kinetic mean temperature, which is higher than the arithmetic mean temperature, is known. In the UK and other temperate climates the mean kinetic temperature is 21°C, in Mediterranean climates 26°C and in hot climates 31°C. The respective relative humidities are temperate 45%, Mediterranean 60%, hot dry or moderate climates 40% and hot humid climates 70%. (These figures are taken from a Guideline on stability tests on medicinal products issued by the EC Committee on Proprietary Medicinal Products [2]). The mean kinetic temperature in any region of the world can also be derived from published climatic data [1].

It is important to remember that the establishment of the shelf-life of a product is a predictive procedure. It is based on data generated on samples stored under conditions that are believed to accelerate any changes occurring at the conditions the product will encounter in the market. All such predictive procedures have a certain degree of probability of success. That probability is least

when it is based on short-term data on samples stored at conditions far removed from actual market conditions. It increases as longer-term data are produced on samples stored under conditions nearer those of the market, but it is always less than 100%. In this sense a stability test can never be regarded as finished in less time than the actual shelf-life of the product. The point at which so-called 'stability clearance' can be given will depend on the product in question, the results obtained on comparator products and experience in the market with those products. The results of stability tests, and the conclusions drawn from them, should not be presented in such a way as to suggest that the product has been proved to be 'stable' but rather as a probable shelf-life under given conditions.

23.11 SUMMARY

A stability test is a process which extends over a relatively long period of time and which involves a substantial amount of laboratory work. It is imperative that such tests should be conducted rigorously and as efficiently as possible. Maximum efficiency can be achieved only if the objectives of the test are clearly defined before the test is scheduled and started. Control products should be included wherever possible since they can greatly facilitate the interpretation of test data. There should also be sufficient flexibility in the test plan to allow modifications (such as changes in the examination schedule) to be made in the light of information that becomes available as the test progresses. There should never be a standard test plan that is applied uniformly to all stability tests. Clear definition of test objectives and careful planning of tests can yield the required information most efficiently and in the shortest time.

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PART 4
PERFUMES: THEIR MANUFACTURE IN PRODUCTS AND PSYCHOLOGY IN USE

24

Perfume and the manufacture of consumer products

Norman J. Van Abbé

24.1 INTRODUCTION

It was a popular notion for countless generations that every medicine must be expected to have an unpleasant flavour. When, at last, truly effective therapy began to foster a less mystical and more rational approach to medication, attitudes started to change. The main obstacle to making every oral medicine pleasant tasting nowadays is the danger of encouraging small children to take too much. In other words, those features of a product which are readily evaluated by users are obliged to keep up with the times; this certainly applies to the flavour and even more, perhaps, to the aroma of a consumer product.

Similarly, disinfectants were formerly expected to have a distinctive odour which would be disagreeable to many people. Household products of a traditionally obnoxious nature are no longer in vogue, however, and the trend is towards the elegant presentation of even the most mundane commodities. An appealing perfume is often virtually essential for the success of the product. Woe betide any manufacturer who pays but scant attention to perfume when the public expects an attractive aroma!

When manufacturers first tried to make products with better aromatic properties, their efforts were quite primitive by present-day standards. Easily obtained essential oils (lemon, bergamot, clove, mint and so on), or their simplest individual constituents such as terpineol, menthol, eucalyptol and geraniol, were used. Increasing competition between brands in the same product sector, and perhaps the refinement of public taste, led to more subtle developments in perfume being demanded, which called for the earnest endeavours of highly skilled perfumers. These experts are now asked right at the early development stages to put forward ideas for perfuming new or reformulated consumer products of many kinds.

Butler, H. (ed.), Poucher's Perfumes, Cosmetics and Soaps, 10th Edn., 717–748

It could be said that fragrance reaches its peak of achievement in the form of concentrated essence perfumes. These include the more modest brands aimed at the average purchaser and also the costly, exclusive ones at the top end of the market. In addition there is growing scope for making good use of a perfumer's expertise by way of fragrances to incorporate into a broad spectrum of 'functional' products, i.e. preparations to deal with easily identifiable and, in many instances, objective user needs. Perfumed 'functional' products range from skin-care cosmetics and toiletries (e.g. sunscreens, antiperspirants and antidandruff shampoos) to many household products such as dishwashing detergents, floor polishes and insecticides, some pharmaceuticals, tobacco and a host of others. In short, anyone closely involved in developing such products ought to think carefully about the ways and means of perfuming them to maximize their consumer appeal.

24.2 BRIEFING A FRAGRANCE SUPPLIER

Nowadays, creative perfumers are seldom found anywhere except on the staff of specialist firms supplying fragrance to finished product manufacturers and for some industrial applications (e.g. for deodorizing effluent). There are, however, a small number of perfumers offering their expert services as independent consultants. Whether a product manufacturer makes use of a supplier's staff perfumer or an independent consultant, a great deal depends on how effectively liaison is achieved. Mutual understanding is essential in the course of evolving a new line of high-class perfumery and equally so to add the finishing touches to a 'functional' product for toiletry or household use. Whichever purpose is intended, a product manufacturer needs at least a rudimentary understanding of the use of fragrance and some ability to communicate the nature of requirements to a potential supplier. Makers of cosmetics inevitably find themselves briefing perfume suppliers quite frequently. They acquire or, perhaps with little justification, imagine they have acquired sufficient ability to explain their needs without risk of misunderstanding. Problems certainly arise from time to time, particularly when new technical or marketing personnel transfer from other fields to assume responsibilities involving perfume, with which they have little or no previous experience. Sometimes firms normally having no concern at all with perfume suddenly become involved, perhaps in the course of diversifying their product range. Quite serious communication problems may be expected. Fortunately the essence houses are accustomed to circumstances of this nature. A fragrance supplier is obviously represented most effectively in briefing sessions by someone adept at interpreting the ill-defined wishes of a potential client. Pitfalls awaiting the inexperienced client include not just failure to find an outstanding perfume ideal for the purpose in fragrance terms, but also disasters such as emulsion breakdown during the manufacturing process or a hopelessly inadequate shelf-life.

The first important aspect is always the **orientation** of a perfume, i.e. its principal odorous characteristics. Essence houses sometimes offer speculative new perfume ideas to product manufacturers who might show some interest in them. Now and again one of these unsolicited samples will obviate any need for a client to try to explain verbally what is wanted to satisfy a current requirement. The suggestion may fortuitously prove satisfactory as it stands or more likely with only slight modification. In the absence of acceptable speculative ideas, a client company has somehow to make known what is wanted and what is to be avoided in perfuming a new or relaunched product. The least satisfactory way for someone who is not a skilled perfumer to try to define the perceived criteria is to do so too precisely in the perfumer's own vocabulary, by referring to odours as 'green', 'woody' and the like. A perfumer and a non-perfumer may well disagree completely, even as to the correct identification of pine and lavender in typical product bases. Yet these are among the most straightforward as well as the most common types of fragrance likely to be met. The chances are that the use of an inappropriate term will be totally misleading and liable to cause unnecessary delay by diverting the perfumer on to the wrong track.

Confusion may sometimes be lessened, but not altogether prevented, by making reference to a past or present leading brand of high-class perfume. Such a reference might well be given as an illustration of the style of aroma desired but never as a request for a slavish copy. The most satisfactory approach, however, is to submit a fully detailed written brief showing as clearly as possible what the product is intended to comprise or achieve, e.g. type of formulation (in terms of composition, physical form and function), proposed packaging, intended geographical or ethnic distribution, target population (sex, socioeconomic status, age groups), possible brand name, anticipated turnover and acceptable perfume costing. Anything else likely to contribute to a clear understanding of the requirement should be included. Providing such a brief, followed by personal discussion with the potential suppliers, should optimize progress towards a suitable outcome in the shortest possible time.

According to the type of product concerned, such as a footspray or perhaps a home laundering conditioner, differences are to be expected in terms of the development stage at which it is most helpful to consider perfume selection. The most profound consideration will be whether perfume is needed at all in some products. If it is, it could be advantageous to discuss this right from the start of product development, or it may not be practicable to consider perfume seriously until the product's development is nearly complete. The difference in approach may, for example, reflect the relative extent of knowledge regarding the likely background odour of the unperfumed product. Whatever the time chosen to think in detail about perfume, the first step will be to make contact with potential suppliers or consultants so as to outline the needs, preferably in the suggested form of a written brief. A creative perfumer or someone not quite so skilled but still well versed in the subject will probably be brought into

discussions at an early juncture. Similarly, the client will be well advised to involve a formulation chemist directly in the deliberations even if perfume requirements are subsequently advanced by other members of staff.

A controversial aspect is the question of how much a supplier needs to know about the nature or composition of a potential client's product which is either under development or complete. Undoubtedly, a perfumer should at least be supplied with plenty of the unperfumed product base as soon as possible, to facilitate studies of the influence of any background aroma and other likely sources of incompatibility. Numerous features of a formulation may have a critical influence on the perfume, particularly on its stability. Ideally, the client and supplier should have complete confidence in each other. There is every reason to believe that each essence house jealously guards its reputation for the strictest confidentiality on behalf of all clients and enquirers. Hence there should be little or no need to hesitate about giving samples of the intended product for perfumers to study along with a complete formula breakdown or at least a clear indication of the salient features.

At this juncture, major considerations are the number of possible suppliers to be briefed for a particular development and the length of time they are given to come up with an answer. There are no universal principles but the pros and cons for various conclusions are worth trying to assess.

Exclusive briefing of a single essence house is occasionally advocated and may well be favoured in order to provide the greatest possible safeguards for confidential handling of the proposition, even though there should be no need for anxiety in this direction. The main argument for exclusive briefing is that perfumers are sure to be most effectively inspired when they know in advance that their efforts will definitely be rewarded if they succeed in putting forward a satisfactory response to a brief. Moreover, when modification of an early submission seems to be indicated, this may be undertaken in stepwise fashion with full consultation and mutual understanding.

The concept of restricting briefing to a single essence house initially at least, is not meant to suggest that a product manufacturer should stay with the same supplier for all requirements. The suggestion is only that for each development or relaunch of a product, the first efforts at finding suitable perfume could advantageously be confined to briefing only one potential supplier. Many product manufacturers (or members of their staffs) subscribe to the notion that particular essence houses are specially good at devising certain kinds of perfume, e.g. 'fresh' types or perhaps household rather than *haute couture* lines. Although each fragrance supplier employs only a small team of creative perfumers, their ability to tackle a wide variety of work need scarcely be questioned. No such firm, large or small, could allow itself to become too specialized if it is to survive in such a highly competitive field. To avoid possible complacency on a supplier's part or even just to discover who is performing really well at a given time (knowing that management and staff changes in the essence house could

influence their effectiveness), the handing of briefs for different products in turn to a succession of different firms must be a prudent approach.

Sometimes the view is advanced that exclusive briefing may be appropriate for high-class perfumery in developing an entirely new fragrance line, but not for perfuming more run-of-the-mill 'functional' products. In demanding the highest achievements of a creative perfumer's artistry, the concentrated essence is unique. In tonnage terms, though, a supplier may stand to gain more by winning orders to supply fragrance for widely used brands of various 'functional' products. The latter do therefore merit serious attention on the part of creative perfumers and indeed everyone else involved in responding to a development brief.

Despite any recommendations to the contrary, a common practice is to offer essentially the same brief concurrently to four or more potential suppliers. Now and again a stipulation is made that no more than three candidate perfumes will be considered from each prospective supplier so as to avoid making the task of selecting a preferred one too unwieldy.

As the initial response to a briefing, some suppliers tend to offer samples taken from a range of 'off-the-shelf' fragrances. Care will be taken to see that the submitted perfumes are at least reasonably compatible with the intended product, e.g. recognizing the special problems in perfuming a soap bar. The offering of 'off-the-shelf' samples conceivably reflects a feeling that the chances of gaining any business at all from a new enquiry are somewhat remote, bearing in mind the practice of multiple briefing. Many attractive perfumes are, however, created in response to enquiries but for various reasons they cannot all achieve instant recognition and some are liable to stay on the shelf waiting for a customer. Offering them in response to subsequent enquiries is both legitimate and sensible. Valuable time may be saved in the development of a new product. 'Off-the-shelf' fragrances should therefore not be regarded as inferior or substandard. Another reason for the availability of these specimens may be that an essence house likes to have a range of fine fragrances at hand in order to demonstrate the capabilities of its team and it is most unlikely to offer anything likely to undermine its reputation.

As multiple briefing is so widely practised, the essence houses tend to expect such an approach as the norm in new product development. They do not resent the challenge of a competitive strategy. Frequent participation in three-way or broader contests may even be preferred to the alternative of infrequently having an opportunity to work on a more exclusive brief. Substantial differences in the size of the various essence houses do not appear to influence their attitudes in this connection materially.

24.3 TIME ALLOWED FOR PERFUME PREPARATION

Whether briefing is exclusive or multiple, and assuming that a descriptive brief is provided along the recommended lines, one of the most crucial factors will be

the time allowed for receiving a response. The typical time-span ranges from a few days to about 3 months, but rarely longer. For a perfumer to assess a client's needs and put together the first outline for a possible response, just a few days may well be sufficient if nothing really innovative is desired. Devising a more original or outstanding perfume undoubtedly takes longer and sufficient time must be allowed.

The creative efforts aimed at originality or particularly attuning the product to its intended image and testing for stability, are not the only time-consuming steps. For example, in 'functional' products, the lasting powers of a perfume may be a significant factor, favourable or otherwise. Residual aroma of the hair after shampooing calls for different perfume characteristics than, for example, the residual perfume on textiles after laundering. Giving proper attention to questions of this nature ought not to be unduly rushed. The behaviour of a perfume at temperatures well above ambient during product application may be another factor for consideration and this will certainly have to be examined experimentally. Essence houses are usually able to offer the services of a technical development laboratory, often with salon facilities and working alongside the perfumers. The staff will be accustomed to tight schedules but miraculous achievements should not be expected overnight.

The characterization of a suitable perfume, like every other feature of new product development, imposes critical demands on development planning. Forethought and rational timing schedules are needed, whether by way of formalized network analysis or some other preferred system, making due allowance for each crucial step as well as for setbacks which can rarely be altogether excluded.

A supplier working on a perfume concept should, given adequate time, ensure that the fragrance itself and product incorporating it have good prospects for a satisfactory shelf-life. In particular, under normal storage conditions, the aroma quality and intensity need to be retained for the appropriate length of time. Stability may generally be predictable from extensive background knowledge and experience with the same raw materials along with limited laboratory testing. A supplier given no more, and often considerably less, than 3 months to devise a new fragrance and to verify its stability, can hardly be expected to guarantee stability of the product for several years in the shops or in the home environment. In any case, product manufacturers have a habit of continuing to modify formulations long after samples have been given to the essence houses for perfuming. In these circumstances the supplier's experience and limited testing cannot possibly be expected to guarantee unequivocally the finished product's long-term shelf-life. The onus is firmly on manufacturers to substantiate experimentally that their marketed products do have appropriate shelf-life properties.

Aspects of stability most commonly involved in relation to perfume added to 'functional' products include the possibility of product discolouration as well as loss of perfume strength or change in odour character during storage. Changes like these are usually oxidative and frequently related to or intensified

by exposure to UV light. Avoidance of product aeration during manufacture, minimizing headspace in the pack and protection against UV irradiation by choosing opaque packaging material or incorporating UV absorbers in the product or in transparent packaging material, are among the more obvious precautions to be taken.

24.4 COST OF PERFUME

The inherent monetary value of a fragrance blend is not easy for anyone other than a supplier to establish because the composition is not normally disclosed. The contribution made by perfume and the influence of its quality on this, in terms of the ultimate success of a product, are widely accepted even though they cannot be quantified. Some sort of premium is, however, quite obviously warranted in recognition of a perfumer's skill and experience and the supplier's ability to provide a consistently good quality blend. Putting a valuation on such intangibles is always difficult and product manufacturers have to judge as best they can by reference to the general run of fragrance costings from competing suppliers of comparable standing in terms of quality and service.

The uncertainties of costing are partially overcome by deciding in advance how much to set aside for fragrance at the time of establishing a preliminary cost estimate for the whole new product or modification. This target figure is next put in suitable form to the prospective supplier along with the written brief. It is then clearly in the supplier's own interest to submit suggestions complying with the given cost indications or to explain why this would not be satisfactory.

Target costing may be expressed on a basis of price per kg of perfume compound or maybe per 100 kg of perfumed finished product initially. Suppliers are accustomed to both ways of arriving at a preliminary costing, though bulk compound would doubtless be sold on a per kg basis eventually. Expression as cost per 100 kg of finished product at the research and development (R & D) stage has the advantage of not constraining the perfumer too closely on how concentrated or dilute the perfume compound needs to be. Compatibility with other product ingredients could perhaps sometimes be improved, for example, by minimizing the use of a diluent such as dipropylene glycol or benzyl alcohol in the perfume compound. This would probably increase the cost per kg of compound even though it will not increase the cost per 100 kg of finished product.

Upgrading or downgrading the quality of perfume for any reason involves policy decisions calling for wide experience and specialized knowledge. Commercial considerations may point towards an apparent need for cost reduction, and continuing to pay a relatively high price for fragrance in an ordinary household product may seem unnecessary. Whether downgrading would have a significantly adverse effect on consumer acceptance of a new product or an existing one is, however, always hard to foresee. Consumer research techniques may

help to provide the answer but their reliability in terms of the long-term acceptance of a downgraded aroma should not, perhaps, be taken for granted.

24.5 MATCHING

For various reasons, such as the effect of escalating costs at a time of inflationary pressure, a supplier may be asked to limit or reduce costs by devising a less expensive version of an existing perfume compound. The aim is invariably to alter the discernible odour character as little as possible. Normally suppliers try hard to comply with requests of this nature as helpfully as possible, if only to retain a major share of the business. Sometimes, however, the request has to be refused because a reasonably satisfactory modification cannot be made at the lower cost demanded by the client.

When the original supplier of a compounded fragrance declines a request for a cheaper version, others are likely to be invited to tender. An alternative supplier is thereby faced with the problem not only of cutting the cost but also of matching the odour characteristics as closely as possible without the benefit of knowing the formula of the original perfume. Modern techniques of instrumental analysis such as GC/MS will go some way towards identifying the main components and may outline their quantitative distribution. Armed with this information, a skilled perfumer may then manage to devise a passable replica of the original. How far such an approach is ever capable of realizing the intention fully is debatable and it is also hard to be sure how much damage may be done to the product's reputation. Circumstances do still arise in which product manufacturers are impelled to seek cost reduction by 'matching' and essence houses necessarily have to strive to secure these accounts.

Some consideration needs to be given to the ethical aspects of perfume matching as they affect supplier and purchaser. First and foremost the creation of a perfume or series of perfumes exclusive to a particular product manufacturer places an onus of strict confidentiality on the original supplier. Disclosure to anyone else would clearly be unethical. Likewise any knowledge the product manufacturer may glean from a supplier about a perfume formula will be confidential. Making use of this for anything but the agreed purpose for which it was divulged would be in breach of ethical obligations. Some details of the composition may have been unravelled by the product manufacturer's analytical staff; although not subject to quite the same constraints, the disclosure of such details to other suppliers for matching purposes still needs careful consideration on ethical grounds. Essence houses are understandably reluctant to take on assignments liable to compromise their ethical standing whatever prospective purchasers feel about their need for matching perfumes.

Matching has another connotation when the term is used to refer to deliberate copying of successful perfumes made by competitors. Whether or not such copying is intended to enable the match to be passed off in a deceitful or fraudulent

manner, the fragrance industry seems united in condemnation of such practices. The best interests not only of fragrance suppliers but also of product manufacturers, and ultimately consumers too, must surely require a hostile attitude towards matching of a dubious nature.

The history of the perfumer's art, much like that of other artists and gifted craftsmen, shows that each brilliant new departure serves to point the way ahead for its successors. In this respect the development of new perfumes by skilled derivation from earlier ideas cannot be considered in any way reprehensible. The distinction between unprincipled copying and justifiable evolution may be subtle but it is nevertheless crucial.

24.6 PERFUME SELECTION AND EVALUATION

On receiving several perfume suggestions from one or more possible suppliers, a product manufacturer has to decide which, if any, to accept for use in a forthcoming product launch. Normally an elimination procedure will be devised with a view to picking a single winner, although modifications will sometimes have to be made as a result of discussion between supplier and client. To what extent a product's success or failure on the market is truly attributable to its perfume is never known for sure. Foreseeing the merits of one perfume rather than another in advance is subject to even greater uncertainty. The elimination process will be devised with a view to minimizing the doubts but only full-scale marketing for a lengthy period really clinches the argument beyond question. The evaluation of several variants under these conditions will not be feasible and personal judgement ultimately has to be relied on to decide which option is most likely to be preferred. Home user tests or regional test marketing help to demonstrate the best way forward but they do have limitations. The effects of merchandizing techniques or particular TV commercials, for example, on the success of a product are extremely hard to assess. So are the effects of other facets of marketing, such as the choice of packaging material and pack design. Simple, short-term perfume preference tests may be seriously misleading as they cannot take account of the myriad of variables that influence consumer choice and satisfaction in practice.

Despite any reservations about the validity of perfume evaluation test procedures, somehow a decision has to be taken. Out of the range of samples to hand, the one most likely to prove satisfactory in the product has to be identified or steps taken to obtain new or modified perfume suggestions. The timing shown in the product development plan will usually be a major factor governing perfume selection. A search for perfection could continue forever unless some kind of discipline is imposed. Factors of importance in the final selection include whether:

1. there is adequate compatibility with the product as a whole during the manufacturing process;

2. there is any deleterious effect on product shelf-life;
3. product performance is affected, favourably or unfavourably;
4. product safety is affected;
5. the perfumed product has an acceptable consumer rating when first compounded, after use and after storage.

These factors are heavily weighted towards a preponderance of technical criteria. For this reason someone such as a senior formulation chemist, or the nearest equivalent in the establishment, should preferably have the main responsibility for perfume selection, even though he or she does not necessarily have the last word.

The range of pertinent factors is a formidable one in terms of the volume and depth of laboratory work that might be devoted to seeking foolproof answers. If the full range of effort was devoted to each of several perfume suggestions for each development project, perfume evaluation would be a mighty undertaking. The capacity of even the largest R & D laboratory could well be swamped. Abbreviated procedures are therefore mandatory. For example, initial odour evaluation may be carried out on samples in which perfume has been blended with separate samples of product base (perhaps a cream or powder). The least satisfactory offerings are thus eliminated before tackling the more time-consuming task of studying physical and chemical interactions during the course of product manufacture. A range of storage tests may be set up under various environmental conditions without deciding in advance how much to do by way of monitoring changes at intervals subsequently. The examination will be decided later when some of the perfumes have been eliminated for various reasons. The scale of inspection work is thus limited according to the number of candidate perfumes still in the running. Some aspects of shelf-life involve minimum time and attention, such as the straightforward recording of visible changes. Other features, such as consumer ratings for odour after prolonged storage, are liable to be very demanding indeed; there will be no incentive to undertake more than necessary of such assessments.

A number of the technical features of a complex product might theoretically be affected adversely by perfume addition. A case could be argued for a broad array of intricate, costly and time-consuming scientific studies. Though instances may be cited of serious colour changes, emulsion separation and similar misadventures following the addition of perfume, the overall record or experience of manufacturing perfumed products would suggest that devastating effects are quite rare. This would seem to justify taking a degree of risk in relation to compatibility, with the assessment based mainly on background knowledge of the formulation and then on predominantly sensory evaluation of the complete product made under laboratory conditions. Simple measuring of pH, for example, along with assay at intervals of therapeutically active or other constituents specially concerned with product performance, would complement the sensory examinations where appropriate.

Passing reference ought to be made to the relationship between perfume and microbiological status of a product. Some perfume compounds could conceivably be preferable to others through a beneficial influence on preservative efficiency associated with antimicrobial properties of the perfume constituents. In practice, however, it appears that the concentration of perfume is seldom enough to have any marked preservative effect. When the state of preservation of the product itself is barely adequate, or if conditions may be foreseen whereby an upsurge of contamination could overwhelm the preservation system chosen, microbial proliferation could well lead to off-odour which would be ruinous to perfume quality. Occasions may thus be envisaged with some types of product where the ability of a perfume to withstand the effects of microbial growth without substantial loss of or harm to its aroma would be worth studying in depth, as well as the relative resistance to biodeterioration of different perfumes or their main components.

In smaller commercial organizations, the last word on perfume selection has long been, and still remains, a prerogative of the chairman, chief executive or, perhaps, their respective spouses. Since all of these people will most likely have had long experience in their particular areas of business and will thus have acquired a finely tuned perception of the best ways to please their customers, it may well be sensible for them to continue making the final perfume selections in the traditional way. What is less certain is the best way to choose between alternative fragrances before launching out into unfamiliar areas, e.g. when a household products firm is contemplating an extension into the toiletries field. Even the most self-assured executive may feel in need of good advice under these circumstances. Commercial understanding and experience are particularly important when it comes to predicting the likely impact of a new or relaunched product on wholesale and retail buyers as well as the general public. The whole platform for a launch will need to take into account the way in which retail buyers are likely to respond because, rightly or wrongly, they will greatly influence crucial factors like the prominence given to store displays.

There is a long history of highly successful consumer products having been marketed initially by small firms which were later assimilated into much bigger ones. This pattern of business development embraces numerous considerations beyond the matter of fragrance but it may seem to offer some evidence to the effect that entrepreneurial 'flair' still has specially good prospects in this direction. By contrast, the process of arriving at a chosen perfume by way of extensive consumer research and deliberation in committee may be a sure recipe for mediocrity.

Selection procedure designed to ensure that the chosen fragrance is well accepted by consumers must be founded upon criteria appropriate for the purpose. Whether choice is by top management, a committee or a lone chemist, the right question is not whether they themselves like the aroma. Their judgement should be applied to the task of predicting whether the target population will take a favourable view of the perfume and allow this to influence their purchases

accordingly. Sometimes those who are making an assessment will personally like the perfume effect and also take a considered view that it will suit the intended market segment but this will not always work out so. Characteristics of a product just right for today's teenagers may well fail to impress middle-aged company executives responsible for decisions on perfume. National and ethnic preferences are liable to be highly unpredictable; they should never be underrated and, if possible, they should always be assessed locally in the relevant territories or by truly representative individuals. Just a few consumer products are evidently saleable worldwide with the original composition exactly as for the home territory, including the same perfume. Experience suggests, however, that a formulation is usually better developed specially for a particular market. Certainly the fragrance requirement ought to be reviewed, if possible, by discussion and research on-the-spot. The essence houses usually have specialized knowledge of regional and ethnic preferences which is freely available to product manufacturers in need of suitable fragrances.

Steps in the process of narrowing perfume choice could include the following:

1. Assessment by one or more individuals in a development laboratory, e.g. by a senior formulation chemist and his staff.
2. Tests on a small in-house panel of 'expert' panellists; these will have been specially selected following earlier checks on the acuity of their olfactory response and their ability to discriminate between samples in terms of odourant type or intensity.
3. Small-scale, short-term tests for immediate perfume impact or impression using 'non-expert' volunteers.
4. Home-use tests by panels, small or large, consisting of volunteers chosen with the greatest care to correspond to the target consumer population.
5. Regional test marketing of perfumed product in a limited area for a sufficient time to gauge the initial acceptance and also to give some indication of repeat sales volume.
6. Examination of the outcome of all the tests by those designated to be responsible for perfume selection.

24.7 ASSESSING CONSUMER ACCEPTANCE

The impression created by any perfume normally depends on how it rates for suitability, originality and attractiveness once it has been made up in the intended form, e.g. as the main component of an alcoholic essence or as a subsidiary ingredient in a compounded product. In the end what matters is whether the perfume makes a positive contribution to the commercial success of the product and whether this success is maintained in repeat sales at a satisfactory level for as long as might have been expected. The exact influence of perfume acceptability on sales achievement is never known. Opinions are always based on viability of the product as a whole along with personal judgement of the influence of the

perfume. An outstanding fragrance will rarely leave room for doubt but rather more marginal suitability and appeal are unfortunately more typical. The contemporary trend towards relaunching popular brands of many kinds of consumer goods at intervals of 2–3 years, however, possibly means that perfume with an auxiliary role does not really need to have long-lasting acceptance. Sometimes relaunch changes are deliberately limited to other product attributes while retaining continuity of brand identity by way of an easily recognized perfume.

To what extent the choice of a perfume warrants detailed and searching assessment depends on the level of expectations for the planned launch or relaunch and the anticipated significance of perfume in this context. Some methods of assessment are undoubtedly more reliable in indicating consumer reaction than others, but whether to invoke them has to be weighed against the cost and time involved.

Whenever people are invited to assess perfume as experimental volunteers, as distinct from deciding for themselves as purchasers what perfumes or perfumed products to use, the ethical implications need to be considered. This applies especially where substantial exposure in a test chamber or other enclosed atmosphere is involved or product has to be applied to and perhaps left on the skin. Safety is an important aspect but whether or when it is *morally* justifiable to ask volunteers to accept a risk, however small this is believed to be, is primarily an *ethical* matter. Predictive safety testing in a laboratory helps to identify the level of risk but cannot eliminate it. Volunteers are entitled to know what risks they could reasonably be expected to incur if they agree to participate.

The issue of ethical justification arises because volunteers cannot exercise the freedom of choice enjoyed by normal purchasers. Both may be liable to suffer injury through exposure to a harmful substance but the moral or ethical position is different for the volunteer who is called upon to obey the dictates of someone else. The absence of free choice is far more important in some ways than the degree of risk involved, so long as a volunteer is not misled with regard to possible risk.

Contemporary views on the ethics of human experimentation are mainly concerned with therapeutic research, if only because mishaps are most likely to have serious consequences when potent pharmacologically active substances are being evaluated with the aid of volunteers. Thus a Code of Practice was established and embodied in the Tokyo Declaration of 1975. Ways in which the ethical requirements for human experimentation may be satisfied in the development of non-medicinal products have not been examined so fully. An article entitled 'The Use of Human Volunteers for Testing Cosmetics and Toiletries' (Van Abbé, 1983, Ref. 5) sets out the main points for consideration as follows:

1. A written protocol is essential, to demonstrate that the work will have a proper scientific basis.
2. The investigators must be clearly identified and appropriately qualified.
3. Volunteers must not be subject to duress and must be free to discontinue participation at any time.

4. Volunteers must have the purposes and risks fully explained to them and be asked to sign a consent form confirming that this has been done.
5. All the relevant facts should be examined by an independent panel or committee competent to assess the scientific merit of the proposed study and to review the steps being taken to safeguard volunteers' interests.

The precise manner in which ethical matters need to be handled in particular circumstances depends to some extent on the frequency and scale of experimentation and the degree of risk to which volunteers are likely to be exposed. So far as perfume is concerned, most investigators probably imagine that the process of odour assessment presents hardly any risk of injury. Serious ethical problems do not appear to be involved but this is not necessarily correct. Perfume has often been alleged to be responsible for initiating skin allergy, although this kind of assertion is not always well founded. The possible association is not readily dismissed and a causal rôle of aromatic substances in asthma could also be a reason for some concern, especially if there is a theoretical risk of substantial exposure, e.g. when perfume chamber tests are used. If perfumed products are applied to the skin and left *in situ,* substantial absorption along with toxic effects at distant body sites might conceivably be involved. Hence it may be unwise to think that ethical aspects of perfume testing may be happily ignored.

No one is likely to suggest that each new perfume evaluation calls for the full gamut of ethical committee approval and associated complexities. The ethical requirements may reasonably be tailored to suit the prevailing needs and the anticipated level of risk. This usually means, for example, that the overall approach to testing in a particular establishment needs to be carefully examined from an ethical standpoint rather than each separate test. Even if the conditions of experiment are believed to involve no more than the slightest risk, each volunteer perfume assessor should be invited to sign a consent form. Such a form should never be relegated to the status of a pre-printed *pro forma,* reiterating formal and inconsequential platitudes. On the contrary, the form needs to be carefully designed with a particular study or set of studies in mind, reminding the volunteer of his or her right to discontinue participation without necessarily giving any reason and explaining the type of experimentation and nature of expected risks, if any. If, as is commonly desirable, steps are taken to exclude individuals with skin allergies, hay fever, etc. and patients currently receiving medical treatment, a volunteer might be invited to confirm that these requirements are fulfilled. Above all, either in writing or verbally, it should be made clear that signing a consent form does not diminish a volunteer's legal rights in any way.

Insurance implications arising from the use of experimental volunteers need additional consideration. The conditions under which liability is covered may impose special requirements for safety evaluation and may also be concerned with the matter of recording the volunteers' consent in suitable form. Further

constraints may relate to the need specifically to inform the insurers if new and previously untried chemicals are involved and there may be particular stress on the qualifications of supervising personnel.

When perfume assessment is deemed to need relatively large numbers of volunteers, the proposed testing is commonly contracted out to an agency independent of the sponsoring company. The ethical aspects, including the question of informed consent, are then primarily a responsibility of the agency, although sponsors of consumer research obviously bear considerable responsibility for the safety-in-use of materials being tested and they need to satisfy themselves on this score in an appropriate manner.

24.8 TECHNIQUES FOR PERFUME EVALUATION

The classical method of studying the characteristics of a fragrance on an absorbent-paper smelling strip is suitable for perfumers accustomed to extrapolating from this method of examination to likely experience under normal conditions of use. Others cannot generally be expected to gain reliable insight into the relative merits of alternative perfumes from such an examination. A better first impression will nearly always come from smelling the perfume after incorporation into unperfumed product base. Particular attention will doubtless be given to the aroma of the perfumed product contained in a prototype pack but an attempt should also be made to simulate conditions during and after use of the product in an essentially normal way.

Laboratory staff, marketing people and even prospective purchasers tend to evaluate perfume by rubbing a little of the product on the skin. This seems a safe and reasonable approach to evaluating a cosmetic type of perfumed product though other, quite different types of product are also sometimes handled similarly; this may be most unwise unless the formulation and its risk potential are known. So far as risk related to the perfume may be concerned, the theoretical possibility of sensitization, leading to allergic contact dermatitis, needs bearing in mind. Such an outcome is rarely if ever reported but this may simply mean that the testing process has initiated a latent condition of hypersensitivity. A recognizable clinical condition of contact dermatitis only becomes manifest later, if or when the person is exposed again to the same offending chemical; in this event, accurate identification of the causative agent responsible for the hypersenitivity may be well nigh impossible. Anyone with a known tendency to skin allergy is clearly wise to take special care with regard to taking part in the testing of new perfumes.

The conditions under which perfumed products are used vary greatly. Arrangements are frequently made to simulate normal usage, taking into account the various types of product involved. Such arrangements are needed anyway for evaluating product performance as a whole but they are usually easy to adapt for in-use study of perfume. Examples include using a hairdressing salon to study

the merits of a perfume for a shampoo before, during and after use; or using a simulated home laundry to evaluate a perfume for inclusion in a domestic laundering detergent. Special large, sealed chambers are needed for studying air freshener performance; in this field, perfume has both functional and aesthetic attributes, each calling for evaluation under carefully simulated use conditions.

The choice of assessors to be entrusted with the responsibility for expressing views on experimental perfumes has already been discussed. Opinions concerning the most suitable arrangements will no doubt continue to differ but the need to simulate 'real-life' conditions as far as possible should not lead to much debate. What is meant by 'real-life' should, however, be interpreted as broadly as possible. For example, efforts should be made in conjunction with the fragrance supplier to ensure that all samples used in a selection procedure are truly representative of bulk output in odour quality and storage characteristics. For obvious reasons suppliers are likely to avoid sending atypical samples if possible, but the risk of unexpected odour changes through unsatisfactory storage may not always be appreciated. Perfume compounds generally benefit from cool storage in well-sealed containers in the dark, preferably with the headspace purged with nitrogen gas. Theoretically the age of both product base specimens used in perfume evaluation and of the perfume compounds should correspond to normal custom. Wide discrepancies in time-scale, e.g. for raw material storage, are found in different factories or even within a single production unit. Variations may be due to factors such as the frequency of purchasing new batches of raw materials, the timing of merchandizing schemes and the rate of turnover of packed stock. Simulating all such variables for the purposes of perfume evaluation is seldom feasible and to some extent fragrance suppliers have to accept a degree of responsibility for supplying compounds with a reasonable margin in terms of stability. All concerned need to recognize that the magnitude of problems that could arise from perfume instability tends to grow as the scale of testing broadens e.g. through consumer research up to test marketing.

The best ways to obtain valid data from consumer research on subjective product attributes such as odour are often debated. Specialists in this field will usually be commissioned to conduct the studies. They invariably wish to discuss the overall study design with the sponsor and usually welcome suggestions concerning questions to be asked of respondents. All concerned with consumer testing are likely to be thoroughly familiar with the need to avoid asking leading questions and with the risk of confusion arising from so-called 'halo' effects. For example, the aim of a particular study might be to assess consumer response to the current and modified version of a perfume compound in a hand lotion. In a comparative study, it might be decided that the lotion with the original fragrance should not be coloured, whereas samples containing the new perfume compound would be given a distinctive pink colour. If users happen to display a fairly pronounced though unrecognized preference for pink-coloured hand lotions, the study might well lead to the erroneous conclusion that they were

strongly in favour of the new perfume even though in reality they were rather indifferent to it. Care will normally be taken to avoid foreseeable risks along these lines, e.g. by making 'test' and 'control' samples as indistinguishable as possible except with regard to the characteristics truly in need of assessment, but this will sometimes present considerable difficulty (if, for instance, one fragrance imparts a colouration to the product as a whole quite different from the colour obtained when using the original fragrance). Efforts to match up characteristics for the purpose of comparative testing should clearly, whenever possible, include all sensory aspects liable to influence a respondent's attitude; partly to obviate conscious bias but also to rule out less obvious 'halo' effects. Easily noticeable differences in viscosity are certainly undesirable and so too are differences in packaging and labelling of samples (except for unavoidable differences in code numbers or instructions for use).

Answers to questions about liking of the product overall may tend to give worthwhile information on perfume ratings, if several perfume compounds are compared in the same product base. Unfortunately questions on perfume as such are liable to elicit misleading answers as most respondents do not have a suitable vocabulary with which to express themselves on this topic. Sometimes direct questions about perfume are undesirable if they direct too much attention to the subject. Instead, it is usual to ask whether there is anything the respondent particularly likes or dislikes about the product. In response to such an approach, unprompted answers singling out perfume attributes should genuinely reflect an individual's true convictions. A two-stage enquiry may be advisable on occasion, starting with unstructured questions that do not channel responses in any particular direction. Supplementary questioning then seeks to reveal a deeper insight into the respondent's feelings by more pointed reference to product characteristics such as perfume. An advantage is that the two-stage approach may succeed in bringing out the nature or strength of any 'halo' effects.

The most convincing approach for studying any product attribute of importance is a test market in the course of which consumers actually buy and use the item under apparently normal commercial circumstances. Whether a sale is effected and, in particular, whether repeat sales follow is what really matters. Any preference test in a laboratory or carried out in other ways to try to simulate market conditions is bound to be at risk of incorrectly forecasting a product's capacity to achieve initial and repeat business. A myriad of factors influences each decision to buy any item offered for sale. Answers to questions under test circumstances always lead to some degree of suspicion that they over-simplify by being unaffected by advertising, promotional deals and the ultimate and most important criterion of having to part with money.

Test marketing is not always an easy or practical undertaking because, for instance, the cost may not be warranted in relation to the commercial or technical importance of the factors to be studied. Another common objection is that test marketing will allegedly alert competitors prematurely and stimulate countermeasures

to pre-empt a product improvement. Possible alternatives may be devised, however, such as the introduction for a brief or longer period of a prospective relaunch product, without drawing too much attention to it, in a relatively obscure territory. Unfortunately this type of experimental marketing is accompanied by the distinct possibility of providing data unsuitable for extrapolation to markets of real consequence. Moreover, the magnitude of error in extrapolation cannot be foreseen. Much scope remains for devising novel and reliable ways to demonstrate in advance the sales potential of new and relaunched consumer products.

The desired conclusion from any perfume evaluation is that the favoured candidate ought to be the most satisfactory when incorporated in the product currently under development. Validity of the conclusion will be expected to depend on the expertise applied in the process of evaluation, including such factors as the relevance of questions asked and the extent to which panellists represent the target population. Arrangements for gathering, collating and analysing data are also important. Nevertheless it may not follow that the majority preference is always the most suitable for the purpose, for several reasons. For example, tests for preservative status and some safety evaluation procedures often continue in parallel with perfume evaluation and consumer research. A preferred candidate may well fail at a regrettably late stage on technical grounds. Alternatively, problems of supply and cost (of fragrance or other raw materials) may emerge belatedly and necessitate reformulation, possibly involving the perfume.

Most of all, the wisdom of trying always to please a numerical majority of consumers with the aesthetic attributes of a new product might itself be subjected to careful scrutiny. Perhaps this is *par excellence* the recipe for mediocrity already mentioned. Might it not be more commercially sensible to look for a powerful minority preference to ensure a solid foundation of brand loyalty? Maybe the answer should depend on the life-expectancy for the brand in the market under consideration. For example, product support depending on a strongly enthusiastic minority could probably be extended progressively in the course of time if this seems to be justified by the early return on investment, thereby making a case for additional promotional expenditure. By contrast, a short-term fashion introduction has to secure the broadest possible franchise as quickly as possible. Such considerations should all influence the final choice of perfume.

24.9 PREDICTION OF SAFETY-IN-USE

The safety-in-use of perfumes has implications for those involved in the manufacture of products containing them and for others exposed in the course of their daily occupation, as well as consumers using perfumed finished products. Even though serious injury due to contact with perfume rarely comes to light, this does not justify complacency. Cause-and-effect related to toxicity is often hard to pin down and this is especially so when the normal route of exposure to a substance is by inhalation or skin contact rather than oral ingestion. Skin

problems involving severe intolerance to sunlight have been attributed to the inclusion of certain so-called nitro-musks, such as musk ambrette, in perfume compounds but the association was initially hard to recognize. Short-term heavy exposure to fragrance chemicals is unlikely except perhaps in some manufacturing processes and life-threatening acute poisoning is therefore virtually excluded. Furthermore, chemical substances with a high risk potential in terms of acute toxicity would be deliberately avoided for use in perfumery for obvious reasons.

Delayed, cumulative or subchronic toxic injury from contact with perfume is not easily ruled out as a possible outcome. The mere fact that the most minute quantities of volatile aromatics induce sensory responses in the brain soon after contact with olfactory receptors in the nose must surely be taken as an indication that such chemicals are capable of displaying pharmacological activity, normally favourable but not necessarily predictable in effects over a relatively long period of frequent exposure. The oil : water partition characteristics of many fragrance chemicals suggest a likelihood of largely unimpeded passage through a variety of physiological barriers. Transfer through the skin is an obvious possibility and penetration across the blood–brain barrier might give access to potentially vulnerable regions of the central nervous system. Toxic changes of a subchronic nature may indicate that distribution around the body, metabolic pathways and excretion kinetics are such as to favour systemic accumulation of a toxic substance, reflecting perhaps an affinity for body lipids. Fortunately some fragrance chemicals tend to be excreted rapidly (the low molecular weight esters, for example), which helps towards an acceptable safety margin.

Occasionally stronger evidence of subchronic toxic risk has shown the need for caution and for a responsible attitude to the predictive testing of perfumery ingredients. For example, the once widely used but now discontinued acetylethyl tetramethyl tetralin or AETT was found to be neurotoxic and to accumulate in the brain tissue of some species under experimental conditions. Although actual harm to humans following exposure to AETT was not observed, the potential hazard of insidious consequences needs to be seen as a clear warning for the future.

Questions about safety-in-use in the perfume field, especially in relation to systemic toxicity, tend to be answered within the supply industry rather than by user companies. Collaboration between the suppliers has reached a high order in recent years by way of the commendable efforts of the Research Institute for Fragrance Materials Inc. (usually known as RIFM), sponsored by the major essence houses. Background information on a wide range of fragrance chemicals has been assembled from the published scientific literature and from suppliers' files. Additional testing has been commissioned where significant gaps in available knowledge were identified. The outcome of these studies has been published as an extensive series of authoritative monographs covering each of the chemicals examined. On occasion RIFM has also given notice concerning evidence of unacceptable risk. Alongside these efforts, the International Fragrance

Association (IFRA) publishes a Code of Practice accompanied by detailed recommendations where appropriate for voluntary limitation by the industry of the use of chemicals believed to be potentially harmful. Several essence houses are known to apply an in-house 'black list' imposing even more stringent restrictions on their perfumers than the IFRA recommendations currently require.

For the manufacture of consumer products including a fragrance, the purchase of perfume compounds only from suppliers willing to certify that these take full account of RIFM findings and comply with IFRA recommendations is strongly advised. Acute, subchronic or chronic toxicity has rarely, if ever, been shown to be substantially augmented when perfume is incorporated into a product base. Safety clearance already established for fragrance chemicals *per se,* e.g. by RIFM, should therefore generally suffice for the safety evaluation of finished products in these respects. Toxicity testing of finished products specifically on account of the perfume is thus hardly ever needed, though it may be required for other reasons. A perfumed product might, for example, be used in such a way as to involve relatively heavy exposure in the case of small children; the available data might not give enough information about dose–response patterns at low body-weight and appropriate testing would then have to be carried out.

Important factors in satisfying requirements for safety-in-use in respect of perfumed cosmetic products are, as indicated, the purchase of raw material only from the most reliable sources and unremitting vigilance in order to foresee and eliminate any abnormal risk. Any circumstances entailing unusual exposure patterns should serve as a warning, suggesting the need for a wary eye on the possibility of unacceptable risk and for excluding potentially harmful ingredients.

Some perfumed products are used regularly for months or years on end and the same perfume constituents may turn up in a number of different products used concurrently or sequentially. The theoretical possibility of long-term toxic changes including carcinogenesis comes to mind. However, there is no evidence to suggest that perfumery chemicals would be prone to acquire carcinogenic potential owing to the concurrent presence of other ingredients in a product; background data relevant to the individual fragrance raw materials, e.g. as shown in RIFM monographs, should therefore suffice. There should be no need to repeat long-term studies previously carried out with individual chemicals in order to allow safety clearance for new formulations with regard to lack of carcinogenic potential. Often the availability of a range of short-term studies for genotoxicity showing favourable results will be adequate so long as there are no theoretical or other grounds for thinking that a substance may be a carcinogen. Fragrance suppliers looking into the possible use of novel chemical substances with a view to their use in perfumery would be expected to consider undertaking a range of studies on mutagenicity but there will rarely if ever be a need for user companies to carry out such work on the perfume compounds they purchase.

The generation of data on percutaneous absorption or uptake through other routes of access to remote tissues may be advisable if the formula for a perfumed product or the proposed manner of use suggest the likelihood of unusually heavy exposure. Although this is unlikely to be applicable with most consumer products, exceptions could perhaps arise. When it is felt necessary to study absorption in detail, a choice between a variety of experimental techniques will have to be made. For example, an *in vitro* model might utilize excised cadaver skin as the experimental membrane or tracer studies could be conducted *in vivo*. Mimicking typical exposure in normal use as closely as possible always seems advisable in absorption studies. The protocol might entail the use of a ^{14}C-labelled ingredient in a radiotracer study, or the chemical could possibly be enriched with a stable, non-radioactive isotope such as ^{13}C, ^{15}N or ^{18}O followed by monitoring with the aid of mass spectrometry. Absorption studies with radiotracers or stable isotopes may sometimes be conceived as human volunteer experiments so long as due care is taken at the planning stage to safeguard the volunteers and reference is made to the relevant regulatory authorities as necessary.

A special case of absorption risk and possible toxicity is the use of perfume in products likely to be inhaled deliberately or incidentally in relatively high dosage. The RIFM monographs and IFRA recommendations take care of nearly all the likely possibilities in this context but inhalation toxicity tests may be needed because of atypical features of the formulation as a whole. If such special studies are undertaken, effects due to other ingredients will naturally be recorded as well as toxic changes, if any, attributable to the perfume. The use of an experimental design with unperfumed controls included helps to establish the extent to which toxicity is definitely associated with exposure to the perfume. Much of what has been stated about the evaluation of inhalation toxicity also applies to various other theoretically possible kinds of toxic potential conceivably related to the use of perfumed products. For example, some risk of reproductive or teratological adverse effects could be postulated. Such risks will be considered in connection with the comprehensive safety studies on individual fragrance chemicals, for example, by RIFM. The process of formulating a consumer product would not normally be expected to enhance significantly any toxic risks of the type envisaged and specific testing of formulations on these lines would not seem to be needed.

Whereas systemic toxicity testing of a perfumed product on account of the perfume content is seldom necessary, local or topical toxicity is more likely to be altered in the course of compounding perfume with other ingredients and more often calls for experimental verification. The main ways in which topical toxicity might be associated with the perfuming of products are:

1. ocular toxicity (damage to eye tissues possibly with impairment of vision);
2. skin irritancy;
3. mucous membrane irritancy;
4. contact sensitization;
5. phototoxicity and/or photosensitization.

The work of RIFM and IFRA has helped to minimize any serious risk of topical toxicity caused by perfume in consumer products, and fragrance suppliers also carry out various types of predictive safety testing on their own raw materials and perfume blends. The question therefore arises whether or when a product manufacturer needs to conduct any safety testing on the formulations to which consumers will be directly exposed.

The scope for diversity in product formulations is so wide that the advice must be given to examine each proposed composition on its own merits to decide what safety evaluation is needed. Sufficient knowledge and experience may be available in-house or expert guidance may have to be sought from external sources. It is always sensible to study carefully the fullest possible background information, if only because this will often show that little or no further safety testing is needed.

The inclusion of perfume rarely seems to convert a non-eye-irritant product into a distinctly irritant one. This is certainly true for those products in which perfume is only a subsidiary component at relatively low concentration. Essence perfumes with a much higher content of fragrance chemicals will usually have to be looked at more critically in this regard. However, even though some odorous constituents such as the phenolics may be potent eye irritants in undiluted form, they hardly ever lead to problems of this type during ordinary use. The lack of difficulty in practice probably arises from the reduction of eye irritancy due to dilution and also the fact that eye irritation is usually dose-related, i.e. the amount of the irritant substance actually coming in contact with the eye tissues is usually so minute that injury is most unlikely.

The only perfumed preparations likely to require testing for ocular toxicity specifically because of their perfume content are probably the more concentrated spray perfumes which could easily be responsible for rather substantial eye contact. Other products with a relatively high perfume content and liable to be splashed in the eye accidentally may also need to be tested to establish the level of risk and the degree of relief afforded by irrigation (rinsing with water). If any distinct evidence of eye irritancy is found, an important factor will be the rate of return to normal of the ocular tissues, i.e. reversibility of the effect.

Skin and mucous membrane irritancy are occasionally predictable on theoretical grounds, in the case of perfume for consumer products, though the nature of the product as a whole may suggest a need for testing anyway as a sensible precaution. So long as sufficient background information is to hand, predictive safety testing for skin irritancy in connection with perfumes could nearly always make use of human volunteers. Initially, a patch-testing approach is likely to be favoured, using 'open' (not occluded) patches or with partial or complete occlusion. The use of occluded patches helps to accelerate responses and perhaps gives greater confidence with respect to probable safety-in-use. False-positive adverse responses are more likely with occluded patch-testing whereas testing without occlusion would be expected to give a more realistic picture of likely

skin tolerance. Details of various patch-testing techniques may be found in the relevant scientific literature. These tests are mostly suitable for carrying out in-house if adequate biological expertise is available; alternatively, several contract research establishments offer the necessary facilities.

Extra care is likely to be needed for products liable to come into direct contact with mucous membranes of the eye or elsewhere. Examples where the application site is usually remote from the eyes would include perfumed skin-care preparations for the napkin area of infants and also intimate hygiene products for adult use. The level of risk in these circumstances of mucous membrane contact may not be particularly worrying but a subjective stinging response (possibly but not necessarily accompanied by objective changes) is more common. Stinging tends to be most noticeable in the relatively delicate areas rather than on fully keratinized surfaces and consumer complaints may be particularly vociferous, even though the extent of true harm is minimal. 'Stinging' potential, however, is not easily and reliably predicted in the laboratory. Predictive test methods using human volunters are described in the literature and some contract research laboratories conduct testing on these lines. Unusually powerful stinging potential of a new or reformulated product may show up during consumer research if the records are carefully scrutinized. Almost unaccountably, products sometimes manage to reach the market before they elicit a noteworthy level of stinging complaints, so there is evidently scope for improved testing. This may also serve as a warning that even seemingly minor modifications to a formulation at a late stage in pre-market development may lead to intolerable stinging.

Various perfume constituents are allergenic to some degree or, in other words, they have some potential for inducing skin sensitization. The typical human environment includes large numbers of potential sensitizers but clearly these are normally tolerated reasonably well by most people. A perfume generally comprises many hundreds of individual molecular configurations, of which maybe only a tiny proportion have any noteworthy sensitizing potential. In practice, allergic contact dermatitis caused by perfumes affects only a minute percentage of exposed persons. Whether odorous compounds such as those to be found in perfumes are specially prone to provoke allergy is unknown; a process akin to hapten formation* may perhaps be involved in evoking a response via the olfactory receptors as well as in stimulating the epidermal Langerhans' cells (Chapter 14, p. 398) trigger off an allergic skin reaction. Different skin allergens span a wide range of potencies. The elimination of those allergens most likely to cause distressing reactions in practice is a worthwhile objective with realistic chances of success. The work of RIFM and IFRA, making use of a vast background of industry experience along with studies by dermatologists, led to the identification of some fragrance chemicals that were relatively potent allergens. Restrictions in use were suggested in some instances and the worst offenders proposed for discarding

* Conversion of a normal protein liable to provoke antibody formation.

altogether. Examples of substances for which such steps have proved necessary are cinnamic alcohol and aldehyde, isoeugenol and phenylacetaldehyde.

In the present state of technology, total exclusion of all of the less potent sensitizers from perfumes would make it impossible to manufacture many or even the majority of highly esteemed fragrances. This would benefit only a small minority of consumers anyway, for most people do not experience any problems at all with perfumes. One reason for the relative lack of allergic response to perfumes containing constituents known to have sensitizing potential is apparently that some other constituents are able to exert a 'quenching' effect. For example, *d*-limonene acts as a quenching agent by abolishing the sensitizing potential of cinnamic aldehyde. In time deliberate advantage may be taken of this phenomenon to improve the skin tolerance to various perfume blends. Meanwhile, careful study to determine acceptable levels of the less potent known sensitizers in perfumery use is a wise course and IFRA has been giving appropriate advice to the essence houses.

Attempting to match existing popular perfumes with totally non-allergenic substitutes having equivalent aroma would be exceedingly difficult and might well greatly increase costs. The problem may sometimes be circumvented by offering an unperfumed variant of a product. Where it is economically viable to launch an extra variant in this way, the idea should certainly help those users prone to allergic skin responses. Exaggerated comment in the media appears to have generated anxiety in many people about perfume allergy and the marketing of special unperfumed products may perhaps lend an undue air of authority to such anxiety. Fortunately most consumers do not have skin problems needing special care and there is therefore no reason to deprive them of the aesthetic benefits of a cherished perfume.

Partly because contact sensitization and consequent dermatitis are numerically so uncommon, reliable predictive testing is bound to be difficult. Potent sensitizers that might have been used in perfumery will hopefully have been characterized already and either eliminated or sharply restricted in use. Product testing now tends to be looking rather for relatively low-frequency risks, e.g. less than one reaction per thousand test subjects. Such a level of response to any kind of biological stimulus invariably gives rise to severe difficulty on statistical grounds alone, quite apart from the daunting methodological and logistic problems involved. The chances of recognizing weak sensitizing potential may perhaps be increased to some extent by testing at exaggerated perfume concentration; dose–response patterns in sensitization are liable to be unpredictable and unfortunately the right conclusions to be drawn from such testing are not easily determined.

Opinions differ about the advisability of predictive sensitization testing on consumer product formulations (as distinct from possible testing on their perfume content) specifically to study perfume-associated risk. Some experts favour limited testing on panels of 100 or 200 human volunteers by means of

standardized patch-tests or in the form of use-tests with careful observation of skin tolerance. Some favour the use of skin patients whereas others consider their exclusion is preferable. Another view is that gradual stagewise increase in the numbers of people exposed under normal use conditions to a new product is the most satisfactory way to learn how well it is tolerated in practice. An important reservation relates to adverse skin responses in which exposure to light plays a part. Photo-activated reactions are liable to represent a serious problem for the individuals concerned, possibly for a long time. Risk potential of this nature fortunately seems to be mainly a property of individual chemical constituents and the testing programmes under way in the fragrance industry ought to ensure that any such constituents will be quickly eliminated from perfume compounds on sale.

Light-related skin toxicity may be classed as either photo-irritancy or photo-sensitization depending on whether or not an allergic mechanism is involved. Reactions such as these tend to affect freely exposed skin surfaces such as the face and may therefore lead to great difficulty in pursuing a person's normal way of life. The offending spectral frequencies are not confined to the UV as might be supposed. In some instances photo-activated skin responses are apparently related to visible light irradiation and so they are exceedingly hard to avoid indoors or out.

Among the wide variety of consumer goods on sale, certain categories likely to be perfumed and to involve substantial skin exposure to irradiation during use may be identified, e.g. after-shave lotions. Several unfortunate incidents concerning actinic dermatitis were found to be associated with the inclusion of perfume constituents greatly favoured for the masculine 'notes' they imparted to after-shaves. Certain coumarin derivatives such as 6-methylcoumarin have had to be discarded and the so-called nitro-musks have either been restricted in use-level or withdrawn owing to the risk of photo-activated skin reactions. Problems like these generally fall on the shoulders of the product manufacturers when they are first encountered though, once the causal factors begin to be recognized, they are normally referred back to the fragrance suppliers. The suppliers in this instance have been deeply concerned indeed to find ways of devising good perfume compounds for male toiletry products devoid of photo-toxic or photo-sensitizing risk.

Opinions differ regarding prevalence in the general public of adverse reactions in the tissues coming in contact with perfumed products and directly due to their perfume content. Some dermatologists, for example, claim that a high proportion of patients attending contact dermatitis clinics give positive patch-test responses when challenged with a standard 'fragrance mix' and/or their own perfumed products. Although this implies a degree of sensitization to perfume, the notion that their dermatitis was actually a consequence arising directly from this is not necessarily correct. Such patients are commonly found to have multiple sensitivities as shown by patch-testing (sometimes vividly described as the 'angry back' syndrome). Probably only one of the substances to which a patient has given a

positive patch-test response was implicated in the original skin condition and this might well have had nothing to do with perfume. Everyone living in a modern community must surely come into contact with perfume in one form or another every day throughout life but contact dermatitis demonstrably attributable to perfume can only be regarded as remarkably uncommon. Care is undoubtedly needed in the manufacture of consumer goods to minimize skin reactions as far as possible and to help those who are unlucky enough to suffer adverse effects. So long as proper care is being taken, there are no obvious grounds for demanding any drastic steps to deal with the skin problems associated with perfume.

The view is sometimes held that cosmetic allergy is a rather widespread problem and that consumers or their medical advisers would benefit from full ingredient labelling on such products. Usually the potential purchaser is able to tell easily enough whether or not a product does contain perfume and if an unperfumed one is preferred the right course to take is clear. If a *bona fide* enquiry is received from a medical attendant on behalf of an individual patient, every responsible product manufacture will doubtless be pleased to cooperate by supplying the fullest available information on product composition (referring back to fragrance suppliers where necessary). However, the blended compositions with which most consumer products are perfumed commonly include many hundreds of odour constituents. Meaningful declaration of perfume composition within the confines of a label or pack is totally out of the question. The most helpful step will usually be to establish whether any substances to which a patient is already known to be sensitive are present.

Circumstances also arise in which a dermatologist or a skin clinic is seeking to establish the nature of a patient's allergic hypersensitivity by means of a series of diagnostic patch-tests. Product manufacturers and fragrance suppliers should always be willing to give full information on product or ingredient composition promptly in strict confidence in response to enquiries arising from investigations on these lines. Samples of perfumed and unperfumed product, perfume compound on its own and individual perfume constituents if available should be sent without delay when requested for patch-testing. Normally the dermatologist will wish to decide what solvent or diluent, if any, to use and will determine the dose or concentration levels for testing. For the cooperating manufacturer to ask for a full report on the outcome of patch-testing seems desirable and entirely reasonable, although such investigations involving perfume rather frequently turn out to be abortive because the patient becomes bored with the proceedings long before a conclusive finding is reached!

A pertinent question is whether strong suspicion or even fully authenticated evidence of causal association between perfume and a few adverse reactions indicates a need to withdraw the formulation from the market or perhaps to make some kind of modification. With consumer products meant to be generally bland and innocuous like nearly all cosmetics, toiletries, soaps and household products, even only one or two instances of severe adverse reaction may call for

drastic steps. A single instance of a severely life-threatening injury or death or a case of irreversible interference with sight, for example, would almost certainly show the need to withdraw the formula and probably to recall the product from the market. Strong evidence for a causal relationship would be necessary and this would be extremely unlikely in relation to perfume. Severity of response and its reversibility if known (i.e. the time taken for the skin response to subside) may influence the decision-making process but usually it is prudent to examine the incidence of patch-test positives in relation to an estimate for the total of people at risk or, in other words, the number of current users calculated from sales data. With this type of approach the most likely conclusion is that there is no need to change the product as the skin problem is a rarity. Maintaining a watchful eye on the possibility of more serious consequences is naturally important as a necessary safeguard for the public, however, as well as for the manufacturer's good name.

The testing carried out by a dermatologist or skin clinic on individual patients to investigate the sources of their skin disorders is correctly seen as a *diagnostic* exercise, primarily of benefit to these patients. A clear distinction should be made between this approach and testing, normally with healthy volunteers attending a laboratory, to provide a forecast of likely effects on the population as a whole; these are described as *prophetic* patch-tests and are often intended to show whether an ingredient could safely be included in a consumer product. Whereas diagnostic patch-testing gives results which apply, in essence, only to particular patients, prophetic patch-tests are meant to provide information on the likely incidence of adverse effects in a much larger population of consumers. Nevertheless any evidence of relatively severe risk shown by diagnostic testing should certainly not be ignored.

Substantial numbers of complaints with a relatively sudden onset and relating to adverse skin or eye reactions soon after introducing a new product or relaunch call for special attention, especially if studies at the R & D stage have not suggested that anything of the sort would be expected. The complaint pattern may suggest that:

1. an unusually potent irritant or sensitizer has been unwittingly included (perhaps by way of an impurity not present in pre-market raw material samples); or
2. the new product has prompted individuals with unduly sensitive skin to find out whether it suits them better than products they have previously found troublesome; or
3. the complainants have previously encountered the same or chemically related sensitizers in other products which *induced* an allergic state but the new product happens to be the source of the sensitizer that has *elicited* a clinical response and incurred the complainant's displeasure; or
4. an ingredient, acting as a histamine liberator in the skin of hypersensitive individuals, is leading to an urticarial response (akin to 'nettle rash').

Allergic contact dermatitis nearly always involves a delay of several days between first exposure to the causative agent and a second exposure following which the elicited reaction first becomes noticeable. If a response occurs more rapidly after first exposure and an earlier encounter cannot be traced, typical sensitization will seem to be ruled out and consideration should be given to the possibility of contact urticaria. This may be more common than is generally supposed, taking either a mild or a more severe course of a short-term or more chronic nature. A crop of urticarial reactions soon after launching a product without forewarning in the course of extensive pre-market testing might suggest an impurity problem with one of the raw materials.

A spate of adverse reaction complaints following a product launch seems to be experienced by every manufacturer now and again, sometimes with little prospect of a quick and easy solution. It may well seem as though some consumers just wait for the arrival of new products to invoke the intolerance to which their skin is always prone. Happily such a phenomenon of 'new product neurosis' usually subsides rapidly without any positive countermeasures. Maybe some people with real skin problems do need to keep trying different preparations and are bound to be sadly disappointed if problems recur when the latest innovation is tried. These unfortunate people presumably exclude themselves quickly from the population continuing to use the product. The complaint rate following an initial peak should soon fall to a more acceptable level if there is no exceptional provoking factor. Management is apt to view with alarm an unusually high complaint rate in the early stages of a costly product launch on which hopes have been staked. During such a period of anxiety R & D has to maintain a balance between discouraging an unwarranted panic response and keeping on the alert for any sign of a serious health hazard. Despite the advisability of a wait-and-see attitude, the prospect of adverse skin reactions leading to unfavourable, exaggerated publicity is a frightening one which may well lead to a premature decision to withdraw the product from sale.

Although consumer products in recent years have enjoyed a remarkably good record of safety-in-use, and adverse effects have been without dire consequences on the whole, those responsible for product safety matters in a manufacturing establishment must always be on the lookout for more critical dangers. Everyone finds it hard to believe that a carefully tested, thoroughly researched product could truly be responsible for major health problems but lack of alertness could prove to be a devastating and unforgivable error from a commercial or health angle or possibly both.

24.10 PURCHASING CONSIDERATIONS

Pure financial aspects of the purchase of perfume compounds from fragrance suppliers cannot adequately be considered in the present context for several reasons, including the diverse questions tending to arise with totally different

kinds of end-products. An important consideration is that a perfume compound is effectively a proprietary speciality exclusive to a particular supplier. This imposes stringent limitations on the way in which competitive buying or multiple sourcing may be used to influence costs. The relationship between fragrance suppliers and their clients frequently embodies a more personal liaison along with the development of greater confidence and trust than would be associated with the purchase of other chemical supplies. Mutual understanding of the special considerations affecting the pricing of perfume compounds and the relevance of increasing offtake, for example, is characteristic of this field.

An intention shortly to place an order for a particular perfume compound for the first time should invariably be subject to the supplier's provision of a letter of safety assurance showing that the compound:

1. takes full account of RIFM findings and complies with IFRA recommendations except where specifically indicated;
2. is believed to be safe for use in the intended manner;
3. complies with relevant legislation concerning the handling of hazardous substances;
4. complies with regulations currently in force in the territory where the product is expected to be sold.

The provision of safety assurances of this kind is a normal procedure within the fragrance industry.

Some purchasers of fragrance insist that, as well as regulatory and industry-recommended restrictions, their own 'black list' is to be enforced with respect to certain named substances not to be included in any perfume compounds supplied to them. Similarly, several essence houses apparently maintain in-house restricted lists and their creative perfumers are prohibited from using these raw materials in new compositions. Although the reasons for such self-imposed discipline cannot be verified, the concerned approach can only be applauded.

Sometimes an occasion arises whereby a supplier needs to remove an ingredient from the formula of a perfume compound, with or without prompting by the client. Actual or impending changes in regulatory status, for example, may show the need for this type of revision but it seems that steps are always taken to keep clients informed. Usually samples will be provided showing proposed modifications designed to retain the original aroma character as closely as possible, for agreement with the client prior to further bulk delivery. The magnitude of such problems is shown by the fact that the need to discard only a single constituent may well result in the revision of 70 or more different perfume compounds supplied worldwide by one essence house to just one multinational product manufacturer. Patience and understanding of each other's difficulties is a paramount requirement!

Many perfumery raw materials are still obtained from natural sources despite the widespread use of synthetics. The existence of a 'green' lobby could well

reinforce the demand for perfumery constituents of natural origin. Fragrance materials from botanical sources incur some risk of noticeable crop variation from year to year or even from farm to farm, as a result of varying standards of weed control perhaps. Such variability may be apparent but, possibly even worse, it may be of a subtle kind, escaping notice at first. Worst of all, crop variance may result in unusual off-odour only after storage. Fragrance suppliers have in the past sometimes stated that their perfume compounds were routinely adjusted to allow for cropwise changes. Nowadays a more satisfactory answer is to restrict purchases as far as possible to growers with good quality control of cultivation based on adequate laboratory facilities, so that year-to-year variances are minimized. Synthetics overcome the hazard of crop variation though they may, of course, introduce other impurity problems.

In addition to a written safety assurance, perfume buying needs to involve agreement on an analytical specification for each perfume compound. Such specifications are often somewhat rudimentary, giving a measure of quality control only in terms of appearance, aroma and simple physical or physicochemical criteria. Control is partly by comparative odour assessment against retained samples from earlier deliveries. There is some risk that these samples will have changed with storage, though this may be minimized by keeping them in well-filled amber glass stoppered bottles in a cool place. Comparison may nevertheless still be misleading if a gradual drift occurs with successive deliveries. Quality assurance by means of high-precision instrumental analysis is possible but how far it helps to ensure consistently good odour quality is uncertain. Future prospects are surely favourable.

A more controversial factor in perfume compound purchasing is the extent to which the buyer is entitled to know the detailed composition of the material supplied. The creation of a perfume has as much to do with Art as with Science and the eventual achievement is a valuable piece of 'know-how' belonging to the particular supplier. However, once the creative work of the perfumer has been finalized, copying presents no insuperable difficulty. Although perfume suppliers have always been inclined to guard their formulae as important trade secrets, the value of this secrecy must have been greatly eroded by modern instrumental analysis.

From the standpoint of a consumer product manufacturer, the formula for a perfume compound is not of any great interest for the day-to-day production and sale of a preparation in which it is incorporated. In relation to safety evaluation and the product manufacturer's ability to maintain a proper stance on regulatory matters, on the other hand, the disclosure of perfume composition by the supplier assumes some importance.

For the purpose of this review of the topic, an appropriate conclusion seems to be that fragrance supplier and product manufacturer should usually be able to reach agreement on the sharing of confidential details of perfume composition subject to strict guarantees on the handling and use of such information.

Where disclosure is agreed, perhaps the most important criteria will be that the details may only be used for safety evaluation and regulatory purposes, that they are available to and stored by nominated expert staff only and covered in these and other respects by a legally binding agreement. This is a totally distinct matter from the issue of ingredient labelling discussed earlier. In general, even where a disclosure agreement is in operation, information would be passed to an external enquirer (such as a dermatologist on behalf of a patient) only by agreement between nominees of the essence house and the product manufacturer.

24.11 CONCLUSION

The perfuming of consumer products must seem to most people quite a simple matter which has been carried out for generations past and which is likely to continue without need of fuss or serious attention. Lately a minority of people have come to regard perfume with great suspicion, implying that a high proportion of skin problems are directly attributable to the unnecessary addition of perfume to otherwise bland and wholly innocent products. The truth is almost certainly to be found somewhere between the extreme points of view. Incorporating an aesthetically satisfying perfume in a safe and cost-effective manner involves many complexities needing to be recognized and, where necessary, clarified. Many facets are changing or developing rapidly so that contemporary ideas may need to be modified in the reasonably near future. Fortunately the fragrance industry has demonstrated exemplary willingness to tackle problems in a highly responsible and truly collaborative spirit. The excellent relationship between this industry and its product manufacturing clientele should immeasurably benefit those whom they seek to serve, the public at large.

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25

The psychology of fragrance and aromatherapy

Jean Ann Graham

25.1 INTRODUCTION

The psychology of cosmetics and fragrance as an academic field of research in its own right began its development at the end of the 1970s. From an initial review defining and outlining the field for cosmetic and toiletry products [1], a programme of empirical research was embarked upon demonstrating the psychological and social effects of using different products, the benefits enjoyed, and motivations for their use.

In the field of psychology of fragrance it is helpful to distinguish a number of categories for study: perfumes (e.g. fine fragrances, colognes); cosmetic and toiletry products that contain perfume (e.g. fragranced skin-care, hair-care and hand-care products); environmental fragrances (e.g. *pot-pourri,* room fresheners, etc.) and finally aromatherapy products (essential oils). The branch of aromatherapy has grown, particularly in recent years and so the psychological aspects of these products in particular need highlighting.

The psychology of fragrance encompasses the following behavioural effects of a product on the user: in respect of others' perceptions (of the appearance, personality, projected image, etc.); self-perception (self-image, moods, self-esteem, confidence and attitudes); interpersonal attraction (liking, sexual attraction, and so on). The field encompasses motivations, or reasons for using or purchasing a product; it even attempts (where appropriate) to relate fragrances to different situations and lifestyles and to link individual fragrances with particular dimensions of personality; and finally it assesses therapeutic effects (mental and physical) particularly relevant to aromatherapy products.

The theoretical background, principles and conceptual framework that apply in the psychology of fragrance are similar to those that apply in the psychology

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of facial make-up [2]. One of the central themes in the field of colour make-up is the 'what is beautiful is good' stereotype, i.e. that if you are attractive, you are assumed to have a more ideal personality than if you are unattractive. There is an abundance of research that demonstrates the benefits of being attractive in a variety of situations and walks of life (see for example ref. 3); those who are attractive have been shown to benefit in both work and social situations. It has been shown that beautifying products [4] enable a person to be perceived as more attractive and to be seen as having a significantly more positive personality. From this research the notion of a 'what has been *made* beautiful is good' stereotype emerged. The benefits extend to self-perception, as when a person perceives herself more favourably with facial make-up. Graham and Kligman [5] have demonstrated numerous benefits from receiving professional make-overs, in terms of how a person perceives herself on a number of dimensions of social behaviour.

In a similar way, perfume can also be used as a vehicle to enable averagely attractive people to enjoy some of the benefits of being more attractive and feeling good; and benefits can accrue from being seen to have 'made oneself beautiful', or to have 'cared for oneself', by using fragranced products or perfumes.

Intuitively, and on the basis of what we have found for other product categories (such as facial make-up) we would hypothesize that fragrance can be uplifting in mood, make a person feel cared-for, affluent, attractive, etc., enhance appeal to other people and bring more favourable social perceptions. Some of these aspects have been demonstrated, to a degree, but there is still need generally for more research data on fragrance.

25.2 HISTORY OF PSYCHOLOGY OF FRAGRANCE AND AROMATHERAPY

25.2.1 The history of fragrance

The history of the use of fragrance in many countries throughout the ages and its links with medicine, health and cosmetics has been covered in Chapter 2. From the perspective of the history of the psychology of fragranced products, at times throughout history perfume enjoyed the status of an expensive luxury often just to be used on special occasions. Queen Elizabeth I, for example, is said to have ordered perfumed cannons to be fired when she entertained the Duke of Anjou [6], an example of the use of perfume to reflect social dominance; in the seventeenth and eighteenth centuries perfume was used more abundantly even than today, including by men. It was more popular to use perfume than to wash – not only people but clothes, animals, furniture, and even money.

In the Rococo era, the conspicuous use of perfumes was not very acceptable as it suggested the person was using perfume to be noticed and was being 'obvious' in using it to attract. *Eau de Cologne,* handkerchief perfume or discreet scents

from lavender or flowers, which might be thought to emanate from floral sachets rather than perfume, were more acceptable.

In the twentieth century, however, throughout the times of the two world wars the economic resources were mostly not readily available for purchase of luxury items such as perfume. For the men, many of whom were in the Services, any hint of a perfumed product (even a scented soap) was regarded as quite unacceptable socially, with an effeminate image. 'Palmolive' soap at that time was sold worldwide and used by men who, when asked if they liked the perfume, would answer with surprise; 'Yes, why? it smells like soap!' It was universally accepted, and did not conflict with the prevailing need to project strong masculinity. Fashion was a matter for women!

Later, when prosperity returned, only men's conservatism prevented acceptance of perhaps a subtly perfumed after-shave or talcum powder, used only occasionally. This quiet corner of the fragrance market was eventually moved only when women wanted their men to smell of the daring men's products; either 'Brut', 'Aramis' or 'Insignia'. Even as late as the 1970s and into the 1980s it was still not acceptable for a conservatively dressed conventional man-in-a-suit to show too much interest in these products. The essentially feminine image that was for a long time throughout this century associated with cosmetics and fragrance was probably responsible for this very slow change in the men's market.

It took until well into the 1980s for the mainstream of society's men to be given the clear message that there was now 'fashion for men', which in turn influenced the growth of men's fragranced products. With this change in attitude the big 'boom' in men's fragrances that was expected and hoped for within the industry eventually started in the latter part of the 1980s and continued throughout the 1990s. There is now much more awareness of, and gradually increasing demand for, men's personal fragranced products, with the major concept behind their sale being that they represent 'today's lifestyle'.

Changes in the men's market have also partly been influenced by changes in the role of women within our society, in turn influenced in the latter half of the twentieth century by the fact that perfume became more and more of an everyday item available to everyone. It became a status symbol to own a luxury perfume with a fashionable name of the moment and to ask for it as a birthday or Christmas gift if too expensive for the recipient to buy.

In the latter part of the 1980s, in the marketing of fragrances for women, the concept of 'psycho-group' [7] emerged, which attempted to match different fragrances to particular lifestyles, social attitudes and social values. With this new psychological approach to fragrance marketing there was a concurrent tendency toward a decrease in 'me-too'-type fragrances and an increase in fragrances conveying some information about the individual, conveying the message, 'I am' or 'individuality'. Throughout the 1980s, as the Western female role and lifestyle changed (and continue to change through the late 1990s) and women have been enjoying more liberty to adopt the lifestyle and personality of their choice, so

choice of perfume increasingly has come to depend on the individual. For example, Paloma Picasso's 'Tentations' perfume is marketed with her 'uniquely personal approach'. She emphasizes the importance of 'being oneself!' as a statement of individuality but – at the end of the day – it is also the most attracting of qualities. 'Tommy girl', marketed as 'a declaration of independence', is an example of a fragrance using the independence/individuality type of theme. However 'Tommy girl' is also marketed as a perfect companion to 'Tommy' ('the real American fragrance' for men), reflecting the underlying importance of the attraction theme. The theme of attraction is strong and all-pervasive throughout the world of fine fragrances.

In the 1990s, the emphasis was very much more on men's products, many available fragranced products being used by both sexes, e.g. 'Wash & Go' all-in-one hair shampoo and conditioner. This contrasts with a period earlier in the century when only women bought the available products. Today it is much more socially acceptable for men to purchase cosmetics and toiletry products, particularly by purchasing 'own-brand' products in large supermarkets or smaller self-service health and beauty stores, such as The Body Shop, and VIRGIN VIE. VIRGIN VIE stores, for example, were launched with simply one fragrance for men and one for women. In larger department stores the men's toiletry products are often located near to the men's clothing, footwear and other accessory departments which should make men feel more comfortable with purchasing them, although some are often seen in a section with the women's cosmetics and fragrances. Careful consideration should be given to what female products might be presented near to male toiletry products.

Sets of products with matching fragrances are popular in a range of smaller stores that sell cosmetics and pharmaceuticals. Thus the range often consists of cologne, after-shave lotion and balm, talcum powders, soaps and deodorants. These are increasingly taking over the market previously cornered by fine fragrances alone. The way many of these products are presented by improved packaging and appeal is partly responsible for the growth in this market. The change in attitude towards products for men has given many men more confidence to use and purchase them, rather than relying on their wives and girlfriends purchasing them and persuading them to use them. There is still room for more improvement in this and for more information to be made available to them regarding existing products to treat specific problems regarding their skin, hair etc., and generally meet their needs.

Different fragrances and products may be appropriate for different subcultures and different segments of the market. Particular products, such as 'Wash & Go' or 'CK1' may be preferred by younger, active, sporty types who want to project that image, whereas other products – for example, shower gels, and deodorants – seem to be more universally accepted.

The presentation of many products conveys a masculine image to men by the appropriate use of colour, for example, black, grey and dark red, and other

aspects of packaging and presentation. With the acceptance of the 'New Man' concept and the 'Men Behaving Badly' idea in the 1990s, we have had a framework for predicting that this market trend will increase because more men will use products designed especially for them. Media personalities still project a macho image while obviously using modern hair-care products, etc. Many companies convey an air of rugged masculinity in their advertising and presentation of their ranges of products; examples are 'Lynx', 'Insignia' and 'Brut'. Now that it is more acceptable for men to use fragranced products similar promotions should be successful.

Male and female fragrances used to be easily distinguishable but this is no longer always the case. In the latter part of the 1990s it eventually became acceptable for men's fragrances to be more unisex; e.g. Calvin Klein's 'CK1' and 'CKBe' deliberately positioned to appeal to either sex. Nevertheless, women still give off strong perfumes more than men do, and mainly to attract. The use of perfumes to provide a long-lasting pleasing scent aura has remained more the domain of the female sex. Men today are usually pleased if a woman exudes a pleasant fragrance, and one that harmonizes with her personal odour.

The dependable success and popularity of unisex fragrances is as yet unclear – more empirical research is required in this area. Are unisex fragrances really wanted? If so, by which age groups in particular? Do men and women really want to use the same products? Is it better to emphasize differentiation between the sexes regarding fragranced products? These are some of the current issues that require more researching, but trends tend to be short-lived.

Jellinek [8] maintains that harmony between a perfume and the person wearing it must not be limited solely to the odour effect but it must also prevail in the psychic domain. In the end he concedes that the personal odour of cultured men and women is so slight that the objective of bringing the perfume into harmony with the wearer's personality comes down primarily to taking psychic factors into account. Given that the psychic make-up of men and women is fundamentally different, if Jellinek is right, then fragrances that differentiate between the sexes should be what is really required. In fact the use of psychological concepts of 'masculinity' and 'femininity' to advertise and market products remains central.

The USA, Europe and Japan have all had tremendous fragrance markets; particularly as fragrance is thought of more and more as an everyday commodity with many uses and benefits, to be used frequently and, with different choices of fragrances, for use on different occasions throughout the day. More research is needed, however, to quantify the motivations and benefits of using men's fragranced products to project different moods and be appropriate for different situations.

The children's market is another important section for growth in the industry: they are the future generation of users. Youngsters sometimes as young as 5 can develop fashion-consciousness. They tend to be well informed on hairstyles and the latest toiletries and cosmetics, and sunscreen products for children (such as

the Boots range), etc. Young boys very commonly use hair gels. Many young people have an interest in fashionable fragrances, particularly in bath and hair products, and this trend is increasing and extending to specialized soaps, foam baths, body lotions and fragranced shower gels. For example, bath product gift sets containing hair and bath products for boys, soaps and bath products for girls, including dusting powder, are available.

Many girls borrow their mothers' products when quite young, so here is another area which could be further promoted. The macho image for boys could be developed further, although they may not be ready yet for their own range of perfumes. They are not so interested in fragrance-free products but they respond to scents of all kinds, especially the fun-type and strongly fragranced products that enliven the senses. Wearing such products would make them feel pleasant and fresh, and in addition draw attention to themselves. If the products have 'natural' association then so much the better; e.g. colourful fruit-scented soaps. A variety of colourful fun-type fragranced products would perhaps help to relieve today's pressures and allow the children to develop the personalities and lifestyles of their choice, though still in line with the fashion of their peers.

More research is needed to assess the young people's particular motivations in using fragranced products, to quantify the benefits they experience in using the products, and to ascertain the future product markets and areas of growth. The psychological and social dimensions that are important to this group will serve as a basis for empirical research to influence the direction for future expansion.

25.2.2 The history of the psychology of aromatherapy

The healing powers of aromatic oils can be traced back thousands of years (the history of aromatherapy products is described by a number of writers – see, for example, ref. 9). The ancient Egyptians used aromatic oils in religious ceremonies; for example, the dead were anointed and embalmed in preparation for the after-life. The Bible contains many references to the use of oils for healing and religious purposes. In the Middle Ages oils normally used to hide unpleasant smells of unwashed bodies were used as a form of protection to fight epidemics and infections. With the progress of scientific knowledge in the nineteenth century oils were replaced by chemical ingredients and these synthetic copies did not have the same therapeutic value and often had negative side-effects.

In the twentieth century essential oils were rediscovered by Professor René M. Gattefosse (a French chemist), who introduced the term aromatherapy in 1928 after discovering the healing properties of lavender essence for burn injury. This work was developed by Dr Jean Valnet and his book *The Practice of Aromatherapy* served as an important foundation for the field.

The aromatherapy section of the fragrance market probably became popular in the 1980s onwards because of its wide range of appeal to those who may be interested in natural remedies, holistic medicine or just a generally healthy

lifestyle, and would appeal to anyone who might be suffering from the stresses of the present age. A variety of aromatherapy-type products are now commonly found in many stores, including health-food stores and chemists. It seems likely that the use of aromatherapy-type products will increase in the new millenium as long as the stressful nature of our society increases.

One outcome of the late 1990s was the dual-purpose product which combines an aromatherapy product with another product with quite a different function, e.g. the Remington foot spa with four aromatherapy treatments; also, hair-treatment products (such as the Biolage range) with built-in aromatherapy treatments – to put you in a nice mood whilst also getting your hair treated. This range is marketed to renew hair (giving it back the silkiness and healthy shine nature gave it) whilst its unique 'Aromascience' fragrance renews peace of mind.

Maggie Tisserand [10] maintains that we are at the beginning of a health revolution: that preventive medicine is the medicine of the future and that as an adjunct to other forms of *medicine*, aromatherapy is one of the important *therapies* of the future. She believes that it will serve not just to treat illness but as a very real protection from environmental pollutants, bacteria and viruses. So in the future, instead of waiting until we become ill, we can protect the body and build up resistance to disease to prevent illness occuring. Aromatherapy is also a 'good investment' in terms of health and beauty – an enjoyable way of feeling and looking good.

25.3 MOTIVATION FOR USE OR CHOICE OF PRODUCTS

Ebling [6] argued that there are a number of social functions of odour, and that women wear perfume not only to attract the opposite sex but also to increase their own feelings of sexuality. Even if there is no male to hand, they use perfume to enhance their individuality, for their own satisfaction, for status and, perhaps, to increase their positive feelings towards male companions. It should not be overlooked, however, that one of the primary social functions of fragrance and deodorizing products is to conceal unpleasant odours of the body and to create an impression of being attractive and clean.

A study in the 1980s by Graham and Furnham [11] found that all cosmetics, including perfume, were evaluated by 14–18-year old males and females as being more attractive for use by females in night-time social situations compared with day-time situations. If we can assume that most benefit can be received from products with the highest ratings, then perfume use by females is the most attractive to the males, and especially in night-time situations. But since the 1980s many people have tended to enjoy all-day perfumes. Perfume tends to be used more now as part of the daily dress to feel clean, fresh and comfortable and ready for the day.

Research on the motivations behind men's use of fragrance still needs more exploration, but attraction of the opposite sex is certainly very important among

them. The men's fragrance market is rapidly increasing. Whereas male and female perfumes used to be easily distinguishable, the distinction is sometimes more blurred. Some women's fragrances resemble, to varying degrees, masculine scents and so, too, some modern-day men's fragrances are 'sweet' enough for some women to want to wear them. Some fragrances are, as we have seen earlier, deliberately positioned to appeal to either sex.

There is still a majority of people, however, that prefers products for each of the sexes to be clearly demarcated. In the early 1990s there was a tendency towards a more romantic, feminine mood to be used to promote and advertise a number of women's fragrances; for example, 'Knowing' by Estée Lauder, 'Nights in White Satin' by Yardley; whereas there was a tendency for the promotion and advertising of men's fragrance to use a more macho image, for example, 'L'Egoiste' by Chanel. In the latter part of the 1990s this trend continued, for example, with the popularity of the female fragrance 'Allure', and the men's fragrance 'Obsession'. There is also a trend towards matching pairs of fragrances for each sex, e.g. Clinique's 'Happy' fragrance for women and men. All in all, there is plenty of choice and the choice is ours.

Hugh Bain [12], market researcher, reports on consumer interviews regarding the motivations of perfume use, which he has conducted in a number of cultures. He does this by exploring awareness of the psychological effects of fragranced products on the perceiver, as well as motivations for using them. Bain talks about three dimensions of perfume effects: (a) messages to certain specific persons (the interpersonal dimension), (b) impressions created on others in general (social dimension) and (c) feelings generated within the user him/herself (inner-directed dimension).

(a) Interpersonal dimension

The desire to be attractive and to attract sexually (whether one or many) is of very high importance, even though the sexual drive may not be at the basis of all of perfume culture. So perfumes should be seen to enhance the body not the room surrounding the person. The qualities and personality aspects being captured that are found attractive may also vary; for example, efficient, professional, *'femme fatale'*, etc.

(b) Social dimension

These days a person's lifestyle is thought to be reflected in the way that person presents himself/herself in public in terms of dress, demeanour and increasingly in terms of smell, so that a person can feel 'unfinished' or incomplete if he/she has forgotten to put fragrance on before going out or as part of the morning's preparations (the large expansion in the commercial exploitation of fragrances in personal grooming may be partly responsible for this). The suitability of a perfume also varies with the circumstances (situation and mood) in which it is

to be used, and it should be chosen appropriately to *support* the person *socially* (and convey the appropriate message) within the social encounters occurring in that situation.

(c) Inner-directed motives

It is thought that a woman will use a perfume on many occasions to please herself, rather than to attract the opposite sex. The motive for this can often appear to relate to a need for fantasy – represented by idealized images of self (for example the glamorous role models and aspirational lifestyles used in advertising and promoting new perfumes).

Other inner-directed reasons given by women for using perfumes are thought to be related to their desire to express their femininity and individuality, and to enhance their self-esteem. The need for social approval and finally for their own self-image (perfume belongs to yourself), to feel better about themselves (by smelling nice); in these kinds of ways perfume use can be very individual.

Finally there are mixed patterns of motivations, where more than one motive may be operating within one person at any given time. For example, a perfume may be used on one occasion to attract someone special (interpersonal), and to project an image (for example, of affluence) generally appropriate to a particular situation (social). The relative weighting of the different motives will also vary depending on the varying circumstances.

Bain concludes that people's motives for wearing perfumes are often sexually determined. However, people often use/choose perfumes for many other reasons aside from sexual ones. He summarizes these other motives as including the desire to reinforce social confidence, to express a mood or personality, to conform to group expectations, to affirm group affiliation, to accommodate to the ambiance of leisure or work environments, to demonstrate wealth and social status and simply for pleasure.

The three dimensions of behavior used (by Bain), to categorize the different areas of motivation for using perfume, parallel the main areas of behaviour delineated by Graham [13] with respect to the psychology of cosmetics and fragrance; namely: interpersonal attraction, others' perceptions and self-perception.

25.4 PSYCHOLOGICAL BENEFITS

25.4.1 Fragrance

For perfume (or fine fragrances) *per se*, research by Baron [14] showed that wearing a pleasant fragrance increased attraction and produced positive shifts in social perception, in an 'informal' dress situation. In further research Baron [15] has shown that males evaluated female job applicants lower when they wore perfume or cologne, female evaluators showing the opposite pattern. However,

Baron's research is limited to a student subject sample in which attitudes may have been 'fashionably' negative at that time. Baron [16] reviews studies exploring further the effects of fragrance in such social situations, and describes how the use of perfume in combination with avoidance of additional non-verbal tactics positively affects 'liking and attractiveness'. Dollase [17] argues that Baron's studies offer additional evidence that self-reference has greater impact on perfume use than does social validation, i.e. that people use perfume because they like it, not because they know its effects on others. He also concedes that we do not yet really understand very much about what happens in the mind of the consumer with regard to the motivation of perfume selection from the inner perspective.

Further current research is needed on other subject groups to demonstrate the substantial benefits that would be predicted from the use of perfume in a whole range of work and social situations, for men as well as women users, and perhaps focusing on different age groups and subcultures depending on the market segments of interest.

We would expect perfume to enhance significantly perceived attractiveness and personality, along dimensions similar to those we know are affected by other products, such as make-up. For example, a person using a pleasant fragrance should be attributed with more desirable characteristics, such as being more sociable, confident, interesting, etc. In other words, the 'what has been made beautiful is good' stereotype should extend to perfume and fragranced products also. We would also expect interpersonal attraction and self-perception to be positively affected by the use of perfume.

25.4.2 Fragranced products

There are also benefits to be enjoyed from fragrance contained within a product such as hand cream. Jouhar *et al.* [18] have investigated this specifically in relation to whether:

1. fragrance within a cosmetic product influences social perceptions of the person (appearance, personality, age, etc.);
2. fragrance within a product affects evaluation of the product.

The research findings showed that the presence of fragrance within a product does favourably modify perceptions of the user's appearance and personality and the product is also evaluated more favourably.

For skin-care products, although their direct effects are cleansing, nourishing and maintaining, their perfuming may also be in order to render the application of a product base more agreeable. The product may otherwise be odourless or unpleasant in fragrance. Problems of perfume addition such as discolouration can occur, and care must be taken to ensure that any materials that might be irritating or harmful to the skin are not used.

Concerning the benefits of fragrance within soap products, although the primary purpose of soap is to cleanse the body, and the fragrances added to soap are not expected to linger for a long time, some added fragrances are intended to leave a pleasing odour behind, or to give a feeling of freshness as well as cleanliness (for men's soaps and shaving soaps more masculine fragrances would be added).

With regard to the benefits of perfuming hair products, again, although the main aim of a shampoo product is to cleanse (the hair and scalp), perfume is added because the consumer is used to it being there and likes it to be there, unobtrusive though it may appear. However, since the odour of the hair is an important part of overall personal odour, the appropriate perfuming of shampoos, conditioners and styling products has become more and more important. The role of healthy, natural fragrances, e.g. fruit scents of apple, avocado, etc., have become particularly popular. A stronger fragrance within hair products is more acceptable now if it conveys a feeling of healthiness and naturalness.

When fragrances are added to most caring and cleansing products, however, only the effects become apparent to others, not the fragrances themselves.

In the perfuming of toiletry products a well-formulated perfume can add the right finishing touch which makes for an excellent product.

When the fragrancing of a product is successful and dominates the market, such as the fragrancing of Johnson & Johnson's baby powder (in which the fragrance becomes associated with emotional correlates of mother's love, safety, etc.), other manufacturers are more or less obliged to use similar fragrances to hope to be successful.

With regard to the fragrancing of decorative cosmetics such as lipsticks, since they are used, among other reasons, for aesthetic purposes and to create a pleasant and attractive, appealing effect, this fact determines to a large extent the direction for their fragrancing.

It has also been found that lipsticks with less 'aromatic' scents (e.g. fruit flavours such as strawberry, peach, cherry, also coffee, vanilla flavours, etc.) and more floral-like or 'perfumery' scents (e.g. rose, violet, jasmine, orange blossom, etc.) are preferred by most consumers. From a psychological point of view this can be explained in that lipstick is not used to beautify the mouth as an organ of food intake but to enhance its erotic attractiveness as an organ of kissing, so pleasant perfumes (not associated with flavourings), and enhancement of the colour of the lips, would facilitate this. Thus a strong desire to attract predominates.

25.4.3 Fragrance and mood

If a consumer wishes to project a certain mood for a particular occasion or situation; if she (or he) is experiencing a certain mood and wants to enhance it; or if she wants to project a mood very different from the one she is already

experiencing, then it is important to know the kind of mood projected by a fragrance, or the situation for which the fragrance is appropriate. The consumer herself can then decide what she needs to feel or project on any particular occasion, and choose the fragrance accordingly. These ways of enhancing the mood are among the benefits of fragrance.

One of the questions that the psychology of fragrance has focused on is whether individual perfumes have their own specific image, mood, personality or lifestyle that they project, e.g. sexy, glamorous, romantic or formal. Psychological research has looked at this and developed methods for relating perfumes to the dimensions that are most meaningful to the consumer.

In one such study [19] psychological concepts were found to be readily associated with specific perfumes, and these relationships between perfumes and psychological concepts can be specified and quantified. Participants in the study were white US females. The results showed how much each perfume was liked or disliked, how positively or negatively it was evaluated on different psychological dimensions, and the situations and age groups that consumers felt each perfume suited.

Research conducted in Germany [20] on 600 female fragrance users, by questionnaire, attempted to relate fragrance choice to personality data. A colour rosette test devised by Haarmann and Reimer was also used. Subjects were asked to select the colour combinations that they found most appealing, and colour preference was then used as an indicator of the person's personality. Four personality categories were used: introverted, extroverted, emotionally stable and unstable. From the deduced personality the fragrance preference and need was then derived. Mensing concluded from this research that fragrance preference is related to psychological factors (among others), and that perfume must appeal to an individual's emotional fragrance need.

There appears to be an assumption in the research that colour preference reflects the actual perfume *need* in line with the personality identified from the colour choice. For example, it is assumed that an extroverted personality would want and need an extroverted type of perfume. However, an already extroverted personality does not particularly *need* an extroverted perfume; rather,' a more introverted perfume would complement and balance the person's personality better. Similarly, a person with a quiet, retiring personality would benefit from an extroverted perfume which would project a more balanced personality and add to the person's own feeling of social confidence.

A direct link between fragrance and psychological concepts has been made in research conducted in the USA [19]. This links individual perfumes for females directly with mood, image, lifestyle and situations, without using colour as an intermediary. The crucial factor is mood and this does not need to be inferred from colour choices. Although colour can help to infer personality, this is not the whole story. Which fragrance a person needs or wants is variable, and depends more on her mood. Perfumes should be geared to match what the

consumer might *wish* to project, regardless of her basic personality. What is important is to get to know and understand the consumer personally and individually, and find out what she needs.

So, the perfume needs only to be clearly identified and marketed as conveying a particular mood, e.g. a quiet, subtle mood; a lively extroverted mood; a soft, romantic mood; or a fun mood. The right fragrance can then be selected on the basis of how the individual aspires to feel. These methods can also be applied to men's fragrances. They can be identified as conveying, for example, a macho or masculine mood or a healthy, active, sporty mood. Further dimensions will be identified from future empirical research on men's fragrances.

More research is needed to investigate self-perceived benefits of fragranced products, i.e. positive changes in mood, self-image, self-esteem, etc. It is likely, however, that the benefits of fragrance outweigh the risks of any adverse effects such as sensitization or toxicity. Skilful formulation of a product can minimize any adverse effects, but these often depend more on the susceptibility of the user than on the particular product. Cooke [21] argues that potential risks of perfumes and fragranced products need to be seen in perspective by evaluating them in the context of the many benefits obtained.

25.4.4 Environmental fragrances

Any range of perfumes can be assessed for their best use; for example, fragrances appropriate for work versus social situations, night versus day wear and so on. Situational appropriateness probably depends on the amount of perfume used.

Research in the USA [19] has related perfumes to different social situations and the different lifestyles that accompany them. Questions have focused on such issues as:

- Are different fragrances associated with different situations?
- Does a particular perfume project an image associated with a certain type of situation? It has been found that the situations and lifestyles appropriate for individual fragrances can be clearly delineated: work, a glamorous night out, etc.

Environmental fragrances have been produced that are claimed to project selected moods, e.g. nostalgic, carefree, romantic; in other words, they act essentially as mood modifiers. In the USA such fragrances have been developed for a number of situations: work, home, school, etc.; so that, for example, fragrance could be emitted automatically to influence behaviour, such as improve productivity in the workplace, make pupils happier in the classroom, control emotions, improve learning abilities and increase concentration. Fragrance supposedly may be used consciously or subliminally to control different aspects of behaviour, e.g. anxiety, lethargy, and depression, by being dispersed through air-conditioners to filter through public places and promote particular feelings.

In Japan, particularly, environmental-type fragrances such as special bath products that fill the room with natural aromas, colognes on the dashboard of a car, and so on, have been implemented. In the USA, products such as the Aroma Disc system, which fill the room with different fragrances, were fairly successful for a short time; but the idea did not really catch on in the UK.

However, a range of other environmentally fragranced products became popular in the UK; for example, *pot-pourris,* air fresheners, room fresheners, fragranced dried flowers and grasses, perfumed sachets and coat-hangers for the wardrobe, perfumed candles and other scented novelties. Social, economic and environmental changes have created more of a need for pleasant, environmental fragrances, especially 'nature' fragrances as the consumer spends more time and money on improving the home environment and creating relaxing, pleasant surroundings. Environmental fragrances are likely to continue to be popular to help alleviate the increasing stress of living.

In the latter half of the 1990s, the distinction between environmental fragrances and aromatherapy products has become blurred in that some products have emerged that have blended the two concepts. Aromatherapy has become a label that is often loosely attached to products – be they room sprays, bath oils or fizzers or other fragranced products.

Scented 'teddy bears', 'bunnies' and other animals have also emerged as a popular way of marketing *pot-pourri* oils and aromatherapy oils, using them to fill such ornamental novelties, to add fragrance to the immediate environment. The fragrance can be renewed easily.

In the workplace e.g. offices, the atmosphere can become very stuffy, particularly in air-conditioned buildings with sealed windows. The atmosphere can easily be freshened with a few drops of essential oil.

Since essential oils are thought to have antiseptic properties their use will also offer some measure of protection from the airborne bacteria with which we are surrounded.

Tests in air-conditioned buildings in which staff suffer recurrent illness and lethargy have shown that the atmosphere can indeed become very unhealthy ('sick building' syndrome). A Japanese company, known to incorporate aromatic vapours into the air-conditioning systems of offices and banks, found that lemon oil increased efficiency and reduced error. Thus aromatherapy products are used as environmental fragrances.

25.4.5 The psychological benefits of aromatherapy

In terms of the benefits of fragrance, interest in 'aromatherapy' has grown rapidly in recent years in the perfume industry and other circles. The word has different meanings depending on one's background and professional school of thought and training. 'Aroma' may mean flavour, fragrance, perfume, essential oils; 'therapy' means treatment of a disease or the means of treating specific

ailments. The aromatherapists use this part of the word to cover alleviation of symptoms or psychosomatic conditions, and aim to effect this by the use of fragrance; not just by smelling nice but by actually doing something for the well-being/health of the client. Many essential oils and aromatic chemicals are said to be effective for a wide range of purposes including curing insomnia and dizziness, and control of appetite, desire to smoke and sexual desire.

There are different understandings of aromatherapy: firstly, in connection with the therapeutic uses of essential oils, when massaged on the skin or ingested; secondly, the aspect of the treatment in which the odour is considered to be the active principle. With regard to the behavioural effects of aromatherapy products on the user (be they essential oils or other types of 'aromatherapy' products, e.g. bath oils/fizzers, foot spas, etc.) such effects might be expected to be mainly in terms of self-perceived mental and physical therapeutic effects.

We would expect aromatherapy products to be uplifting in mood, making a person feel cared for, more relaxed, more refreshed, invigorated, etc. These are the kinds of claims surrounding the different types of products.

The validity of the claims for aromatherapy lie in demonstrating benefits: (a) psychologically, or (b) physiologically/medically. It is unclear whether claims for the oils used are in all cases quantified and substantiated with rigorous research data.

Shirley Price's [22] description of a number of case histories of aromatherapy practices, from her own and other people's, indicate that most of the improvements reported are on the physical/medical level with substantially less attention focused on addressing any psychological changes taking place. These could be investigated further and more systematically.

Some research has been conducted on the effects of fragrances on mental states. 'Behavioural conditioning' with aromatherapy can be used to control mood fluctuations, to beat stress, fight pain, or induce sleep. The purpose of the aroma is always to affect mood – for example, to soothe or calm the client. There is also the associated aspect of its relationship with relaxation. Where an aroma is presented accompanying relaxation therapy, the relaxation response can eventually be elicited, by association, when the aroma alone is presented.

There is some evidence that aromatherapy can be helpful in ameliorating some medical conditions. Schiffman [23] reports that relaxation therapy combined with odours (especially human odours such as sweat) appears to be helpful in cases in which there is a history of difficulty in becoming pregnant. It is said to promote acceptance and comfort with the odour of one's sexual partner. Schiffman also reports the observations that pleasant odours (such as chocolate and fruits), used in conjunction with relaxation therapy, can actually diminish the intensity of pain, and unpleasant odours such as butyric acid can increase the sensation of pain. When the same pleasant odours delivered during the therapeutic session are experienced at a later time, they are often able, on their own, to reduce the pain and elicit a relaxation response. Thus aromas to alleviate pain

have been in use for centuries in Eastern countries; the presence of pleasant odours in the recovery room has been observed to shorten the recovery period.

Schiffman also describes studies which appear to show that aromas relieve depression when used in conjunction with relaxation therapy, drugs and psychotherapy. She describes the use of food aromas for treating eating disorders in elderly and obese patients, again in conjunction with relaxation therapy, to desensitize the patient to the food aromas. Further extensive research is needed to uncover fully the psychological and biological mechanisms involved in the modification of mood and behaviour using aromas.

Pilot research in the 1980s has shown how natural fragrances can bring benefits for multiply handicapped, profoundly retarded children (with a mental age of less than 1 year, and with severe mobility limitations) [24]. By allowing them to explore various fragranced products, psychological and social benefits to the children were observed. When presented with a range of naturally fragranced products these children, who would normally be incapable of much of a response, appeared to respond to the more strongly fragranced products, such as tangerine aromatherapy oil, large, coloured, fruit-scented soaps, and lip balms flavoured with kiwi fruit and Morello cherry. The fruit scent seemed to awaken the children's senses at the same time as providing an enjoyable learning experience. The indication is that natural fragrances seem to act as very positive behavioural motivators for the development of some sensory awareness in the profoundly retarded child, thereby generating a potentially therapeutic value within this community.

In general there is need for more formal and systematic research studies that demonstrate the specific psychological and physiological claims being made for various aromatherapy products.

25.5 NEW THEORETICAL DEVELOPMENTS IN THE PSYCHOLOGY OF FRAGRANCE AND AROMATHERAPY

Some psychological aspects of cosmetics as well as perfumery are described in Paul Jellinek's book, *The Psychological Basis of Perfumery* [25], as edited and revised by his son J. Stephan Jellinek. Central in Paul Jellinek's theory was the notion that 'modern perfumery seeks to create or reinforce sexual attraction'. This is restated often in women's popular press particularly, and forms the basis of a lot of perfume advertising. Jellinek's view of cosmetics was that they are used entirely for aesthetic reasons and act as aphrodisiacs. There are, however, other factors influencing the use of fragranced and cosmetic products.

Perhaps we can say that Jellinek's approach *was* the psychological basis of perfumery but that it no longer is. It contrasts very much with the psychology of fragrance as the field has been defined and studied by psychologists in the past two decades. Our approach is very different, and different empirical questions are asked today; we make observations of, and measure, the behaviour of people

with respect to fragrances, and tackle many more issues. The field has expanded to encompass the many social and psychological benefits of perfumery including effects on self-perception and others' perceptions, as well as interpersonal attraction.

Graham [13] describes how the theoretical background, principles and conceptual framework that apply in the psychology of fragrance are similar to those that apply in the psychology of cosmetics, and this continues to be the case in the light of more recent evidence.

The conceptual framework used by Hugh Bain [12] to describe the dimensions of fragrance use (or why people use perfumes) is similar in essence to the framework used to launch the psychology of cosmetics [1]. This parallel between the two fields can be seen to emerge further.

Research data indicate that the psychological and social motivation for use of decorative cosmetics in the 1990s was only in small part (5%) motivated by interpersonal attraction factors, but rather, in much larger part (52%) by a 'feel-good' factor among other things [26]*. Any detailed exploration of motivation for perfume use in the 2000s is likely to reveal a similar picture, and this requires further exploration.

A 'feel-good' factor has been shown to emerge within the context of each field. J. Stephan Jellinek [25] describes research conducted among 317 US female college students in 1992 [27]. In this research, which explored women's motives for using fragrance, it was found that a 'feel-good' factor which emerged accounted for 73% of the respondents' answers. Seventy-three per cent of the respondents gave as the reason for using fragrance: 'part of my beauty routine'. Only 48% chose 'attractiveness to others' (of both sexes) as a reason for fragrance use, and only 35% gave 'to attract the opposite sex' as applying to themselves.

This can be seen to parallel the research in the field of psychology of cosmetics, by Graham [26], in which a 'feel-good' factor motivating colour cosmetic use was also found to emerge much more strongly than attraction.

In a review of Paul Jellinek's work it is suggested by Graham [28] that, although very sound as an industry textbook, this volume highlights the need for more input from psychologists in this area. One of the few psychologists [17] contributing to *The Psychological Basis of Perfumery*, re-interprets findings from consumer studies. He holds the view that a perfume becomes the expression of a woman's own feelings – a 'self-anointment' as it were – and the satisfaction that comes with its use stems from a strong internalization of symbolic values. This adds another to the number of possible and plausible motivations for perfume use.

The variety of ways in which fragrances have been shown to affect behaviour need to be delineated, and all the issues covered, including identifying the gaps

*This research was sponsored by Avon Cosmetics.

in the database where we know research is needed but may not have been done yet. At this stage outlining the field with a clear and useful reference framework of this kind is necessary for its development.

Adequate coverage of the field should encompass the study of motivations for use of fragranced products and delineate the psychological and social benefits enjoyed from use of fragranced products in terms of effects on self-perception, moods, feelings, attitudes, self-esteem, confidence and self-image and effects on others' perceptions (or the image conveyed). Within this framework the role of fragrance in influencing interpersonal attraction is also considered, but it is not necessarily the main issue.

As we have advanced in knowledge in this field, the number of unanswered questions could be said to have increased, as have the number of researchers and research studies. The task of tackling the field of psychology of fragrance is therefore an ambitious one. It is an interesting subject that needs to be effectively conveyed.

Certainly there is need for good solid textbooks presenting a succinct overview of the field to reflect the growth of interest and research attention in this direction over the past two decades. This is particularly in order to keep us aware of new developments and their application to meet the needs arising within the industry.

Overall, there has been quite a lot of stimulus to consider psychology seriously as an aspect of perfumery and, as a result, the field of psychology of fragrance and aromatherapy has actually developed quite considerably.

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