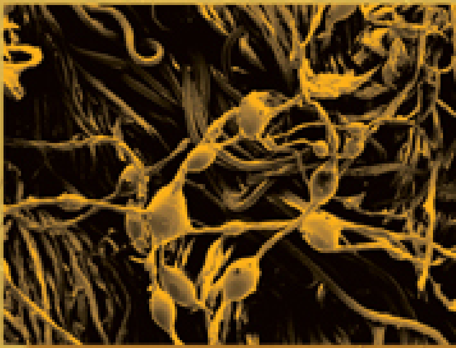
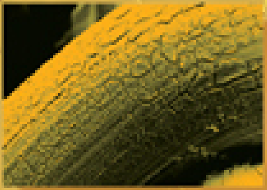
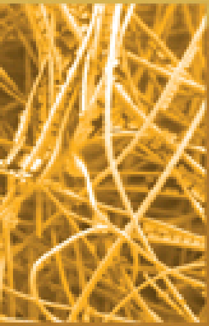
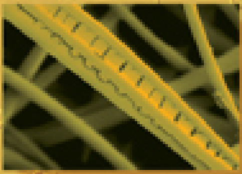




NANOSOLS and TEXTILES





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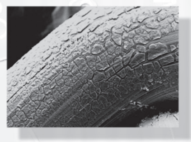

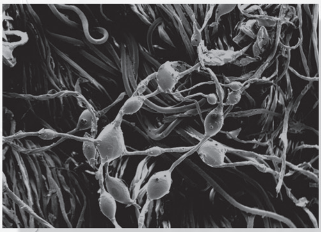

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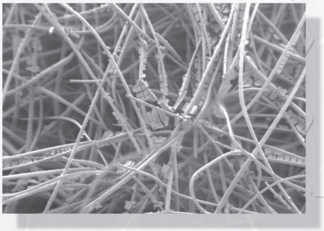

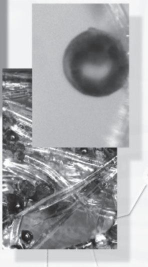

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I would like to dedicate this book to my academic teacher,
Prof. Dr. Eckhard Schollmeyer, and thank for his guidance and support.

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Dedicated to my academic teacher Prof. Dr. Horst Böttcher, who made this book possible and helped me with interesting discussions.

Boris Mahltig

Preface

Textile materials are materials for the daily use. Everyone wears clothes, uses linen and every apartment is equipped with curtains and carpets. For thousands of years we use our clothes to protect us against the weather, as well as to keep us warm and dry. At the same time, textiles are important for fashion reasons. Carpets separate our feet from the cold floor, they absorb the noise if one walks over the floor and they embellish the rooms. Since these applications of textiles are very old one can state that the production of textile is a very traditional business. Besides the traditional textile applications the area of technical textiles is very important and a growing part of the textile industry. Comparable with the conventional textiles many of these technical textiles can be found everywhere and everybody uses such technical textiles although not everybody notices them. Some examples are the conveyor belt at the cash desk in the supermarket, the safety belt and the airbags in the cars or the roofs of the modern sport arenas. Further examples are enumerated to give an idea in which products technical textiles are applied:

- in building trade textiles are used to reinforce concrete
- bullet-proof vests protect against weapons
- modern architecture uses textile materials in building trade
- many components in cars, aircraft and even space vehicles are reinforced with fabrics
- in medical applications textiles are used, for example, as implant material
- …

Textile materials offer a number of advantages that make them essential for clothes as well as for technical textiles. Fabrics can be draped in many different forms – if needed thousands of times, they can be prepared to be flexible as well as inflexible, they show a certain permeability for air, vapour and liquids and textiles combine an enormous stability (especially tensile strength) with comparatively low weight. Fabrics can be produced with large surfaces and are simultaneously comparatively light in weight. In many cases textile approaches therefore offer solutions favourable in price and performance.

Up to the beginning of the 20th century textile materials based either on animal (e.g. wool, silk) or plant fibres (e.g. cotton, bast). With the rise of synthetic fibres these became ever more important for the textile industry. In the decades after the synthetic fibre materials were invented polymer scientists developed fibre polymers for a lot of applications. During this time the idea was to produce a certain polymer for certain applications, but market economy lead to a narrowing of the assortment of fibre polymers available. No new fibre polymer was introduced in the market successfully for many years, and many of the fibre polymers lost their commercial relevance. Today approximately 50 % of the textiles are made of cotton and the rest is mainly based on polyester and polyamines plus some minor materials [Schenek (2001); Koslowski (1997)]. In 2006 nearly 80 % of the textile fibres produced in the world were polyester and cotton [www.ivc-ev.de]. Some studies say that in several years the only fibre materials of importance will be based on cotton or polyester (which means poly(ethylene terephthalate), the synonym for polyester in textile industry) and the polyolefines (polypropylene and possibly polyethylene). At the same time as this reduction of the variety of fibre polymers that are commercially available the number of applications for textile materials increases impressively. Especially the market for technical textiles shows high rates of economic growth. The demand for new materials or for materials with new or additional properties is immense. Against the background of facts mentioned before this means that these new materials have to be developed dealing with the fibre polymers available. Due to this reason the surface modification of fibre materials is an important topic of textile research worldwide.

The modification of textile fibres is carried out by commonly used chemical or electro-chemical application methods. Many of the classical textile finishing techniques (e.g. hydrophobization, easy-care finishing) that are already used since decades are amongst these methods. Dyestuffs, polymers or monomers are applied to the fibre material and are deposited either permanent or often only temporarily. Modern techniques are applied more and more parallel to these. One of these modern techniques is, for instance, the treatment with corona or plasma. Corona treatments allow one to modify the surface of the polymeric material either by surface etching or by introducing oxygen-rich groups onto the polymer surface. Plasma treatment can add a huge number of functional groups to the polymer surface, depending on the process gases in the plasma chamber. The literature reports, for example, the deposition of fluorine rich surfaces, leading to highly repellent fabrics [Bahners et al. (2001)]. The plasma techniques offer far reaching possibilities, but the technical effort is comparatively high due to the fact that the processes often have to be carried out under reduced pressure or at least under exclusion of oxygen. Besides plasma treatment electron beam technologies as well as different photonic technologies (UV-, laser treatment) [Praschak et al. (1998) & (2000)] are applied to achieve certain functionality.

One of the different new approaches and possibly one of the most promising for surface modification of textile materials – and certainly not only of textile materials – is the sol-gel technology which was probably one of the most important developments in material science during the last decades. The sol-gel technique offers far reaching possibilities for creating new surface properties. In the literature a tremendous amount of functionalities can be found that have been achieved by application of sol-gel coatings. Sol-gel technology promises the possibility to tailor surface properties to a certain extent, and to combine different functionalities in a single material. At the same time the application of sols can be carried out with techniques commonly used in the textile industry. Finishing of textiles can, for example, be carried out in a simple dip or padding process followed by a thermal treatment in a stenter frame.

In this book we concentrate on the use of so-called nanosols for modification of textile materials. Nanosols are colloidal solutions of nanosized metal oxide particles in aqueous or organic solvents or mixtures of both. Due to the high surface area of the small particles the nanosols are metastable. During a coating process the particles will aggregate as well as condense, initiated by evaporation of the solvent and, for instance, by thermal treatment. These processes mostly result in dense three-dimensional metal oxide networks. The basic inorganic nanosols used for such coating procedures can be modified over a wide range, leading to coatings which exhibit many new functionalities. Nanosol coatings can be easily applied to a huge number of materials such as glass, paper, wood, metals, synthetic polymers, natural fibre material and thus also to textiles. In comparison with many other materials textiles products combine, for example, high flexibility and usually low thermal resistance. The conditions for the treatment and the composition of the nanosols have therefore to be adapted to the particular demands of textiles.

The intention of the authors was not to write a book explaining the principles of sol-gel technique or of nanosols. Concerning this a number of excellent books are available, most of them will be cited frequently in this book. This work gives an overview of possible applications of nanosols for the modification of textiles.

Boris Mahltig and Torsten Textor

Content

Chapter 1

Nanosol Preparation and Application

Nanosols are colloidal solutions of nanometre sized metal oxide particles in aqueous or organic solvents. Due to the very high surface area of such small particles the nanosols are metastable, thus, for example, during a coating process the particles will aggregate due to the evaporation of the solvent, easily forming a three-dimensional network. Nanosol particles exhibit diameters in the range from a few nanometres up to 100 nm, while coatings formed by nanosols can reach a thickness of up to several hundred nanometres. The length scale of a nanosol coating can therefore cover a broad range of the structural elements starting from molecules up to three-dimensional, large-scaled objects such as fibres forming a textile. Depending on the curing parameters the inorganic metal oxide based networks will be mainly amorphous after moderate heat treatment (so-called *xerogels*), if a treatment at high temperatures of, e.g., 500°C and more is carried out the networks form increasingly crystalline structures.

The basic nanosols can be modified in a wide range, leading to numerous new functionalities that can be applied to various surfaces in comparably simple coating processes (Figure 1.1). The nanosol coating is therefore a suitable tool for modifying a large number of materials, such as glass, paper, synthetic polymers, wood, metal and, of course, textiles.

As a result of the particular properties of textile materials, e.g. high flexibility or low heat resistance, the nanosol process has to be adapted for the treatment of textiles. This chapter will give an introduction to the preparation, modification and application of nanosols with respect to special demands for treating textile materials.

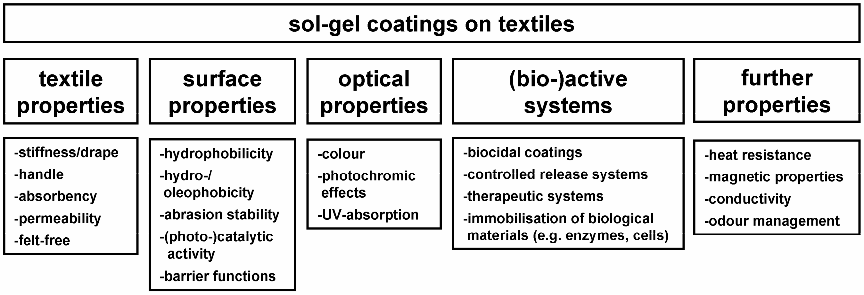


Figure 1.1 Selected examples for the improvement of textiles by application of sol-gel coatings.

1.1 General aspects of the preparation of nanosols

Nanosol coatings are usually prepared by using the sol-gel process [Hench et al. (1990); Brinker et al. (1990a)]. This process can be basically divided into three steps: formation of the nanosol by hydrolysis of the precursor material and subsequent condensation reactions, the coating process, then drying or curing. The precursors are either inorganic metal salts or metal organic compounds such as metal alkoxides or acetylacetonate. Alkoxy derivatives of metals or semi-metals are most widely used, whereby hydrolysis transforms them into the corresponding hydroxides. These hydroxides are mostly unstable in higher concentrations and therefore tend to undergo subsequent condensation reactions. The condensation reactions lead to the formation of particles with sizes in the nanometre range. The conditions used for the preparation of the sols (e.g. solvent, pH-value, temperature, concentrations, salt concentration) determine the development of the particles as well their size. Hydrolysis can be carried out under acidic as well as alkaline conditions. Nonaqueous sol-gel routes are also possible [Niederberger (2007)]. Nanosols hydrolyzed under acidic conditions usually result in weakly cross-linked condensation products with a denser layer structure after coating, whereas alkaline-catalyzed sols tend to particle aggregates with larger pores [Brinker et al. (1990a)]. Frequently used precursors are, for example, tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS), titanium(IV)isopropoxide $Ti(OC_3H_7)_4$ or

$Al(OC_4H_9)_3$ [Hench et al. (1990); Liu et al. (2007)]. The product of the reaction described is the so-called nanosol, which is a liquid dispersion of low viscosity (usually in the range of 1 to 6 mPas) containing nanosized particles. This nanosol can be easily applied to numerous substrates, forming dense layers after the evaporation of the solvent. The main steps for preparing sol-gel derived coatings are depicted in Figure 1.2.

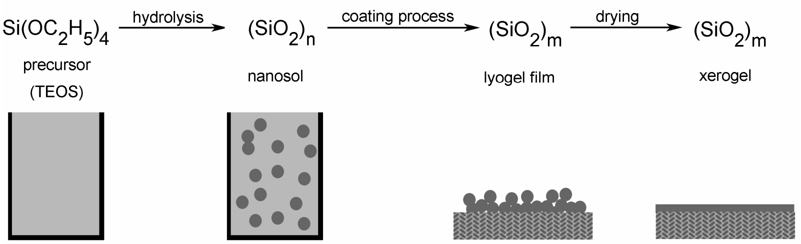


Figure 1.2 Main steps for the preparation of nanosol coatings (sol-gel process), here shown for a silica coating.

Due to the small size and the high surface area the particles tend to aggregate, so the nanosol itself is metastable [Schmidt (2006)]. The aggregation can either lead to a gelation process or to precipitation of metal oxides. In both cases the sol cannot be used as a coating material any more. The stability of a sol is affected by many parameters, most important are the type of particle and the solvent composition. Furthermore the pH-value, the amount of water, the solid content or the presence of salts determine whether a sol is stable. Certain sols are stable for several years while others will gel within minutes, or even seconds [Estella et al. (2007); Norisuye et al. (2000)]. A significant stability enhancement can be for example achieved by dilution of nanosols with ethanol or other alcohols. In certain cases the gelification process will be accelerated by dilution with water. The diagram in Figure 1.3 shows the correlation between the time until various silica sol gels gelify as a function of the dilution with water. In addition the diagram shows that a modification of the sol, for example with organically modified silanes can increase the storage time. Even if a nanosol is still liquid and can be used as coating solution, ageing of the nanosol particles occurs. Ageing means not only a continuous agglomeration and gelation of the sol, but also the precipitation of aggregates is possible. The ageing can have a significant influence on the properties of the resulting coatings, especially on coating thickness, roughness and porosity [Fidalgo et al. (2003a)].

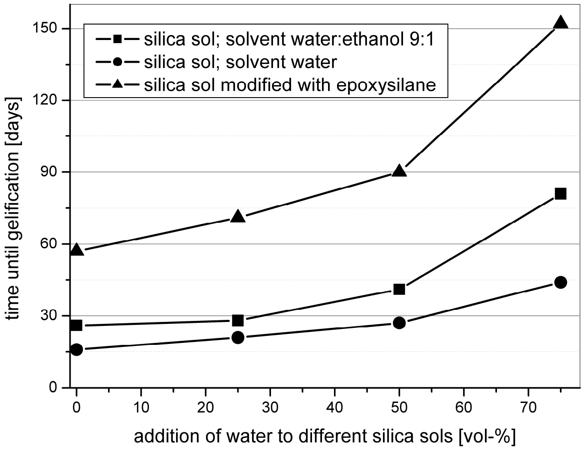


Figure 1.3 Enhancement of the stability of different silica sols with increasing dilution using water.

Most sols are prepared starting from alcoholic solutions of alkoxysilane precursors like TEOS. TEOS can also be used as precursor for the hydrolysis in pure water, since ethanol is released during the hydrolysis reaction. In the latter systems the precursor and water have to be stirred vigorously because TEOS and water are immiscible, as schematically depicted in Figure 1.4. Furthermore the TEOS concentration has to be kept at a comparatively low level to achieve stable nanosols [Wright et al. (2001); Mahltig et al. (2005b)]. An alternative method to prepare aqueous nanosols is the removal of the organic solvent by evaporation by passing air through the sol while simultaneously substituting it with water [Böttcher (2000); Amberg-Schwab (2003)]. Using this method the resulting mean particle size in the aqueous nanosol is quite similar compared with that the originally ethanol containing sol. Figure 1.5

shows the particle size distribution of correspondingly prepared sols with different amounts of ethanol.

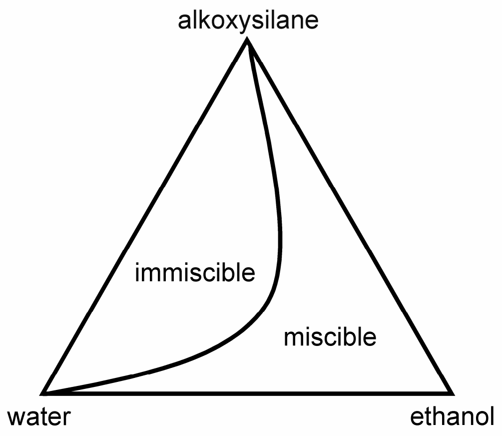
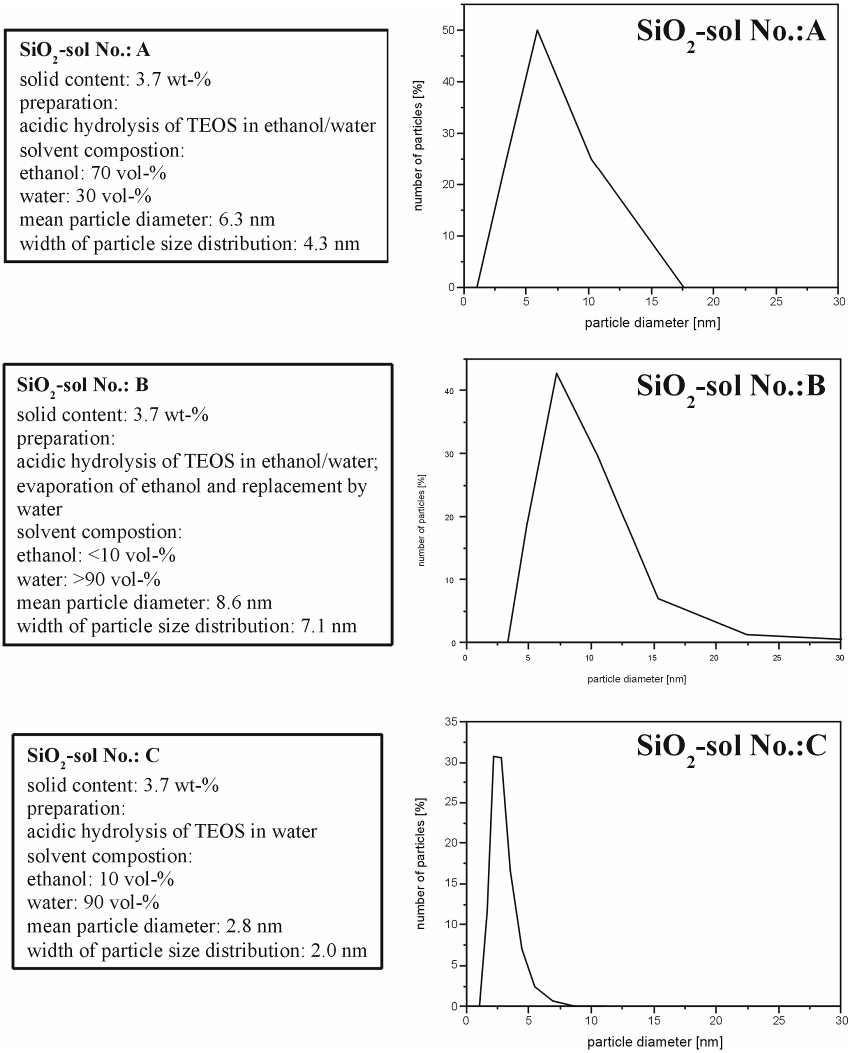


Figure 1.4 Schematic phase diagram of the system alkoxysilane, water and ethanol.

For many industrial applications solvents will be completely unacceptable, but if only small amounts of solvents do not cause problems, highly concentrated sols can be produced by using solvents such as diethylene glycol. These solvents allow the preparation of stable sols with comparably high concentrations in the range of 30 wt-%. A corresponding product supplied by CHT R. Breitlich GmbH is commercially available under the name iSys MTX [Koch (2006)]. The sol is delivered with high solid concentrations in diethylene glycol and can be either applied pure or diluted with water. For application in industry the dilution with water is highly recommended, leading to an aqueous sol with low content of organic solvents. The stability of the basic sol is at least six months, after diluting it with water the stability will be greatly decreased, but it will be enough to guarantee proper processing.



SiO_2-sol No.: A
solid content: 3.7 wt-%
preparation:
acidic hydrolysis of TEOS in ethanol/water
solvent compostion:
ethanol: 70 vol-%
water: 30 vol-%
mean particle diameter: 6.3 nm
width of particle size distribution: 4.3 nm

SiO_2-sol No.: B
solid content: 3.7 wt-%
preparation:
acidic hydrolysis of TEOS in ethanol/water; evaporation of ethanol and replacement by water
solvent compostion:
ethanol: <10 vol-%
water: >90 vol-%
mean particle diameter: 8.6 nm
width of particle size distribution: 7.1 nm

SiO_2-sol No.: C
solid content: 3.7 wt-%
preparation:
acidic hydrolysis of TEOS in water
solvent compostion:
ethanol: 10 vol-%
water: 90 vol-%
mean particle diameter: 2.8 nm
width of particle size distribution: 2.0 nm

Figure 1.5 Particles size distribution of differently prepared silica nanosols.

In addition to the above described sols derived from metal alkoxides aqueous sols can also be prepared by the hydrolysis of metal halides or other salts. Examples mentioned here are the preparation of alumina sols from $AlCl_3 \times 6\ H_2O$ [Kurokawa et al. (1998)]; aluminium lactate [Zhang et al. (2007)] or the synthesis of titania nanosols starting with $TiCl_4$

[Toshikazu et al. (2004); Ishibai et al. (2006)] or titanium (IV) sulphate [Kishimoto et al. (2003)].

Probably the most favourable silica nanosols can be produced from aqueous sodium metasilicate ($Na_2SiO_3 \times 5H_2O$) by using ion exchange techniques [Thim et al. (2000)]. Such sols are produced on an industrial scale, starting with silica (sand) and sodium carbonate that are mixed in the melt, forming sodium silicates. These silicates can be dissolved in hot water or steam, forming water glass. By ion exchange the sodium can be removed from the solution, during this gentle neutralization orthosilicic acid is formed. Due to the already mentioned low stability of the orthosilicic acid condensation reactions occur, subsequently leading to the formation of colloidal silica particles. The stabilization of these particles is guaranteed by adjusting a certain sodium oxide concentration. Many aqueous dispersions of colloidal polysilicic acid are commercially available, some examples are given in Table 1.1. These sols contain up to 50 wt.% of solid material and are stable for at least six months.

Table 1.1 Several commercially available silica dispersions.

Trademark	Producer
Ludox	Grace
Nyacol	Nyacol Nanotechnologies, Inc.
Levasil	H.C. Starck
Köstrosol	Chemiewerke Bad Köstritz

1.2 Modification of nanosols

Nanosols can be modified in many ways to achieve new or additional functional properties. By adding new properties to a sol, the sol coated surface will be suitably provided with the corresponding functionalities. The modifications can be carried out by adding particular compounds, either to the precursors before hydrolysis, or to the prefabricated nanosols. A huge number of additives can be employed leading to manifold functions. An admittedly incomplete overview of selected examples is listed in Table 1.2. On the one hand the additives can be simple monomolecular compounds such as certain silanes or other reactive monomers, dyestuffs or any ionic compounds. On the other hand oligomers, synthetic as well as natural polymers, polysiloxanes or even proteins can be added. Even embedding of living cells has recently been reported [Böttcher et al. (2004)].

Table 1.2 Selected examples of functionalisation of sol-gel coatings.

Functionalisation	Additive / Component	References
Hydrophobic	Alkyltrialkoxysilanes	Mahltig et al. (2003); Textor et al. (2001a)
	Hydrophobic polysiloxanes	Mahltig et al. (2003); Textor et al. (2001a)
	Urea/polysiloxane	Vince et al. (2006)
Oleophobic	Fluorocarbon polymers	Cerne et al. (2004); Yeh et al. (2007)
	Fluorinated alkyltrialkoxysilane	Satoh et al. (2004); Textor et al. (2001a)
Improved abrasion stability	Epoxyalkyltrialkoxysilane	Textor et al. (2001 & 2003); Schramm et al. (2004); Liu et al. (2007)
	Methyltriethoxysilane	Lee et al. (2002)
Well hand feeling	Epoxysilane / polyetheramine	Yan (2006)
Antiwrinkle	Dimethylolethylene urea	Huang et al. (2006b & 2007)
Heat resistance	Zirconium / aluminium oxide	Benfer et al. (2002)
Flame resistance	Antimony oxides	Petrow et al. (1974); Hennige et al. (2005)
	Phosphoric acid	Chapple (2006)
Dyeing	Organic dye stuff	Dubois et al. (1996); Trepte et al. (2000); Min et al. (2003); Mahltig et al. (2004a & 2004b); Juan et al. (2005)
	Infrared dye	Prosposito et al. (2000)
Photochromic	spiroxane	Hoffmann et al. (1995)
UV protection	Organic UV-absorber	Müller et al. (2004); Zayat et al. (2007)
	Organic UV-absorber / TiO_2	Mahltig et al. (2005a)
	TiO_2	Xin et al. (2004 & 2005); Xu et al. (2005a)
	Zinc oxide	Textor et al. (2003); Li et al. (2007d); Huang et al. (2006c)
Shielding of X/α-rays	Barium sulphate	Qu et al. (2002)

Table 1.2 (continued): Selected examples of functionalisation of sol-gel coatings.

Hydrophobic	Alkyltrialkoxysilanes	Mahltig et al. (2003); Textor et al. (2001a)
Luminescence	Epoxy- and aminosilanes, polymers	Han et al. (2002); Ramos et al. (2002)
Antistatic	Aminosilane	Xu et al. (2005b)
	SnO_2	Wu et al. (2004)
conductive	tetrathiafulvalene	Zlatolas et al. (2007)
magnetic	Fe_3O_4	Thomas et al. (2006),
superparamagnetic	Fe_3O_4	Xu et al. (2005d) Zorjanovic et al. (2004)
Photocatalytic	TiO_2 / anatase	Iwashita et al. (2000); Daoud et al. (2004b & 2004c); Liuxue et al. (2008) Textor et al. (2003) Textor et al. (2007a)
Biocidal	Organic biocides	Böttcher et al. (1999); Haufe et al. (2005)
	TiO_2 / anatase	Daoud et al. (2005)
	Silver	Mahltig et al. (2004c); Tarimala et al. (2006)
	Copper	Kim (1993) Trapalis et al. (2003)
	Zinc oxide	Vigneshwaran et al. (2006)
Controlled release	Benzoic acid	Böttcher et al. (1997)
	Fragrances	Carturan et al. (1997)
	dopamin	López et al. (2007)
Enzyme immobilization	Oxidase	Betancor et al. (2005)
	Lipase	Chen et al. (2002)
	papain	Li et al. (2007)

In principal two main types of modification of nanosols are defined: chemical and physical modification.

The chemical modification is performed with additives which are able to form covalent bonds with or within the metal oxide particles during the preparation process [Schubert et al. (1995); Haas et al. (1999a)] (Figure 1.6). Such chemical modifications could be the result of a co-condensation of different types of metal alkoxides, for example of tetraethoxysilane (TEOS) with other metal alkoxides ($Me(OR)_n$). Following this approach metal oxide compounds composed of different metals in a variable ratio can be produced. The most frequently used metals are silicon, aluminum, titanium, zinc and zirconium, the literature shows many more examples [Chu et al. (2003); Kong et al. (2005); Jeong et al. (2006)]. Depending on the reaction conditions and the reactivity, the resulting particles can consist of mixed oxides or core-shell structures might be formed, where core and shell are based on different oxide compositions [Kong et al. (2005); Zhang et al. (2006b)].

Another approach for chemical modification is the co-hydrolysis and cocondensation of trialkoxysilanes R'-$Si(OR)_3$ that are modified with an organic rest R'. These alkoxysilanes can be introduced covalently into an inorganic metal oxide network. The organic group can act simultaneously as a network modifier (Figure 1.7), that changes properties of the resulting coatings such as the porosity [Tan et al. (2006b)]. One should note that the use of modified alkylalkoxysilanes can influence the reaction kinetics of the sol-gel polymerisation. Especially silanes exhibiting bulky organic chains could lead to lower reactivity under both acidic as well as alkaline conditions [Tan et al. (2006a)].

Hydrophobic or even oleophobic surfaces can be designed by introducing alkyl- or fluoroalkyl groups into the coating material. If the organically modified alkoxysilanes used are modified with functional groups based on epoxy- or methacrylic compounds these groups can also be used to achieve cross-linking of organic domains parallel to the development of the inorganic network [Nass et al. (1990); Liu et al. (2007)]. Due to the mentioned combination of inorganic and organic functionalities the resulting materials are often specified as inorganic-organic hybrid polymers (other descriptions used are Ormocer®, Nanomer® or Ormosil). The above described chemical modification of the xerogel networks is illustrated in Figure 1.6. In general every compound, that is miscible with the precursors or the sols and that is able to form a covalent bond to the metal oxides and that does not increase the gelation intolerably can be introduced into the sol-gel derived networks. Even larger and more complex organic compounds such as dyes or active agents can be bonded covalently using the approach described [Trepte et al. (2000)].

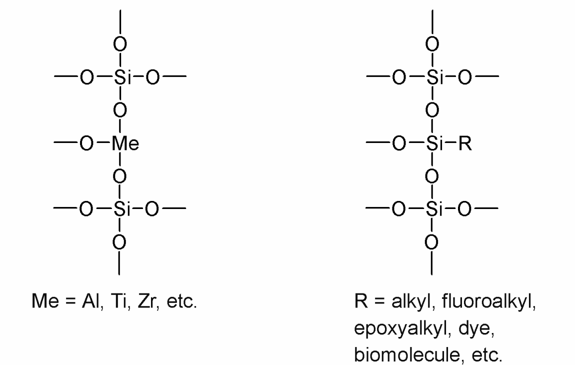


Figure 1.6 Chemical modification of nanosols.

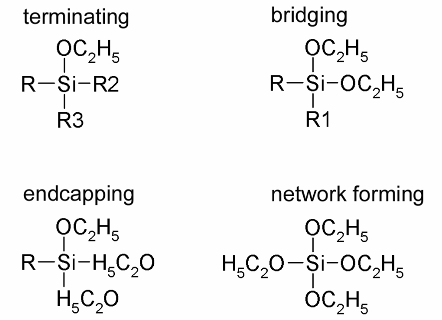


Figure 1.7 Modification of inorganic network by different silane precursors.

The modification of nanosols can also be carried out with additives that are homogeneously incorporated and immobilized into the metal oxide matrix without forming covalent bonds. These additives are usually larger molecules such as polymers, pigments, dyestuffs, active substances or biomolecules. The incorporation can occur by adding the additives either before, or after hydrolysis of the precursors (Figure 1.8). Both routes will lead to comparable composite structures and immobilization behaviour since it is assumed that encapsulation actually occurs during the formation of the network. The immobilization of additives within the inorganic matrix is very efficient and can be controlled by several means, for example, the composition and structure of the oxide matrix, by the additive content or, for example, by the

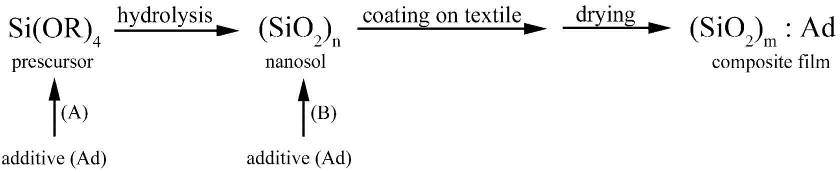


Figure 1.8 Modification of nanosol coatings by physical incorporation of additives.

addition of pore forming agents [Böttcher et al. (1997a); Wei et al. (1999)].

1.3 General aspects of the textile coating process with nanosols

In general, nanosols are coating agents useful to functionalize a broad range of different materials. Applications are often reported for hard materials like metal or glass [Celzard et al. (2002)] and also for softer materials from natural sources like wood [Mai et al. (2004), Mahltig et al. (2008)]. Basically the same nanosols used for coatings applied to such materials can be also used for preparation of coatings on highly flexible materials such as textiles or paper. Nevertheless the nanosol compositions as well as the application procedures have to be adapted with respect to the particular demands of the textile substrates as required by the textile industry. Table 1.3 shows a comparison between basic industrial requirements for applying sol-gel coatings on inorganic substrates as glass or metal and applying it to a textile material [Lutz (2006); Brückmann et al. (2006)].

Table 1.3 Typical properties and requirements that have to be taken in account if using sol-gel systems for coating glass/metal or for finishing textile material [Lutz (2006); Brückmann et al. (2006)].

	Conventional sol-gel systems used for coatings on glass or metal	Typical demands for application in textile industry
storage time	limited; cooling is necessary	stable for several months, storing at room temperature
solvent	Inflammable	aqueous systems are preferred, no use of flammable liquids
application / concentration	batch processes, such as dipping / ~ 1000 g/l	continuous processes / ~ 50 g/l

The main limitation for a nanosol application with respect to textiles is determined by the comparatively low thermal stability of most textile materials which is usually below 200°C, for many materials significantly lower (compare typical examples in Table 1.4). Only some special fibre materials e.g. those based on PEEK (polyetheretherketone) or PEI (polyetherimide) and of course the inorganic fibres such as glass fibre can be treated at higher temperatures [Robert et al. (1999)].

Table 1.4 Examples for thermal properties of selected man-made fibres [Kowalski (2000)].

Fibre	Melting temp. (decomposition temp.) [°C]	Heat stability in air up to [°C]	Ironing temp.* [°C]
PA 6	215–220	120	150
PA 66	255–260	120	180–200
m-aramide	(~370)	180–200	
p-aramide	(~550)	180–200	
PET	250–260	120–160	150–200
Elastane	230–290	120	150–180
PE (HD)	124–138	70–90	
PP	160–175	~120	130
PAN (homopolymer)	~320	140	150–180
PVC	(240–260)	< 65	
Viscose	(175–190)	120	150–180
PTFE	327–342	180	
Glass		300–400	
Carbon fibre	3600	300	

* The ironing temperature indicates the peak temperature that the material will withstand at least for a limited time.

One has to keep in mind that a thermal treatment at temperatures below 200°C will only form inorganic xerogels, the preparation of ceramic oxide coatings with a higher density would need temperatures higher than 500°C. For the deposition of sol-gel coatings composed of mixed metal oxides or metalized metal oxides thermal treatments with temperatures often higher than 400°C are necessary. An increase of the xerogel density as well as a decrease of its porosity without curing at extremely high temperatures can, e.g., be achieved by adding certain metal or semi-metal oxide pigments to the sols [Hennige et al. (2005)].

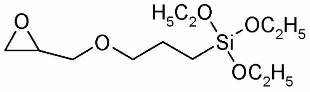
An alternative method to realize more crystalline or metalized nanosol coatings could be offered by the sol preparation under hydrothermal conditions [Demazeau (2007); Mahltig et al. (2007)] or also by the "benzyl alcohol route" [Pinna (2007)]. The hydrothermal synthesis is a convenient way to realize crystalline metal oxide compounds without thermal aftertreatment of the coatings. By this method the necessary thermal treatment can already be carried out during the nanosol synthesis and further treatments can be performed at lower temperatures. Due to the decrease of nanosol stability with increasing temperature the synthesis at higher temperatures is however not suitable for every type of nanosol. In this case an appropriate alternative could be a microwave treatment during sol-gel synthesis [Tompsett et al. (2006)], which can be applied either under hydrothermal conditions but also under a standard atmosphere [Liuxue et al. (2008)]. In contrast to a conventional heat source, the microwave couples directly with the molecules of the entire reaction mixture and activates most molecules that possess a dipole moment or are ionic. The resulting rapid rise in temperature accompanied by the direct activation of reactants make shorter reaction times possible [Hayes (2004)]. Examples are the microwave-assisted solvothermal synthesis, which allows the fast synthesis of high quality metal-organic framework crystals [Ni et al. (2006)], the enhancement of Ostwald ripening of TiO_2 particles [Wilson et al. (2006)] or the formation of the crystalline TiO_2 form anatase from amorphous TiO_2 sols [Liuxue et al. (2008)].

As mentioned above, on the one hand a thermal aftertreatment at higher temperatures should be avoided to reduce degradation and deformation of the textile materials. Nevertheless, on the other hand for many sol formulations a moderate thermal treatment at about 120°C after the sol is applied to the textiles is appropriate. This treatment speeds up the gelation and drying process of the coating and simultaneously enhances the adhesion between coating and substrate. A thermal aftertreatment has therefore to be adapted with regard to the type of textile coated and to the applied nanosol coating.

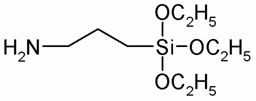
As shown in Table 1.3 the type of nanosol solvent used is of great importance for industrial applications, as there is a strong demand for aqueous and non-inflammable solvents. In case of nanosol application on textiles, the solvents are not only important for nanosol preparation and stability. The solvent can have not only a strong influence on the formation of coating onto the textile but also on the coating adhesion. With regard to textile application different explanations can be found in literature how the solvent composition influences the formation of the sol-gel derived coatings on textiles or fibres. For example, the grafting of a polymer layer onto wool is significantly influenced by the solvent composition. The best values are achieved with appropriate mixtures of water and ethanol, due to a balance of a fibre swelling by the solvent and an activation of the fibre surface [Chauhan et al. (1997)]. In fact, by using nanosols with same particle composition but different solvents, coatings with different properties are obtained. The wettability of organic substrates such as textiles by different solvents also plays an important role. In many cases it can be observed that nanosols with an organic solvent lead to smooth coatings on fibres while the same sol with water leads to coatings forming cracks [Mahltig et al. (2005b)]. This effect occurs mainly for the synthetic fibres that are relatively hydrophobic. A certain amount of a less polar solvent than water improves the wetting of such materials and thus improves the resulting coatings.

It has to be taken into account that a cosolvent can influence the process of hydrolysis of alkoxide groups by transesterification reactions. It has also been reported that different organic solvents need not necessarily affect the reaction and the resulting sol-gel films will have unchanged properties. The deposition of prefabricated silane oligomers is only slightly affected by using different organic solvents [Watson et al. (2001)]. Differences in film morphology and thicknesses observed are explained by different solvent evaporation rates during the gelation process [Fidalgo et al. (2003b)] but also with the ageing of the nanosol [Fidalgo et al. (2003a)].

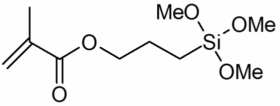
An important factor for the application of nanosol coatings for textiles is the adhesion of the coating to the fibre surface to prevent the coating from flaking off, for example during use or washing. In the case of materials like cotton or cellulose the adhesion of the sol-gel coating is easily improved by chemical condensation of silanol groups with the hydroxyl groups on the textile surface [Salon et al. (2005)]. The chemical condensation of prehydrolyzed alkoxysilanes on cellulose is known to occur after thermal treatment at above 100°C [Abdelmouleh et al. (2002)].



(3-Glycidoxypropyl)triethoxysilane



Aminopropyltriethoxysilane



Methacryloxypropyltrimethoxysilane

Figure 1.9 Chemical structure of functional silanes containing reactive side-chains.

In addition the adhesion can be enhanced by using crosslinking agents, such as alkyltrialkoxysilanes with epoxy or amino functions on the side chains [Trepte et al. (2000); Schottner (2001)]. Examples of useful additives are shown in Figure 1.9. The organic group of these agents can form covalent bonds to various substrates. Epoxy groups might for example react with hydroxyl or amino groups on fibre surfaces, or methacrylic groups could be grafted to polymer surfaces, while the alkoxy functions condense with the inorganic network of the sol-gel matrix. Beside the modification of nanosols by adding aminofunctional silanes, highly diluted aminosilane compounds can be also applied as primer, thus increasing the adhesion of the subsequently applied nanosol coating [Mackenzie et al. (2003)]. Table 1.5 summarizes the functional groups and the polarity of the most important fibre polymers.

Table 1.5 Functional groups available on different fibre materials.

Fibre material	Reactive groups	Hydrophobic/hydrophilic*
Cotton	-OH	Hydrophilic
Wool	-OH, $-NH_2$	Hydrophilic
Polyester	Endgroups –COOH, -OH	Comparably hydrophobic
Polyamides/Aramides	Endgroups $-NH_2$, -OH	Hydrophilic
Polyacrylonitriles	-CN	Hydrophilic
Polyolefins	---	Strongly hydrophobic

* The designation is a textile valuation.

Many fibre polymers do not have reactive groups on their surfaces, so direct chemical bonding to the nanosol coating is not possible. In this case, the polymer surface has to be activated in order to achieve sufficient adhesion between the nanosol coating and the fibre.

A number of methods are known in textile industry to functionalize textile materials to increase wetting behaviour and adhesion properties. One of these methods is corona treatment. The polymer surface is partially oxidized by treating it with an oxygen plasma. As a result the number of polar surface groups, e.g. hydroxyl or carboxyl increases [Chan et al. (2000)]. Other methods to increase the surface energy or to deposit functional groups are certain low pressure plasma treatments with reactive atmospheres [Friedrich et al. (1994), Akovali et al. (1996), Carlsson et al. (1993)] or photo-oxidation processes, e.g., by excimer-UV-lamps, quasi monochromatic lamps that are able to oxidize polymers such as polyester without affecting the bulk material [Praschak et al. (1998 & 2000)]. Zorjanovic et al. described a pretreatment that is comparable to the process of disperse dyeing well known in the textile industry [Zorjanovic et al. (2004)]. Polyester fibres are treated with a long-chain alkyl amine in an autoclave at a temperature higher than the glass temperature of the polymer. Under these conditions the non-polar alkyl chain will diffuse into the polymer (which is only possible due to the increased mobility of the polymer chains above the glass temperature), the polar amine group will not. After reducing the temperature below the glass temperature the alkyl chain remains fixed in the fibre and the functional amine group can for example be used to improve the adhesion to coatings based on epoxy-modified nanosols [Zorjanovic et al. (2004)]. The result of the mentioned pretreatment is schematically depicted in Figure 1.10.

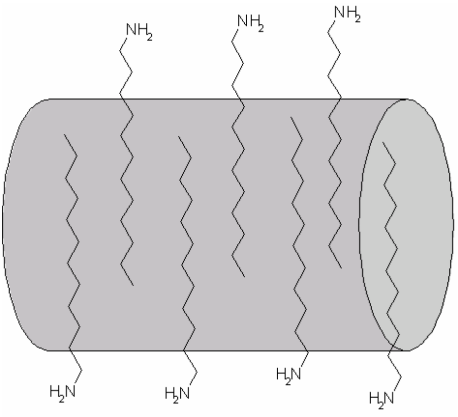


Figure 1.10 Functionalization of a polyester surface by immobilizing long-chained alkyl amines in a process comparable with disperse dyeing.

Another approach is the use of fibres that are based on copolymer materials containing alkoxysilane groups. Covalent bondings between the silanols or alkoxysilanes that are part of the copolymers and those of a silica sol are easily formed [Jang et al. (2001)], nevertheless special fibre materials have to be prepared, which will hinder the commercial application.

1.4 Application process

The application of nanosols to the textile materials can be carried out by conventional procedures used for textile finishing (Figure 1.11). Such procedures are mainly simple dipping, padding or spraying processes [B. Wulfhorst (1998); A. Giessmann (2003)]. Even printing processes using nanosols can be realized on textiles. Probably the simplest method is dipping of a textile sample into the nanosol. The fabric is immersed in the sol, remains there for a certain time, it is taken out and it either dries under the ambient conditions or it is thermally cured in an oven or a stenter frame. This general approach to finish textiles with nanosols will be described in more detail in the following chapters, since it can be carried out with techniques conventionally used in the textile industry.

Other curing procedures may also include a plasma treatment, the use of lasers, IR or UV radiation. Comparable procedures can also be carried out with fibres or yarns instead of fabrics [Liuxue et al. (2006); Krüger et al. (2006)].

Since the solvent uptake of a textile fabric is extremely high compared with polymer film padding, the latter process is more common in the textile industry. The solvent uptake of a textile is in the range of 100 % (depending on the fabric as well as the fibre material). The padding process is a dipping process, followed by squeezing. The squeezing process is advantageous for several reasons, on the one hand the amount of liquor absorbed by the fabric can be reduced drastically. On the other hand the squeezing guarantees uniform distribution of the sol covering the complete product. This is particularly important when using aqueous nanosols for the treatment of hydrophobic fibres that show a comparably low wettability [Gu et al. (2000)]. High amounts of sol absorbed by the fabrics might be disadvantageous for different reasons. The production speed would be decreased and/or the energy consumption would be increased since more solvent has to be evaporated. Additionally the amount of solvent necessary would be larger. In addition to these economical and ecological disadvantages a higher amount of sol absorbed means an increased coating thickness. The coating thickness is of tremendous importance for the resulting textile properties as will be described later (see Chapter 2). To achieve a certain coating thickness either the concentration of the sol has to be adjusted or the pressure applied by the squeezing rolls.

For certain applications or finishings full penetration of the textile by the sol is not necessary. As an example, repellence might only be needed on one side of the product. In these cases the sol application cannot be carried out by dipping or padding. For this the casting of the nanosol or a spray application treating only one side of the textile fabric are useful methods. Possibly the use of sols with higher concentrations might be required or be advantageous. In contrast to the simple dipping process these techniques allow one to adjust the amount of sol applied to the fabric more precisely. The above mentioned application techniques are depicted schematically in Figure 1.11.

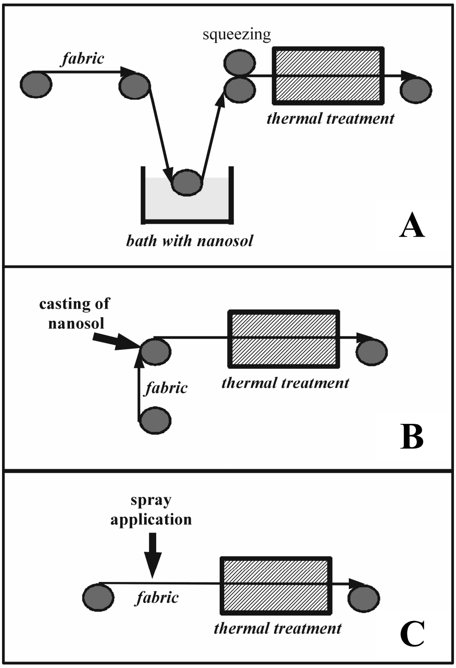


Figure 1.11 Schematic drawing of nanosol finishing of textiles by conventional application techniques, A: padding, B: casting, C: spraying.

A continuous dip coating process can usually be divided into four stages: *immersion, deposition, drainage and evaporation* [Brinker et al. (1990a)]. After the textile leaves the nanosol bath the solvent evaporates during the drainage. Squeezing stops the drainage while the evaporation process continues until the textile is fully dried. Figure 1.12 illustrates the four stages introduced by Brinker et al. in case of a padding process.

Due to an increase of the particle concentration as a consequence of the evaporation of solvent an aggregation and agglomeration of particles occurs. The proceeding processes lead to a gelation of the nanosols. As a consequence the deposited film builds up to the final xerogel layer after complete removal of the solvent [Brinker et al. (1990b)].

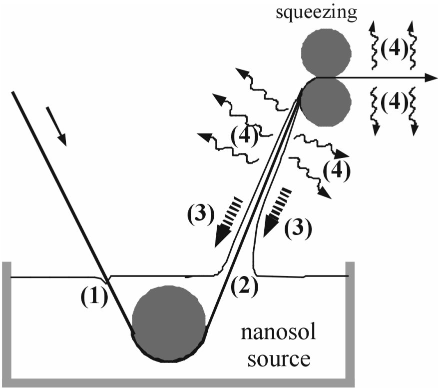


Figure 1.12 Stages of a continuous dip-coating process: (1) immersion; (2) deposition; (3) drainage; (4) evaporation.

In comparison with the dipping process the nanosol application by spraying differs in a particular way. The evaporation of solvent does not start after deposition but already after the nanosol spray drops leave the spraygun. The solid content and the viscosity of the nanosol will therefore be increased to a certain extent before the sol wets the textile. Examples of the changes in the nanosol concentration and viscosity are shown in Table 1.6. Especially for those sols prepared with highly volatile solvents like acetone the aforementioned changes may be significant, especially with respect to wetting speed and film formation.

Table 1.6 Changes in the solid content and the viscosity of certain nanosols during a spray process.

Sol composition	Solvent concentration [vol.%]			Solid content [wt.%]		Viscosity [mPa s]	
	Water	Ethanol	Acetone	Sol	After spraying	Sol	After spraying
SiO_2	80	20	---	10.2	10.5	2.5	2.4
SiO_2	9	91	---	20.5	23.1	2.4	2.8
SiO_2	9	35	56	23.0	27.0	1.3	2.2
SiO_2/PMMA	9	35	56	29.4	36.1	5.3	12.0

Since the fabrics will not be completely immersed in the nanosol the wetting will be also different compared with the padding process. If the amount of sol applied to the surfaces is very low the textiles might not be wetted completely and the deposition of a corresponding nanosol might be limited to the front side of the fabric. The spray application is advantageous for several reasons. Among others the amount of coating material applied to the surface can be reduced as well as adjusted exactly. In the case of the padding process the liquor uptake is in the range of 70 wt-% or more of the textile weight. For the application of thin coatings the nanosols must be therefore strongly diluted.

If the wetting is limited to the front side of the treated material, so-called double-face effects can be achieved. It allows preparation of textiles with a hydrophobic and a hydrophilic side. This is, amongst others, of interest for sports wear. The hydrophilic side worn on the skin can transport the humidity outwards while the hydrophobic outer side will repel rain.

Beside the mentioned advantages of spray application some drawbacks must be mentioned. The complete immersion guarantees complete wetting of the product which – in the very most cases – leads to a uniform distribution of the coating material covering the complete substrate. The uniform spray application for large surfaces in a continuous process is a general problem – not only for sol-gel coatings. Especially for these minimum application techniques irregularities might lead to enormous problems. Simultaneously incomplete coverage of the fibres might decrease the durability of the nanosol coatings applied.

Another phenomenon that can be observed if textiles surfaces are coated by a spray application can be observed on the SEM micrograph shown in Figure 1.13. Many drop-like particles surround single fibres of a knitted fabric. Such drops will not (or rarely) be found for padded samples. Figure 1.14 shows SEM micrographs of samples that were also coated by spray coating. In this case the spray was applied to woven fabrics. The number of drops observed for these samples was much lower, only single fibres that poke out of the fabric showed corresponding drops.

Figure 1.13 Spray application onto cotton – deposition of silica nanosol modified with PMMA polymer (sample kindly prepared by H. Haufe & K. Muschter, GMBU Dresden).

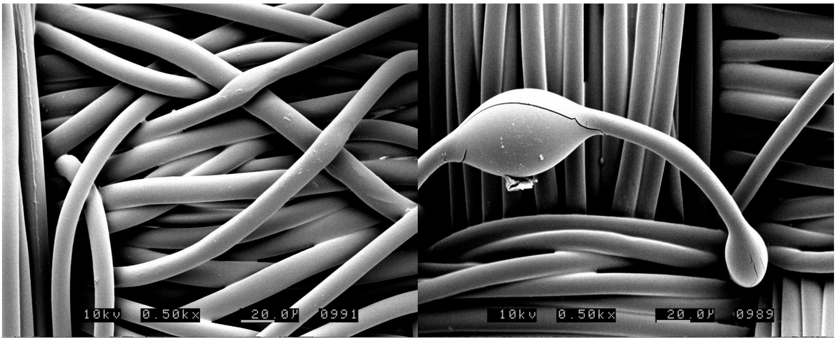


Figure 1.14 SEM micrographs of a polyamide fabric treated with a nanosol by spray application. Xerogel “drops”, as on the right micrograph, can only be observed for fibres poking out of the fabrics.

The above mentioned phenomena could be explained according to the theory of, among others, de Gennes, who states that a drop will never spread out along a fibre [Borghi et al. (2005)]. In the case of the fabric the wetting will be forced by the capillary forces, if a fibre sticks out of the surface these forces will not act. Borchard-Wyart [M. Daoud and C.E. Williams (1999)] explains why complete wetting of a film is possible but complete wetting of a fibre is not. In the case of wetting a film the solid-liquid interface has the same area as the liquid-air interface. In the case of a fibre the liquid-air interface is larger than the liquid-solid interface. The phenomenon can be also observed in nature – a spider web on a foggy morning will show a lot of droplets and even if the fibres are hydrophilic no spreading will occur.

Irrespective of the employed application technique the use of nanosols with increasing concentration will lead to an increased thickness of the coatings and simultaneously to an increased occurrence of a bridging of nearby fibres which results in a lower flexibility of the treated fabric [Gu et al. (2000); Textor et al. (1999)]. Additionally a higher sol concentration might cause less uniform coatings on the textile since highly concentrated sols might contain more agglomerates and precipitates compared with more diluted sols. Irregular structures of several micrometer size could be the result of the deposition of those larger aggregates and precipitation beside the regular deposition of nanosol coatings [Mahltig et al. (2005b)]. Examples of bridging are shown in the SEM micrographs in Figure 1.15.

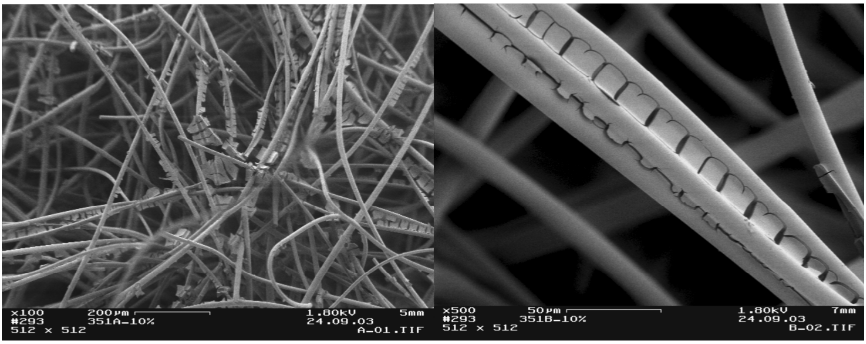


Figure 1.15 Fibres of a carbon felt coated with a highly concentrated silica sol (SEM-image kindly supplied by M. Mertig and N. Schreiber, Max-Bergmann Center of Biomaterials, TU-Dresden).

Under mechanical stress thick nanosol coatings and bridges between fibres crack. Furthermore thick layers tend to crack during the drying process [Brinker et al. (1990a)]. A more detailed description of effects determined by the coating thickness and the development of bridging will be given in later pages of this chapter.

A model for film formation and fibre bridging is presented in Figure 1.16. Fractures of thin bridges will result in fins, whereby broad bridges often leave the bare fibre surface (compare Figure 1.17) [Krüger et al. (2006)]. Crack formation resulting in bare fibre areas can lead to ineffectiveness of the functional coating. For water repellent finishings a cracked coating might e.g. impair the repellence if the water is sucked into the crack or even into the fibre due to capillary forces. To achieve regular fibre coatings with higher amounts of applied nanosol, multiple coatings from diluted sols could be an appropriate method. A multiple coating using diluted sols is reported to lead to more homogeneous coatings and less uncoated fibre areas compared with single coating procedures using higher concentrated sols [Krüger et al. (2006)].

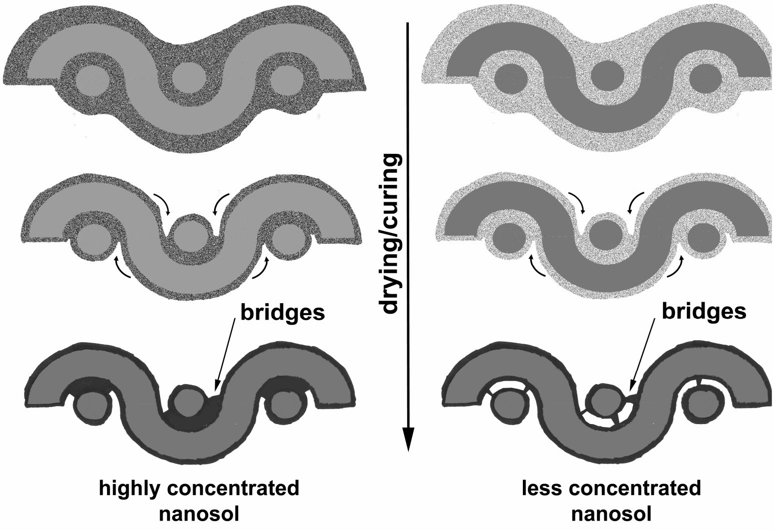


Figure 1.16 Model for film formation and fibre bridging during the drying process of the nanosol film between fibres. For less concentrated sols on the right handed side and for highly concentrated sol on the left handed side [Krüger et al. (2006)].

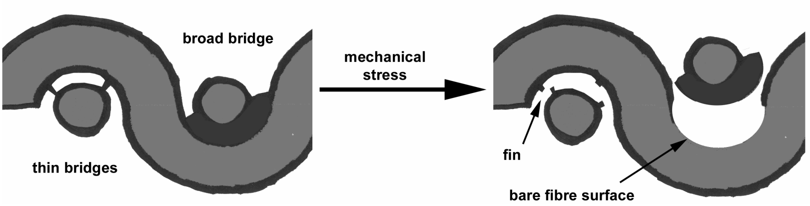


Figure 1.17 Fracture of thin bridges results in fins of nanosol coating material. Fracture of broad bridges leads to bare fibre surfaces [Krüger et al. (2006)].

Even with repeated coating procedures cracks and surface damage will however occur if the nanosol coating exceeds a certain thickness (depending on the coating material). This phenomenon was described experimentally for ZrO_2 and Y_2O_3 coatings and thermodynamic calculations corroborate the theory that the crack formation is directly related to the film thickness [Miller et al. (1990)]. It could be explained by a shrinkage of the coating networks during the evaporation of the solvent, leading to tensions in the resulting films as schematically depicted in Figure 1.18.

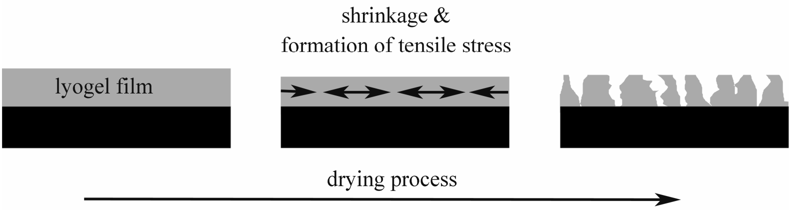


Figure 1.18 Schematic illustration showing the consequences of stress generation resulting in crack formation during evaporation of solvent from the gel films [Kozuka et al. (2000)].

The occurrence of the stress or crack formation during the gelation can be explained by the formation of pores within the gel that are filled with the solvent. During the continuing evaporation of the solvent and the further condensation of the gel these pores collapse, resulting in the aforementioned increase of tension. The process is schematically depicted in Figure 1.19 (left hand side). These tensions will increase with increasing film thickness. At a certain thickness the above mentioned cracks will therefore appear [Brinker et al. (1990a)]. For example in case of coating of carbon felts with alumina sols – even with repeated coating procedures – crack formation was observed for a thickness higher than 800 nm [Suzuki et al. (2006)]. It is also reported that beside the thickness of a coating the curing conditions (speed and temperature) might also influence the formation of cracks to a certain extent. Figure 1.20 shows an example of the formation of cracks for a titania coating. In general the estimation was made that inorganic films thinner than 500 nm do not tend to crack formation, while it seems impossible to prepare inorganic sol-gel films thicker than 1000 nm without cracks [Brinker et al. (1990a)].

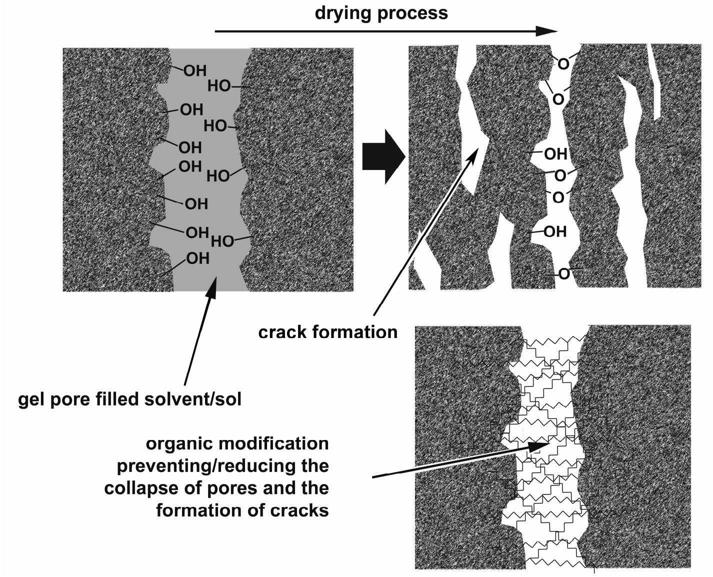


Figure 1.19 Comparison of condensation and pore collapse in titania gel films with and without the polymer PVP [Jing et al. (2007); Kozuka et al. (2000)].

As mentioned above, not only the thickness of the coating, but also the nanosol material itself determines the tendency to crack formation significantly. Furthermore the crack formation can additionally be reduced by organic modification of inorganic nanosols. An increased proportion of organic materials allows the preparation of thicker coatings free from surface defects. For this purpose, e.g., the addition of the organic polymer polyvinylpyrrolidone (PVP) is reported to be advantageous [Jing et al. (2007); Kozuka et al. (2000)] (Figure 1.19, right-handed side). The organic domains will reduce the shrinkage of the pores and simultaneously increase the flexibility of the networks, which lowers the tension occurring.

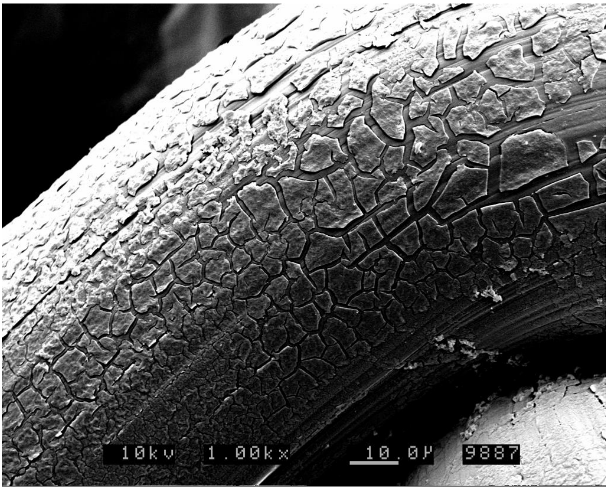


Figure 1.20 Crack formation of a thick TiO_2 nanosol coating on a propylene fibre.

1.5 Fibres derived from sols

The focus of this book is set on finishing of textile materials with nanosols. Interesting approaches are described preparing fibres and nanofibres using the sol-gel technique. Some examples are given here, for more detailed information the authors refer to the corresponding literature, e.g., [Tanaka et al. (2005); Chatterjee et al. (2002); Venkatesh et al. (1999)].

Sols can be used as basic solution for the spinning of fibres. By this method, simple glass fibres are prepared by dry spinning of silica sols [Peltola et al. (2001); Celzard et al. (2002)]. By spinning directly from appropriate sols, inorganic composite fibres can be prepared, not only based on pure SiO_2 but also on other metal oxides or mixtures of both. Basically two different kinds of sol-gel based fibres are described – inorganic/organic or pure inorganic composite fibres.

Inorganic/organic composite fibres can be prepared by compounding silica or metal oxide sols with organically modified alkoxysilanes as described above. Composite fibres can also be prepared by spinning mixtures of fibre forming compounds such as acetylcellulose and silica sols [Tanaka et al. (2005); Chen et al. (2005); Kulpinski et al. (2005)]. Purely inorganic composite fibres are prepared from inorganic sols based on different metal oxides. In contrast with the coating of textiles with inorganic sols, the temperature range for the preparation of fibres based on these sols is not limited. Due to the fact that no textile substrate or any organic compounds are present, thermal treatments of up to 900°C and higher can be carried out without causing decomposition.

New inorganic composites as ZrO_2/SiO_2 or Al_2O_3/SiO_2 are available if processing temperatures are not limited to 200°C [Beasley et al. (1963)]. Another important example is the ternary system SiO_2-CaO-P_2O_5 which can be used as a framework for both mineralized and non-mineralized structural tissues. These additionally bioactive fibres are prepared employing a high velocity spray process [Domingues et al. (2001)] or by air-spraying [Oréfice et al. (2001)]. The mentioned spinning processes mostly result in fibres with diameters in the range of about 10 μm deposited as a fibre sheet.

Besides some excellent properties, such as thermal stability or a good solvent stability the inorganic fibres are disadvantageous for some reasons. The inorganic fibre material is more brittle and has lower flexibility and elasticity compared with conventional fibre materials. Thus the possibilities for the production of fabrics based on these materials is limited. During the weaving process the weft fibres have to be moved between the warp fibres with very high velocities. Additionally the warp und weft fibres are bent with a very small curve radius at the selvage. The mechanical stress during the conventional weaving process is often a limiting factor for the production of fabrics based on the inorganic fibres. To allow the production of fabrics or knitted fabrics, the fibres have to be sized and the production speed has to be reduced.

The spinning process itself is more expensive. On the one hand the precursors for preparing the composites are often comparably expensive. Here a coating with a nanosol might be a better alternative. In the case of spinning, the whole fibres are made from sol-gel material while by coating only a thin layer is necessary to apply the functional properties onto a polymer fibre. On the other hand it is more difficult to spin inorganic materials compared with organic polymers because of the mechanical disadvantages mentioned above.

The production of fibre sheets based on the inorganic fibres is comparably simple. Thus for certain applications it might be advantageous to prepare inorganic fleeces. If the tensile strength of such fleece layers is too low the deposition of the fibres onto a supporting layer might be necessary.

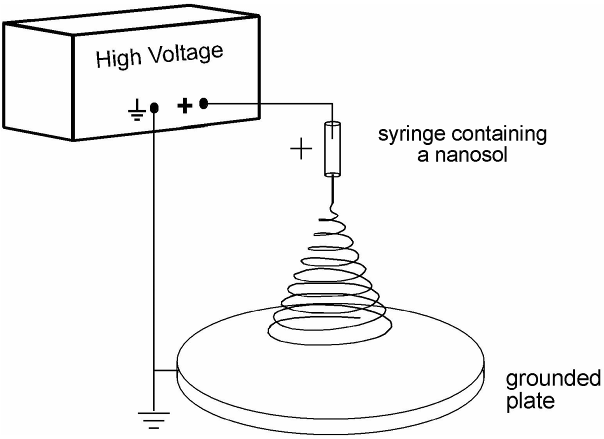


Figure 1.21 Basic setup for preparation of nano-fibres by an electrospinning process.

A comparatively new method for fibre preparation is electrospinning using a strong electric field to force the fibre development [Ramakrishna et al. (2005)]. This very special method is of high interest since it allows the production of fibres with very small diameters down to several nanometers. The electrospinning process is not limited to conventional polymers, it can also be carried out to prepare fibres derived from nanosols [Choi et al. (2004)]. The electrospinning involves the application of a strong electric field to a capillary connected to a reservoir containing an inorganic nanosol. Under the influence of the electrostatic field, a pendant droplet of the sol at the capillary tip is deformed to a conical shape. If the voltage exceeds a threshold value, electrostatic forces overcome the surface tension, and a fine charged jet develops. The jet moves towards a plate acting as counter electrode. The solvent of the nanosol starts to evaporate immediately after the jet is formed. The result is the deposition of a thin inorganic fibre on a substrate located above the counter electrode. The basic setup as used for an electrospinning process is depicted schematically in Figure 1.21. Figure 1.22 shows a SEM micrograph of silica fibres (derived from a nanosol) spun by the described process.

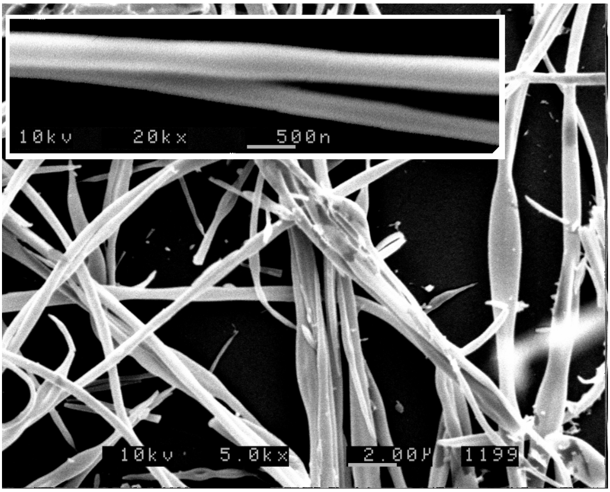


Figure 1.22 SEM image of electro-spun nanosol fibres of prepared from a comparably simple silica sol.

The deposited fibres form a fleece [Choi et al. (2003)]. Titania or titania/silica fibres with very fine diameters of about 120 nm can be prepared by electrospinning of TiO_2 or TiO_2/SiO_2 nanosols. [Choi et al. (2004); Watthanaarun et al. (2005)]. Although these fibres are very thin, they are stable in a calcination process from 500°C up to 1200°C. The titania based materials could for example find applications as photocatalytic systems.

The general advantages of such fleeces based on nanofibres are the combination of light weight and high surface area. The inorganic fleeces are of high interest e.g. for the preparation of catalytic materials since besides having a high surface they allow a high throughput of liquids or gases. Additionally the materials promise a good solvent and temperature stability. Nanofibres are also of interest for the preparation of certain filter materials, e.g. for the filtration of very small particles [Bahners et al. (2008)]. Further applications are also reported for antimicrobial filter material based on electrospun nanofibres modified with nanoparticular silver [Voigt et al. (2006)].

Chapter 2

Nanosols and Textile Properties

It is probable that no other material is more associated with comfort than textiles. For clothing the comfort aspects are of high importance on the one hand to achieve the greatest possible acceptance of the product by the customers, but also for sanitary reasons. To give an example, fibres with a high stiffness and a high amount of filaments sticking out of the surface could cause skin damage on a micrometer scale and are significant cause for skin irritation. In the case of textiles worn in direct contact to the skin it is also of importance to achieve sufficient water uptake capability of the product in order to reduce skin irritation to a minimum [Höfer (2006a)]. Apart from clothing textiles, a curtain is expected to show a certain *fabric drape*, or coverings need a certain *touch*. All these parameters and many more are connected with comfort. The definition of comfort respectively the measurement of comfort from a scientific point of view is a challenge for textile researches since decades. Textile properties as *fabric's drape* or *touch* can not be evaluated with a simple measurement and therefore it is difficult to describe questions concerning the *fabric's drape* or *touch* by certain values. Many researchers have attempted this, and a huge number of testing methods are known [Holme (1984)].

This chapter will show some examples in what way a number of selected textile properties are affected by coating with simple silica nanosols. This information will help to understand and assess the influence of nanosol coating not least on the textile comfort. Since the nanosol coatings are of particular interest for technical textiles the focus of the investigations is not set on clothing only.

On the following pages the influence of a simple silica nanosol, without any special modification, on two basically different materials is shown. The materials selected are a bleached cotton fabric and a polyester fabric as used for technical applications. We repeat, that in the context of textile material polyester is equivalent to polyethylene terephthalate (PET), if another polyester is described within this book, the correct chemical name will be given. The two materials cotton and polyester were selected since cotton and polyester are the economically most important textile fibre materials in the world. In 2006 approximately 80 % of textile fibre materials were based on these two materials (Information from the Industrievereinigung Chemiefasern e.V., cp. Table 2.1), and it is expected that especially the use of polyester is most likely to increase than decrease within the next years [Schenek (2001); Koslowski (1997)]. The effects of nanosol coatings that will be described are examples for the fabrics made of these two materials. The results can certainly not be transferred directly to other fibre material, but they will give a good idea.

Table 2.1 World-production of textile fibres in 2006, Source: (www.ivc-ev.de).

Fibre polymer	Amount [1000 tons]
Polyamides	4,100
Polyacrylics	2,500
Polyester	27,700
Cotton	25,800
Cellulosic fibres	3,500
total amount of synthetic fibres	37,800
total amount of textile fibres	68,300

Cotton as a natural fibre and polyester as a synthetic one differ in many properties. Cotton fibres contain comparatively high amounts of water (approximately 10 wt.%), while the polyester fibre is usually not able to absorb more than 0.2 wt.%. Cotton is a cellulosic fibre with a high ratio of hydroxyl groups that make it hydrophilic and that are available for polar interaction or potential surface reactions. The aromatic polyester is comparatively hydrophobic and the number of functional groups is low since it is limited to hydroxyl or carboxyl end groups of the polymer chains available at the surface. Investigations of [Knittel, personal correspondence] carried out with commercial polyester films, showed that typically amounts of only 10^{-8} mol/cm^2 of hydroxyl groups are available. The surface of the polyester fibre is comparatively smooth and uniform, while the cotton surface is structured and covered with pores. SEM micrographs shown in Figure 2.1 give an impression of the topographic differences of the natural and the synthetic fibres employed. For all these described differences it might be expected that the two materials will show differences in behavior during and after coating with nanosols.

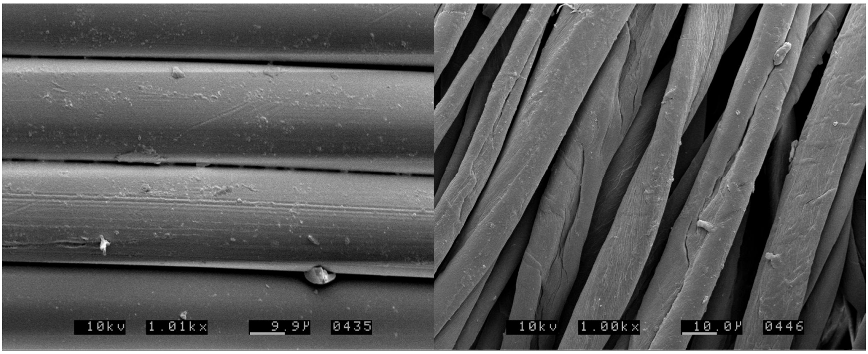


Figure 2.1 SEM micrographs of a polyester (left) and a cotton fabrics (right) used for the nanosol coatings described on the following pages.

Due to the aspects discussed above the amount of liquor that is absorbed during the dipping in a padding process is higher for the cotton compared to polyester. The liquor uptake of cotton in the investigation presented was about 95 wt.% compared with only 30 wt.% for the polyester. After passing the padding machine the cotton contained about 60 wt.% of the liquor, the polyester 19 wt.%. A higher increase of the mass per unit area can therefore be observed for the finished cotton as expected. The corresponding data are shown in Figure 2.2. The maximum increase shown here is about 14 wt.% for the cotton and 6.5 wt.% for the polyester samples.

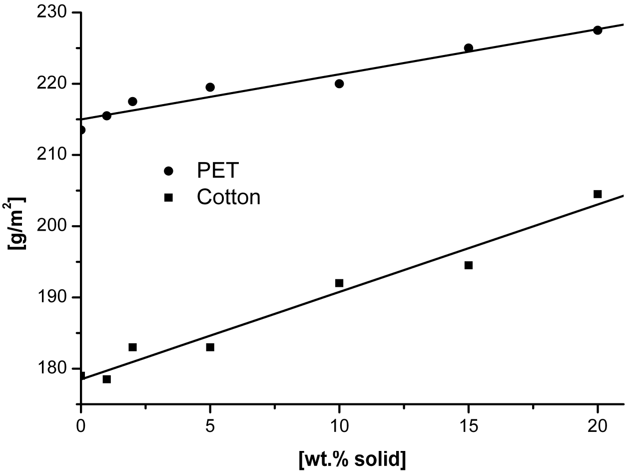


Figure 2.2 Change in mass per unit area for polyester and cotton after coating with a silica sol with varying solid content.

2.1 Mechanical properties

The more the mass per unit area increases, the more the stiffness of the fabric increases. The stiffening occurs due to the lower flexibility of the inorganic coating material and – especially if sols with higher solid concentrations are applied – due to the development of bridges between the fibres, mentioned above (cf. Chapter 1.4). The increase in the bending stiffness (measured according to DIN 53362) is depicted in Figure 2.3. As one can see coatings carried out with sols of a low solid content will only lead to a slight increase in the stiffness. The photographs shown in Figure 2.4 visualize the effect for a viscose material modified with simple silica sols at various concentrations. Regarding the corresponding SEM micrographs the close connection between the occurrence of bridging between fibres and the stiffness is obvious. For the more diluted sols, no sticking together of the single fibres can be observed, whereby for higher concentrated sols the fibres are interconnected (compare Figure 2.6).

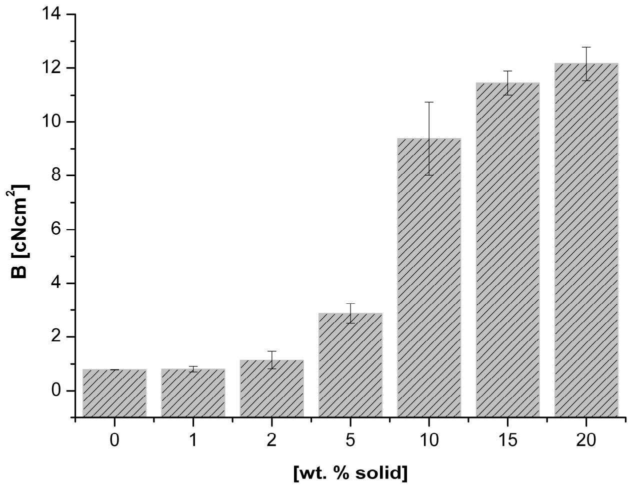


Figure 2.3 Change in the stiffness in bending B (Cantilever procedure according to DIN 53362), here shown for cotton (here warp). For detailed information concerning the measure B see the mentioned DIN standard, in abbreviated form it is a measure for the length of a fabric that can be pushed over an edge before it sags to a certain extend (B includes the mentioned length as well the mass per unit area).

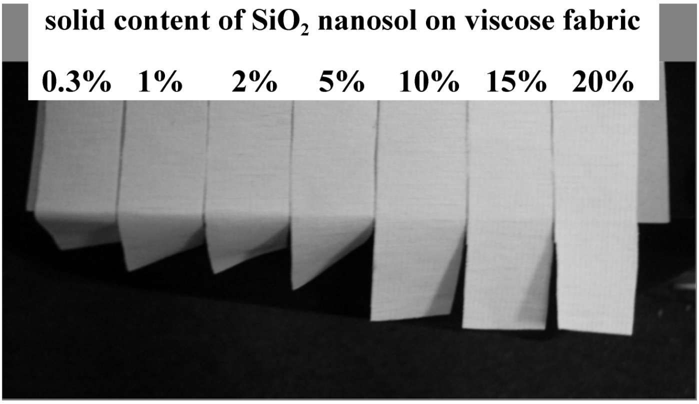


Figure 2.4 Photographs of viscose fabrics finished with silica sols with increasing concentration, demonstrating the increasing bending stiffness.

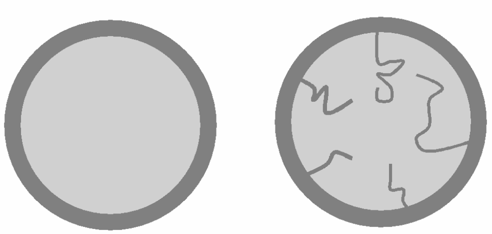


Figure 2.5 Schematic drawing of the distribution of a sol-gel derived coating on a synthetic fibre, here polyester (left) and a natural fibre as cotton (right). The porous structure of the cotton fibre allows formation of inorganic matrices within the fibre.

Comparable results can be observed for the polyester fabrics, but the stiffening effect is not as distinct for the synthetic fibre material. On the one hand this could be explained by the much higher sol uptake of the natural fibre and on the other hand by the fact that the sols cannot penetrate the polyester fibre, therefore the silica coating will only be on the fibre surface. Conversely the sols can penetrate the cotton fibre leading to a higher stiffening of the single fibre, since the inorganic matrices will also form within the fibre. The described distribution of the inorganic material for synthetic as well as natural fibre materials is shown schematically in Figure 2.5.

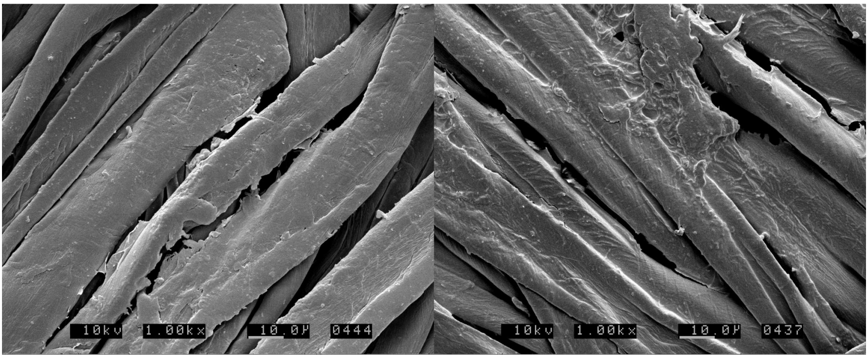


Figure 2.6 SEM micrographs of a cotton fabric coated with a silica sol with a solid content of 2 wt.% (left handed side) and 20 wt.% (right handed side), the grey fabric is shown in Figure 2.1 (right handed side).

The crease resistance of a fabric gives information about the ability of a fabric to flatten itself after it was folded. It can be measured by the so-called angle of recovery (according to DIN 53891), ideally the material is able to flatten completely which correlates with a recovery angle of 180°. The angle of recovery of polyester and cotton fabrics is only slightly influenced by simple silica sols. It is interesting to observe that the values increased for sol-gel coated samples and only for comparatively highly concentrated sols will a decrease be observed. Values for a polyester fabric are presented in Figure 2.7. Even for the silica sol with a solid content of 20 % the recovery angle is slightly higher (better) than for the unmodified fabric. The run of the curves for cotton are comparable, but for the highly concentrated sols the recovery angle will be lower than for the unmodified fabrics.

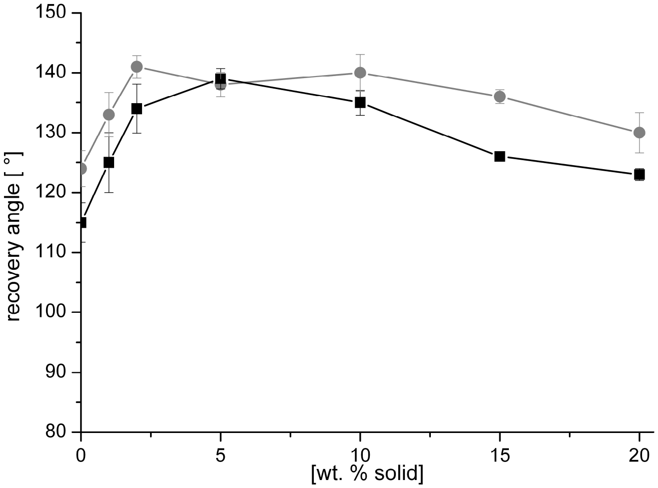


Figure 2.7 Change of the recovery angle in a crease resistance test (according to DIN 53981) for a polyester fabric coated with silica nanosols of different concentration. (circles = weft, squares = warp).

As mentioned at the very beginning of this book, one of the main advantages of textile fabrics is the combination of a light-weight, flexible product with excellent mechanical strength. Further important characteristics of textile materials are therefore the tensile strength as well as the elongation at the breakpoint and the force that is necessary to tear a fabric.

The tensile strength (measured by a tensile test with strips of textile fabrics, DIN 53857) of the cotton used in this studies increases only very slightly while the elongation at break is reduced with increasing sol concentration up to 18 %. Regarding the polyester tested here the tensile strength is affected to a greater extent. The treatment with the mostly diluted nanosol used in this study (only 1 wt.% solid content of the silica sol) already leads to an increase of approximately 10 % in warp and 30 % in weft direction. In addition only a slight increase of the tensile strength for fabrics coated with silica sols of higher solid content compared with the results for fabrics finished with more diluted sols can be observed. The elongation at break for the coated polyester decreases with increasing sol concentration in the range of 10 %. The corresponding results for the polyester are shown in Figure 2.8.

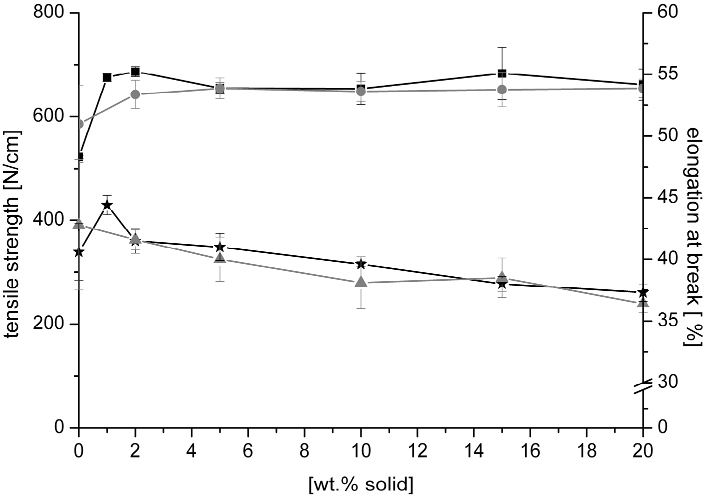


Figure 2.8 Tensile strength (black squares = warp, grey circles = weft) and elongation at break (black stars = warp, grey triangles = weft) for strips of a polyester fabric treated with a silica nanosol with varying solid concentration.

It is known that the finishing or coating of fabrics might weaken the materials respecting the resistance to tear propagation. The results of corresponding measurements for nanosol treated fabrics confirm this. The experiments discussed in this chapter show that the influence of the silica finishing is much smaller for the cotton fabrics than for the synthetic material. In the warp as well as in the weft direction a certain decrease of the tear propagation force can be observed, the maximum decrease is in the range of 25 %. The synthetic fabrics exhibit, as is well known, a much higher resistance against tear propagation but simultaneously the polyester fabric are distinctly more affected by a nanosol coating. As shown in Figure 2.9 the force to tear the fabrics decreases by at least 56 % in this particular case.

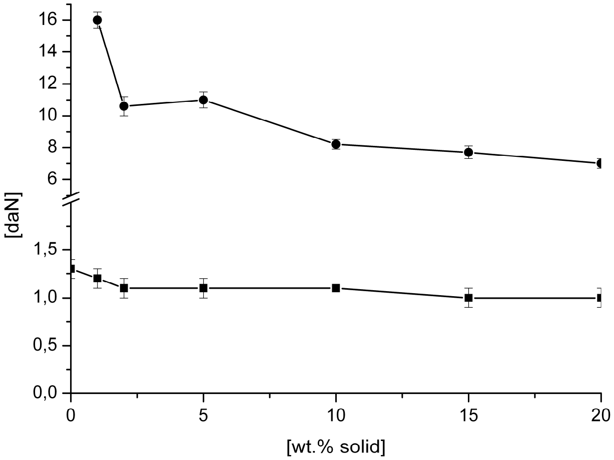


Figure 2.9 Tear propagation force of a polyester and a cotton fabric (warp, according to DIN 53895-2), finished with a silica nanosol of varying solid content.

The decrease described can at least be explained partially by a higher yarn slippage resistance. The nanosol coating reduces the ability of the fibres to displace; this could either be explained not only by the above discussed bridging of the fibres, but also by an increase of the friction between the single fibres. This explanation is supported by the fact that especially for the very smooth surface of the untreated polyester fibres the fabrics do not tear because the fibres shift too much, leading to a complete deformation instead of a tearing. The fact that the strongest relative decrease occurs after applying the sols with a low solid content indicates that the bridging is less important for the effect, since the bridging is negligible for the highly diluted sols. To investigate the yarn slippage resistance measurements were carried out following the approach of [Berndt et al. (1983)]. The corresponding results for a technical polyamide are shown in Figure 2.10. According to Berndt et al. the force necessary to pull out single fibres of a fabric is a good measure for the yarn slippage resistance. In the example shown here the application of a nanosol with a solid content of only one weight percent already leads to an increase of the pull out force by more than 50 %. A further increase of the solid content leads to a further increase of the pull out force due to the already discussed bridging of the fibres by the coating material. The results support the above mentioned assumptions and simultaneously indicate that sol-gel coatings can act as a non-slip agent.

In fact, the use of sol-gel technique to improve the yarn slippage resistance has been known for many years – silicic acid aquasols (e.g. Köstrosol®, Levasil®) prepared from water-glass are established in textile industry and were used before anyone knew about nanotechnology.

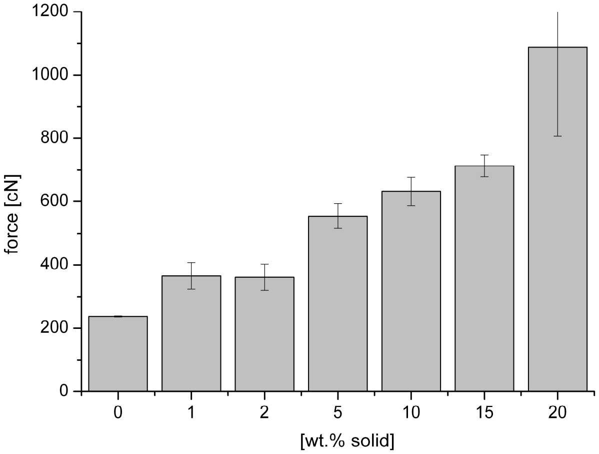


Figure 2.10 Measurement of the pull-out force of fibres for a polyamide fabric coated with a silica nanosol of varying solid content.

As previously mentioned, the hand of a fabric is of importance especially for clothing textiles, linen curtains or upholstery fabrics. Conventionally textile industry uses softeners to improve the hand of fabrics and as for every conventionally treated textile nanosol treated fabrics can also be finished with softeners to enhance the soft handle and therefore improve the sense of well-being. Softeners can either be applied on a textile already treated with a nanosol, or, if soluble, be added to the nanosol before application. Many different types of fabric softener are known and used for textile finishing [Bajaj (2002); Hausch (2001); Zyschka (2001)]. A simple classification of softeners into six categories is given by [Bajaj (2002)] (Table 2.2).

Table 2.2 Classification of softening agents by [Bajaj (2002)].

Softener category	Typically used softener agent
Cationic	Quaternary ammonium compounds
Anionic	Sulphated oils, sulphated alcohols
Nonionic	Polyoxyethylene derivatives, wax emulsions
Amphoteric	Imidazoline, carboxylate, amine oxide
Reactive	Compounds similar to reactive dyes exhibiting reactive groups and long chained softening groups
Special	Silicones

Quaternary ammonium compounds used as cationic softener are chemically quite similar to quaternary antimicrobial agents used to produce biocidic nanosol coatings, as will be described in Chapter 7. Some examples for those cationic softeners are presented in Figure 2.11. These compounds can be easily combined and applied together with a nanosol. The softener will be embedded into the nanosol coating during the sol-gel process. The softener is however likely to release from the coating during a washing procedure. In this way a more porous and eventually damaged coating will be left on the fibre surface, it might therefore be more advantageous to apply the softener in a second step onto the already coated fabric. Even the post-treatment using a softener might however lead to disadvantages. Due to the positive charge and the more hydrophilic nature of the quaternary ammonium softener it has to be kept in mind that the employment of these materials is not possible, for example, if the sol-gel coating is applied to improve the water repellence of the textile.

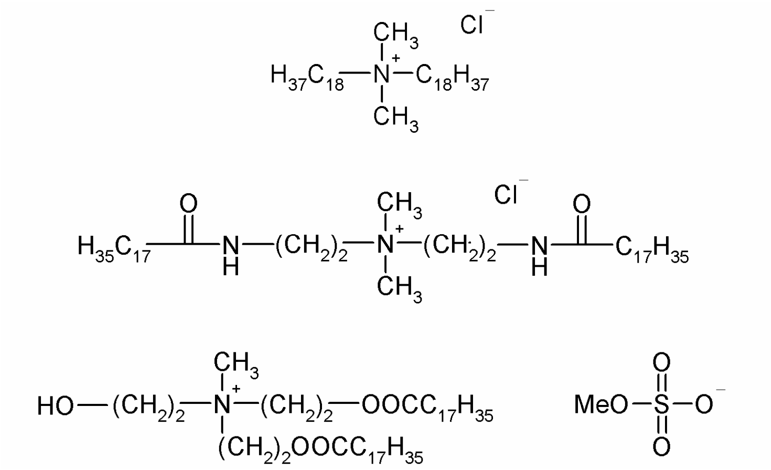


Figure 2.11 Examples of cationic softeners, quaternary surfactants [Poppenwimmer et al. (1999); Hausch (2001)].

The use of silicone softeners might be more advantageous for the combination with nanosols since they are more hydrophobic. Some examples are given in Figure 2.12. These silicones exhibit a chemical analogy to organically modified silica sols. Even for the modified silica sols the share of organic components is however low compared to the share of organic components of the mentioned silicones.

If soluble, the silicone softeners can be easily mixed with the nanosols before applying the sols to the textile. It is useful to choose silicone softeners with reactive groups that are able to bond chemically to the nanosol matrix. One should however be aware that the modification of a sol with silicone softeners could significantly change the properties of the sol – e.g., change the sol stability – and additionally the properties of the resulting coating. Softeners will mainly influence the surface energy and therefore properties more or less related to water-, oil- or soil repellence, in addition antistatic properties could be affected. Some useful softeners for combination with nanosols are given in Table 2.3.

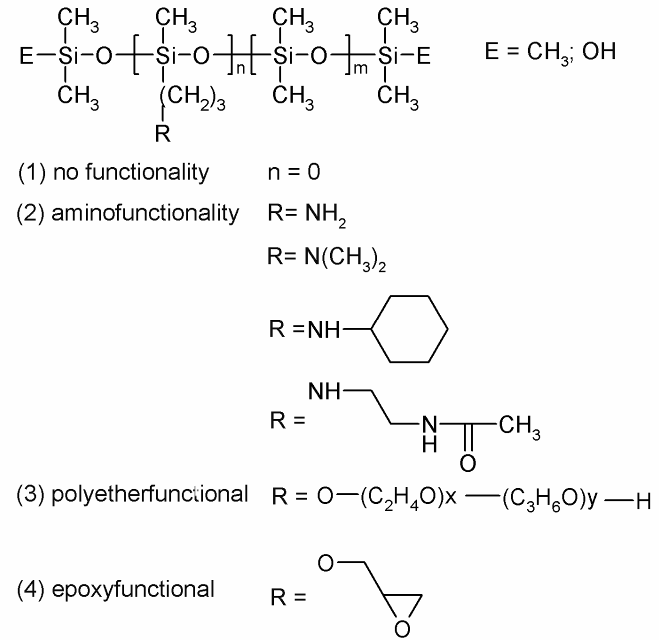


Figure 2.12 Chemical structure of some silicone softeners [Bajaj (2002); Hausch (2001)].

Table 2.3 Some useful fabric softener for combination with nanosol treatment of textiles (supplier CHT R. Beitlich GmbH – Germany).

Fabric softener / Trade name	Composition
HANSA AS 8020	Aminofunctionalized polysiloxane
HANSA ASM 9020	Amino/amidofunctionalized polysiloxane
HANSA SQ 2020	Polysiloxane with side chains containing quarternary groups
HANSA ESE 6960	Elastomeric silicone with epoxy modified side chains

Numerous experiments with the mentioned softeners were carried out by the authors, showing subjectively good, sometimes excellent results in the handle of the fabrics. Since a measurement of the handle or the declaration of the handle by a certain objective value is difficult (the author is of the opinion that it is up to now impossible) no values can be presented that support the above mentioned improvements.

2.2 Wettability, water absorption and storage properties

As mentioned above the kinetics of water uptake as well as the amount of water that can be absorbed are of especial interest. In addition, the proportion of humidity that is stored in a textile is of importance for clothing physiological reasons or for technical applications. The absorption of water (or of any other liquid) by a textile is largely determined by two parameters. The first is the surface energy of the fibre material, and the second the capillary effects of the yarn and the fabric. Both will be influenced by every coating material. While for a hydrophobic synthetic fibre such as polyester the absorbed liquid will be absorbed onto the fibre surface only (the polyester is able to absorb a negligible amount of 0.2 wt.% of water) a natural hydrophilic fibre will also absorb liquids into the fibre itself. The absorption into the fibres can occur due to an adsorption by the polymer accompanied by a swelling or by an intrusion of the liquid into pores in the fibres [Rouette (1995)].

A coating covering the surface of a fibre can influence the absorption in many ways. The coating can act as a barrier, preventing a direct contact of the liquid with the fibres, stopping or at least decelerating the absorption by the fibre material. The coating can also influence the capillary forces by blocking pores, reducing the capillaries and crevices and by changing the wettability of the surface. Since the sol-gel derived coatings will be able to influence all the above mentioned parameters it is worth investigating the influence of a comparatively simple sol-gel coating in this chapter. Certain sol-gel coatings to improve the water and oil repellence, e.g. to prepare self-cleaning textiles will be discussed in a following chapter, since this topic is of special interest for textile finishing.

A simple test to investigate the suction of a fabric is the TEGEWA drop test [Schmidt et al. (1987)]. A drop of water falls from a particular height onto a textile sample and the time until the drop is soaked up completely is measured. The graph depicted in Figure 2.13 shows the corresponding results for cotton and polyester fabrics coated with aqueous/alcoholic TEOS-nanosols of increasing solid content. Both grey fabrics soak up a drop of water within seconds. For both fabrics an immense increase of the drop penetration time can be observed after treatment with the mentioned nanosols. In the case of the cotton fabric, a comparatively small increase occurs for the more diluted sols, while for the polyester fabric even the sol with only one weight percent solid content leads to an increased drop penetration time of nearly one hour (in this studies the test was always stopped after one hour).

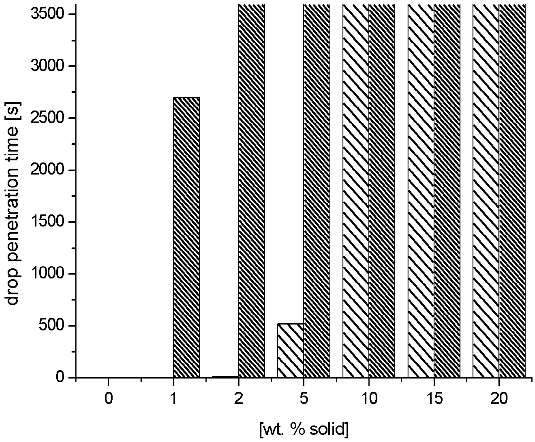


Figure 2.13 Results of the TEGEWA-test, evaluating the time a drop of water needs to completely penetrate (soak into) a fabric. The test was carried out with cotton (sparse) and polyester (dense) fabrics treated with TEOS based nanosols with different solid content. (If the drop penetration time exceeds 3600s the test is terminated).

Another test to determine the suction ability of a textile material is described in DIN 53924, that investigates the velocity of soaking water by a fabric (*method by determining the rising height*) (cp. Figure 2.14). A hanging stripe (cut in weft or warp direction) is brought in contact with a liquid surface. The height that is reached by the liquid soaked up is measured after certain periods (30 s, 60 s and 300 s). Corresponding results for a polyester and a cotton fabric are shown in Figure 2.15. The results confirm the results of the TEGEWA test (cp. Figure 2.13). Compared with the grey fabric the nanosol treated material soaks up the test liquid (dyed water) much slower in case of fabrics coated with strongly diluted nanosols, while those samples coated with sols of higher concentration do not absorb water at all.

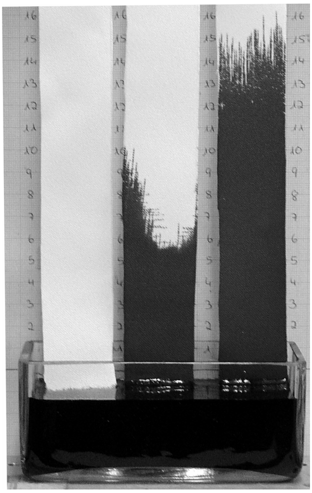


Figure 2.14 Photograph showing the capillary rise method. The lower edge of three different samples is dipped into a water bath (dyed for better visualization). The right sample is an untreated cotton fabric, the one in the middle was treated with a silica sol of low concentration (2 wt.%), the left one with a silica sol of high concentration (20 wt.%).

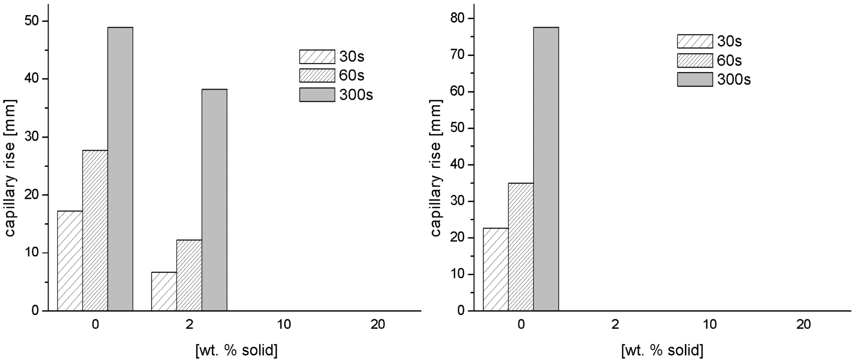


Figure 2.15 Results of a test using the capillary rise method, according to DIN 53924. The lower edge of a hanging PET-fabric (right hand side) or a cotton fabric (left hand side) is immersed into water and the rise of the liquid is measured after 30, 60 and 300 seconds.

The decreased suction shown in Figures 2.13 and 2.15 cannot be explained by changes in the surface energy only since, e.g., for polyester the coating is expected to lead to an increased surface energy, which should produce better wetting ability. While the surface energy of polyester is in the range of 43 mN/m, the surface energy of silica surfaces is in the range of 78 mN/m. The changes in the absorbency of the fabrics must however, at least to a certain extent, be explained by changes in the capillarity of the fabrics that occur, e.g., due to the bridging of the fibres.

The determination of the amount of water that is absorbed or adsorbed after completely immersing similarly coated polyester or cotton fabrics in water leads to the progression shown in Figure 2.16. The higher the solid content of the sol used for coating the lower the resulting water uptake. While the grey fabrics used here showed an uptake of about 120 wt.% the fabrics coated with a highly concentrated silica sol took up only about 35 wt.% for the polyester and about 60 wt.% for the cotton fabric.

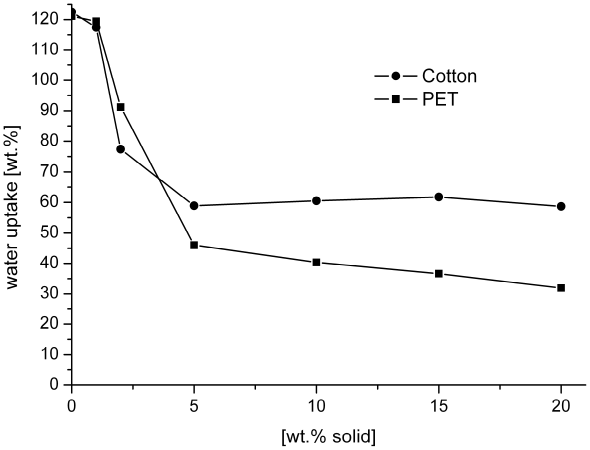


Figure 2.16 Water uptake of differently coated polyester as well a cotton fabrics after a complete immersion into water for about 60 seconds. Samples were coated with alcoholic silica sols of different solid content.

The absolute values certainly depend also on the textile construction as can be seen in the results exemplarily shown in Figure 2.17. Different polyester fabrics were treated with an identical silica sol, all treated samples show different changes in the water uptake as a consequence of the coating with nanosols, the general tendencies are however comparable. The same is valid for the drop penetration time.

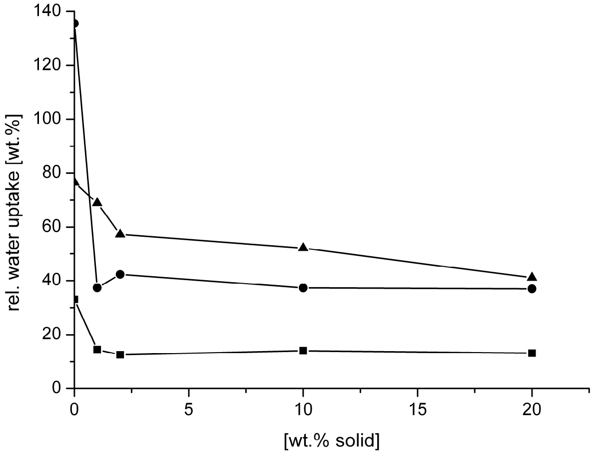


Figure 2.17 Water uptake of different polyester fabrics after complete immersion into water for about 60 seconds. Samples were coated with alcoholic silica sols of different solid content.

2.3 Appearance

For many applications changes in the appearance of textile material will not be accepted. Possible colour deviations or a yellowing of the substrates have therefore to be observed. The simple silica sols are basically colourless; thus changes in the finished textile's appearance are not to be expected. Table 2.4 summarizes the results of corresponding measurements investigating changes in the degree of whiteness. The changes are as expected not significant, neither for the cotton nor the polyester sample. Sols based on other oxides might influence the colour of a textile coated. Titania sols are known to yield coatings that show a slightly yellowish colour. Furthermore many sol-gel materials are known that show certain colours, e.g. iron oxides, modified titania or silver containing composites [Zorjanovic et al. (2004); Yin et al. (2006); Mahltig et al. (2004c)].

Table 2.4 Influence of coatings based on a simple alcoholic silica sol on the degree of whiteness of a polyester and a cotton fabric (according to Berger).

sol concentration	whiteness, according to Berger	
wt.% solid	cotton	PET
0	78.7	146.5
1	79.5	149.8
2	79.5	150.5
5	77.8	148.4
10	77.4	149.6
15	77.7	151.1
20	77.1	149.8

2.4 Air permeability

As described in Chapter 1 and shown in numerous SEM micrographs the sol-gel derived coatings will mainly cover the fibre surface and only for comparatively highly concentrated sols the resulting coatings will form bridges between the single fibres. For many applications the air permeability of a fabric is an important property of the textile products. Especially textiles that are in skin-contact during use must have at least a certain air and vapour permeability to prevent sweating. Many conventional coating materials will simply close up the open structure of a textile material and therefore hinder any transport of air or vapour.

The comparatively thin coatings yielded by the application of nanosols will not close up the open structure of the textile materials, therefore it is expected that the permeability will not be decreased to a significant extent, at least as long as the abovementioned bridging of the fibres does not take place in too high a degree. The results confirm these expectations. Figure 2.18 shows the air permeability of a cotton fabric that was treated with silica sols of various solid contents. At least a slight variation of the values can be observed, but they are here not significant.

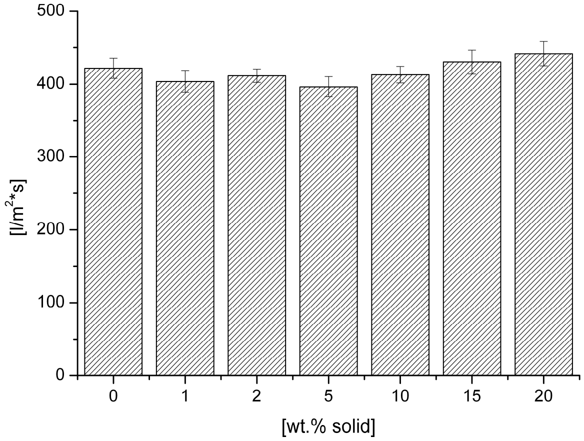


Figure 2.18 Air permeability of a cotton fabric coated with a simple silica nanosol of increasing solid content (measured for a sample size of 50 cm^2).

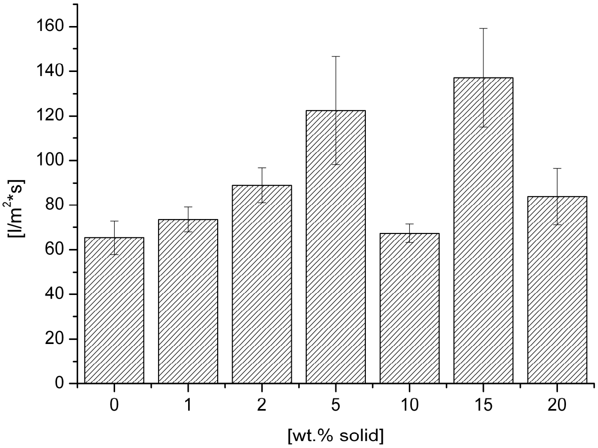


Figure 2.19 Air permeability of a polyester fabric coated with a simple silica nanosol of increasing solid content (measured for a sample size of 50 cm^2).

Other measurements that were carried out with a polyester fabric that showed an initially lower permeability showed different results. The corresponding results are shown in Figure 2.19, for these samples even a distinct increase of the air permeability occurs for samples treated with sols of increasing solid contents. Not until a certain sol concentration did the air permeability decrease to values comparable with the grey fabric. It should be mentioned here that the grey fabrics were padded with the solvent used for the sol preparation and dried under the same conditions as the sol-gel treated ones before measuring the permeability.

Figure 2.20 shows results of the measurement of the air flow through another cotton fabric (as a function of pressure) that was modified with nanosols of different solid content. In this example again an increased flow through can be observed with increasing sol concentration.

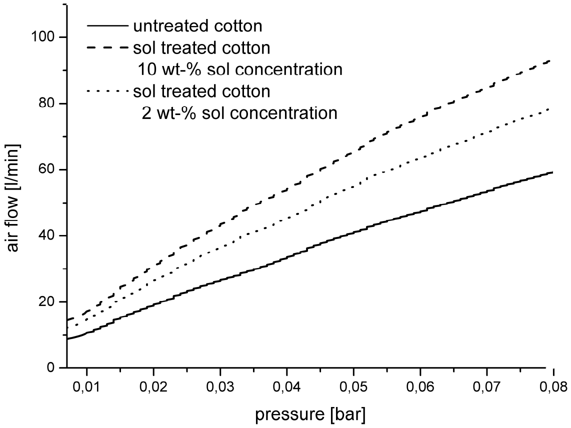


Figure 2.20 Air flow through cotton fabrics (untreated and treated with silica nanosols of different concentration) as function of pressure (data gained using a Porometer 3G; WSI Wenman Scientific Corp.).

The specific changes of the air permeability of a sol-gel treated textile will certainly be influenced not only by the sol but also by many parameters with regard to the textile used (among others, construction, density, thickness, hairiness, sizing agents that might be removed by the sol). Nevertheless the results shown above indicate that the sol-gel derived coatings will at least in almost all cases not influence the air permeability negatively.

Chapter 3

Fibre Protection

As described before one of the reasons using textile materials is the combination of a light-weighted, flexible material with high (tensile) strength. A number of impacts weaken or even destroy the textile materials. Such influences could e.g. be of mechanical, thermal, chemical or biological nature. An abrasive force as an example will ablate the fiber and therefore reduce the fiber diameter or it will even cut the fiber into pieces. As a result a fabric will loose its tensile strength and fail under load. For this, the abrasion resistance is one of the limiting factors for the life cycle of a product as e.g. a conveyor belt or a rope. Certain materials that are used in contact with chemical substances or in aggressive atmosphere must withstand these conditions. The polyester fiber as an example will be degraded by a hydrolytic process if, e.g., treated with basic liquids or hot steam. Some fiber materials, especially the synthetic fibers are easily inflammable which is a problem for two reasons. On the one hand these materials will be easily destroyed by flame contact. On the other hand the burning material is a dangerous threat since the propagation of a fire will be supported and the combustion products are a terrible hazard not least for human beings.

For the above mentioned reasons an important aspect of the surface modification of textile materials is, e.g., the improvement of the mechanical and thermal stability, the increase of the flame resistance or the protection against aggressive atmospheres.

3.1 Improved wear-resistance

The modification of textiles with silica particles in a sol-gel process is reported to lead to ceramic-like composites with higher density and improved mechanical properties [Liu (1996)]. Scratch resistant and transparent hybrid polymer coatings based on expoxy-functionalized alkoxysilanes or methylalkoxysilanes that are modified with silica nanoparticles are also described [Haas et al. (1999a & 1999b); Amberg-Schwab (2003); Lee et al. (2002)]. The modification of silica sols with few amounts of organosilanes like methacryloxypropyltrialkoxysilane is reported to increase the hardness of the nanosol coating. Comparable materials are employed for several years to protect plastic lenses of spectacles or compact discs against scratches. In contrast the combination with other metal oxides like TiO_2 or ZrO_2 might lead to a decrease of hardness and therefore to less abrasion stability (compared to the silica modified systems) [Chan et al. (2000)].

For thin coatings the abrasion or scratch resistance is a function of the thickness of the protecting layer, for a given material it can be stated that the thinner a coating the lower its scratch resistance [Lin et al. (2004); Wirasate et al. (2005)]. This fact is a limiting factor especially for textile application. One has to remember, that the flexibility of a coated fabric is, amongst others, depended on the thickness of the coating applied. This will be no problem for a compact disk or a lens since the demands for a sufficient flexibility are comparably low. But for textile materials the abrasion resistance always has to be a compromise between sufficient flexibility and required coating thickness. An increase of flexibility can certainly be achieved by modification of the particular sols with organic cross-linkers, network modifiers or softener, but one has to keep in mind that an increase of organic materials will most likely also influence the coating’s abrasion resistance.

Nevertheless the treatment of textiles with inorganic nanosols can lead to improved abrasion stability. A better shrink-resistance of fabric materials containing keratinous fiber like wool could be also possible by treatment with modified silica sols [Nakazato et al. (1990)]. An example for improved abrasion stability of textiles is given by [Böttcher (2001)]. Polyester sieves used in paper production are exposed to an extreme abrasive mechanical load, limiting the product's life cycle. The coating of such sieves with an alkyl-modified silica sol leads to an improvement of the abrasion resistance. The amount of material abraded by an abrasion test customary in this industry (*Einlehner Test*) is reduced for a sol-gel coated polyester. These results are proven by the measurement of the reduction in the sieve thickness and the loss of weight. Selected data are summarized in Table 3.1. Both measures are significantly reduced for the nanosol coated sieves emphasizing the improved abrasion resistance.

Table 3.1 Abrasion (Einlehner test) on nanosol coated polyester fabrics (tested by W. Best / Heimbach GmbH & Co KG., Düren /Germany) [Böttcher (2001)].

Sample	Distance* [m]	Increase of temperature [°C]	decrease of thickness [%]	loss of weight [%]
grey fabric	25,000	67	5.67	2.24
Alkylmodified nanosol coating	25,000	63	2.83	1.15
grey fabric	50,000	77	8.41	3.59
Alkylmodified nanosol coating	50,000	73	4.85	1.28

* *distance* is a measure for the simulated continuous stress

The improvement of abrasion resistance due to a nanosol treatment is reported for numerous different types of textile materials such as cotton, polyamide and glass fibers [Textor et al. (2003); Schramm et al. (2004)]. For treatment of cotton it is, e.g., advantageous to modify pure silica sols by the addition of epoxysilanes like 3-glycidylpropyloxytrimethoxysilane (GPTMS). By this, the adhesion of the nanosol coating to the fibre is increased, thus enhancing mechanical stability. The improvement of adhesion is caused by chemical bonding that results from the opening of the epoxy ring of GPTMS and the reaction of the hydroxyl groups on the cotton surface [Schramm et al. (2004); Park et al. (1999)]. An enhancement of abrasion stability is also stated by the addition of alumina pigments embedded into the nanosol coating [Hennige et al. (2005)].

As reported [Textor et al. (2003)] nanosols based on the above mentioned epoxysilane and an organic cross-linker (here bisphenol A), additionally filled with a certain amount of alumina nanoparticles, can also be applied to prepare coatings that improve the wear-resistance of a textile material, e.g., based on glass fiber. The photograph presented in Figure 3.1 shows glass fiber samples after performing an abrasion test (*Martindale Test*), while the grey fabric was completely destroyed after less than 100 rubbing cycles the coated fabric withstand more than 10,000 cycles without any visible damage.

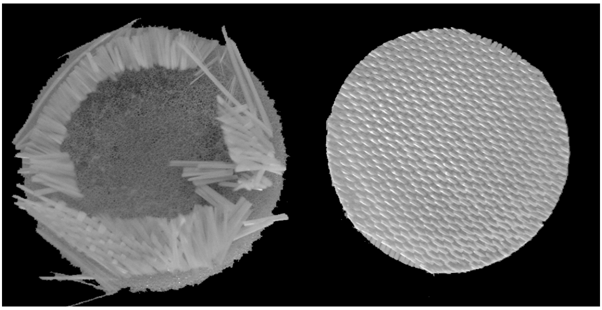


Figure 3.1 Photographs of glass fibres fabrics after carrying out a Martindale abrasion test, the left, completely destroyed sample was a grey sample, the right one coated with an organically modified nanosol.

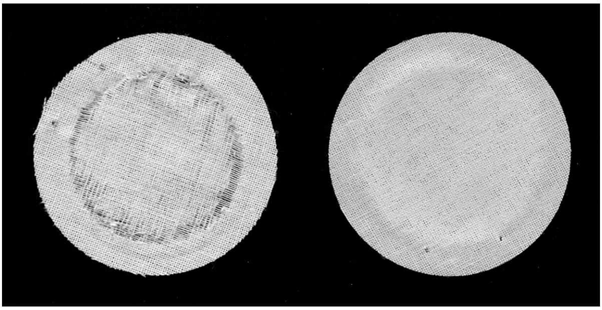


Figure 3.2 Photographs taken of cotton samples after performing a Martindale test. The left, strongly abraded sample is the grey cotton fabric after **20,000** scrubbing cycles, the right sample is a cotton fabric coated with the same sol as described for the glass fiber (cp. Figure 3.1) after **100,000** cycles.

The effect is impressively high for the glass fiber that is known to have a very low wear resistance but other materials finished with the same sols also show an improved resistance. The photographs shown in Figure 3.2 compare the resistance of a cotton sample with and without an alumina modified sol-gel coating. After 100,000 rubbing cycles the sol-gel coated cotton sample is in a better condition than the grey sample after only 20,000 cycles.

3.2 Increased fire resistance or flame retardance

Flame retardancy of textile materials is of an enormous interest not least since every year thousands of people world-wide die at home in fires. A burning cigarette falling on the mattress or the sofa, or a curtain in contact with a candle is often enough to set the house on fire. Especially in Great Britain and in the United States the statutory provisions for the materials used in such applications are extremely high. For technical textiles used in danger zones or those employed in high-temperature applications there is also a huge demand for finishings that at least yield high flame retardancy better a flame resistance.

The purely inorganic sols are themselves incombustible; therefore they are not expected to increase the inflammability of fiber materials. A certain flame retardant activity gained by inorganic nanosol coatings are expected to be the result of a barrier effect. This barrier hinders the flow of oxygen to generated volatiles during thermal decomposition. By this the temperature of glowing combustion is increased. However two facts can lead to a low ability of thermal shielding. First, the nanosol coatings have to be applied very thin onto textiles. Second, the inorganic xerogel matrices are porous, so they probably could not act as sufficient oxygen barrier. Nevertheless in literature SiO_2-sol coatings are reported for fiber treatment to realize a certain flame retardant activity [Kashiwagi et al. (2000); Hribernik et al. (2007)]. In the reported case the more significant parameter is the porosity and not the thickness of the sol-gel coating. A SiO_2 coating of 100 nm thickness with low porosity is reported to lead to better flame retardance than a 400 nm thick but more porous coating [Hribernik et al. (2007)].

Quite the contrary astonishing effects can be observed sometimes. In a certain case (unpublished) the authors modified a flame retardant polyester fabric (Trevira CS®) which does, e.g., not burn after ignition with a lighter. After modification of the mentioned fabric with a sol-gel coating (that was flame retardant itself) the composite did not show any flame retardant properties but burnt completely (as shown in Figure 3.3). Such unexpected synergetic effects have to be taken in account, but do not exclude the possibility of preparing flame retardant sol-gel coatings for textiles.

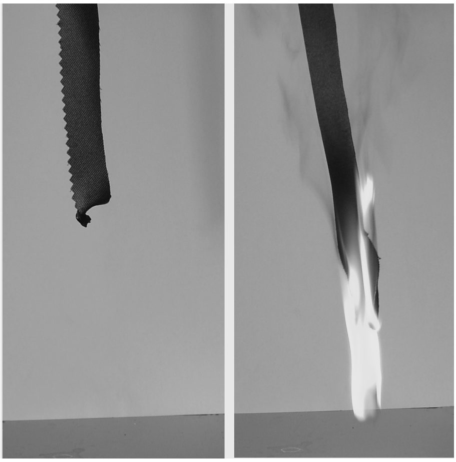


Figure 3.3 Trevira CS fabrics after treatment with a lighter. The grey sample (left handed) was in contact with the flame for 15 seconds without inflammation, the fabric only melts and forms some char. The other sample was coated with a purely inorganic silica coating; inflammation took place after contact with the flame immediately.

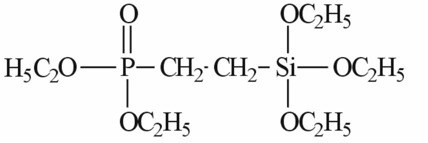
Flame retardants work with a number of different mechanisms, since coatings prepared by sol-gel technology can be combined with a huge number of material several approaches can be adapted for coating textile materials with appropriately modified sols.

Flame retardants as alumina or magnesia hydroxides that degrade endothermically and remove heat from the surrounding could be incorporated into the sol-gel matrix but since the total mass of these compounds will be extremely low – as introduced, coatings applied have to be very thin to guarantee a certain flexibility – compared to the textile itself an significant effect is unlikely.

More promising could be the approach to incorporate chlorine or bromine containing substances. Such materials are used often for fire protection. During a fire the halogen compounds decompose, releasing hydrogen chloride respectively hydrogen bromide. These will react with highly reactive hydroxyl and hydrogen radicals in the flame, forming less energetic chlorine or bromine radicals. Radical processes in the flame are mainly promoted by hydrogen as well as the hydroxyl radicals and are therefore mainly responsible for the propagation of a fire. The reduction of these radicals will slow down the initial burn rate and increases the time to flashover. Brominated species that are used as flame retardants are, e.g., polybrominated diphenyl ether, polybrominated biphenyl or brominated cyclohydrocarbons.

Phosphorous containing materials as, e.g., phosphate esters are used as flame retardants that act as a shielding [Song et al. (2005)]. The phosphate esters incorporated in a coating (or forming the coating itself) will be converted to char by a fire, forming a protective layer. These barrier layers hinder the transport of oxygen to the polymer and simultaneously act as a shield against the radiant heat. Intumescent additives, e.g., based on ammonium polyphosphates or dicyandiamide will expand during decomposition and therefore also form a thick char layer acting as the described shield against oxygen and heat. A limiting factor by using such materials in combination with inorganic nanosols might be the fact, that the applied layers and therefore the expanded char layers will be comparably thin.

The employment of nanosols is a well established method to enhance the fire and heat resistance of wooden materials [Saka et al. (1997); Mai et al. (2004)]. For these applications, silica nanosols were usually modified with phosphorous compounds such as diethylphosphite or phenylphosphonic dichloride. In comparison to the application on wood, until now there have been less reports of enhancing the fire resistance of textiles by nanosol treatment. The reason may be that the impregnation of wood with nanosols usually leads to comparably high amounts of sol uptake. Therefore an enhancement of fire resistance can be realized more easily compared to the treatment of textile fabrics. The use of metal oxide sols made of SiO_2, TiO_2, Al_2O_3 and their mixtures is reported to improve the heat resistance of textile filters up to temperatures of 300°C [Benfer et al. (2002)]. The air permeability of these filters is not or only slightly decreased by the nanosol treatment, simultaneously the abrasion resistance of the textile filters can be improved. Simple silica sol coatings modified with fluorinated silane compounds are furthermore used to enhance the flame resistance of nylon carpets [Satoh et al. (2004)]. As already mentioned above an additional improvement of heat and flame resistance should be expected by incorporating phosphorous-containing flame retardant compounds into the nanosol coatings applied to textile fibers [Horrocks et al. (2000)]. Excellent values of flame retardance of treated cotton are actually achieved by the combination of different silica sols with phosphorous compounds like orthophosphoric acid or diammonium hydrogen phosphate [Chapple et al. (2006)]. Unfortunately the rinsing stability of the flame protective properties is comparably low, limiting possible applications. Most probably the flame retarding phosphorous compounds are not chemically bonded to the nanosol coating and due to their good solubility in water they are washed out during first water contact. Due to this, the use of, e.g., phosphatealkyltrialkoxysilanes which could be covalently bond to the sol-gel derived networks should be more advantageous – an example is shown in Figure 3.4. The flame retarding properties of such compounds in epoxy containing silicon and phosphorous hybrid *ceramers* is well described by [Chiang et al. (2002)].



$$H_5C_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OC_2H_5}{|}}{P}}-CH_2\text{-}CH_2-\overset{\overset{\displaystyle OC_2H_5}{|}}{\underset{\underset{\displaystyle OC_2H_5}{|}}{Si}}-OC_2H_5$$

Figure 3.4 Example for a phosphatosilane compound (here diethylphosphateethyltriethoxysilane) that can covalently bond to a silica based matrix and is therefore protected against washing out.

Apart from modified silica sols employed for flame retardant treatment sols containing antimony oxide (Sb_2O_5) particles are also reported to improve the flame retardant properties [Petrow et al. (1974)].

These antimony containing sols are usually applied in combination with chloride or bromide containing compounds. It is assumed that *antimony oxide halogen* compounds generated in-situ interrupt oxidizing reactions that are responsible for the flame propagation and therefore act as flame retardant. The application of antimony oxide can either be performed with an Sb_2O_5 sol or by embedding of antimony oxide pigments into a conventional nanosol coating which is reported by [Hennige et al. (2005)].

3.3 Barrier coatings

Barrier coatings as the above described char layers acting as oxygen and heat barrier are only formed during a fire but there is also a certain demand for barrier coatings protecting a textile material permanently. Polyester is known for its excellent solvent resistance as well for a good stability in acidic atmospheres (under ambient conditions). But then under basic conditions it will be degraded hydrolytically. The same behavior can be observed for glass fiber based materials. On the other hand polyamide-based materials show a certain weakness against hydrolytic decomposition in acidic atmospheres. Polyesters as well as polyamides and even the high-tech polymers as the aramides will furthermore be degraded in superheated steam. Some investigations with regard to the ageing behaviour of fiber materials were, e.g., carried out by [Bahners et al. (2002 & 2003a)]. It has to be stated that in principle the most fibre materials show sufficient stability for a lot of application, but especially for long-term application or in industrial applications under certain atmospheres the fibre protection will play an important role. To give an example an air filter’s life cycle in an air conditioner will not be limited by the hydrolytic stability of the fibre material the life cycle of a filter used in hot-gas filtration will.

Numerous papers are written describing sol-gel based systems with certain barrier properties. [Amberg-Schwab et al. (1996)] prepared alkoxysilane based inorganic-organic hybrid polymer systems as coating material for polyester that guarantee excellent barrier properties against water vapour and oxygen as well as against numerous organic materials used as flavours. [Bahners et al. (2003b)] investigated the ageing behaviour respectively the decomposition of different fibre materials under various atmospheric conditions. The mentioned paper reported of interesting results with regard to sol-gel derived thin layer coatings applied to the fibre materials.

Investigations were carried out by the authors [Textor et al. (2002a & 2002b)] with technical polyamide, polyester as well as glass fibre fabrics that are equipped with barrier layers based on a sol-gel coating. Glass fibre, e.g., is of industrial interest in building trade, to substitute steel reinforced concrete by glass fibre reinforced concrete. Glass fibre is of advantage for several reasons, it is light weighted compared to steel but nevertheless offers a high strength. Additionally it is more flexible and what is the main advantage it does not show corrosion. Steel reinforced concrete must have a certain thickness to protect the steel against weathering effects, glass fibre would allow to build more filigree structures. The only problem is, that concrete sets for about four weeks and has pH-values of about 14 and as introduced glass fibre is sensitive against basic atmospheres. For the above mentioned investigations glass fibre fabrics were coated only with a thin layer of a sol-gel coating mainly based on 3-Glycidyloxypropyltrimethoxysilane and were afterwards stored in different atmospheres. Afterwards the tensile strength was taken as a measure for the hydrolytic degradation of the fabrics. Figure 3.5 summarize the corresponding results proving an excellent protection of the fibre material under basic conditions.

As mentioned above concrete sets for several weeks, therefore experiments were carried out storing fabrics in an ammonia atmosphere for about two weeks. A strong decay of the tensile strength of the grey fabric can be observed as expected for the complete storage time, the remaining strength after two weeks is only about 20 % of the initial one. The coated fabric shows no decay for the complete storage time, proving that the thin hybrid polymer coating protects the fibres sufficiently acting as a barrier. The results can also be taken as an evidence that the sol-gel derived coatings homogeneously cover the fibre surface, since defects in the coating are expected to allow punctual hydrolysation of the fibre in the ammonia atmosphere which would also lead to a decrease in the tensile strength, that was not detected.

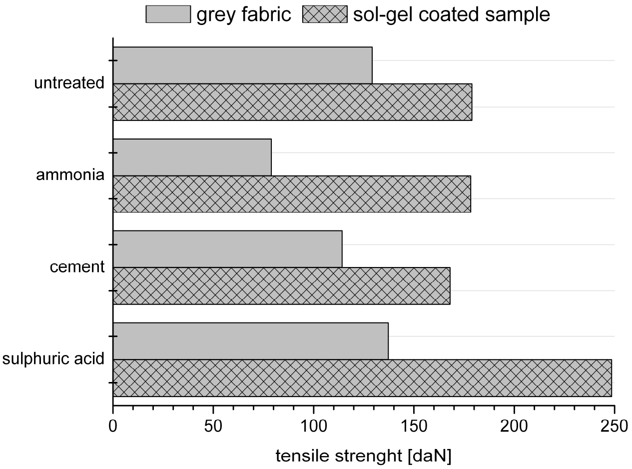


Figure 3.5 Tensile strength of coated (patterned) and uncoated (grey) glass fibre fabrics before respectively after storing in different atmospheres. (ammonia = 24h saturated ammonia atmosphere, 60°C; cement = 6 days in a concentrated concrete solution, 60°C; sulphuric acid = 6 days storage in a closed vessel over concentrated sulphuric acid (with free SO_2), 60°C).

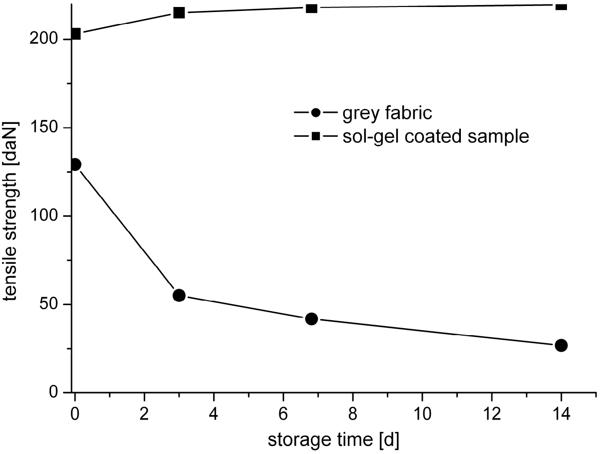


Figure 3.6 Tensile strength of a coated (dark grey) and an uncoated (light grey) glass fibre fabric after a storage in an ammonia atmosphere at a temperature of 60°C for up to two weeks.

The results above show that appropriate coatings can act as barriers against liquid as well as vapour or gaseous atmospheres.

Several conditions have to be taken into account, as the homogeneous coverage of the fibre material, a certain impermeability of the coating and certainly a sufficient durability of the coating itself under the particular conditions. The sol-gel technique with its idea of modular composition of materials seems to be ideal to develop hybrid polymers that fulfil these requirements.

3.4 UV protection

Numerous synthetic fiber polymers show a comparably low resistance against ultraviolet radiation. Examples of some polymers that are decomposed by UV-light are polyester, *p*-aramide or poly-*p*-phenylene-benzobisoxazole (PBO) fibers. While for clothing applications the light-stability of polyester is sufficient, certain applications ask for an improved resistance. As an example a textile roofing will be exposed to sun-light for years and a decomposition of the fiber material would lead to a decreased mechanical strength.

For many products an improved UV-resistance is achieved by a modification of the fiber polymer (before the spinning process) with UV-absorbing pigments as, e.g., titania or by employing organic molecules acting as radical scavengers.

For the sake of completeness it shall be only shortly mentioned here, that sol-gel derived coatings can be applied that shield the UV-light and guarantee a certain protection of the fiber polymer. Approaches to do so will be discussed in a subsequent chapter (Chapter 5.2), when the interaction of sol-gel coatings with light will be described in more details.

Chapter 4

Improved Water, Oil and Soil Repellence

Probably one of the first applications of textiles was the protection of man against the weather, for example, against rain and snow. Textile finishes to prepare water-repellent fabrics were therefore and still are important products in textile industry. Not only the umbrella or the rain coat should be water repellent, but also many other textile materials. This repellence is often not limited to simple hydrophobicity, for many applications repellence for all kinds of oils and soil are additionally expected. Textiles in everyday use like carpets, curtains, upholstery or tablecloths are only some possible products that need a suitable finish. Such textile materials are often advertised as easy-to-clean or easy-to-care.

Besides the above mentioned materials used in the household the repellence properties of many technical textiles are also of great importance. Conveyor belts as used in food or tobacco industry have to meet a number of criteria. The product that is conveyed must not stick to the surface. Especially in food industry the products are often a mix of aqueous and oil based ingredients. Additionally it has to be easy to clean residues from the belt in order to meet hygiene standards. Another example might be filter materials: the intervals in which filters have to be cleaned or exchanged strongly depend on its repellence properties. If a material has to be cleaned less frequently its product life time could be increased on the one side, on the other side the manufacturing process needs be interrupted less frequently. Sol-gel modified filter materials for filtration of diesel fuel in automotive applications are already commercially available [Chabrecek et al. (2005)].

The production of repellent surfaces is also of high importance for textiles used in medical applications. As all the other materials used in the operation theatre textiles must be sterilizable and possible contamination must be prevented as far as possible. During an operation surgeons need cloths that can drain off high amounts of liquids and that simultaneously stay clean. An interesting task is moreover the development of bandages or plasters for wound treatment that are less adhesive to the healing wound. In many cases the wound healing is prolonged since the removal of the wound dressing leads to an impairment of the regenerating skin (a detailed discussion of this topic is given in Chapter 8).

Besides products that combine water and oil repellence, products that show only oil repellence in combination with hydrophilic properties might be advantageous for certain applications. Filter materials could be invented which are able to separate polar or hydrophilic substances from non-polar or oleophilic substances.

In many cases a water barrier is achieved by completely covering the open structure of a textile with a dense polymer layer or by producing laminates by incorporation of certain membranes like Gore-Tex® or Sympatex®. A covering of the open structure of a fabric can not be realized by a sol-gel coating, since the coatings applied have to be very thin as already described in Chapters 1 and 2. The focus in this chapter is therefore set on the application of nanosols aiming at a reduction of the surface energy of the finished fibre material.

4.1 Hydrophobic coatings

Simple inorganic nanosols like silica sols are already more hydrophobic than some of the natural fibre materials such as cotton or other cellulosic materials. These sols already influence the repellence or the absorbency of such materials. Most of the synthetic fibres, such as polyester, polyethylene or polypropylene are comparatively hydrophobic, whereas the polyamides and polyacrylic fibres are relatively hydrophilic. A list summarizing some surface energies is given in Table 4.1. Increased water repellence can, as is well known, only be achieved if the coating surface energy is below that of the substrate. Unmodified inorganic sols will not therefore be able to improve the hydrophobic properties of a polyester or of a polyolefin. As mentioned in Chapter 2, changes in the absorbency of a fabric are not equivalent to its hydrophobicity alone.

Table 4.1 Surface energies of selected polymers and inorganic oxides [Arkles (1977)].

Material	Critical surface tension [mN/m]
Polytetrafluoroethylene	18.5
Polypropylene	31.0
Polyethylene	33.0
Poly(styrene)	34
Polyvinylchloride	39
Polyester	43
Polyamide 6.6	46
Glass, soda-lime (dry)	47
Silica, fused	78
TiO_2 (anatase)	91

In general it can be stated that a simple inorganic nanosol will be not meet the demands of the textile industry for a water-repellent or an oil or a soil repellent textile. This statement is especially true if a basically inorganic nanosol is modified, for example with epoxyalkylsilane, that is often used amongst others to enhance a adhesion of a coating to the textile surface. Modifications with various organic or organically modified additives such as epoxysilanes might even increase the hydrophilic properties of inorganic nanosol coatings [Song et al. (2003); Textor et al. (1999)] The introduction of polar groups into the sol-gel derived networks will, as expected, increase the surface energy of the resulting coatings.

By suitable modification using compounds with hydrophobic functionalities nanosols can be prepared yielding low surface energies and thus guaranteeing a certain repellence. Such modifications can either be carried out by a covalent bonding between the hydrophobic components and the inorganic building blocks or by physical embedding hydrophobic substances in the networks. In many cases alkoxysilane compounds with alkyl or fluoralkyl side chains are used. These compounds are advantageous because during the hydrolysis of the precursors as well during the gelation process the hydrophobic compounds will be chemically bonded to the inorganic nanosol [Mahltig et al. (2003); Daoud et al. (2004a & 2006); Brambilla et al. (2007)]. A number of suitable alkoxysilanes are shown in Figure 4.1.

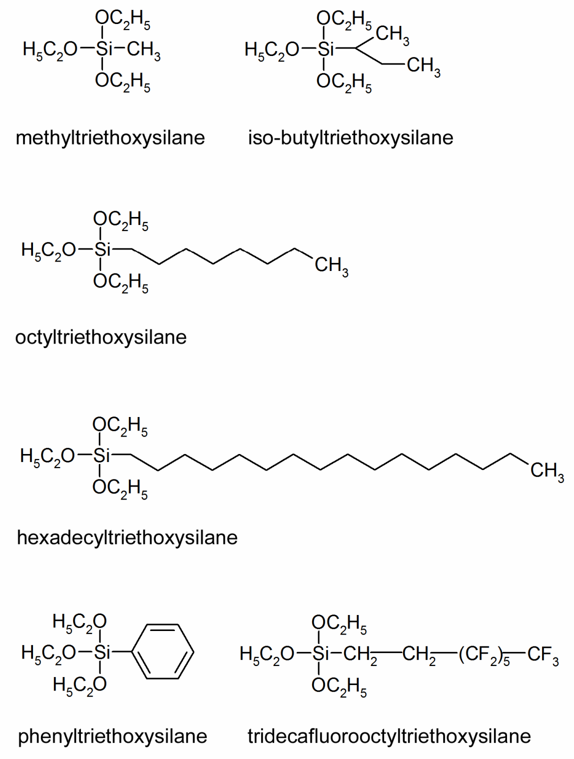


Figure 4.1 Examples of hydrophobic silane monomers.

Another way to prepare highly repellent surfaces is to modify the sols with reactive polysiloxane compounds [Shindou et al. (2003)]. Examples are shown in Figure 4.2. The challenge is often to find or optimize a suitable combination of the hydrophobic additive with the comparatively hydrophilic inorganic metal oxide component of the nanosol. This is especially the case if water is used as main solvent for nanosol preparation [Mahltig et al. (2005b)] since the use of additives with low surface tension in a mainly aqueous sol will lead to phase separation.

This phase separation can be avoided by use of polysiloxanes containing hydrophobic groups as well – necessary for achieving the demanded hydrophobic surface modification – as hydrophilic side chains providing a sufficient solubility in water. Appropriate compounds are to be found among some products of the Dynasylan™ group (Evonik) based on a fluorinated polysiloxane modified with hydrophilic aminosilane side chains.

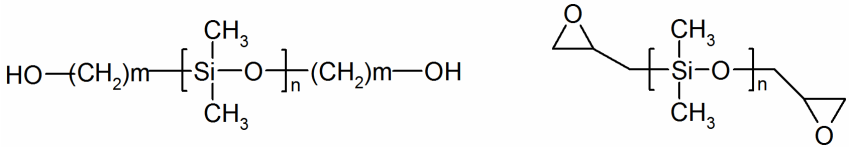


Figure 4.2 Selection of polysiloxanes employed for hydrophobic modification of nanosols for textile application.

Even small amounts of hydrophobic alkyltrialkoxysilanes below 0.5 wt.-% added to a silica sol can yield a strongly hydrophobic effect. [Mahltig et al. (2003); Daoud et al. (2004a & 2006)] reported the preparation of highly repellent textiles following the approach described. The small amount of hydrophobic additives necessary for a significant change of the wetting behavior can be explained by a gradient in the surface tension of the different compounds building up the network during the gelation process. Due to this gradient the more hydrophobic components will accumulate at the surface of the evolving film [Fabbri et al. (2006)]. So, compared with the bulk the surface of the resulting material will be enriched with the hydrophobic components. Figure 4.3 shows an example of the influence of a certain share of a hydrophobic additive on the wetting behavior of a sol-gel coated surface. The unmodified sol-gel coating applied to a polyester foil will lead to a contact angle of water below that of the pure polyester, which is 76°. Addition of only 1–2 vol.% of a hydrophobic compound to the sol will lead to an increased contact angle of nearly 100°.

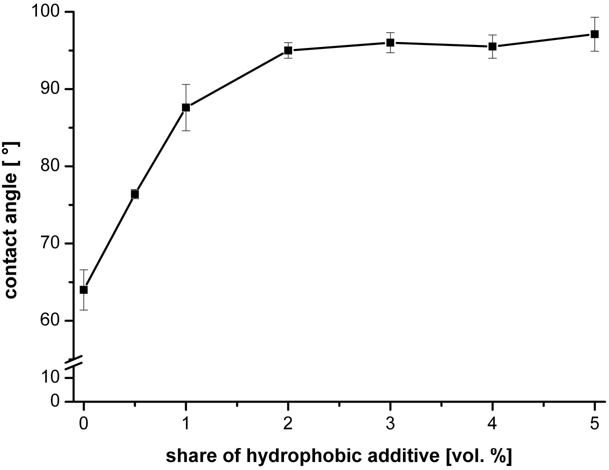


Figure 4.3 Influence of different shares of a hydrophobic (fluorinated) alkoxysilane additive on the contact angle of water on a coating based on a sol derived from an epoxysilane. The coating is applied onto a polyester foil, to suppress influences of the surface structure of a textile on the contact angle.

The length of the alkyl side chain of the alkyltrialkoxysilane additive used is more important for the absolute change in the surface energy that can be achieved than its concentration (which corroborates the above mentioned theory that an additive distribution gradient is built up). The water repellence determined by measuring the contact angle of water on coated surfaces increases significantly with an increasing length of the alkyl side chain (at a given concentration of the hydrophobic concentration). Highest values with contact angles of about 100° on coated glass are achieved by using side chains with at least 12 carbon atoms. The results of corresponding experiments are summarized in Figure 4.4. One has to keep in mind that longer alkyl-chains will lower the solubility in aqueous sols, therefore a certain proportion of other solvents or the use of sufficient surfactants might be necessary.

The analogous phenyltrialkoxysilane may also be used as the hydrophobic additive alternatively to alkyl-modified silanes. The hydrophobic effect gained by this phenylsilane is slightly smaller than expected for the analogous alkylsilane exhibiting six carbon atoms in the alkyl side chain (compare Figure 4.4 also).

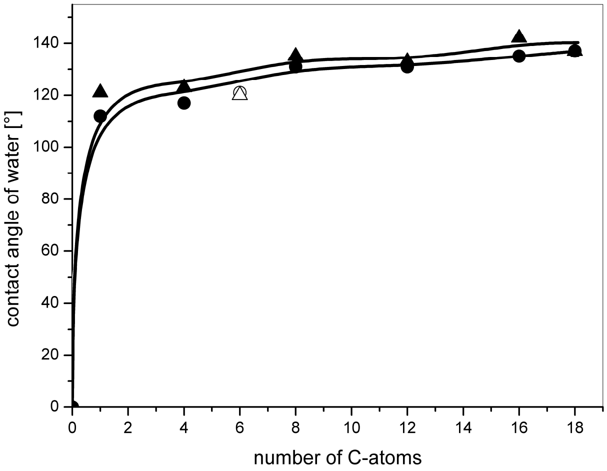


Figure 4.4 Nanosol coatings modified with 4 wt.% of hydrophobic alkyltriethoxysilane additives with increasing chain length or phenyltriethoxysilane on different substrates (triangle = CO/PES, circles = polyamide, open symbols = corresponding results for the phenyltriethoxysilane modified sols) – the solid lines are guides for the eye. [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

For preparation of aqueous sols containing a comparatively high share of water the use of less hydrophobic silanes with shorter alkyl side chains might be necessary, with regard to the sol stability. In these cases a compromise must be found between the required repellence and stability. Hydrophobic finishes for textiles according to the described approach are, for instance, realized by modification with octyl-modified [Mahltig et al. (2005b)] as well as propyl-modified alkoxysilanes [Textor et al. (2002b)]. For certain approaches hydrophobic finishes can also be carried out by preparation of sols based on the hydrophobic silanes only. These finishes, however, often have lower durability and are in many cases more expensive when compared with the composites described above.

The surface energy or contact angle for the water cannot be taken as the only parameter to assess the water, oil or soil repellence of a textile material. As already mentioned in Chapter 2, among other factors the fabric construction, the denier, the hairiness as well as the structure influence e.g. the topography or the capillarity of a fabric are significant.

For this reason, more *textile related* evaluation methods should be employed to achieve specific information concerning the repellence or wetting characteristics. A more significant testing method for this purpose is, for instance, the measurement of liquid or water uptake after complete immersion or after carrying out a spray test. Figures 4.5 and 4.6 show results of corresponding tests. The tests generally confirm the results gained by measurements of contact angles. Even by addition of a low concentration of about 0.1 wt.-% of an appropriate alkoxysilane to the nanosol the water uptake of a coated textile can be additionally decreased. For the example presented here, only about 1 wt.-% of the alkylsilane additive employed is sufficient to reach a plateau value for the repellence with regard to the water uptake. A further increase of the additive amount does not additionally reduce the water uptake (compare Figure 4.5).

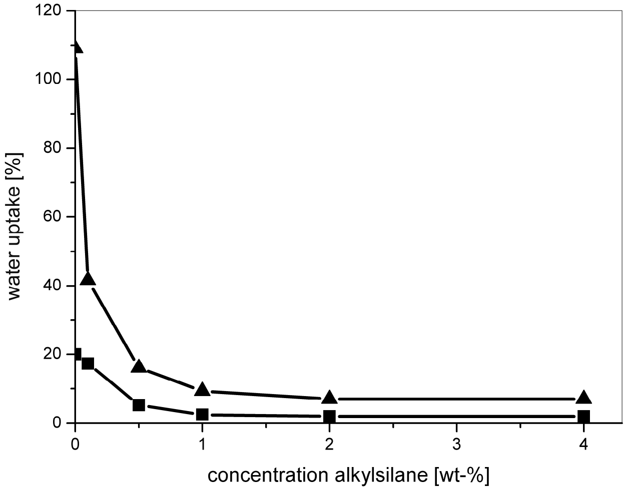


Figure 4.5 Water uptake of a CO/PES-fabric finished with nanosols containing hexadecyltriethoxysilane of increasing concentration after carrying out a spray (square) or a dipping test (triangle) with water [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

Figure 4.6 shows the development of the water uptake of a coated polyester/cotton blended fabric depending on the length of the alkyl chain of the additive used for modification of the applied nanosol. As seen above, regarding the influence of different additive alkyl chain lengths on the contact angle it can be stated that an increasing chain length leads to a decreasing water uptake for chain length up 12 carbon atoms. The use of additives with longer alkyl chains will not decrease the water uptake any more.

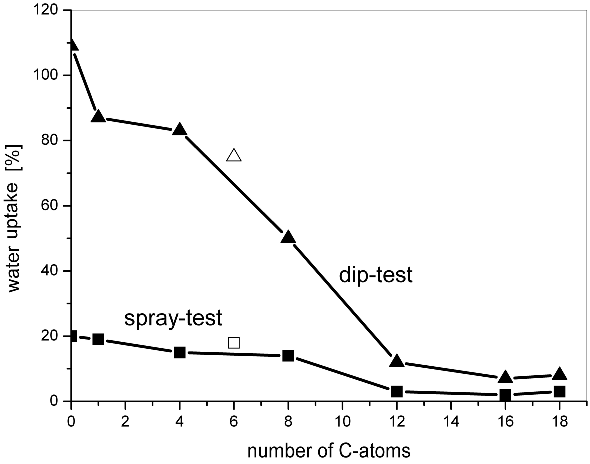


Figure 4.6 Water uptake of a CO/PES-fabric finished with nanosols containing alkyltriethoxysilane additives with increasing length of the alkyl chain and phenyltriethoxysilane (open triangle) after dipping (solid triangle) or spraying (squares) with water. (For the grey fabric the water uptake was 99 % after spraying and 157 % after dipping) [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

The amount of water that is soaked up by a fabric can be separated into the amount that is adsorbed on the surface, mainly driven by capillary forces or the surface energy, and the amount of water that is absorbed within the fibres itself. The results depicted in the figures above only show the static water uptake. Since the sol-gel derived coatings are more or less porous it can be expected that especially the coatings with a comparably high surface energy will basically slow down the velocity of the water uptake by the fibres themselves [Amberg-Schwab et al. (1998)]. Thus even a simple nanosol coating with a comparably low hydrophobicity protects the fibre against water, since it builds up a barrier between the water and the fibre. These coatings themselves exhibit, as mentioned above, a certain porosity and are not hydrophobic. Thus a decelerated migration of the water to the fibre material might take place (depending on the surface energy and the porosity of the sol-gel matrix) determining the speed of water uptake. Highly hydrophobic coatings will prevent (or at least weaken) the water migration through the barrier. The proposed migration of water to the fibre is illustrated in Figure 4.7.

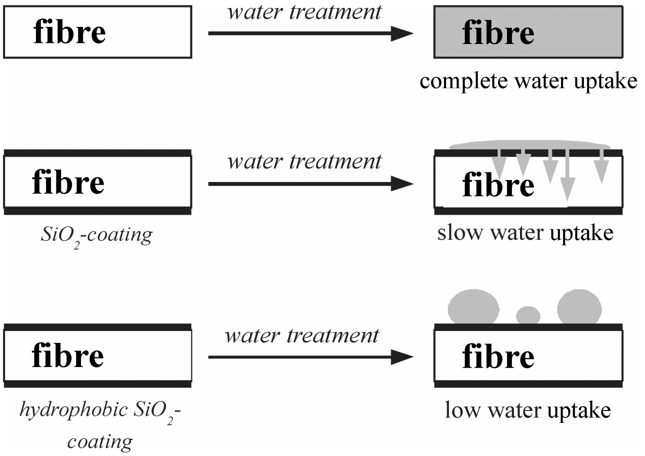


Figure 4.7 Schematic drawing of the above described model for the water uptake of sol-gel coated fabrics.

For synthetic fibres with a low water uptake ability such as polyester – which is not able to absorb more than 0.2 wt.% of water – this effect can be neglected (provided that the amount of water stored within the thin sol-gel layers can be also be neglected). Especially natural and cellulosic fibre materials are however able to absorb comparatively high amounts of water, therefore the migration of water might be significant.

If the fibres absorb water this is mostly accompanied by swelling that could, in the worst case, lead to disruption of the nanosol layers.

It can be stated that to guarantee a low water uptake with inorganic nanosols even in case of long-time exposure the application of sols with highly hydrophobic additives is preferable. Following the above concept, less hydrophilic coatings will only decrease the water uptake if the migration of the water is prevented, which could, for example, be achieved by suitable modification, mostly with organic polymers, of the sols that lead to coatings with higher network density or lower porosity [Yeh et al. (2007a); Ogoshi et al. (2005)].

For preparation of hydrophobic textiles by nanosol coatings it might be important to carry out sufficient thermal curing after the application. This curing might be necessary, as mentioned above, to improve the adhesion of the coating to the substrate. Curing or heating might also be required, especially for the long chained alkyl groups, to permit rearrangement of the alkyl chains [Poppenwimmer et al. (1999)]. Analogously, a loss of hydrophobicity during washing can be regained by thermal treatment such as ironing [Naßl et al. (2002); Mahltig et al. 2003)]. The loss of hydrophobicity during the washing procedure can be explained by a change in the alkyl chain orientation in the warm washing water. During a heat treatment in the dry state, the hydrophobic groups will be able to rearrange leading to a recovery of the hydrophobic effect. These effects are also known from fluorocarbon finishes as conventionally used in textile industries. [Duschek (2001)].

As described above, not only monomeric hydrophobic additives but also hydrophobic polymers are used to modify nanosols. The main limitation for using hydrophobic polymers in combination with the nanosols is the low solubility of polymers in a nanosol. As mentioned above this is especially the case if water based solvent systems are needed. To increase the solubility of the polymeric additives solvents as THF, acetone or toluene could also be used for nanosol synthesis [Yeh et al. (2007a)]. A huge number of different types of hydrophobic polymers can be used for nanosol modification. Advantageous are especially polysiloxanes exhibiting both hydrophobic as well as hydrophilic functional groups. The hydrophilic groups will increase the solubility in the sol, while the hydrophobic functionalities will accumulate at the surface of the product during the gelation process and therefore guarantee sufficient water repellence. The hydrophobic polymers can either be simply physically embedded into the sol-gel derived network or polymers with suitable functionalities that can cross-link or condense with the inorganic nanosol matrix can be employed to increase the durability of the effect [Vince et al. (2006)]. An example of an appropriate siloxane is given in Figure 4.8. The hydrophobic polymer backbone is modified with hydrophilic urea groups, simultaneously the polymer is terminated with alkoxy silane groups, allowing condensation reactions with the inorganic sol. Such urea/polydimethylsiloxanes are used to prepare organic/inorganic hybrid polymer sols achieving a high sol stability. The washing fastness of the resulting hybrid polymers on, for example, cotton is reported to be very promising [Fir et al. (2007)].

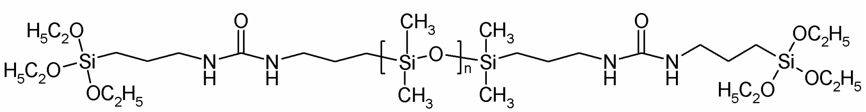


Figure 4.8 Structural formula of diureapropyltriethoxysilane that can be used for preparation of hydrophobic organic/inorganic hybrid polymer sols. Hydrophilic urea groups enhance the solubility, while the alkoxysilanes simultaneously allow covalent bonding to the inorganic matrices [Vince et al. (2006); Fir et al. (2007)].

Substrates coated by nanosols based on, or modified with vinyltriethoxysilane (VTEOS) can yield highly hydrophobic surfaces. The critical surface tension of a glass surface treated with pure VTEOS is very low, 25 mN/cm [Arkles (1977)]. Polymer foils coated with pure vinylalkoxysilane sols exhibit contact angles against water higher than 100° [Textor (2002a)]. Analogous vinyl modified nanosol coatings can be applied onto textiles. Such experiments were carried out with textile substrates, coated either with a vinyltrimethoxysilane (VTMS) based sol or a nanosol derived from a mixture of VTMS and TEOS. The fabrics were treated with UV-light (using various light sources) after the application of the sol, to initiate cross-linking of the vinyl functions of the network resulting after previous thermal curing. The effect of the

UV-treatment (in an inert atmosphere) on the water uptake is depicted in Figure 4.9. After irradiation the water uptake exhibits a certain decrease compared with the coated fabric without additional UV-treatment.

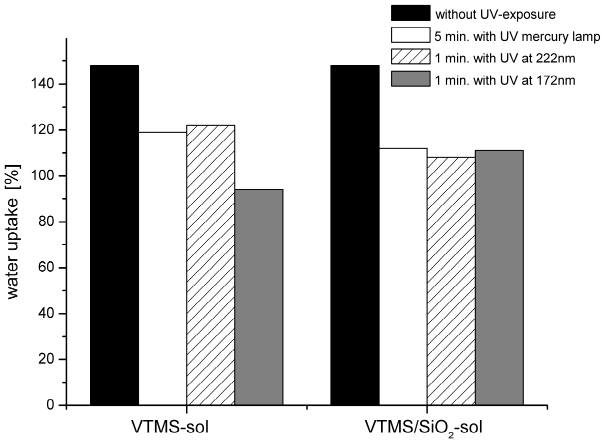


Figure 4.9 Differences in the water uptake of cotton samples treated with vinyl modified sols before and after a UV-treatment.

The decreased water uptake due to the irradiation with ultraviolet radiation can be explained by cross-linking of the vinyl groups [Sanchez et al. (2005)]. Photo-polymerization processes, as schematically depicted in Figure 4.10, lead to an increased network density of the hydrophobic coatings and therefore decrease the permeability for water.

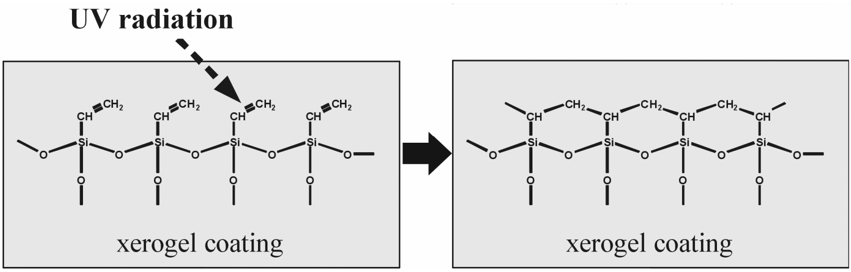


Figure 4.10 Schematic drawing, illustrating the subsequent cross-linking of vinyl groups for a textile coated with, for example, a sol based on or modified with vinyl-modified alkoxysilanes such as vinyltrimethoxysilane (VTMS).

The presence of oxygen during the UV-treatment could promote unwanted photo-oxidation processes that should on the one hand increase the surface energy and therefore lower the water repellence and on the other hand the cross-linking of the hydrocarbons would be inhibited the described increase of network density would therefore not occur.

4.2 Oil and soil repellent coatings

Oil and soil repellent coatings are of high commercial interest as easy-care and easy-to-clean applications, not only for textiles. Up to now, repellence of oil or oil like soils with nanosol coatings can only be realized by modifying nanosols with fluorinated compounds [Böhringer (2002)]. Nevertheless, many suppliers claim to have fluorine free oil repellent nanosol finishing for textile treatment. Until now such a product has not introduced into the market.

In consideration of the physical fundamentals the creation of an oil repellent surface without employing fluorine compounds must be impossible. To prevent wetting by a liquid material brought into contact with a surface the liquid has to show a lower surface energy than the surface of the sample to be wetted. Table 4.2 shows the critical surface tension of a number of molecular building blocks. On the one hand those building blocks are mentioned that dominate in oil-based soils, on the other hand those of fluorine based oil repellents are given. The only functional groups that lead to a lower surface energy than $–CH_3$ are $-CF_2-$ and $-CF_3$. Keeping in mind that wetting can only be prevented if the surface has a lower surface energy than the wetting material, a sufficient repellence against all hydrocarbons can only be achieved by fluorine compounds. Wetting with certain oils or fats with higher surface energy can certainly be also prevented by fluorine free surfaces with lower energy but this repellence would be limited to a limited number of soiling substances. Even nature, that created so called super-repellent surfaces – for example, the leaves of the watercress or the lotus plant – was not able to create oil repellent surfaces. The reason is that in those natural products no $–CF_3$ groups are available. Nevertheless a number of different approaches leading to fluorine free oil repellent surfaces have been investigated. One example is based on moveable silica particles placed on preadsorbed polycations [Cousins et al. (2005)].

Table 4.2 Critical surface tensions of different molecular building blocks [Duschek (2001)].

Surface composition	Critical surface tension [mN/m]
-CF_3	6
-CF_2- (polytetrafluorethylene, “flat fluorocarbon chain”)	18
-CH_3 (oriented paraffin)	24
Silicone	24
-CH_2- (polyethylene)	31

To achieve oil repellent nanosol based coatings fluorinated additives such as monomeric perfluorinated alkylsilanes, e.g., trifluoropropyltrimethoxysilane, polysiloxanes with fluorinated side-chains or fluorinated surfactants can be used [Satoh et al. (2004); Textor et al. (2001)]. Fluorinated alkyl-alkoxy compounds are useful as additives but they can also be used as precursors in polycondensation reactions leading to fluorinated polymerized particles which are used as coating agents [Akamatsu et al. (2001)]. In general, the combination with fluorinated compounds is often limited by their low solubility in the nanosols, again especially in aqueous systems. For this reason one usually uses polysiloxanes containing aminoalkyl-sidechains in addition to the fluorinated chains or to use fluorosurfactants modified with hydrophilic groups that increase the solubility of the fluorine compounds. A selection of fluorine containing surfactants that can be employed to prepare low-energy surfaces with nanosols is presented in Figure 4.11.

In the case of the modified nanosols one has to take into account that the modification of the sol might influence not at least the adhesion of the resulting coating materials, which is important for the durability of the coating. The preparation of nanosols from methylalkoxysilanes and perfluoroalkylsilanes in combination with small amounts of aminopropyltriethoxysilane is reported to be advantageous. In this case, the aminopropyl group improves the adhesion to the treated textile materials and leads to a promising wash fastness [Zhang et al. (2006)].

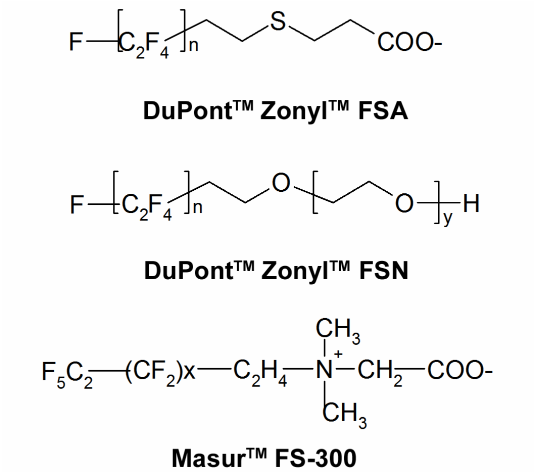


Figure 4.11 Selection of fluorosurfactants employed for nanosol modification to achieve oil-repellent coatings.

By application of fluorine modified nanosols, textiles can be equipped with excellent repellent properties against water as well as a huge number of oil-based or oil containing soils. Pretreatment of textile materials with a silica sol before application of a conventional fluorocarbon is also reported to lead to surfaces with excellent water and oil repellence. The repellence after a washing procedure is reported to be improved compared to the application without pretreatment [Yeh et al. (2007a & 2007b)].

Figure 4.12 shows photographs of textiles finished with different hydrophobic and/or oleophobic nanosols. The textiles are stained with different soilings that are common in everyday use. Untreated textile surfaces will be stained by water, coffee, wine and oil. The alkyl-modified surfaces are protected against the water-based soils, while only the fluorine modified samples repel the hydrocarbon based oil. The samples shown in Figure 4.12 that are finished with a sol modified with a fluorosurfactant lead to an excellent repellence for oil, while water-based materials are completely soaked up. This phenomenon could be explained by the amphiphilic nature of the fluorosurfactant, composed of fluorinated alkyl chains and hydrophilic groups.

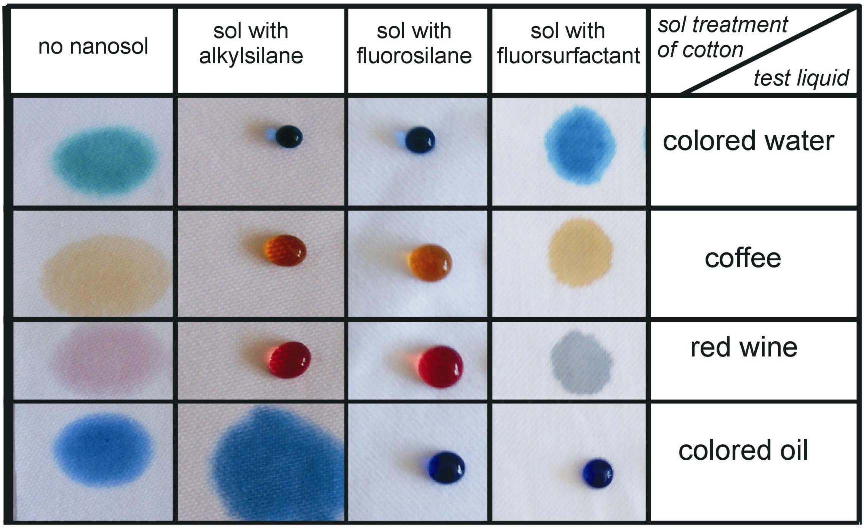


Figure 4.12 Different soils dropped on a cotton fabric treated with differently modified sols. Photographs are taken two minutes after applying the drops onto the fabrics.

Applications of sol-gel based finishes for textiles are, for example, reported for nylon carpets [Satoh et al. (2004)] and polyester curtains [Müller et al. (2004)]. It is stated that fluorinated nanosol applications lead to similar or even better soil repellent properties compared with *conventional* commercially available fluorocarbon resin dispersions [Müller et al. (2004)]. An advantage of the sol-gel based systems might be that the amount of fluorine components can be reduced due to the abovementioned enrichment of the mostly expensive low energy compounds on the coating surface during the gelation process. A reduction of the amounts or even a replacement of certain fluorine compounds is especially of interest since the materials are known to accumulate in the environment because they show a high persistence and are not biodegradable [Prescher et al. (1985)]. Due to this fact many producers now investigate methods to replace the systems conventionally used in textile industries.

Fluorinated nanosols are also tested to improve the repellence of polyamide fabrics as used for textiles employed in hospitals. One demand for textiles worn in the operation theatre during surgery is the prevention of blood penetration through the protective clothing. At the same time the additional requirements for these clothes are extremely high. The products have to guarantee excellent wearing comfort, since surgeons sometimes have to do very concentrated work for hours. Sol-gel based finishes promise possibilities to create highly repellent fabrics while only slightly affecting, for example, the stiffness or the breathability of the fabrics (compare Chapter 2).

The water vapour transport through a silica sol treated fabric is reported to be very promising [Rische et al. (2003)], so an improvement or preservation of air permeability and breathability is expected even after applying a repellent finish. Corresponding data are given in Figures 4.13 and 4.14.

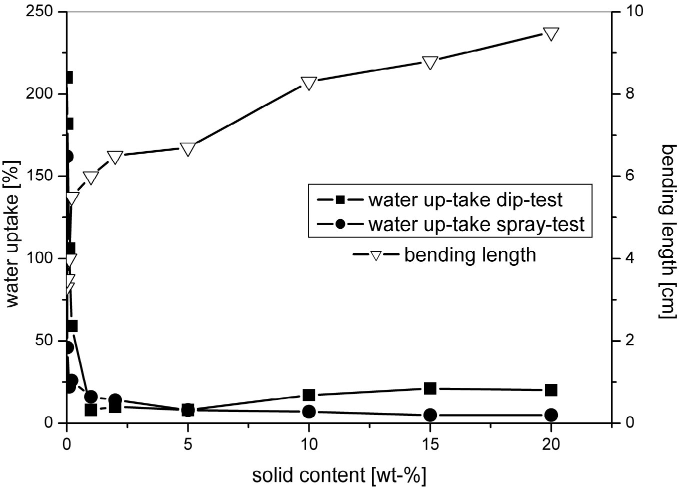


Figure 4.13 Fluorinated nanosol coatings on polyamide fabric as employed in clothing worn in operating theatres. Water uptake and bending length of fabrics as function of the solid content of the nanosol used.

The water uptake of a tested fabric is decreased to a minimum level even employing very low amounts of fluorinated nanosols, while simultaneously the stiffness in bending is comparably slightly increased (compare Figure 4.13). Regarding the air permeability, the finished textiles even show an increased permeability as long as the nanosols employed are diluted sufficiently (compare Figure 4.14). The use of nanosols with a higher solid content will not increase the repellence significantly but will increase the stiffness and lower the air permeability.

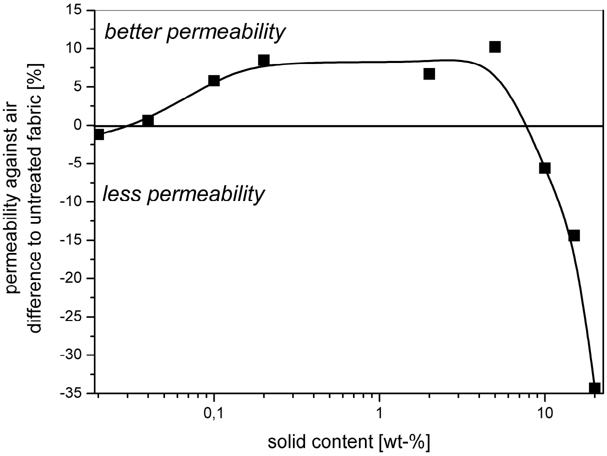


Figure 4.14 Fluorinated nanosol coatings on polyamide fabric as employed in clothing worn in operating theatres. Air permeability of fabrics as function of the solid content of the nanosol used. The solid line connecting the measured data is a guide for the eye only.

4.3 Self-cleaning properties

In principle the labelling of textiles as self-cleaning if they are equipped with a simple low-energy surface is misleading, this really means that these textiles are easy-to-clean. Basically two types of self-cleaning surfaces are distinguished in literature – photoactive or photocatalytic surfaces, based for example on photocatalytically active TiO_2 [Bozzi et al. (2005)] and superhydrophobic surfaces, often named Lotus surfaces [Barthlott et al. (1997); Fürstner et al. (2000); Li et al. (2007e); Zhang et al. (2008)]. The combination of both types in a single coating is also described [Hsieh et al. (2005)]. In all cases, for cleaning an interaction with the environment is necessary. This is irradiation with UV-light for photocatalytic coatings and water exposure as rain, or at least a certain orientation for superhydrophobic surfaces. Photoactive coatings exhibit in addition antimicrobial properties, they will therefore be intensively discussed, in the context of other antimicrobial coatings in Chapter 7.

As mentioned above, self-cleaning surfaces are often named as *lotus-like surfaces* [Patankar (2004); Hennige et al. (2006)]. This name is used with repect to self-cleaning surfaces that can be observed in nature. The wings of numerous animals as well as certain leaves show extremely high repellence – one of these leaves is that of the lotus plant. Nearly every soiling that is deposited on a lotus leaf can be removed by rinsing the surface with water [Barthlott et al. (1997); Fürstner et al. (2000)]. Analogous to the lotus leaf, self-cleaning superhydrophobic surfaces are defined as surfaces from which soiling can be completely removed by treatment with pure water.

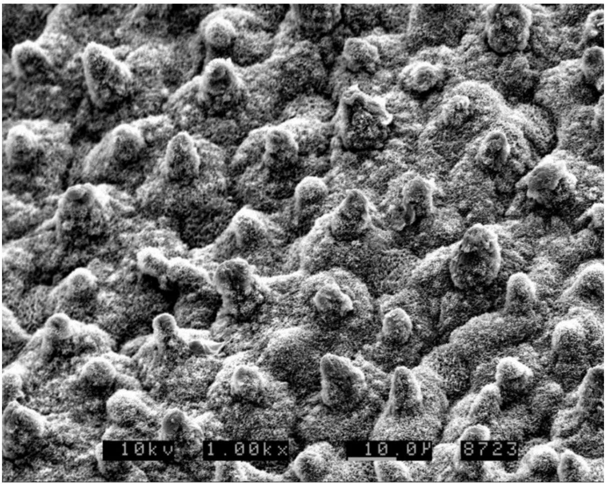


Figure 4.15 SEM image of the surface of a lotus leaf (Nelumbo nucifera).

The lotus leaf surface is covered by self-assembled hydrophobic waxes forming a nanostructure upon an underlying microstructure, built from cell wall structures and cuticular folds. Figure 4.15 shows a scanning electron micrograph of a lotus leaf surface. The existence of nanostructures onto a microstructure is named hierarchical topography [Neinhuis et al. (1997); Löthman et al. (2006)]. The super-repellence of the lotus leaf is explained by a combination of this hierarchical topography and a simultaneously highly hydrophobic surface. A sketch illustrating the so-called Lotus-Effect® (the Lotus-Effect® is patented! [Bartlott (1999)]) is depicted in Figure 4.16.

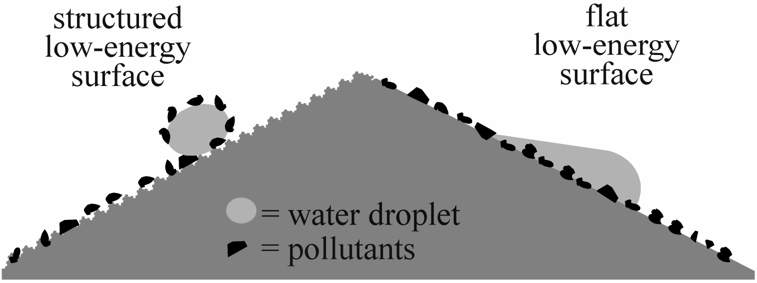


Figure 4.16 Sketch illustrating the removal of soils by water from a self-cleaning – hierarchically structured and hydrophobic – surface and the behaviour on a smooth/flat low-energy surface (adapted from [Wong et al. (2006)]).

The combination of a hierarchical surface topography and hydrophobic properties leading to superhydrophobic surfaces is certainly not restricted to natural surfaces – several bio-mimetic approaches to transfer the concept to inorganic surfaces as metals or glass have been implemented [Herminghaus (2000); Löthman et al. (2006); Li et al. (2007e)]. The hierarchical topography leads to a surface exhibiting a certain roughness. Compared with a smooth hydrophobic surface a water droplet deposited will exhibit a decreased effective contact area (liquid-solid) on a rough hydrophobic surface (Figure 4.17). The water droplet contacts the structured substrate only on the peaks of the surface profile, thus enclosing air within the valleys that are not wetted [with respect to Cassie (1948), Cassie & Baxter (1944)]. The contact angle is therefore determined by a composite interface that is consisting of the solid and the entrapped air. Since the contact area between the droplet and air is much bigger compared to the contact area with the substrate, the air will mainly influence the resulting contact angle [Herminghaus (2000); Patankar (2004)]. Thus a rough hydrophobic surface has higher contact angles of water compared to a chemically identical but flat perfectly plain surface. A comparison is experimentally given, for example, by Su et al. with a water contact angle of 105° on a plain surface and an angle of 168° on the chemically similar but rough surface [Su et al. (2006)]. Water droplets draining off from such an artificial superhydrophobic surface are able to pick up soils and remove them from the surface while on the plain surface the soils are at least shifted by rinsing, as is schematically depicted in Figure 4.16. Since this effect is based on the high surface tension of pure water, the self-cleaning effect is not present when rinsing with water containing surfactants.

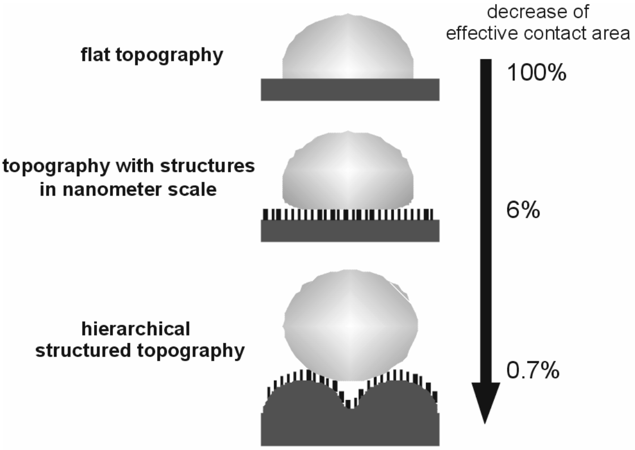


Figure 4.17 Influence of the topography on the effective contact area between a drop of water and hydrophobic solid surfaces of different topography [Stegmaier et al. (2003)].

Nanosols themselves contain particles on the nanometer scale and should be an ideal means to built up coatings with a particular topography combining nano- and microsized structures. Nevertheless, the coating with nanosols can lead to smooth surfaces with low roughness, due to the low stability of nanosol particles and their high tendency for aggregation and network formation (Figure 4.18). Thus, in order to create nano-structured coatings by nanosol application, the stabilization of the nanosol particles is advantageous. This stabilization can be performed by surface modification of sol particles [Schmidt (2006)], e.g., by combination with long-chained alkyltrialkoxysilanes.

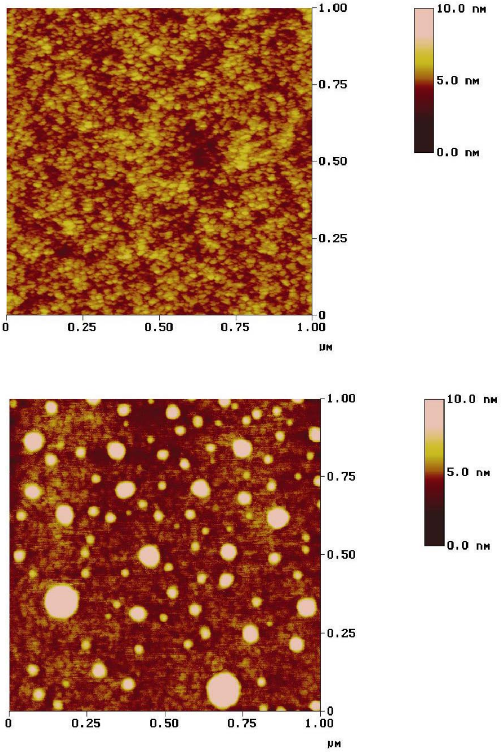


Figure 4.18 SFM images of nanosol coatings on glass surfaces. Top: coating derived from an epoxysilane modified silica sol; Bottom: coating derived from a silica sol modified with epoxy- and hexadecylsilane compounds.

It is also possible to prepare stable and larger silica particle with sizes of several hundred nanometers by alkaline hydrolysis [Stöber et al. (1968), Costa et al. (2003)]. Such sols are reported to be useful to enhance, for example, the roughness of a textile surface. As furthermore described in literature a second treatment with a fluorinated silane coupling agent will finally lead to superhydrophobic properties [Yu et al. (2007)]. An interesting approach is to form Stöber particles from silane precursors directly onto the textile surface by a sol-gel reaction and to add a hydrophobic modification afterwards [Hoefnagels et al. (2007)]. This process is quite similar to the modification of already formed SiO_2 particles by hydrophobic alkyltrialkoxysilanes for hydrophobic modification of fabrics [Pipatchanchai et al. (2007)].

In order to attain a combination of nano- and microstructure, the combination of nanosols with larger particles or pigments is also an appropriate approach. This combination is reported to lead to self-cleaning properties on textile substrates [Textor et al. (2004b), Hennige et al. (2006)]. For this, epoxy modified silica sols are used as a primer coating on felts. As a second coating a mixture of the modified silica sol with Aerosil® particles (silica nanoparticles prepared by flame pyrolysis) is applied. The use of the highly agglomerated Aerosil® particles leads to the necessary micro-sized topography on the textile surface. The hydrophobic properties are achieved by additional treatment of the particles with alkyl silanes, fluoroalkyl silanes or disilazanes [Textor et al. (2003b); Hennige et al. (2006); Pipatchanchai et al. (2007)]. The self-cleaning properties of such treated textiles has been proved. At present the use of self-cleaning textiles is however restricted, because of the low abrasion stability of the hierarchical structured coating [Stegmaier et al. (2003)].

Chapter 5

Changing the Light Absorption of Textiles

For most consumers light absorption of textiles means only the color of a textile. For fashion reasons the color of a textile is one main argument for the buying decision. In view of an increased awareness of health not only the absorption of visible light but also the absorption of ultraviolet radiation is of growing importance since the number of people suffering from skin cancer increased dramatically within the last decades. Especially light colored textiles offer only weak protection against the hazardous UV-radiation. Simultaneously organic dyestuffs used for conventional dyeing of textiles could, for example be protected against bleaching by an UV-absorbing barrier.

Absorption is not only an important topic for fashion reasons. As mentioned in various chapters before, a number of synthetic fibres are decomposed by UV-light, therefore UV-absorbing finishes are of high interest, for instance for outdoor application or textile architecture [Xing et al. (2007)]. Beside protection against ultraviolet radiation other topics such as adaptive coloration or absorption or reflection of infrared radiation are of great interest especially for the abovementioned applications. Adaptive coloration could allow variation of the translucence depending on the weather conditions, while reflection of the IR-radiation in sunlight could be useful for climate management to save energy necessary for air conditioners.

Different approaches to achieve certain absorption properties by application of nanosols can be used. The main requirement for changing the light absorption of a textile by nanosol finishing is that the modified sol is able to absorb and/or reflect visible, ultraviolet or infrared light either over a broad range of the spectrum, or at certain wavelengths. Inorganic nanosols can be prepared that absorb light without further modification. Coating derived from nanosols based on TiO_2 or TiO_2/SiO_2 [Xin et al. (2004a); Xing et al. (2007)] show absorption of UV-light with a comparatively high extinction coefficient. Other metal, metal oxide or semi-metal sols also show certain absorptions. An interesting aspect is the fact that the color of many sols depends on the size of the colored particle. As an example, for very small semiconductor particles the color is determined by the so-called quantum size effect [Kreibig et al. (1995)]. The optical properties of materials have been shown to depend on the size of nanoparticles (schematically illustrated in Figure 5.1).

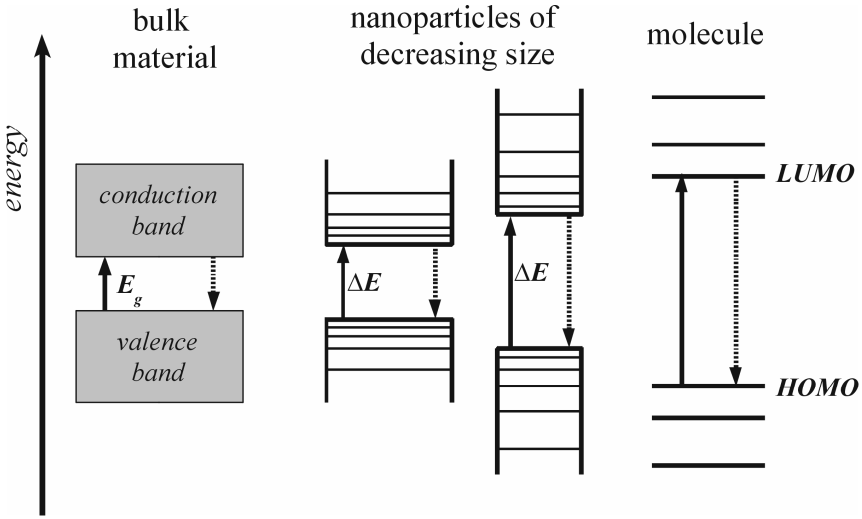


Figure 5.1 Schematic drawing illustrating the quantum size effect.

While the optical properties of single molecules are determined by the energetic gap between molecular orbitals (mostly the HOMO – highest occupied molecular orbital and LUMO – lowest unoccupied molecular orbital), the absorption of semiconductor bulk materials are usually characterized by the so-called band gap between the unoccupied conduction and the occupied valence band. For very small particles – in the range of several nanometers – the number of orbitals located in the valence and the conduction band is drastically reduced. Therefore the number of orbitals is so low, that instead of quasi-continuous bands discrete orbitals can be observed. The occupied as well as the unoccupied orbitals repell each other. This repulsion determines the gap between the HOMO and the LUMO. A reduction in particle size will decrease the number of orbitals and therefore lead to lower repulsion. As a result the energy gap between HOMO and LUMO becomes larger. For a colored nanoparticles the absorption band shifts to shorter wavelength with decreasing particle size.

Another well known example for a size dependent color are metal sols, for example those based on gold colloids. For these colloids the color is among other factors influenced by size dependent scattering of visible light [Mie (1908); Miura et al. (1953)].

The optical properties of nanosols can also be changed by adding light absorbing compounds which can easily be embedded physically into the nanosol or even chemically bonded to the sol particles or the developing xerogel network. Following this approach organic as well as inorganic dyestuffs and pigments are, for instance used to change the absorption in the visible range of light [Avnir (1995); Xuening et al. (2000); Böhmer et al. (2000)]. Even embedding of chlorophyll from leaf extracts into silica matrices has been reported [Vázquez-Durán et al. (2006)]. The UV-absorption can be changed by embedding organic UV-dyes [Dong et al. (2000); Zayat et al. (2007)] into the nanosol matrix. By incorporation of certain near-infrared absorbing dyes into silica sol systems the absorption in the range from 800 nm to 1200 nm can be modified [Wang et al. (2004); Prosposito et al. (2000)]. An interesting invention relates to embedding IR-reflective pigments as additives for nanosol coatings applied to textile materials [Hennige et al. (2005)]. Pigments prepared from different lanthanide oxides show the necessary properties. Textiles equipped with IR-reflective properties provide a protection against heat radiation. Such heat reflecting materials are of great interest, for example for protective clothes worn by firemen or for architectural textiles.

It is also of interest that the light fastness properties of dyed textile fabrics can be improved by a sol-gel posttreatment [Luo et al. (2003)] or a pretreatment of textile fabrics with sols during the dyeing process. The improvement of fastness might focus on the one hand on a reduction of the leaching of a dyestuff during washing. On the other hand, protection of the dyestuff against photodecomposition due to the incorporation into a sol-gel derived network has been reported [Dubois et al. (1996)].

5.1 Dyeing

As mentioned above a comparatively simple approach to dye textile materials by nanosols is the preparation of colored sols by addition of an organic dyestuff, or a mixture of organic dyestuffs. The dyeing process is carried out by a simple dipping or padding process followed by drying, for example in a stenter frame. During the coating and the subsequent drying process the dyestuff molecules are embedded into the inorganic matrix derived from the nanosol.

By embedding dyestuff into the inorganic matrix the washing fastness [Mahltig et al. (2004a)] and the photostability [Dubois et al. (1996)] can be enhanced. Two mechanisms have been suggested for the discoloration of a textile – that was dyed by applying a colored nanosol – during a washing procedure [Trepte et al. (2000)]. In the first one the embedded dye may be leached out of the nanosol coating and in the second one the coating and thus the dyestuff is removed from the fibre surface completely (compare Figure 5.2).

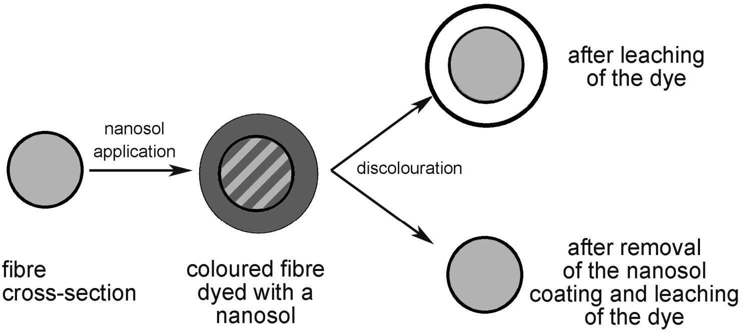


Figure 5.2 Dyeing and leaching of textiles with dye containing nanosols, adapted from [Trepte et al. (2000)].

To improve or achieve sufficient washing fastness of the coloration based on a nanosol dyeing process both the interaction between the dyestuff and the surrounding metal oxide matrix as well as the adhesion between the coating and textile fibre have to be sufficient.

The effectiveness of embedding a dyestuff into an inorganic coating is determined by several parameters and therefore different methods can be used to improve the durability. The following enumeration summarizes some approaches for optimizing the fastness of sol-gel derived colorations:

- Physical embedding of the dyestuff molecules: The immobilization of smaller molecules in the nanosol matrices is usually less effective. It can therefore be expected (if other interactions may be neglected) that the larger the dyestuff molecule, the better the immobilization and the slower the leaching process [Mahltig et al. (2004b)]. This is especially the case if colored pigments are embedded instead of dyestuffs that are dissolved molecularly [Böhmer et al. (2000)].
- Interaction (e.g. polar, nonpolar) between the dyestuff and organic functionalities of an appropriately modified nanosol matrix, such as different alkyl, phenyl or vinyl groups covalently bonded to a silica network [Panitz et al. (1998); Butler et al. (1998); Canva et al. (1992)].
- Electrostatic interaction between the dyestuff molecules and the inorganic matrix: Inorganic nanosol coatings exhibit an electrostatic net charge depending on their isoelectric point and the prevailing pH-value. Silica coatings having a pH value of about 4 at the isoelectric point exhibit a negative net charge at pH = 7, so positively charged dye molecules exhibit an attractive electrostatic interaction with the silica matrix. These dyes are more stable against leaching than uncharged or negatively charged dyes [Shah et al. (1992); Mahltig et al. (2004a & 2004b)]. This approach is comparable with the processes conventionally applied in industry for dyeing synthetic fibres such as those made of polyacrylonitrile. A negatively charged fibre surface is treated with a cationic dyestuff [Raue (1984)]. The absorption of charged polymers onto silica surfaces is also well

known and is, for instance, described by [Mahltig et al. (2001a & 2001b)].

- Complex formation between dyestuff molecules and parts of the inorganic xerogel matrix: If the dyestuff molecules are able to form complex bonds to parts of the inorganic nanosol matrix the leaching stability is significantly enhanced even if the dye molecule is of small size and exhibits the same electrostatic net charge as the inorganic matrix. One example described in the literature is embedding the dye Alizarin S Red in a nanosol-based coating of silica/alumina, thus achieving a promising washing fastness [Mahltig et al. (2004b)]. The complex formation mentioned has been used for textile dyeing since the Middle-Ages. So-called mordant dyes are applied in combination with metal salts (Al, Cr, Cu, Fe and many more) that reduce the solubility of the dyestuffs and therefore increase the durability of the dyeing.
- Establishing covalent bonding between the dye and the nanosol matrix: This can for example be achieved by applying dye molecules that are derivatives of alkoxysilane compounds. These derivatives can, for example, be added during the hydrolysis step of a sol preparation [Schottner et al. (1998); Trepte et al. (2000); Spange et al. (2002)]. A corresponding derivative is shown in Figure 5.3. Another approach is the use of so-called reactive dyestuffs. The reactive functionality of the dyestuff can, for instance be used to form covalent bonding between nanoparticles or silica gels as reported by [Blaaderen et al. (1992); Xuening et al. (2000); Burns et al. (2006)]. In the case of surface deposition of the dyestuff onto the particles nano-sized colored core-shell materials are achieved that are evaluated for application as potential pigments for textile finishing [Wang et al. (2006)].

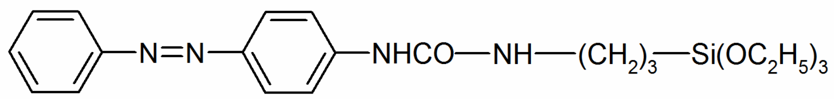


Figure 5.3 Example of a dyestuff molecule modified with an alkoxysilane functionality that allows chemical bonding, for example, to a silica sol matrix. (N-4-phenylazophenylyol-N-triethoxysilylpropyl urea) [Trepte et al. (2000)].

As mentioned above the light fastness of dyes can be enhanced by incorporation into an inorganic nanosol coating. Even embedding in a pure SiO_2-sol coating with no further additive enhances the photostability, an example is shown in Figure 5.4. The enhancement is suggested to be the result of: (I) isolation of the dye from contamination, (II) reduction of the translational and rotational freedom of the dye molecules and (III) protection against other products from photodecomposition and, for instance, atmospheric ozone [Díaz-Flores et al. (2000)]. Beside the protection by simple embedding an enhancement of photostability could be also the result of electrostatic interaction between dye and the surrounding matrix. Due to the ionic interaction of a positively charged dyestuff molecule and a negatively charged silica matrix the energy of the photo-excited dyestuff molecule can be dissipated by transfer to the surrounding silica matrix [Wegmann (1958); Mahltig et al. (2004a)].

A further improvement of photostability has been reported for modification of a purely inorganic nanosol by addition of epoxysilane or perfluoroalkylsilane compounds in small amounts [Mahltig et al. (2004a); Hou et al. (1994); Hoffmann et al. (1995)]. Photostability is of certain importance for colored textiles in case of an intense exposure to UV-radiation, for instance sunlight. Co-embedding of UV-absorbers and the organic dyestuff into the sol-gel derived matrices can distinctly improve the bleaching stability. Corresponding results proving the increased stability are also presented in Figure 5.4.

Instead of the described embedding of dye molecules the nanosol can also be used for pretreatment carried out before a dyeing process or for posttreatment of a previously dyed textile [Min et al. (2003); Juan et al.

(2005); Mahltig et al. (2006)]. The washing fastness as well as the lightfastness can be enhanced by this nanosol application. In the case of pretreatment the nanosol coating acts as a sort of adhesion promoter which improves the durability, while by posttreatment a protective layer covers the previously deposited dye.

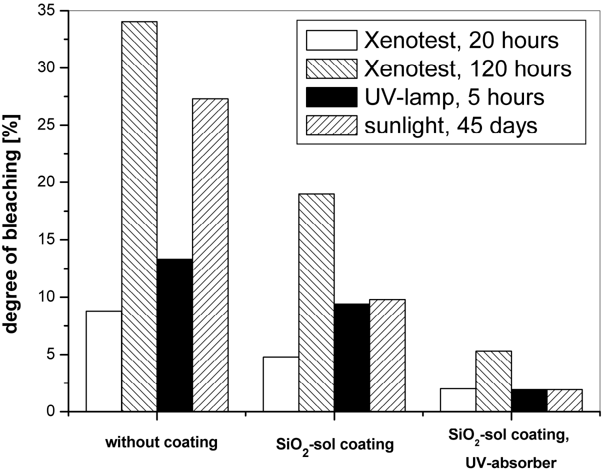


Figure 5.4 Photobleaching behavior of CO/PES blended textiles, dyed with Malachite Green embedded in a silica matrix. To improve the photostability a phenylacrylate derivative (SEMA 20163TM) is used as an additional UV-absorber [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

Embedding organic or inorganic color pigments into nanosol coatings can be carried out [Böhmer et al. (2000); Hennige et al. (2005)] as an alternative to the use of molecularly dissolved organic dyes. One advantage of applying organic pigments compared to homogeneously distributed dyestuffs molecules is a deeper color of the dyed textile, for instance due to light scattering by the pigments. Simultaneously the immobilization of the pigments is expected to be more effective because of the size and since the dyestuffs will not be dissolved and washed out so easily. Conventional pigments have particle sizes in the range of micrometers or slightly smaller. For proper embedding the pigments have either to be ground, or the applied coatings must have a sufficient thickness to incorporate the pigments. To increase the thickness of the nanosol based coatings the amount of organic modification has to be increased because otherwise, as explained in Chapter 1, the coatings would crack and/or the coatings lead to an unacceptable increase in the textile stiffness. The particle size of pigments should therefore be as small as possible, but at most not larger than 100 nm. To prepare homogeneously colored surfaces a proper dispersion of the pigments in the nanosol or the solvent is necessary. Since, as mentioned, the color depth is influenced by the particle size a compromise between particle size and color depth has to be found which best meets the demands.

Promising results were, for example, achieved by using polymeric stabilizers to embed small pigments in silica sols [Böhmer et al. (2000)]. The combination of organic color pigments with ZnO sols applied to cotton fabrics has been reported to guarantee a sufficient wash fastness [Li et al. (2007d)]. An overview on some organic color pigments, suitable with respect to the primary particle size, is given in Table 5.1.

Table 5.1 Organic color pigments useful for combination with nanosols (pigments available from Clariant) [Böhmer et al. (2000)].

Color index	Composition	Mean particle size [nm]
Pigment red 149	Perylene	25
Pigment red 122	Quinacridon	40
Pigment red 257	Ni-isoindolin	70
Pigment violet 19	Quinacridon	60
Pigment blue 15:1	Cu-Pht cyanine	30
Pigment green 7	Hal. Cu.-Phtcya.	35
Pigment yellow 83	Diaryl	40

A well known example for the application of inorganic color pigments in combination with nanosols is the use of colloidal silver as yellow colored additive [Mahltig et al. (2004c)]. Suitable recipes have also been developed employing pigment pastes containing predispersed inorganic pigments of colored metal oxide compounds. A selection of such pastes is given in Table 5.2.

Table 5.2 Useful pastes of inorganic color pigments in 40 % methoxypropanol (pigments available from Habich GesmbH, Austria).

Paste	Composition	Color index	CAS
Iron oxide paste; red	Fe_2O_3	Pigment Red 101	1332-37-2
Iron oxide paste; yellow	FeOOH	Pigment Yellow 184	14059-33-7
Iron oxide paste; black	Fe_3O_4	Pigment Black 11	1317-61-9
Strohgelb paste	Ni, Sb, Ti – oxide	Pigment Yellow 53	8007-18-9
Cobalt blue paste	Co, Al – oxide	Pigment Blue 28	1345-16-0
Grasgrün paste	Co, Ti – oxide	Pigment Green 50	68186-85-6
Moosgrün paste	Co, Cr – oxide	Pigment Green 26	68187-49-5

5.2 UV protection

Solar radiation covers a broad spectrum starting in the range below 200 nm. The range up to 280 nm is strongly absorbed by oxygen and ozone and thus by the earth's atmosphere. Especially the absorption by ozone is reduced due to the development of the well known ozone hole. In general it can be stated that a certain proportion of the UV-radiation in the range from 280 nm to 400 nm reaches the earth's surface. This part of the solar radiation is responsible for browning, but simultaneously this radiation is able to cause health damage such as sunburn, allergies, skin-ageing and in the worst case, skin cancer [Hilfiker et al. (1996); Lapidot et al. (2003); Zayat et al. (2007)]. The exposure of humans to UV radiation increased in recent years due to a changed leisure behavior with more frequent and longer sunbathing. In addition, and probably more alarming, the ultraviolet radiation dose is strongly increased due to a continuous decrease in the thickness of the ozone layer. While only very low doses of the shortest ultraviolet wavelengths (so-called UV-C) reach the earth's surface, the UV-B and UV-A radiation become a growing threat. The UV-B radiation penetrates the upper skin layers (epidermis), while the UV-A radiation also reaches the deeper areas also (dermis). An exposure to this radiation can lead to allergic reactions and accelerated skin ageing and as mentioned in the worst case to the development of skin cancer [Hilfiker et al. (1996); Osterwalder et al. (2000)].

Textiles were basically used for protection against weather conditions for thousands of years. Due to the mentioned changes of the atmosphere, but also for fashion reasons the requirements for sun-protecting textiles increased in recent years since especially the light shaded textiles that are predominantly worn in summer offer weak sun protection. Textiles of darker shades mostly offer a comparatively high UV-protection, because the dyestuffs used absorb ultraviolet as well as visible light strongly. Besides the dyeing of a textile the protection certainly depends on the fibre material used – a polyester fibre is based on an aromatic material and will therefore guarantee a higher UV-absorption than say, a cotton fibre. Optical brightening agents used in laundering detergents can additionally improve the blocking of UV radiation by a textile material. It is certain that the construction of the fabric also influences the possible radiation transmission, for instance the material thickness or the setting of threads will strongly influence the protection properties [Osterwalder et al. (2000)].

Several approaches to increase the ultraviolet protection by a given fabric are known. One variant is the pigmentation of the fibre material (before the spinning process) with titania (nano-)particles in rutile form, which is known as a strongly UV-absorbing inorganic pigment. Another approach is the use of auxiliaries for textile finishing that act as organic UV absorbers either on the fibre surfaces, or incorporated into the fibre polymer. Such organic UV-absorbers are mostly colorless aromatic compounds. The disadvantage of these compounds might be seen in a comparably low durability or a certain toxicity or allergenic potential.

Sol-gel technique or nanosols offer a very promising approach to realize highly effective UV protection coatings for textiles. Nanosols containing inorganic particles such as zinc oxide [Textor et al. (2003); Wang et al. (2005); Huang et al. (2006c); Li et al. (2007d)] or titania [Xin et al. (2004); Daoud et al. (2004c); Abidi et al. (2007); Xing et al. (2007); Onar et al. (2007)] are reported to absorb UV-radiation strongly. Products correspondingly prepared show strongly increased absorption, mainly in the range from 200 to 400 nm because the mentioned nanoparticles have a high extinction coefficient for ultraviolet radiation. Regarding the UV/Vis-spectra one observes a steep drop of the absorption curves at the transition from UV to visible light. This steep drop guarantees a high protection against ultraviolet radiation but also a colorless finishing, which is important in preventing a change in the textile appearance (compare Figure 5.5).

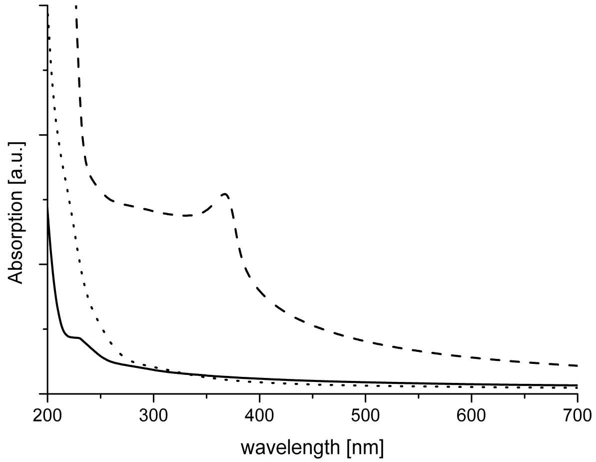


Figure 5.5 UV-Vis-spectra of a polyethylene film (straight line), the PE film coated with a hybrid polymer (dotted line) and the film coated with the hybrid polymer filled with approximately 10 wt.% ZnO (dashed line).

The combination of TiO_2 with silver particles leads to excellent UV protection that is durable against washing but simultaneously to a certain coloration of the textile in the visible range [Onar et al. (2007)]. The preparation of nanosol coatings filled only with TiO_2 or ZnO particles smaller than 50 nm is for that reason advantageous since these coating will not only remain colorless but also transparent (but only for the visible light!), because no light scattering occurs within the filled coatings. Titania (in the rutile from) and zinc oxide strongly absorb radiation with an energy higher than their bandgap energy (e.g. $E_{gap}/TiO_2 = 3.0$ eV; $E_{gap}/ZnO = 3.2$ eV). These energies correspond with a wavelength of 413 nm for the titania and 387 nm for the zinc oxide.

Organic UV-absorbers such as phenylacrylates or benztriazols (see Figure 5.6) can also be embedded into silica-sol based coatings [Lapidot et al. (2003); Dond et al. (2003)] using conventional methods.

The fixation will be comparable to the previously described dyeing of textiles with nanosols.

Figure 5.6 Structural formula of organic UV-absorbers useful for embedding into nanosol coating, left: the benztriazol derivative Tinuvin 213^{TM}; right: the phenylacrylate derivative SEMA 20163^{TM}.

To achieve an improved durability chemical bonding between the organic UV-absorbers and the alkoxysilane compounds employed can be useful. This method allows direct covalent bonding of the organic UV-absorber to the inorganic matrix of the nanosol coatings [Böttcher et al. (2006a)]. An example for the described immobilization process is depicted schematically in Figure 5.7. Alternatively the UV absorber can also be bound to a polysiloxane used as polymeric additive for a nanosol as reported by [Payne et al. (2003)].

Since the organic and inorganic absorbers show characteristic absorption spectra depending on the specific compounds, the particular absorber will most probably not absorb energy over the complete UV-A, UV-B and UV-C bands [Abidi et al. (2007)]. It can therefore be expected that a single absorber will not achieve the maximum protection. Protection against UV light can, however, be ideally completed by nanosol coatings combining inorganic and organic UV-absorbers [Mahltig et al. (2005a)].

Alternatively a fluorescent whitening agent can be used in combination with a TiO_2 sol to increase the UV-absorption especially in the UV-A region. The additional use of such fluorescent whitening agents simultaneously decreases the slight yellowing of the textile that often occurs when applying titania based nanosols for UV protection [Xu et al. (2005a)].

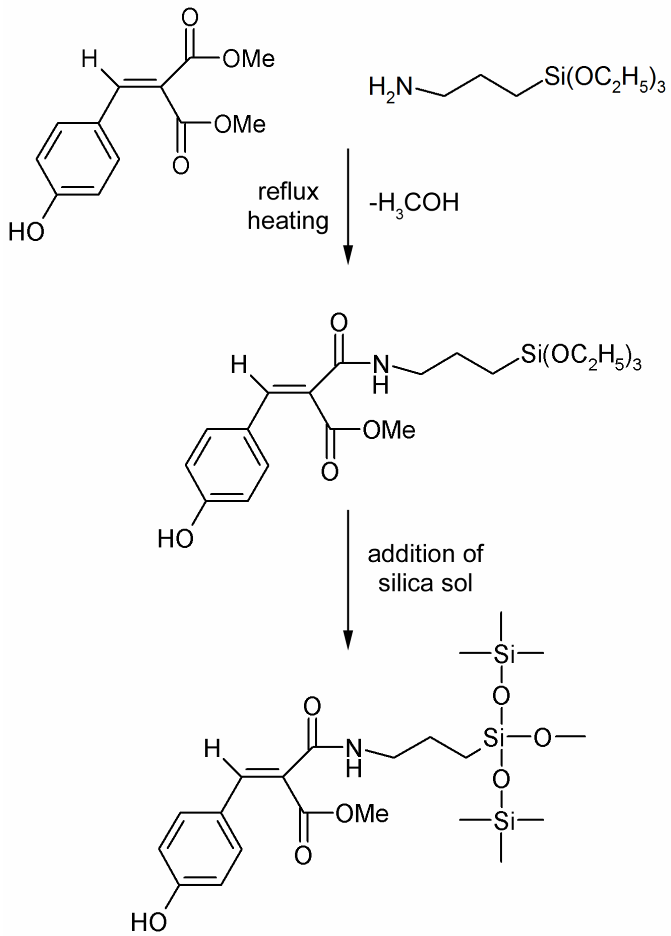


Figure 5.7 Diagram clarifying the chemical bonding of UV absorber SEMA20107 ™ to a silica nanosol matrix according to [Böttcher et al. (2006)].

Figure 5.8 compares three UV/Vis-spectra of the diffuse reflectance of a cotton fabric finished with differently modified nanosols. The evaluation of the diffuse reflectance spectra reveals that nanosol coatings modified with inorganic as well as organic UV-absorbers lead to an improved UV-absorption. The combination of both yields very high absorption over a wide range.

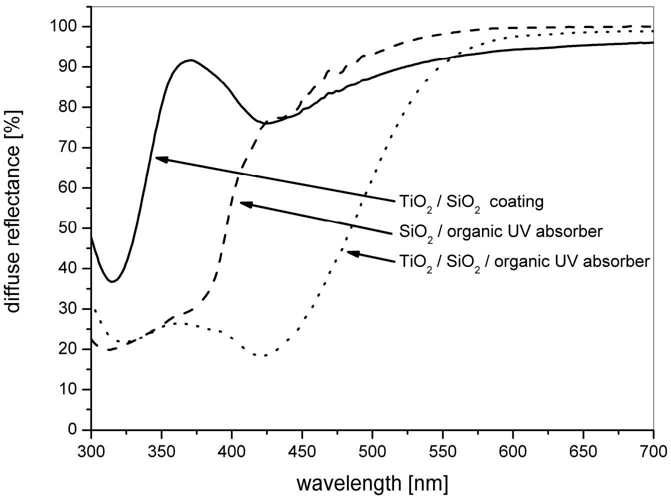


Figure 5.8 UV/VIS-reflection spectra of cotton treated with nanosols modified with organic and inorganic UV-absorbers [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

5.3 Photochromic coatings

Photochromism (Greek: *chroma* = color) is the description for the reversible modification of a material induced by visible or ultraviolet radiation leading to a change in the color or of the absorption spectrum. The reverse reaction can either be initiated by light of a different wavelength, by heat [Wöhrle et al. (1998); Christie (2001)] or it can also take place spontaneously if the light inducing the color change is excluded.

Such an effect is of interest for textile applications for several reasons. An interesting application would be the realization of textile roofing, shadings or marquees that change to a darker color during sunshine and discolors in times with less brightness. Such products could level the illumination intensity within textile buildings such as tents, or are useful for textile materials like curtains or rolling shutters. In addition, for fashion reasons clothing which changes color when leaving the house could be a gimmick. If, the reverse reaction of a photochromic color-change does only take place at a certain temperature this could be useful to store information. Furthermore it could be of interest for product safety. The disappearing of a label that is only visible until a temperature sensitive textile was exposed to a certain temperature could warn the operator or show the producer a false use of the product in case of customer complaints.

A variety of photochromic materials is known. These can be divided in inorganic and organic materials. The inorganic photochromic substances are mostly colorless solids that form electron-hole pairs during illumination, which act as color centers. Typical examples are alkali halogens, doped calcium fluoride or certain titanates. Perhaps the best-known example is silver chloride used in glasses that darken depending on the sunshine intensity. The inorganic photochromic substances are often incorporated in glass. Since the processing temperatures for such systems are far above the maximum temperature allowable for textile processing these materials are excluded for textile application. Nevertheless, an application on textiles might be offered by the use of silver loaded titania films. These films are prepared from TiO_2 nanosols and the silver is formed at room temperature by irradiation with ultraviolet light [Ohko et al. (2002); Kawahara et al. (2005)].

In the case of organic substances showing photochromism the effect can be explained by reversible photo-isomerization processes or photolysis reactions yielding a color change. Many organic substances such as fulgides, thioindigo, stilbene or anthraquinone derivatives show photochromic behavior. Another intensively investigated class of materials undergoing the mentioned reversible photo-isomerization reactions are the spiropyrans. The initially colorless molecules change their color to blue by a light-driven isomerization. An example of isomerization of a spiropyran is shown in Figure 5.9. The so-called leuco form of the molecule shows a sp^3-hybridized carbon that separates the oxazine from another aromatic part of the molecule. By light-induced isomerization the separation of the aromatic parts is broken up and a conjugated system is formed that absorbs visible light. When the irradiation stops, the leuco from will reform.

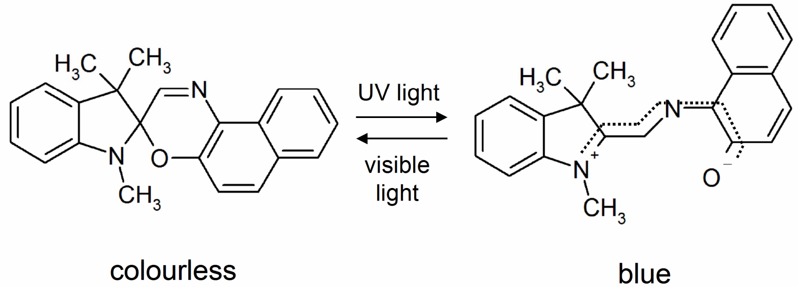


Figure 5.9 Schematic drawing of the photo-isomerization of a spiro-compound changing its color to blue when irradiated with ultraviolet radiation. (Dyestuff: 1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphtha[2,1-b][1,4]oxazine], *Photorome I*).

Sol-gel derived hybrid polymer networks can act as host for such dyestuffs [Hoffmann et al. (1995); Textor et al. (2003)]. Photochromic organic dyes such as the one described here often show poor thermal and photochemical stability. For application onto textiles this stability has to be improved to guarantee a sufficient product life. It is reported that the stability can be improved by embedding the dyestuff molecules into inorganic nanosol matrices. The preparation of nanosols by co-hydrolysis of epoxysilanes and fluorosilanes, or by using methylimidazol thus lead to an enhancement of the photostability [Hou et al. (1994)]. The photochromic effect is also reported to increase by embedding the dyestuffs into such a nanosol matrix [Hoffmann et al. (1995)].

The preparation of photochromic sol-gel coatings for textiles is complex since the dyestuffs are also sensitive to heat, which limits the curing temperatures. At the same time the molecules must be embedded in a way that immobilizes the dyestuff sufficiently, but allows the isomerization as shown in Figure 5.9. If the isomerization is hindered by the surrounding matrix the color shift cannot occur.

The photo-chromic modification of polyester fabrics is described by [Zimehl et al. (2004)]. A hybrid polymer based on (3-glycidyloxypropyl)trimethoxysilane and Bisphenol A in a specified mixing ratio is modified with the spyropyran 1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3′-[3H]naphtha[2,1-b][1,4]oxazine (*Photorome I*). The resulting sol was applied by a simple padding process followed by curing at a temperature below 100°C. Figure 5.10 shows the difference in the transmission of light through the finished textile. A light source was used that emits ultraviolet and visible light. If the UV-light is blocked by a filter we find a higher transmission in the region between 500 and 650 nm, since the colorless leuco form of the dyestuff is predominant. The removal of the UV-filter leads to an increased absorption in the mentioned region, indicating the isomerization.

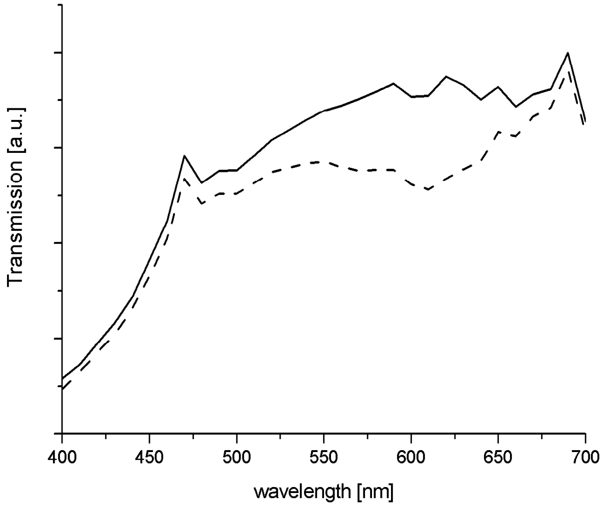


Figure 5.10 Transmission of visible light measured for a polyester fabric coated with a photochromic coating. During the irradiation ultraviolet radiation of the lamp was either blocked by a filter (continuous line) or not (dotted line). Reprinted form [Zimehl et al. (2004)]. With kind permission of Springer Science + Business Media.

To visualize the effect, the photochromic sample prepared was masked with a pattern (forming the letters “NANO”) and illuminated with a UV-lamp. Immediately after the irradiation the pattern was removed and a photograph was taken. A corresponding picture is shown in Figure 5.11. The letters “NANO” appeared during the treatment; without illumination with UV-light the letters will disappear within minutes due to the formation of the leuco form of the spiropyran.

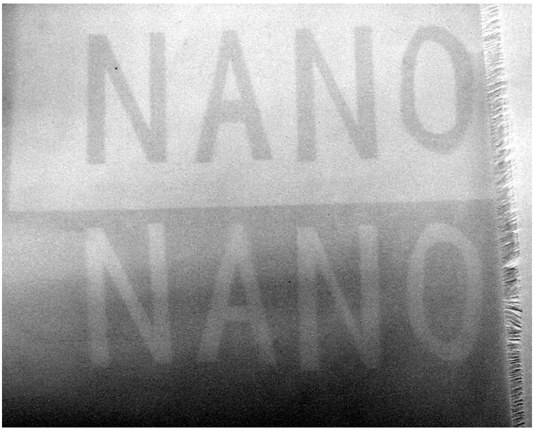


Figure 5.11 Polyester fabric modified with a photochromic nanosol coating. The sample was masked with a pattern (positive and negative) and irradiated with a UV-lamp. Photograph was taken immediately after irradiation, since the color will completely fade within minutes.

Chapter 6

Electrical and Magnetic Properties

Most fibre materials used for textile production are electric insulators. Exceptions are, for example, graphite fibres or metallic fibres that are sometimes worked into a fabric or even used to manufacture complete products. The electrostatic properties of conventional textiles vary extremely, starting with surface resistances in the range of 10^{13} ohm for PTFE-based materials to cotton with approximately 10^{6} ohm under ambient conditions. The broad range of surface resistance of textile materials depends not only on the type of fibre material but also on the topography of the fabric as well on potential substances deposited onto the fibre surface. To give an example Table 6.1 shows how certain production steps can be applied to influence the surface resistance of a textile material. Thermal treatment, for instance, influences the compactness, topography and also hydrophobic properties of a felt might change the surface conductivity within a certain range.

Table 6.1 Surface resistance of different fibre felts. The front and the reverse side of the felt differ due to a difference in thermal treatment during felt production.

Material	Surface resistance [ohm]	
	Front – thermally treated	Reverse – open fibre structure
Polytetrafluoroethylene PTFE	7×10^{13}	7×10^{13}
Polypropylene PP	1×10^{13}	8×10^{12}
Polyester PET	1×10^{10}	1×10^{10}
Polyphenylenesulfide PPS	1×10^{10}	4×10^{9}
Viscose VIS	3×10^{9}	3×10^{9}
Polyamide PA	2×10^{9}	2×10^{9}
Polyacrylnitrile PAN	3×10^{9}	1×10^{9}

As a result of a high surface resistance fabrics can be electrostatically charged, for example, by rubbing, to a level that allows spark formation. Such an electric discharge is not only uncomfortable but it could lead also to damage, for instance, possible damage of electronic (micro-)devices. A safety risk might also arise because of the possible inflammation of explosive gaseous mixtures as a consequence of the spark formation. For these reasons, the treatment of textiles with antistatic agents is carried out for certain applications. Up to now, commercially available products show only low durability, especially with regard to the washing fastness. At the same time the antistatic finishes lower the repellency of the surfaces, resulting in stronger soiling during use.

The use of nanosol coatings to apply antistatic properties is very promising. The combination of antistatic additives with sol-gel derived coatings is expected to yield at least an enhanced fastness of the finishing effect. It was possible to retain the water and soil repellence while attaining the required conductivity. Examples and detailed discussion will be given in section 6.1 below.

Beside antistatic textiles the application of conductive textiles also gained high importance recently [Coyle et al. (2007)]. Conductive textiles are usually defined as having a resistance below 10^3 ohm. Examples are, among others, found in applications for electromagnetic interference (EMI) shielding in clothes or for heating elements used in automobile seats. It has been reported frequently that the constant exposure to comparatively strong electromagnetic fields or a high radiation exposure could cause health problems. For this reason, the protection against electromagnetic radiation, for example, by appropriate working clothes or home textiles such as curtains or blankets is of increasing interest [Stegmaier et al. (2002)]. Another important field of application for conductive textiles or fibres is the development of misleadingly so-called *intelligent* or *smart textiles.* These products integrate microelectronic applications into textile materials, which demands high conductivity, for instance, to transport information [Coyle et al. (2007); Möhring et al. (2006].

[Knittel et al. (2006)] report the development of textile solar cells. Besides the basic challenge of preparing a flexible solar cell on a textile substrate an important problem to solve is to guarantee the transportation of the charge to use the generated electricity.

Electric properties are also related to magnetic properties due to the fact that a moving electric charge produces a magnetic field. Nanosols containing particles made from ferromagnetic materials such as Fe_3O_4 can be employed to prepare (ferro-)magnetic coatings. Nanosized particles below a critical size prepared from normally ferromagnetic bulk materials will show a so-called superparamagnetism. These materials will only show a magnetisation as long as they are influenced by an external magnetic field – without such a field, the magnetisation will disappear without any hysteresis. (The occurrence of superparamagnetism is the reason why the density of data storage media is limited, below a critical size no storage is possible due to the abovementioned effect.)

To summarize, with regard to textile applications of nanosols there are three main topics concerning electric properties: *antistatic, conductive* and *magnetic* or *super-paramagnetic* finishes. These topics will be discussed in the following sections and recent developments for nanosol application on textiles are presented.

6.1 Antistatic coatings

As described above, different fibre materials exhibit very different electrostatic properties. Under ambient conditions a polyester fabric can achieve a surface resistance [according to DIN 54345] of approximately 10^{14} ohm, while a comparable cotton fabric achieves a surfaces resistance of only about 10^{8} ohm [Behr (1991)]. The surface resistance even for different fabrics prepared of a comparable fibre polymer can differ over a broad range, for instance, due to different conditions during fibre production or fabric treatment. As an example, PET fabrics with a surface resistance of up to 10^{15} ohm are reported [Xu et al. (2005b)] but also lower values of 10^{10} ohm are measured for certain PET fibre felts. The differences are strongly influenced by the appearance of the fabric or the surface topography. Measuring the surface resistance of a fabric cannot be compared with measuring the surface resistance of a flat film or a metal sheet. It can nevertheless be generally stated that fabrics prepared from hydrophobic fibre polymers as polyester or from polyolefines fabrics show a higher surface resistance compared with natural fibre materials such as cotton or viscose (Table 6.2).

Table 6.2 Surface resistance of fabrics made of different materials in correlation with the humidity uptake. Measurement were performed at 21°C and 65 % atmospheric humidity [Behr (1991)].

Fabric	Surface resistance [ohm]	Humidity uptake [wt-%]
PP	10^{15}	< 0.1
PVC	10^{14}	0.2
PET	10^{14}	0.3–0.4
PAN	10^{14}	1.5
PA	10^{12}	4
Cotton	10^{8}	8–10
Viscose	10^{7}	10–12

The main reason for the difference in the surface conductivity of different textile materials is in the different water uptake of the materials. Polyester fibre has a water content of below 0.4 wt-%, while cotton retains up to 10 wt-%. The comparably low surface resistance of the natural fibres is due to the conductivity of the water on the polymer surface. As a result of the low amount of water available at the surface under ambient conditions, the polyester can be electrostatically charged to a level that allows the abovementioned spark formation, the cotton cannot. The voltage that can be achieved for hydrophobic fibre materials is in the range of up to 35,000 V or more [Schwab et al. (2007)].

To summarize: a fibre retaining a higher amount of water reduces the problem with electrostatic charging since the water reduces the surface resistance. Besides the chosen material, the electrostatic charging strongly depends on the climatic conditions. During the winter months the relative humidity in buildings is decreased. The problem with spark formation is therefore more probable, since the water adsorbed onto the textile surface strongly depends on the relative humidity in the environment.

Every surface modification such as a hydrophobic or oleophobic finishing will influence the amount of water adsorbed on the fibre surface and therefore also influences the surface conductivity. As a rule of thumb, it can be stated that a surface resistance below 10^9 ohm prevents spark formation. The antistatic properties of textiles are classified by four different ratings. The corresponding ratings, as defined, e.g., by [Behr (1991)] are summarized in Table 6.3.

Table 6.3 Ranking for antistatic properties of textiles in correlation to surface resistance [Behr (1991)].

Classification	Corresponding surface resistance [ohm]
Very good	$< 5\times10^9$
Good	$5\times10^9 - 5\times10^{10}$
Average	$5\times10^{10} - 2.5\times10^{11}$
Insufficient	$> 2.5\times10^{11}$

Depending on the specific use the prevention of spark formation is of different importance. The electric shock which everyone knows when walking over a carpet made of synthetics (especially during the winter month) is mostly more unpleasant than dangerous. Charging of textiles used in industrial environment might become hazardous, since a spark can ignite inflammable materials or destroy sensitive microelectronic components. Now and then newspapers report conflagrations occurring at gas stations or air bags that are activated spontaneously. For filter materials the charging is of importance, since a charged surface can improve the removal of particles and therefore increase the efficiency of the filter. But for other products one has to prevent particles from being attracted by a textile surface, among other reasons, in order to avoid soiling. In the weaving process, during production of fabrics, the weft fibres are moved with extremely high velocities. Friction of the fibres will also lead to electrostatic charging, not only for this reason are the fibres sized. The sizing, by covering the fibres with starch reduces the friction and simultaneously prevents the charging since the starch is able to absorb a sufficient amount of water. The size is removed after the weaving, it is therefore necessary that the starch can be easily removed.

If an antistatic effect has to be guaranteed for long time applications the finishes need to have sufficient durability. Up to now the conventional antistatic finishes do not meet the requirements of a durable modification. Conventional antistatic materials used for finishing work clothes have to be reapplied after a certain number of washing cycles.

Approaches that lead to a sufficient durability are the incorporation of conducting fibres such as metallic or carbon fibres, either during the weaving process, or by subsequent stitching [Marcincin et al. (2005)]. This approach is very complex compared with finishing and more expensive since the handling and incorporation of such fibre materials is more difficult (and sometimes the fibre itself is more expensive). Instead of mixing conventional fibres with conducting fibres, the fibre material itself can be filled to achieve a certain conductivity. By incorporation of, for example, carbon black into the polymer matrix the fibres become conductive if the percolation threshold is exceeded. Alternatively to the incorporation the deposition of metal layers onto the fibres, for instance, by physical vapor deposition or by electrochemical approaches can be employed to achieve conducting surfaces. In addition, the preparation of fibre polymers filled with conductive particles and the application of PVD are comparatively expensive and time consuming approaches in comparison with conventional textile processes.

As mentioned before nanosols can also be used to apply antistatic coatings onto textiles. The antistatic effect is, as previously explained, mostly caused by an increase in the uptake of (atmospheric) humidity caused by a hydrophilic nanosol coating. Due to this, in principle three types of antistatic nanosol coatings should be distinguished.

- purely inorganic coatings, without any further organic modification [Yoneda et al. (1986); Terrier et al. (1995)]
- inorganic coatings, modified by physical embedding of charged or hydrophilic organic additives which increase the humidity uptake, mostly used modifications are charged polymers or surfactants [Matsushita et al. (1990); Roth et al. (1997 & 2000)]
- inorganic/organic hybrid coatings, chemically crosslinked to charged or hydrophilic groups, for instance, formed from ammonium or

aminoalkyltrialkoxysilanes [Haas et al. (1999b); Amberg-Schwab (2003); Xu et al. (2005b)]

Pure inorganic metal oxide sol coatings will not usually increase the surface conductivity because they exhibit a highly insulating behaviour, having no intrinsic conductivity. Nevertheless, even pure nanosol coatings can lead to a decrease of surface resistance after coating textiles, due to an increased humidity uptake by the more hydrophilic coating. Examples are given in literature for combinations of TiO_2 with Al_2O_3 sols [Yoneda et al. (1986)] or for a SiO_2 sol modified with an alumosilicate [Yamada et al. (2004)]. To increase the antistatic effect of these coatings a modification with carboxylic acids or alcohols is however suggested. A sol prepared from neodymium nitrate has also been reported for textile application. In this case, the antistatic effect is expected to be the result of the incorporation of neodymium cations (@Nd^{3+}) into the xerogel network [Kissel (1991 & 1992)]. Pure silica sol coatings will at least only slightly decrease the surface resistance of textiles (Table 6.4). A decrease to values of $R < 10^{10}$ ohm can be achieved by employing appropriate additives [Schottner (2001)]. By modification of silica sols with hydrophilic polymers, surfactants or even alumina the surface resistance of PET fabrics has been decreased to values in range of 10^8 ohm (see Table 6.4), which is a sufficient value for an antistatic treatment regarding the classification given in Table 6.3.

Table 6.4 Surface resistance of polyester fabrics with differently modified nanosol coatings.

Coating	Additive	Surface resistance [Ω]
Uncoated polyester	---	8.2×10^{11}
SiO_2	---	1.6×10^{10}
SiO_2 / PMMA	---	5.5×10^{9}
SiO_2/Al_2O_3	---	1.5×10^{8}
SiO_2	Chitosan	1.6×10^{12}
SiO_2/Al_2O_3	Chitosan	4.4×10^{11}
SiO_2	Hydrophilic polysiloxane	3.2×10^{8}
SiO_2	Fluorsurfactant	1.0×10^{8}
SiO_2	Cetyltriammonium bromide	3.9×10^{8}
SiO_2	Poly (styrene sulfonate)	1.3×10^{8}
SiO_2	TWEEN 80®	2.5×10^{9}

Many examples for antistatic coatings can be found in patent literature. These coatings are mostly realized by simple physical embedding of surfactants or charged polymers into inorganic nanosol-based networks. Selected patents and the antistatic additives used are summarized in Table 6.5. The use of chitosan as antistatic finishing for polyester has been described by [Eom (2001)]. Other results achieved by the authors also employing chitosan prove that a simple mixing of hydrophilic compounds will not necessarily yield improved antistatic properties (compare Table 6.4).

Table 6.5 Overview on antistatic nanosol coatings realized by physical embedding of different additives.

Patent literature	Antistatic additive
Yoneda et al. (1986)	Carboxylic acids or alcohols
Matsushita et al. (1990)	Non-ionic surfactants, cyclic alcohols
Roth et al. (1997 & 2000)	Cationic surfactants, fluorsurfactants, polystyrenesulfonate, celluloseacetate
Kohlert et al. (2004)	Electrically conductive polymers
Chen (2006)	Hydrophilic polymer

With the exception of the application of conductive polymers (which will be described later), the antistatic effect of the nanosol coatings described here mainly depends on the higher humidity uptake at the surface caused by more hydrophilic coatings. A combination of antistatic properties and water/oil/soil repellent surfaces seems therefore to be mutually exclusive. It is expected that a strongly repellent material like PTFE will lose its repellent properties after application of an antistatic finishing. Nevertheless, especially the combination of repellence and antistatic properties is strongly demanded.

The application of three different antistatic nanosols applied to felts made of three different fibre materials is shown in Figure 6.1. It is obvious that the water repellent property of a PTFE felt is decreased by all the nanosols applied. The oil repellent property is only maintained by the nanosol modified with a fluorosurfactant, while the modification with the other additives leads, as expected, to a complete loss of the repellence. It should, however, be stated that with silica/alumina based nanosols antistatic treatments were achieved that simultaneously improved the repellence of the PP and PET felts employed. Nanosol modified with fluorosurfactant can be used to realize oleophobic felts with additionally antistatic properties. These materials are, for example, of special interest for developing industrial filter systems.

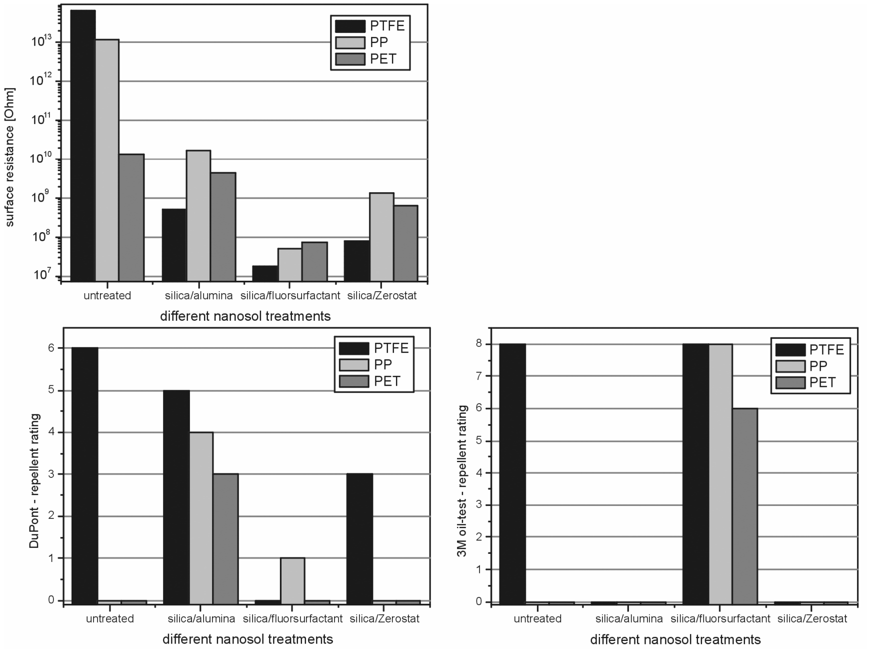
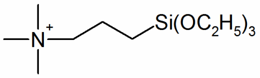
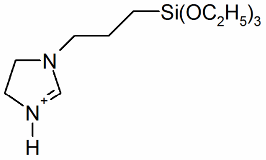


Figure 6.1 Different felts (PTFE, PP, PET) modified with sol-gel derived coatings for improving the antistatic properties – comparison of antistatic and water/soil repellent properties, (Zerostat is an antistatic agent commercially available (supplier Ciba) based on a hydrophilic non-ionic polycondensate).

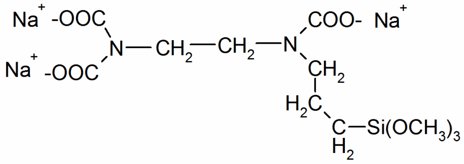
Charged or hydrophilic compounds naturally show a high solubility in aqueous media. For this reason, the antistatic nanosol coatings containing such components are expected to exhibit only low washing fastness. The washing fastness is, however, one of the important properties for textiles used as clothes or home textiles. The chemical or covalent modification of the inorganic nanosol matrix with organic groups exhibiting ionic or hydrophilic functionalities is advantageous with respect to the mentioned durability. The co-condensation of the inorganic nanosols with charged ammoniumalkyltrialkoxysilanes [Haas et al. (1999b)] or with aminopropyltriethoxysilane (APTS) [Xu et al. (2005b)] leads to promising results. Selected useful silanes are depicted in Figure 6.2.



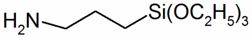
N-trimethoxysilylpropyl-trimethylammonium



dihydroimidazolyl-propyltriethoxysilane



trimethoxysilylpropylethylendiamin-triacetat



aminopropyltriethoxysilane (APTS)

Figure 6.2 Reactive ammonium and aminosilanes employed for preparation of antistatic nanosols [Haas et al. (1999b); Xu et al. (2005b)].

Nanosols prepared from APTS (compare Figure 6.2) can reduce the surface resistance of polyester fabrics significantly. Even after 30 washing cycles according to AATCC Test 135-2000 a reduced surface resistance – compared with the grey sample – can still be detected (Figure 6.3). The figure also shows that the antistatic effect of the APTS coatings is strongly related to the atmospheric humidity. A decrease of the relative humidity from 65 RH% to 45 RH% leads to an approximately tenfold increase in surface resistance.

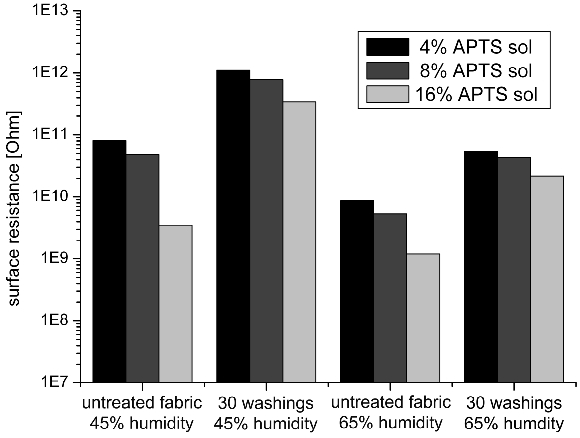


Figure 6.3 Antistatic properties of PET fabrics treated with aminopropyltriethoxysilane sols (APTS sol) of different concentrations. The antistatic properties are determined for the as-prepared and washed samples at different atmospheric humidity (adapted from [Xu et al. (2005b)]. The untreated PET fabric shows a surface resistance of 10^{15} ohm.

Beside charged polymers or surfactants intrinsically conductive polymers could also be used as antistatic additives for nanosol coatings [Wouters et al. (2004); Kohlert et al. (2004)]. Selected conductive polymers are depicted in Figure 6.4. Polythiophene compounds are used for nanosol modification in numerous investigations. Up to now, applications are reported for coatings on plain polymer substrates only, for instance, polyester foils. By using polythiophene as additive, nanosol coatings with a surface resistance of about 10^6 ohm can be achieved as reported by [Wouters et al. (2004)]. Besides using conductive polymers as additives to realize conductive sol-gel coatings the cohydrolysis of precursors such as tetrathiafulvalene (TTF) with siliconalkoxides has been reported [Cerveau et al. (2004); Batail (2004)]. The preparation of intrinsically conductive sol-gel modified fibres (e.g. polypropylene or polyester) by using TTF containing sol-gel coatings has been recently reported [Zlatolas et al. (2007)].

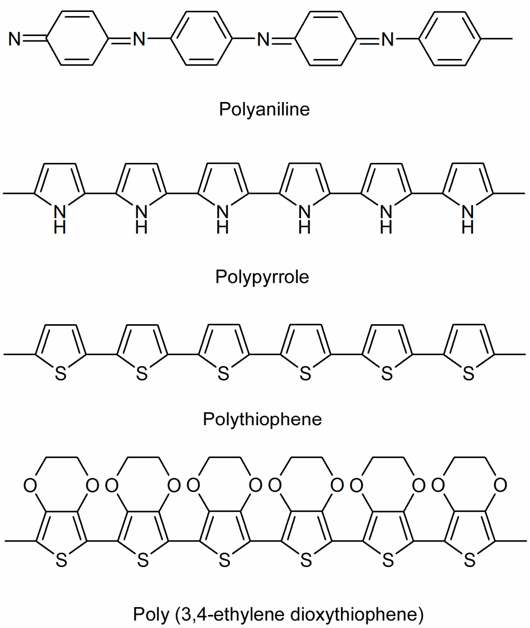


Figure 6.4 Some typical intrinsically conductive polymers (semiconducting form) [Kirchmeyer et al. (2005)].

6.2 Super-paramagnetic coatings for textile materials

The preparation of magnetic coatings or polymers by use of magnetic pigments has been known since decades. Before the cassette recorder was replaced by CD players almost everyone used tapes that contained magnetic metal oxide particles (for example, iron or chromium oxides). The materials had to be permanently magnetized for storing data or music. A very interesting effect occurs if the particle size of these ferromagnetic materials is reduced to a certain value. Below a critical size the particle magnetic properties will change from ferromagnetic to superparamagnetic.

Conventional ferromagnetic materials will be magnetized if brought into a magnetic field. A certain magnetization will remain after the magnetic field is switched off (or if the ferromagnet is removed from the field). This effect occurring for ferromagnetic materials is called the hysteresis effect. Figure 6.5 illustrates the form of a typical hysteresis curve. The curve shows the magnetic flux density B as a function of the magnetic field intensity M that is applied to the ferromagnetic material. If the material was never exposed to a magnetic field, no magnetization can be observed. The first exposure to a magnetic field will lead to a progression along the dotted line. Afterwards changes in the magnetic field intensity will lead to changes in the magnetic flux density along the solid line – the material is permanently magnetized.

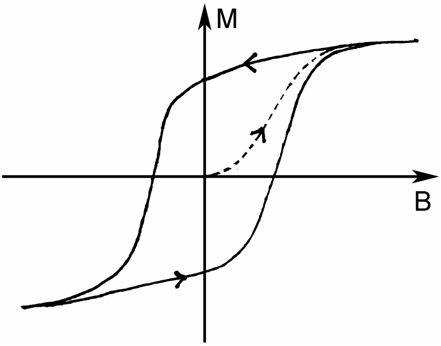


Figure 6.5 Typical hysteresis curve for a ferro-magnetic material.

The permanent magnetization is a consequence of a permanent organisation of the so-called Weiss areas in the ferromagnetic material. Within these areas the magnetic dipole moments of a ferromagnet are parallel. Under certain conditions and if the particle size of the material is reduced to a certain critical size, this permanent orientation of the Weiss areas will not occur.

When particles of sufficient size are brought in a magnetic field, they are magnetized, the magnetization follows the dotted line in Figure 6.5, the Weiss areas will organize. After the magnetic field is switched off this organization will collapse, the material will show absolutely no magnetization, the magnetization will follow the dotted line in Figure 6.5, superparamagnetic materials do not show hysteresis.

For magnetite (Fe_3O_4), a typical ferro-magnetic material, the critical size is approximately 25 nm. Preparation of such particles can be carried out by following classical sol-gel routes or by flame pyrolysis [Chang et al. (1997); Thomas et al. (2006); Raileanu et al. (2007)]. The preparation of superparamagnetic Fe_3O_4/SiO_2 composite particles is possible by using a sol-gel process based on an inverse miniemulsion [Xu et al. (2005d)]. Fe_3O_4/SiO_2 nanocomposites are also prepared by using colloidal Fe_3O_4 particles as additive for a sol-gel process with silica [Raileanu et al. (2007)]. For all synthetic routes one has to guarantee that no agglomeration occurs, otherwise the superparamagnetic properties would disappear.

The example summarized here follows the sol-gel approach to prepare the nano-sized particles and to stabilize them against agglomeration. The preparation of magnetite particles can, for example, be carried out by hydrolyzation of mixtures of iron (II) and iron (III) chlorides under specific conditions [Zorjanovic et al. (2004); Jeong et al. (2007)]. The general reaction is shown in the formula below.

$$2FeCl_3 + FeCl_2 + 4\ H_2O \rightarrow Fe_3O_4 + 8\ HCl$$

A TEM-micrograph of the resulting particles is depicted in Figure 6.6. Note that the iron oxide particle size prepared by the above synthesis is about 12 nm.

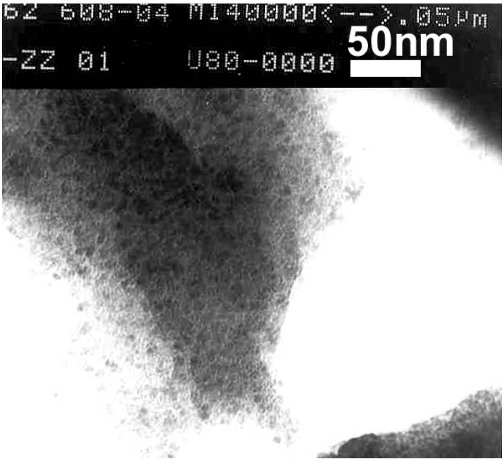


Figure 6.6 TEM-micrograph of iron oxide particles prepared as described above (particle size approx. 12 nm). [Zorjanovic et al. (2007)] reproduced by permission of Koninklijke Brill NV.

Additionally XRD measurements can be used to investigate the crystal structure of the nanoparticles. The X-ray diffraction analysis indicates that the particles depicted in Figure 6.6 consist of magnetite. The signals in Figure 6.7 agree very well with the theoretical values for Fe_3O_4 (magnetite).

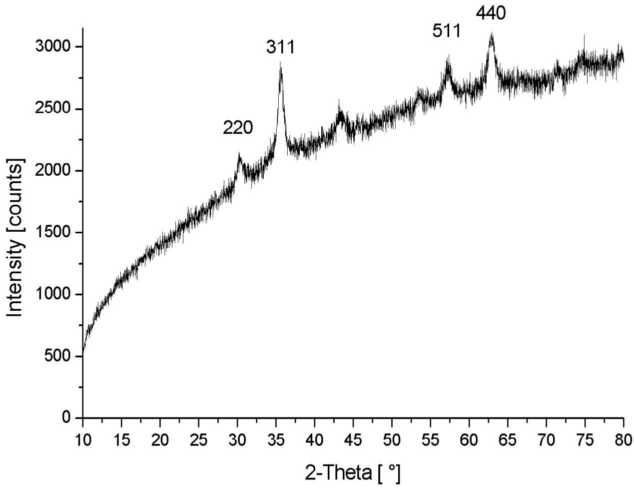


Figure 6.7 XRD-spectra of iron oxide nanoparticles, proving the preparation of magnetite. [Zorjanovic et al. (2007)] adapted by permission of Koninklijke Brill NV.

After washing and redispersing the iron oxide particles with 2-propanol, the dispersions are modified with 3-glycidyloxypropyl trimethoxysilane (GPTMS) to prevent agglomeration. The alkoxysilane is condensed on the particle surface, resulting in a steric stabilization of the particles. This stabilizing step can simultaneously be used for the further preparation of coatings filled with the magnetite nanoparticles. The steric stabilization and the subsequent formation of a three-dimensional network is depicted schematically in Figure 6.8. In a first step hydroxyl groups on the particle surface condense with the alkoxysilane groups of the GPTMS. The GPTMS bonded to the particles stabilizes them sterically. The epoxy-function of the silanes can be used to cross-link the composite e.g. after a coating process leading to a three-dimensional superparamagnetic network.

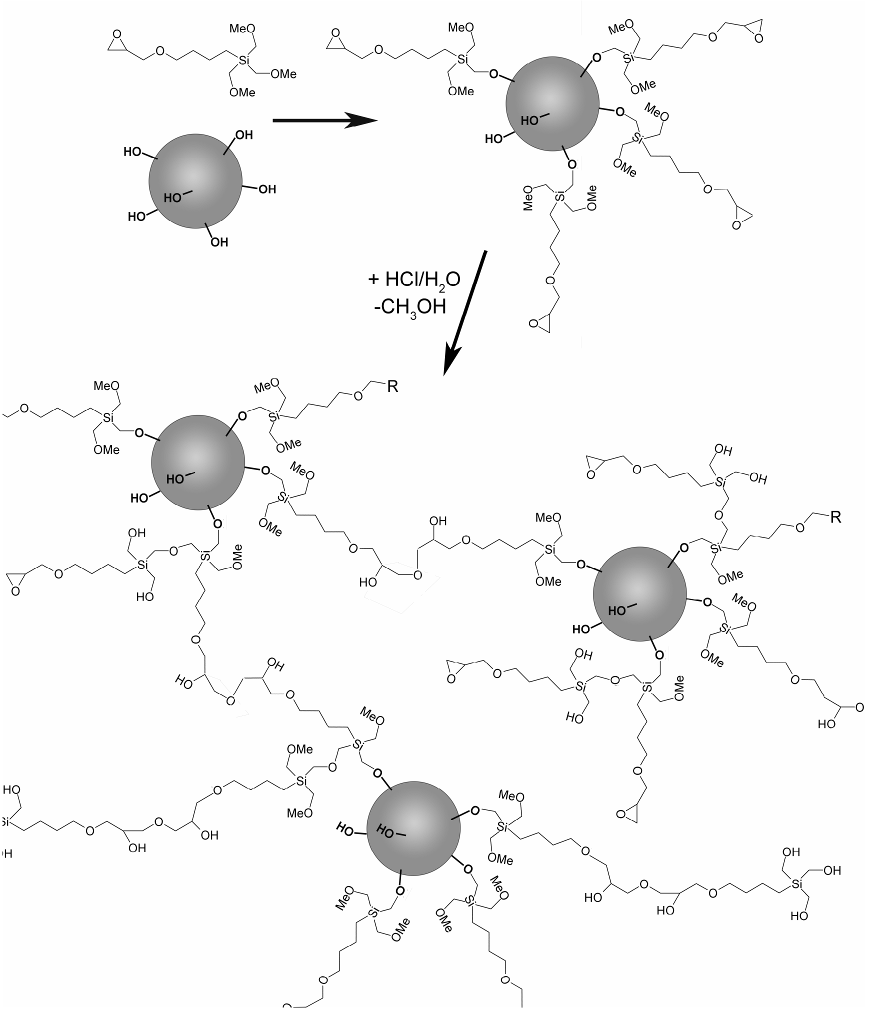


Figure 6.8 Steric stabilization of the iron oxide nanoparticles and subsequent formation of a three-dimensional hybrid polymer network.

To check whether the material produced shows magnetic properties, either the sols or the resulting coatings can be brought in contact with a permanent magnet. As depicted in the photograph in Figure 6.9 a stable sol filled with iron oxide nanoparticles is attracted by a magnet.

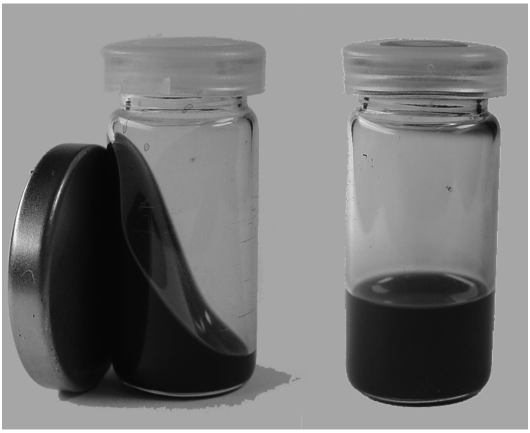


Figure 6.9 Photograph of a sol filled with magnetite nanoparticles. The complete sol containing the magnetic particles is attracted by a permanent magnet.

The pictures presented above prove magnetic behaviour, but not that it is superparamagnetic. The superparamagnetic properties can be investigated by certain magnetization experiments.

The material to be investigated is first cooled down to a temperature of 10 K. A constant magnetic field is applied to the sample (in the experiments described here it was 100 Oe), then the sample temperature is steadily increased to 300 K. The resulting magnetization of the material is measured during this procedure, which is called Zero Field Cooling (ZFC). After the ZFC process has been carried out so-called Field Cooling (FC) is started. The sample is again cooled down to 10 K but the cooling process is now carried out with an applied magnetic field of 100 Oe. The magnetization characteristics of the ZFC and the FC are similar for a material that shows the superparamagnetic effect, they differ as long as the material does not show the effect. By investigation of the curve progression of ZFC and FC experiments the temperature depending appearance of the superparamagnetic behavior can be detected. The temperature above which the superparamagnetic behavior occurs is called the blocking temperature (T_B).

The diagram in Figure 6.10 shows the ZFC and FC experiments for the magnetite powders as well as for a polyester sample that was prepared by embedding the abovementioned powders into GPTMS matrices. In both cases the curve progression proves the superparamagnetic behavior. The blocking temperature calculated for the powder was about 145 K, the T_B for the composite was approximately 95 K. The higher T_B for the powder might indicate a higher agglomeration of the magnetite particles compared to the coating composite proving the concept of stericly stabilizing particles by modification with organically modified alkoxy silanes. The magnetite particles produced here definitely show a superparamagnetic behavior at ambient temperature, other superparamagnetic materials, for example, some of those commercially available show a superparamagnetic behavior at elevated temperatures. Such material can be permanently magnetized at ambient temperature (therefore it will also show hysteresis) and the magnetization could be set to zero again by thermal treatment.

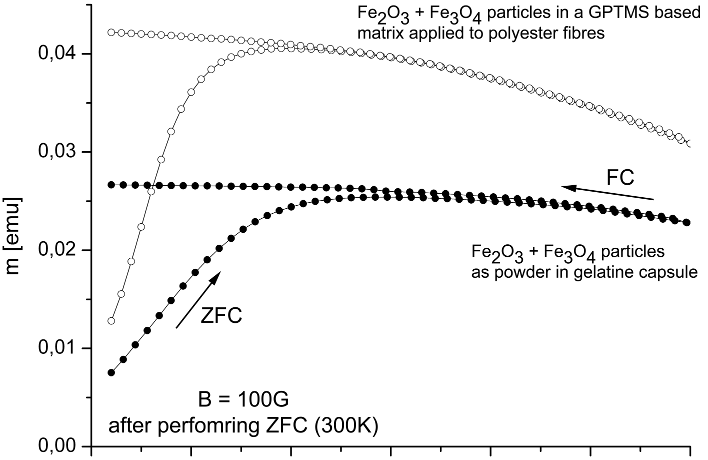


Figure 6.10 Resulting curves of ZFC and FC experiments carried out with a magnetite nano powder and a composite of the same magnetite particles modified with an alkxoysilane, coated to a polyester surface. Blocking temperature (T_B) of the powder sample is approx. 145 K, T_B of the composite material is 95 K. (The work was carried out in cooperation with the group of Prof. Kleemann University Duisburg-Essen, Germany). [Zorjanovic et al. (2007)] adapted by permission of Koninklijke Brill NV.

Chapter 7

Bioactive Nanosol Layers

Bioactive materials have been intensively investigated, especially during the last decade. Sol-gel derived bioactive materials as well as bulk material in the form of thin layers are topics of a huge number of research papers published during recent years. Nevertheless up to now there is no clear definition of what can be described as a *bioactive* nanosol layer. The following section will explain what – from the authors' point of view – should be covered by the term *bioactive nanosol layer*.

The term biocer (*bio*logical *cer*amics) describes inorganic nanosol materials with embedded biological components such as enzymes, proteins or even complete cells [Livage et al. (2001); Betancor et al. (2005); Pierre (2004); Böttcher et al. (2004); Gadre et al. (2006); Nguyen-Ngoc et al. (2007); Smitha et al. (2007); Coradin et al. (2007)]. New composite materials are prepared by embedding biological components into the inorganic xerogels. They then have permanent, or at least temporary, corresponding biological functions.

A more comprehensive definition covers every type of nanosol coating showing any kind of biological function, not only those containing biological materials. This definition would also include inorganic bioactive components such as silver containing nanosol coatings behaving antimicrobially [Mahltig et al. (2004c)], titania coatings interacting with biotin and protein [Huang et al. (2006)] or aluminosilicate coatings improving the biocompatibility [Leivo et al. (2006)]. Furthermore, nanosols modified with organic components exhibiting certain activities can be summarized under the designation

discussed here. An example is the modification of surfaces employing poly(ethylene glycol)s to prevent biofouling.
In general, three different types of bioactive nanosol coatings can be distinguished (Figure 7.1):

Immobilisation: The bioactive agent is completely embedded into the nanosol coating. This is the case for embedded proteins or glycosamines leading to an enhanced biocompatibility of the coated material [Böttcher et al. (1999c); Brasack et al. (1999 & 2000)], e.g., for analytical devices [Arsene et al. (2002)] or for antimicrobial polymer surfaces [Appendini et al. (1997); Kurt et al. (2007)]. Such coatings are of interest, not least for textiles that are worn in direct contact with skin (such as bandages or underwear). To achieve, for instance, high wash fastness the active substances have to be incorporated in such a way that no leaching occurs.

Reaction: Strictly spoken this classification is also a part of *immobilisation*. The bioactive agent is also completely embedded into the coating but it is able to interact, for instance, with reagents available in the surrounding media. An example of this type of bioactive coating is found in the immobilisation of enzymes. When the bioactive composite is brought in contact with the corresponding educts, the enzymes entrapped into the xerogel will catalyze the conversion. Such biocatalytic coatings were, for example, described by [Braun et al. (1990 & 1993); Raileanu (2002 & 2006); Li et al. (2007)]. The immobilization of enzymes is advantageous for several reasons. The enzymes can be removed from the reactor or the products without residues, the product is thus free of proteins and the enzyme can be easily reused. At the same time, the stability of the enzymes might be increased due to the incorporation, which is of interest especially for sensitive (temperature, pH, solvents) and/or expensive enzymes. Another possible field of application that seems to be very interesting is the use of embedded bioactive materials to prepare so-called biosensors [Yao et al. (1995); Wu et al. (2000a)].

Release: The bioactive agent is not permanently embedded but can be released to the surrounding media and therefore interact with biological systems [Böttcher et al. (1997a)]. In this case the nanosol matrix acts as depot for the active substance. Typical examples are nanosol coatings releasing antimicrobial compounds [Mahltig et al. (2004c)] or systems for controlled drug delivery [López et al. (2007)]. An important requirement for preparing such systems is to adjust or determine the speed of the release process. The release must be fast enough to guarantee sufficient effectiveness, but at the same time it must be slow enough to guarantee a sufficient effective period. If such release systems are applied to textiles that are washed leaching or inhibition of the active substance during laundry has to be prevented. All these factors can be adjusted within a certain range by the composition of the nanosol.

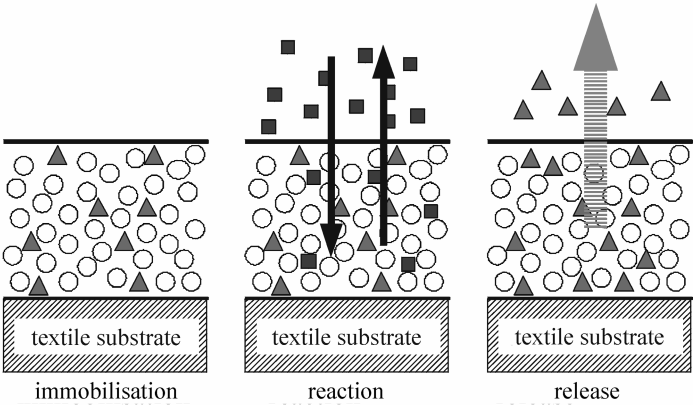


Figure 7.1 Schematic drawing explaining the three types of bioactive nanosol coatings [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

7.1 Antimicrobial coatings

Probably the commercially most important bioactive nanosol systems are at present antimicrobial coatings, also named self-sterilizing coatings [Tiller (2007)] or hygienic coatings [Johns (2003)]. The settlement of microorganisms on textiles is favoured for several reasons. A fabric offers a large and structured surface allowing good adhesion and, for example, excellent water storage properties. With regard to temperature and humidity a textile in contact with the skin offers optimum conditions for the growth of most organisms. For these reasons, there is an enormous demand for antimicrobial finishes, especially for natural fibres with their high water uptake capability [Mathis (2003)].

Antimicrobial coatings on textiles could prevent the degradation of textile fibres, limit the incidence of bacteria, reduce the formation of odour following the microbial degradation of perspiration and protect users by avoiding the transfer and spread of pathogens [Mucha et al. (2002); Höfer et al. (2006a)]. The economic as well as ecologic importance of antimicrobial textiles is therefore significant. The main applications are found for military clothes, medical textiles, but also for sports and leisure wear [Elsner (2006)]. The European market for the abovementioned products in 2003 was already about 28,000 tons, corresponding to 180 million m^2 [Girrbach (2003)] (Table 7.1).

Table 7.1 Application of antimicrobial textiles in Europe 2003 [Girrbach (2003)].

Application	Turnover in million m^2
sportswear	21
outerwear	14
footwear	32
underwear	41
home textiles	34
filling materials	21

With regard to conventional clothing, sports-wear, home-textiles or, for instance, outdoor-textiles like tents or marquees, the antimicrobial property is crucial for convenience and/or optical reasons – the T-shirt should not smell, the marquee should not be mildewed.

For applications in the medical sector the application and development of antimicrobial textiles which act nonselectively are of special importance. Selectively acting microbes will enhance the spreading of multiresistant germs (MRSA), the consequence of which is that ordinary antibiotics will lose their effectivity. The demand for a hygienic environment especially in hospitals will therefore increase even more [Shiotani (2004)]. Antimicrobial finishings for clothes used in hospital or for linen could be an important part to guarantee hygienic conditions.

Another important application of antimicrobial coatings is the employment as antimicrobial wound dressing to avoid the contamination of wounds by any germs [Ovington (2001)]. Simple plasters or bandages could be modified with sufficient nanosols which support the healing process.

Beside the protection against dangerous germs, antimicrobial textiles are used as therapeutic product for relief of several diseases. The therapy of neurodermitic skin can be supported by use of antimicrobial clothes preventing secondary infections by yeast or bacteria [Smolik (2000); Werfel (2001); Johannsson (2003)]. As a result, the need for other drugs such as cortisone containing ointments is decreased, which is especially important for the therapy of the neuroderrmitic skin of children due to the well-known adverse reactions to the pharmaceutical ingredients. Analogously the consequences of diabetes could be reduced by special footwear with antimicrobial properties [Eckardt et al. (2005)].

Commercial products which are already available are made of special fibres with embedded organic biocides such as bisphenols, biguanides or incorporated silver. Other products are blended fabrics with silver-coated nylon (e.g. X-Static^{TM}) [MacKeen et al. (1987)] or chitosan fibres [Knobelsdorf et al. (2000); Knittel et al. (2002)].

Despite this wide range of certain applications mentioned a finishing material that can be employed for every common fibre yielding a defined antimicrobial efficiency combined with a low biocide consumption is highly desirable.

Due to the particular interest in coatings to prevent biocontamination, different strategies to realize an antimicrobial textile by nanosol treatment will be reported in the following sections. Photoactive coatings destroy germs by an oxidation process during light exposure. Nanosol coatings containing nondiffusible antimicrobial additives will be described, or those using the controlled release of embedded biocides. Approaches following these strategies are summarized in more details on the following pages.

7.1.1 Photoactive nanosol coatings

Photoactive coatings can be implemented by application of nanosols containing TiO_2 [Pelton et al. (2006); Zainal et al. (2007)]. Beside the amorphous TiO_2 typically three different types of crystalline titania species are known – brookite, anatase and rutile. A sufficiently high photocatalytic activity is usually only achieved by crystalline titania in the anatase modification [Isley et al. (2006)] but also rutile crystals containing small amounts of anatase have been reported to show photocatalytic properties [Bickley et al. (1991)]. The anatase modification exhibits antimicrobial properties under exposure to daylight or UV light due to photomineralisation or oxidation processes taking place on the semiconductive titania surface [Watanabe (1993); Hirano et al. (2004); Rajagopal et al. (2006)]. Coatings based on mixtures of TiO_2 and SiO_2 are reported as advantageous for antismear, sterilization or deodorizing effects [Chiou et al. (2004); Ohara et al. (2003); Jun (2001); Xu et al. (2005c); Novotna et al. (2007)]. Beside the antimicrobial effect, such photocatalytic coatings could lead to the oxidation of soils deposited on the surface and are therefore used to realize so-called "self-cleaning surfaces" [Bozzi et al. (2005); Qi et al. (2006 & 2007), Textor et al. (2007)].

Different mechanisms are discussed to explain the photocatalytic effect. [Bozzi et al. (2005)] describe two types of reactions. The first proposed mechanism is explained by a direct activation of the titania by the absorption of ultraviolet radiation. The band gap of the semiconductor anatase is 3.2 eV, therefore radiation with wavelengths below 386 nm is absorbed, resulting in the formation of electron/hole pairs. In the presence of oxygen, the electrons in the conduction band are trapped by molecular oxygen from the surrounding atmosphere to form oxygen radicals (Figure 7.2). These radicals are very reactive species that are able to decompose most organic stains as well as biological contamination in subsequent reactions. Another mechanism proposed by Bozzi et al. describes a photocatalytically enhanced oxidation induced by visible light. In contrast with the mechanism described above, this one only explains the decomposition of coloured soils which absorb visible light. The decomposition is initiated by a transfer of electrons in the excited coloured material to the conduction band of anatase. The mechanism is schematically depicted in Figure 7.3. Both mechanisms explain, for example, the degradation of hydrocarbons yielding carbon dioxide and water.

Traces of humidity or water are also reported to be responsible for photocatalytic processes. Since hydroxyl ions are oxidized by transferring an electron into the valence band of the excited semiconductor, thus yielding hydroxyl radicals. These radicals are, just as the oxygen radicals, very reactive species which undergo subsequent reactions, for instance with organic soiling resulting in a degradation of these materials.

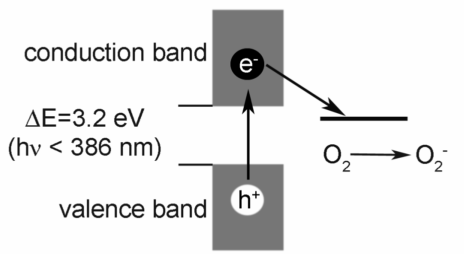


Figure 7.2 Suggested scheme for the formation of oxygen radicals due to the irradiation of anatase with UV light. The formation of the radicals is reported to be one of the initial steps in discoloration of grease due to the UV-irradiation of anatase [Bozzi et al. (2005)].

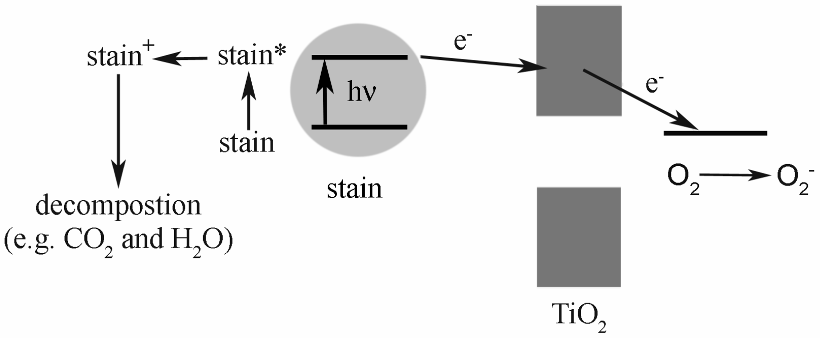


Figure 7.3 Suggested scheme for the discoloration, for example, of red wine or coffee stains due to TiO_2-induced photocatalysis by irradiation with visible light [Bozzi et al. (2005)].

Other titania-based materials with an excellent photocatalytic activity for degrading soils and bio-contaminents are achieved by a preparation of $TiO_{2-x}N_y$ compounds [Yin et al. (2006); Ozaki et al. (2007)]. The nitrogen doping of the titania leads to a narrowing of the band gap due to a mixing of N2p and O2p orbitals, the light absorption of the photocatalytic material is therefore shifted to the visible light range. Analogously, photoactivity induced by visible light is also reported for S-doped TiO_2 crystals [Ohno et al. (2004); Umebayashi et al. (2003); Ho et al. (2006)], N-S-co-doped TiO_2 [Xie et al. (2007b)] and Pt modified TiO_2 [Ishibai et al. (2008)]. All these materials are themselves coloured, which might be a significant disadvantage for functionalisation of textiles materials, since they affect the appearance of the product.

Crystalline nanosized TiO_2 is commercially prepared by the aerosil®-process starting with $TiCl_4$. A highly photoactive TiO_2 achieved by this process is, for example, the Aeroxide P25 (Evonik) containing 80 % anatase [Bickley et al. (1991)]. TiO_2 made by the aerosol process is a powder with a strong tendency to particle aggregation, which might be disadvantageous for several applications. For preparation of a coating agent this powder has to be redispersed and combined with a polymeric or inorganic binder. Embedding of anatase nanopowders into nanosols is also possible. As an alternative, the preparation of TiO_2 coatings of high quality can be carried out by application of TiO_2 nanosols made by hydrolysis of, for example, titanium alkoxy compounds. The coating process from TiO_2 nanosols leads, however, to predominantly amorphous TiO_2 layers, showing comparatively low photocatalytic activity. To reach an enhanced activity the transformation of the amorphous material to crystalline anatase is necessary [Bozzi et al. (2005)].

The transformation of amorphous TiO_2 to anatase is usually performed by thermal (post)treatment at temperatures higher than 300°C [Lee et al. (2005); Barau et al. (2006)] which excludes the finishing of most textile substrates. Woven fabrics made from glass fibres coated with photoactive titania have been reported, they can be used for the decomposition of organic substances. The coatings are prepared at temperatures higher than 200°C [Iwashita et al. (2000); Robert et al. (1999); Horikoshi et al. (2002)]. An alternative method to avoid thermal post treatment at temperatures of several hundred degrees Celsius is offered by the hydrothermal treatment of the amorphous TiO_2 coatings [Yanagisawa et al. (1997); Matsuda et al. (2003); Tadanaga (2006)]. Photoactive nanocrystalline anatase coatings on cotton are produced from amorphous TiO_2 sol-gel films by treatment with boiling water for 180 minutes [Daoud et al. (2004b & 2005c)].

Beside different approaches that demand post treatment of the amorphous TiO_2 coatings efforts have been made to prepare TiO_2 nanosols containing nanoparticles in the anatase modification directly. These nanosols can be used for coatings with highly active surfaces without any additional treatment.

The direct preparation of nanosols containing anatase in aqueous medium has also been described. In this case the anatase formation is supported by the addition of a triblock-copolymer Pluronic P-123 ($PEO_{20}PPO_{70}PEO_{20}$) [Han et al. (2005); Serrano et al. (2007)]. Furthermore a simple *dip-pad-dry-cure* process for treatment of cotton with titania sols is reported by [Qi et al. (2006)].

The nanosol preparation by hydrolysis of titanium alkoxy precursors can be also performed under *solvothermal* conditions (in a pressure-vessel) [Lee et al. (2001); Mahltig et al. (2007); Xie et al. (2007a)]. By this method the thermal treatment necessary for anatase formation is carried out during the hydrolysis of the precursors. A further thermal treatment after the application is not necessary, thus simple finishing of textile materials can be carried out using these nanosols yielding photocatalytic surfaces. Under solvothermal conditions a process temperature of at least 140°C is sufficient to initiate the formation of crystalline anatase, yielding crystalline phases with a size of of about 5 nm (Figure 7.4) [Mahltig et al. (2007)]. However, to enhance the photocatalytic activity significantly the solvothermal process has to be carried out at at least 180°C or in presence of polymeric stabilizers such as the abovementioned Pluronic P123. Even if no anatase phase was determined by X-ray scattering analysis a certain photoactivity of coated textiles was observed (Figures 7.4 and 7.5).

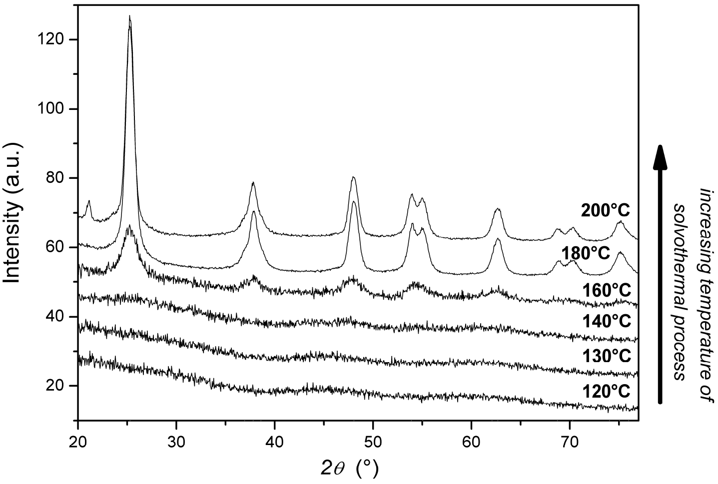


Figure 7.4 WAXS patterns of TiO_2 prepared under solvothermal conditions in presence of Pluronic P123 with increasing process temperatures from 120°C to 200°C. The duration of the solvothermal process is set to two hours (measurement and data evaluation performed by E. Gutmann, TU Dresden).

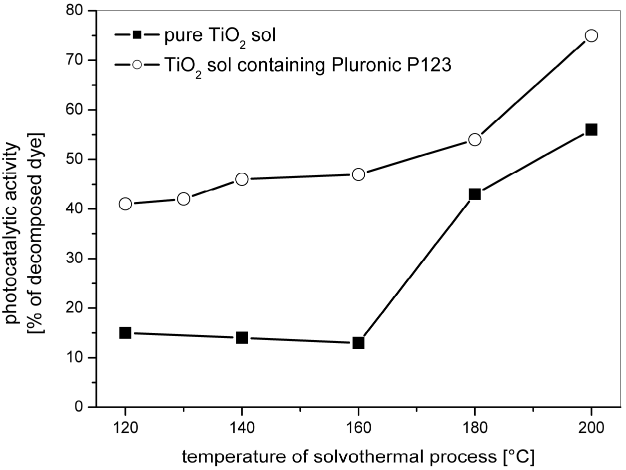


Figure 7.5 Photocatalytic activity of coatings derived from TiO_2-sols prepared by solvothermal synthesis. The sols were applied to viscose fabrics. The photocatalytic activity is determined by the rate of decomposition of the organic dye Acid Orange 7 after 4 hours illumination with ultraviolet radiation [Mahltig et al. (2007)].

Bacteria tests carried out with a cotton fabric treated with a titanium hydrosol. During irradiation the reduction of germs as *Staphylococcus aureus* or *Escherichia coli* was higher than 95 % for the correspondingly finished fabrics. Even after 50 washing cycles the antimicrobial effect was still present [Xu et al. (2006)]. An alternative method could be the preparation of titania by sol-gel synthesis by reflux heating at 95°C. In this way the temperature needed for anatase formation in an additional treatment after the coating process is reported to be decreased to a value of about 220°C. These temperatures could be tolerable conditions for some thermally stable textile materials based on high-temperature fibres, for instance, those used for filter materials [Hart et al. (2007)].

By choosing certain preparation conditions, the formation of anatase is also reported for a synthesis by reflux heating without a further need for thermal treatment of the coating [Yang et al. (2006); Liuxue et al. (2008)]. In this case, especially advantageous is the use of microwave irradiation for heating the reflux, to gain a much higher crystallinity of the anatase phase [Liuxue et al. (2008)]. This fact could be explained by the more effective heating with microwave irradiation. Compared with conventional heating processes, the reactants are directly stimulated by microwaves, so the sintering of the formed TiO_2 particles could be more rapid and effective [Sharma et al. (2001); Peiro et al. (2001)].

A further enhancement of the photocatalytic activity of TiO_2 is reported for anatase combined with SiO_2 [Jung et al. (1999 & 2000)]. The use of SiO_2 or other inorganic materials as binder for TiO_2 particles on cotton fabrics is also quite advantageous for other reasons. The silica binder does not decompose due to the photocatalytic action of TiO_2, as could be expected for organic binder molecules. A silica or any other inorganic matrix could be simultaneously useful to protect a coated textile, since a decomposition of the fibre polymer itself by the photocatalytic effect can certainly not be inhibited. The enhancement of photoactivity of TiO_2 in presence of SiO_2 is proposed to be the result of the reflection of light by the silica component. In case of low film thickness, the ultraviolet light may not be absorbed completely by the titania, so a reflection of the transmitting light by SiO_2 will lead to increased absorption [Langlet et al. (2002); Yuranova et al. (2006)].

The addition of silver is also reported to enhance the photocatalytic activity of anatase [Tran et al. (2006)]. Here the photoactivity depends strongly on the silver concentration and best values are reported for 2–4 mol-% of Ag in TiO_2 films [He et al. (2002)]. It must be stated that the combination of silver with titania does not necessarily lead to an increase in photocatalytic activity, in some cases a decrease for silver containing systems has also been reported. It is expected that the influence of silver strongly depends on the type of organic compounds undergoing the photocatalytic mineralization process [Tran et al. (2006)]. In contrast with the combination with silver, combinations of titania with noble metal clusters, for instance, platinum or rhodium are reported to be more effective [Bickley et al. (1991); Wold (1993); Millon et al. (2007)]. It is concluded that in presence of the noble metal the transfer rate of photoelectrons to the titania surface leading to oxidation processes is increased [Nosaka et al. (1998)] (Figure 7.6).

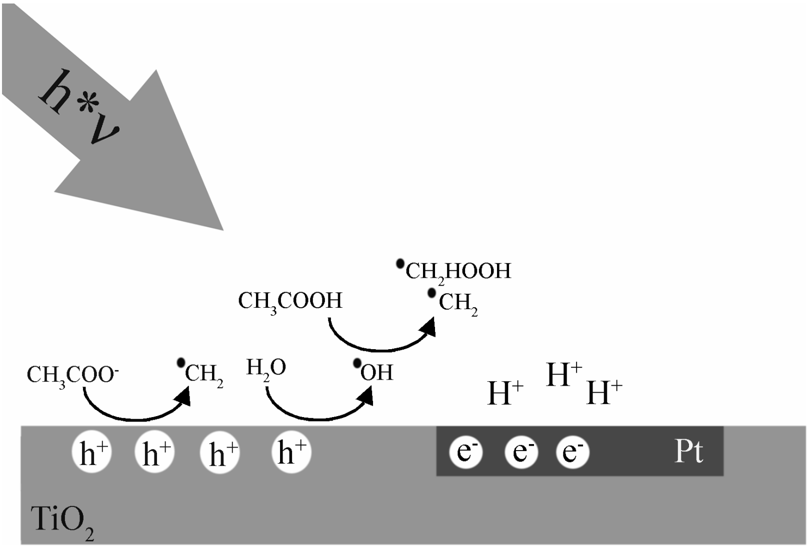


Figure 7.6 Adsorbed organics can be either oxidized directly or can react with hydroxyl radicals near the titania surface (picture adapted from [Nosaka et al. (1998)]).

In the TiO_2/noble metal composite, the generated photoelectrons e^- are transferred and trapped to the noble metal part. The photo-holes h^+

are directed towards the TiO_2 surface (Figure 7.6). In this way the photogenerated charge carriers are more separated and a e^-/h^+ recombination should be less probable. As a result, the quantum yield of the process is enhanced [Kamat (1993)]. Furthermore, an enhancement of the photocatalytic activity is reported for p-doped TiO_2 and CeO_2/TiO_2 composites [Yu (2007b); Yang et al. (2007)] and TiO_2/Fe oxide composites [Yuan et al. (2007)].

An effective way to prepare nanosols with metallised titania particles that can be employed for textile finishing is again the solvothermal process. This method allows a one-step formation of metallised particles by a parallel reduction of the noble metals and the formation of the titania nanoparticles starting from mixtures of the corresponding metal salts and, for instance, titanium alkoxy precursors [Böttcher et al. (2006); Mahltig et al. (2007)]. The so prepared nanosols can be easily applied to textile materials. Thermal post treatment to gain additional reduction of noble metal salts is then redundant.

7.1.2 Nanosol coatings containing nondiffusible antimicrobial additives

A long-term antimicrobial protection for textiles can be realized if nondiffusible antimicrobial additives are combined with an inorganic nanosol coating that guarantees a sufficient durability. A successful immobilization of potentially toxic biocides will simultaneously avoid any transfer of harmful components. Due to the small radius of action such coatings are, however, less effective in cases of extensive contamination. Nondiffusible systems are either realized by direct covalent bonding of the biocide to the nanosol matrix or by a complete embedding of biocidic polymers [Haufe et al. (2005); Andresen et al. (2007)]. Biocides typically used for a covalent modification of coatings derived from nanosols are polycationic components or quaternary ammonium compounds (QACs) (examples given in Figure 7.7).

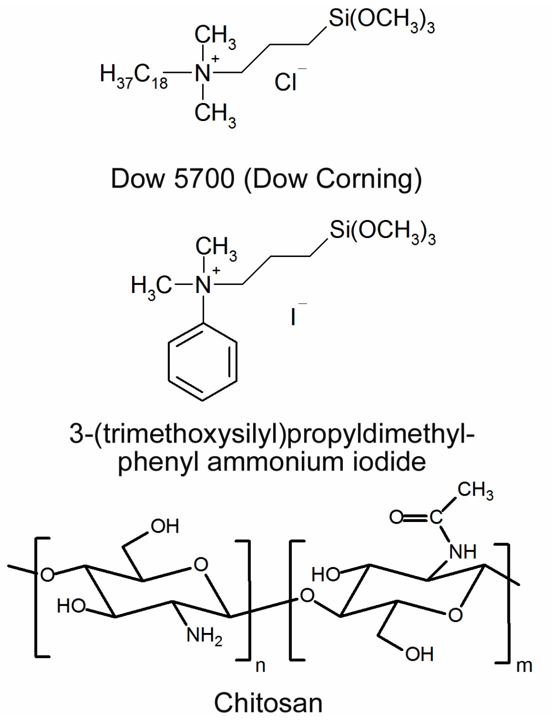


Figure 7.7 Selected examples of organic biocides that can be employed for preparation of *nondiffusible* antimicrobial coatings based on nanosols.

The antimicrobic effect of such materials is explained as follows: the positively charged sides of the biocidal additive interact with the negatively charged microbial cell membranes leading to a leakage of proteinaceous and other intercellular constituents [Chen et al. (1999 & 2000); Kuroda et al. (2005); Ishitsuka et al. (2006)]. The effect might even decrease with increasing alkyl chain length [Klibanov (2007)]. Beside QACs with alkyl side chains, systems with phenyl groups have also been reported to exhibit antimicrobial activity [Marini et al. (2007)] (Figure 7.7). It is well known that in many cases the shape of a biocidic substrate surface strongly influence the activity. Such influences on the biocidic activity have also been reported for sol-gel derived coatings modified with QACs [Brizzolara et al. (2007)]. In fact, to gain an optimal antimicrobial effect by QACs it seems to be necessary to optimize the coating composition with respect to the alkyl chain length of the active compounds, but also with regard to the number of charged groups [Klibanov (2007)]. Such QACs systems are often also described as “nano-daggers”. Effectively acting coatings can be prepared by modifying nanosols with poylcations, here by bonding long-chained tetraalkylammoniumtrialkoxysilanes to a silica-based network. A useful additive is, for example, the Dow Corning product DC 5700 that is depicted in Figure 7.7 [Isquith et al. (1972)]. These compounds can either be applied directly to cotton or polyester textiles, or after prior hydrolysis initializing the formation of a sol. The cohydrolysation or subsequent cocondensation with, for example, tetraethoxysilane can also be carried out to achieve durable and highly effective coatings. Algicidal and antibacterial properties of textiles correspondingly coated are maintained even after repeated washings. Some commercial products are available, for instance, under the label of Microban™ technology. As reported by [Sauvet et al. (2000); Tomsic et al. (2005)] biocidal QACs structures can also be achieved by preparation of sols based on chloro-trialkoxyalkylsilanes and different trialkylamines. The application of these compounds on cotton lead to sufficient bactericidal effects but these coatings are reported to be less effective against fungal contamination. Due to the presence of hydrophobic alkyl chains, the application of QACs is expected to additionally influence the wettability of the treated surfaces [Tomsic et al. (2005)]. Further useful materials employed for embedding antimicrobial polymers are, for example, cationic biopolymers such as chitosan [Knobelsdorf et al. (2000); Lim et al. (2003)], *N*-alkylaldonamides [Maliszewska et al. (2001)] or antimicrobial enzymes such as lysozyme [Appendini et al. (1997)]. Chitosan is a soluble poly(D-glucosamine) with antimicrobial properties that is, among others, employed as textile auxiliary. It can also be easily combined with nanosol based coatings for modification of textile materials [Lim et al. (2003)]. Chitosan is obtained by conversion of non-soluble chitin. Since crustacean shells are basically made of chitin, chitosan is mainly produced from waste material of the sea-food industry – thus chitosan can be regarded as a renewable raw material. It is commercially available with different molecular weights and varying degrees of hydrolysis. The inhibition of the growth of fungi, yeast and bacteria by chitosan-based systems is reported for the acidic pH range [Begin et al. (1999); Rabea et al. (2003); Gerasimenko et al. (2004)]. Besides antimicrobial properties, chitosan-impregnated textiles offer some advantageous dermatological properties such as the support of vascularisation and wound healing, chitosan is at the same time highly biocompatible.

Due to the solubility of chitosan, the application of pure chitosan for textile finishing achieves insufficient durability against washing. Embedding the biopolymer into silica coatings is reported to improve the washing stability and to stabilize the optimum pH range for biocidal action [Haufe et al. (2005)]. Silica coatings modified with chitosan are of particular interest since the antimicrobial composite is completely based on non-toxic and ecologically harmless natural products.

7.1.3 Nanosol coatings with controlled-release of embedded biocides

As previously mentioned, antimicrobial nanosol coatings that act as controlled release systems can be prepared by modification of the sols or by adding the active agents to the precursors used. The active agents are only physically embedded within the sol-gel derived networks. The usually employed agents are non-volatile materials. Thus the release of biocides mostly starts after contact with liquid media.

The preparation of controlled-release systems based on inorganic nanosols has been reported to be advantageous for several reasons. As long as the active agents are embedded within the matrices they are protected against degradation, for instance by environmental influences. The leaching process is at the same time decelerated, the effective period is therefore prolonged [Edge et al. (2001)]. In general, controlled release systems based on nanosols offer a high variability since nearly every inorganic or organic biocide may be embedded. Choosing appropriate biocides is limited by only a few conditions. A sufficient solubility of the biocide in the nanosol solvent is necessary and furthermore possible influences of the active agent for the sol stability have to be taken in account. Taking this into account, a tremendous number of controlled-release systems can be prepared, even immobilized enzymes can be used to achieve an antimicrobial activity [Ibrahim et al. (2007)]. Furthermore, different biocides can be co-immobilized in order to enhance the antimicrobial effect and to diminish the risk of resistance [Mahltig et al. (2004c); Haufe et al. (2005)].

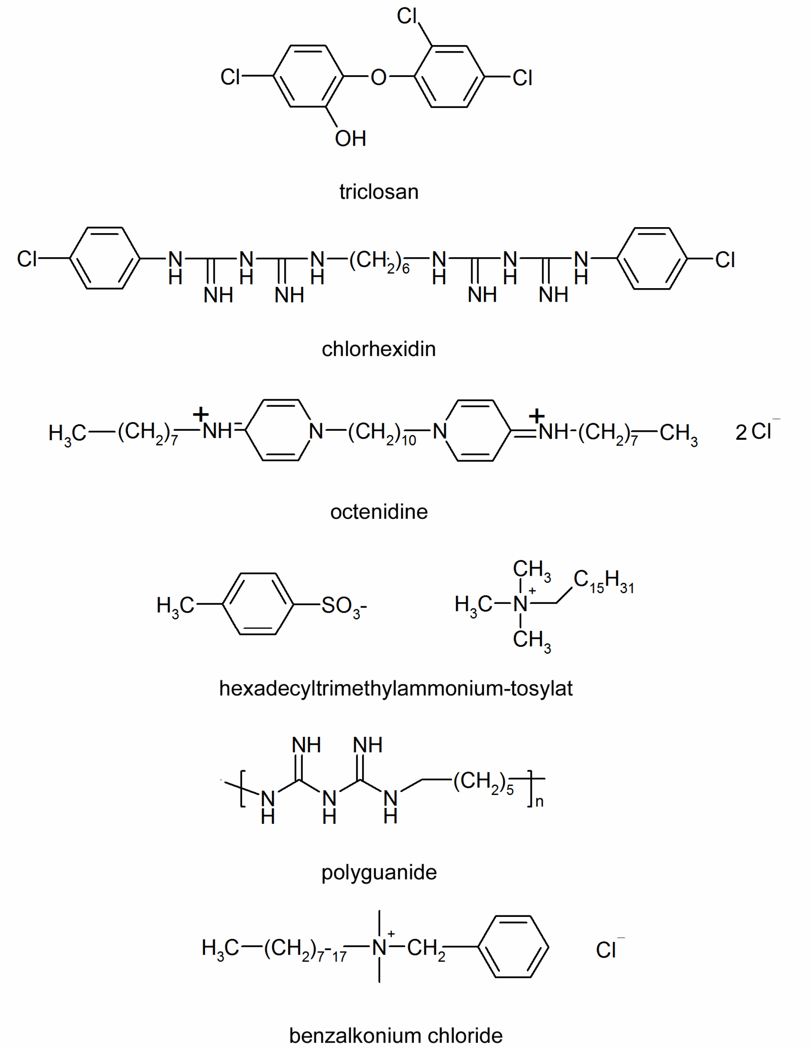


Figure 7.8 Organic biocides useful for preparation of controlled release systems based on sol-gel coatings.

The release of biocides can be controlled by different parameters:

(1) size and solubility of the biocide [Mahltig et al. (2004c)]
(2) the amount of the biocide in the inorganic nanosol
(3) application of polymers or pore forming leachable materials like saccharides; changing the pore structure of the resulting network [Böttcher et al. (1997 & 1999a); Wei et al. (1999)]
(4) additives affecting the polarity of the sol-gel layer, for instance, alkyltrialkoxysilanes

Frequently used organic antimicrobial agents are based on phenols (triclosan), biguanids (chlorhexidine) and QACs as cetyltrimethylammonium bromide (CTAB) or octenidine (Figure 7.8).

Beside the use of organic biocides numerous inorganic biocides are an appropriate tool to destroy bacteria or at least inhibit their growth. An intensively investigated example are nanosized particles of metallic silver [Lee et al. (2003); Blaker et al. (2004); Catauro et al. (2004); Mitterhuber (2005)] or copper [Trapalis et al. (2003a & 2003b)] or metal oxides such as ZnO [Li et al. (2007c)]. Extremely small metal ion concentrations of the mentioned metals are sufficient to effectively damage microorganisms. For silver ions high antimicrobial activity for at least four hours has, for example, been reported at concentrations of only 50 ppb [Cliver (1971)].

The mechanism for the antimicrobial action of silver or other metallic particles has not yet been clarified and is often described as the *oligodynamic effect*. It is stated that not the metal itself but a release of the ionic silver species Ag^+ is responsible for the antimicrobial effect [Lansdown (2006)]. The mechanism is, however, not fully clarified, it is a key point that the Ag^+ ion binds to receptor groups and proteins of bacteria, fungi or yeast.

In contrast to macroscopic silver materials, diffusible cations are formed to a higher extend at the very large surface of metal colloids by atmospheric oxidation in the presence of water [Fan et al. (2002)]. For this reason, nanosized silver particles embedded in inorganic nanosol matrices are expected to achieve higher antimicrobial efficiency compared with thin silver layers deposited on surfaces. Textiles made of cotton or polyester that were treated with nanosized silver particles exhibited excellent antimicrobial effects against gram-positive and (preferably) gram-negative bacteria: only 0.006 to 0.5 ppm are reported to be able to effectively inhibit bacterial growth [Lee et al. (2003 & 2004)].

For textile applications one has to keep in mind that a release of high amounts of ionic silver can also cause skin irritation. It can also be expected that fast leaching of high doses of silver ions will reduce the product lifespan. A proper leaching behaviour is also of particular importance in order to guarantee good washing stability. An appropriate method is to embed colloidal metallic silver in a nanosol matrix. The release rate of silver ions from silver colloids immobilized in an inorganic xerogel is low compared with simple fibre impregnation with $AgNO_3$, but higher than for bulk metallic silver [Lansdown (2006)].

Many different methods have been described in the literature for preparing silver modified nanosol coatings [Steele et al. (1994); Zhou et al. (2000); Mahltig et al. (2004c); Xing et al. (2007b)]. A short overview of different preparation methods is given in Figure 7.9.

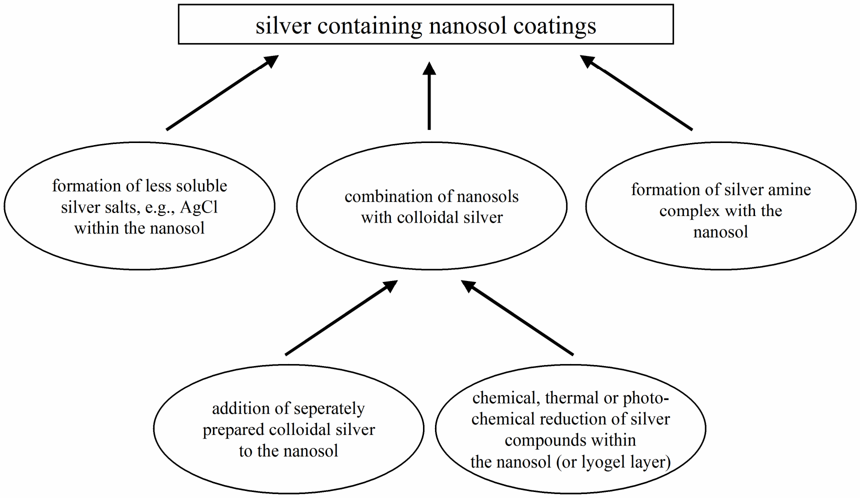


Figure 7.9 Preparation of silver containing sol-gel coatings.

The approach used influences the coating properties significantly; the release of silver and the antimicrobial efficiency have been reported to vary over a broad range. Investigations revealed that nanosol coatings modified with colloidal silver exhibit comparably low rates of Ag^+ release, while coatings with silver amine complexes (from silica nanosols co-condensed with 3-aminopropyl- and N-(2-aminoethyl-3-aminopropyl)trimethoxysilane) show comparably high levels [Suyal et al. (2004)].

In principle three general approaches have to be distinguished for preparation of sol-gel derived coatings modified with metallic silver clusters:

(1) silver colloids separately prepared in a previous reaction are added to an inorganic nanosol [Tarimala et al. (2006)].
(2) silver particles are formed directly within the sol – e.g., from $AgNO_3$ – by using a reductive agent such as ascorbic acid or $NaBH_4$ [Martínez-Castanon et al. (2005); Jiang et al. (2007)] or by the reduction of AgCl by light exposure [Wu et al. (2000b)].
(3) the silver clusters are prepared after the formation of the xerogel, for example by reduction of $AgNO_3$ with hydrogen [De et al. (1996)] or by thermal reduction [Weiping et al. (1997); Kawashita et al. (2000)].

A comparatively simple approach for producing silver-containing silica sol coatings for textiles is the thermal reduction of silver salts within the xerogel after application on the fibre. The decomposition of $AgNO_3$ leading to the formation of silver clusters within silica matrices has been reported to take place at temperatures higher than 300°C [Weiping et al. (1997)]. These thermal conditions certainly exclude most textile materials. However, in presence of reductive agents the process temperature can be decreased to values significantly lower than 200°C. TEM micrographs of as prepare silica coatings with included silver nanoparticles are depicted in Figure 7.10. Corresponding results are achieved by the modification of pure inorganic sols with crosslinking reductive agents as epoxyalkyltrialkoxysilanes [De et al. (2001)].

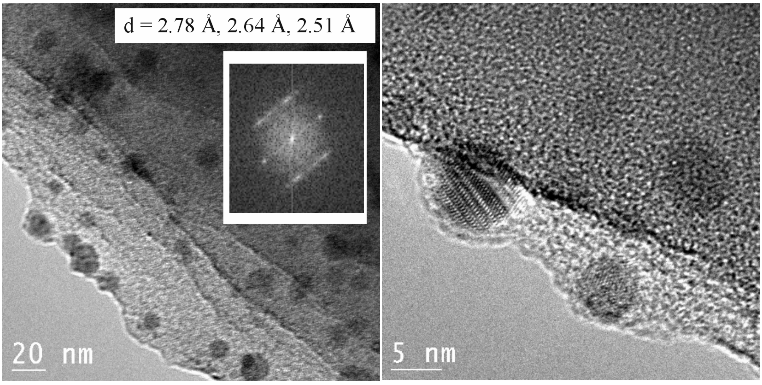


Figure 7.10 TEM images of silver nanoparticles in silica sol based coatings. The silver formation is performed by thermal reduction of $AgNO_3$ (kindly supported by P. Simon, Max-Planck-Institut for Chemical Physics of Solids, Dresden, Germany).

The thermal reduction of silver ions could also be supported by residual alcohol within the gel layer as reported by [Mahltig et al. (2004c)]. These results are similar to the results reported for the formation of silver particles by alcohol reduction in case of employing alkylalkoxysilanes [Mennig et al. (1997); Hah et al. (2003)]. The formation of nanosized silver particles, for instance, on a coated textile can be easily followed by measuring the propagation of the yellow coloration which occurs due to the plasmon resonance of silver [Kreibig et al. (1995)]. The VIS spectra of viscose samples coated with a silica sol modified with $AgNO_3$, followed by different thermal treatments presented in Figure 7.11 exhibit the corresponding propagation of the absorption at about 420 nm. For temperatures higher than 150°C a strong reflection at 420 nm can be observed that occurs due to the formation of silver nanoparticles as a consequence of the reduction of silver ions or of silver nitrate.

The results summarized in Figure 7.12 show that reduction of the silver salt within the networks already occurs at a temperature of about 120°C, but the formation of metallic silver is distinctly accelerated at higher temperatures, as the results for 150 and 180°C show.

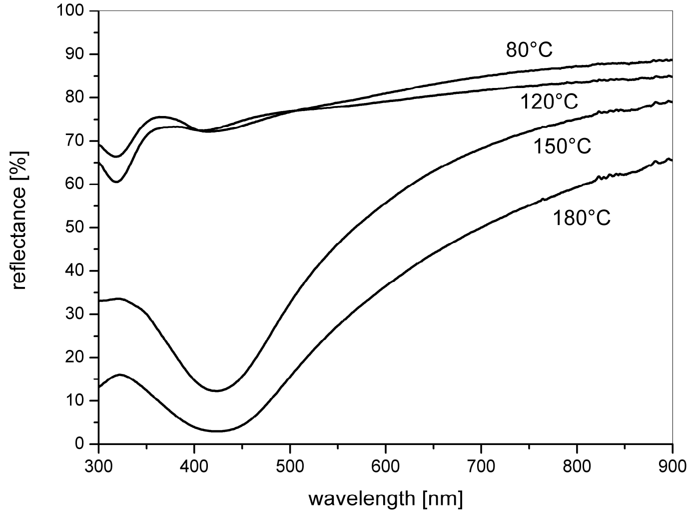


Figure 7.11 Diffuse reflectance of viscose fabrics coated with a silica sol modified with $AgNO_3$ – The thermal post treatment of the coated textile samples is performed for one hour at various temperatures.

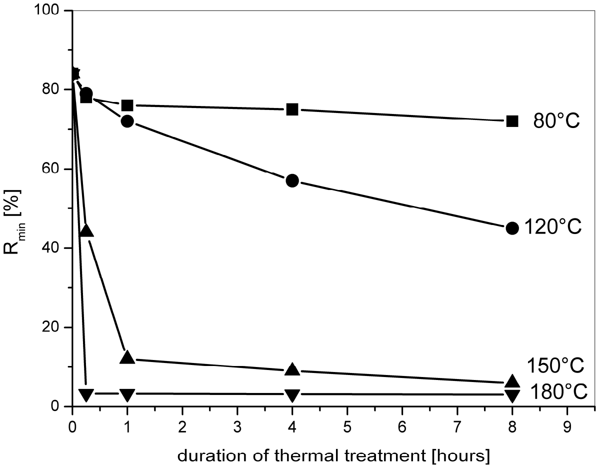


Figure 7.12 Silica sol-based coatings modified with $AgNO_3$ deposited onto viscose fabrics. Reflectance at the minimum of corresponding UV/VIS spectra ($\lambda = 420$ nm) as a function of the duration of the thermal post treatment at various temperatures.

It has been shown that the release rates of silver ions from a silica coating prepared from alcoholic nanosols strongly decreases with increasing annealing temperature and time, which is explained by the above described thermal reduction of silver salts within the matrix starting at a temperature of about 150°C. This is also in agreement with the heat-induced formation of silver nanoparticles at a temperature higher than 120°C observed in silica hybrid films, as reported by [Shibata et al. (2004)].

Due to the slow oxidation of silver appropriately incorporated within the sol-gel matrix, it will take a certain time to release the minimum dose of silver ions that is necessary to guarantee an appropriate biocidal activity. For this reason it could be advantageous to embed silver in combination with organic biocides that exhibit faster diffusion. Some of the common organic biocides were shown in Figure 7.8. Since some of these are delivered as chlorine salts it should be mentioned that these might lower the biocidal activity of the silver due to the well-known formation of silver halides, which have very low solubility. The abovementioned hexadecyltrimethylammoniumtosylate (HTAT) is an advantageous organic biocidal compound for combination with silver-modified sol-gel coatings. By application of nanosols with different biocides not only a delayed antimicrobial activity can be avoided, but the antimicrobial efficiency is also broadened [Haufe et al. (2005)] and the risk of resistance is reduced. As an example, the combination of silver particles and chitosan within porous silica matrices is reported to be advantageous for antimicrobial applications. Such nanosol materials are, for instance, used to develop coatings for non-woven materials used in antimicrobial air filter systems [Nakamura et al. (1995)].

For certain composites the biocidal effect of as-prepared silver modified nanosol coatings is stable for numerous washing cycles (cp. Figure 7.13). Sufficient values with respect to washing stability are achieved with silver particles formed by thermal decomposition of $AgNO_3$. The corresponding products showed an unchanged biocidal activity even after 40 washing procedures. The use of colloidal silver suspension or chitosan in combination with silica nanosols results in coatings with a lower durability, nevertheless these samples maintain a certain activity after up to ten washing cycles.

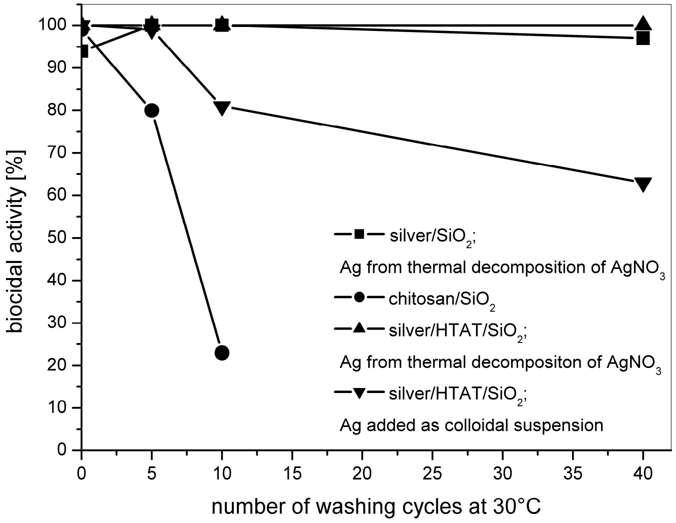


Figure 7.13 Changes in the relative biocidal activity (tested with *E.coli*) of polyamide fabrics treated with differently modified silica sol due to repeated washing procedures at 30°C. Washing was carried out using a domestic washing machine.

With regard to a possible use of the antimicrobial textile materials in hospitals, besides having wash fastness the materials must withstand sterilisation processes. The sterilisation of textiles used in hospitals is usually carried out with hot water steam at 121°C and at a particular pressure. All silver containing coatings presented in Figure 7.13 exhibit an unchanged high biocidal activity after a corresponding sterilisation process. The chitosan containing system shows a certain decrease of biocidal properties, due to partial thermal decomposition of chitosan taking place under the abovementioned conditions.

7.1.4 Embedding volatile biocidal compounds (VBCs)

So far the controlled release systems were based on the immobilization of non-volatile biocides. The release of the biocides embedded within these systems basically occurs in contact with humidity or liquids. By using volatile biocidal compounds (VBC) the biocides are not necessarily released into a liquid medium but also into the adjacent gaseous atmosphere. These systems are therefore discussed separately.

Coatings which release biocides into the adjacent atmosphere are of special interest, for instance, for textile materials used for packageing. During storage or transport of certain sensitive materials the packageing material has to guarantee sufficient antimicrobial protection by releasing biocidal components. A main advantage is that by slow release into the gaseous phase, the surface of the packed material can be protected against bio-contamination without any direct contact.

The preparation of corresponding materials is, for example, reported by [Suppakul et al. (2003)]. SO_2 releasing compounds, allyl isothiocyanate and different natural aromatic oils were immobilized within sol-gel derived networks. Since the porosity of the inorganic matrices used for immobilization can be controlled, the release of volatile materials can also be controlled or delayed within certain limits. This control enables the preparation of antimicrobial coatings employing VBCs which yield a sufficient long-time activity [Haufe et al. (2002)]. Appropriate VBCs must exhibit high volatility combined with high biocidal efficiency at low or minimal inhibitor concentration. Useful biocidal compounds with high volatility are, for instance, organic acids, alcohols, biphenyls, phenol- or cinnamate derivatives (see Figure 7.14).

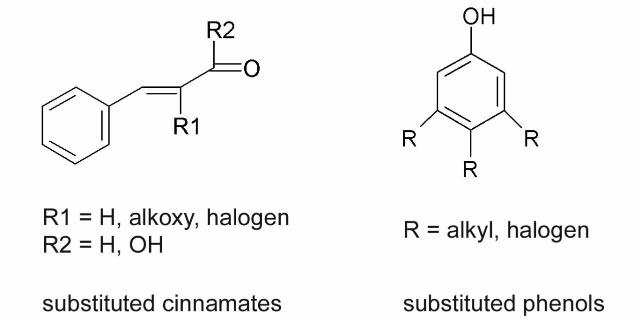


Figure 7.14 Examples for volatile biocidal compounds (VBCs).

Other advantageous substances are biocide-releasing compounds. These compounds themselves are nonvolatile materials, but they release or separate volatile biocidal components such as H_2CO, SO_2 or NO under certain conditions. Suitable compounds are, among others, hemiacetals and hemiaminals.

The release of embedded VBCs from a silica sol-gel coating into the surrounding atmosphere is mainly determined by the vapour pressure and water steam volatility of the VBCs. Other parameters influencing the efficiency of the products are the mass ratio of silica and the VBC, the molecular mass as well as the size of the VBC molecule and the thickness of the coating applied. Accelerated release of the agents can also be achieved by the incorporation of volatile (inert) carriers, such as the terpene derivative borneol, which promotes the release of the biocidal compounds. The antimicrobial effect of such systems has been demonstrated in the use as coatings for cover sheets that are employed to protect potato-dextrose culture plates against fungi *Aspergillus niger* [Haufe et al. (2005)] (Figure 7.15). Such coatings have been successfully tested in practice for the protection of food or wood.

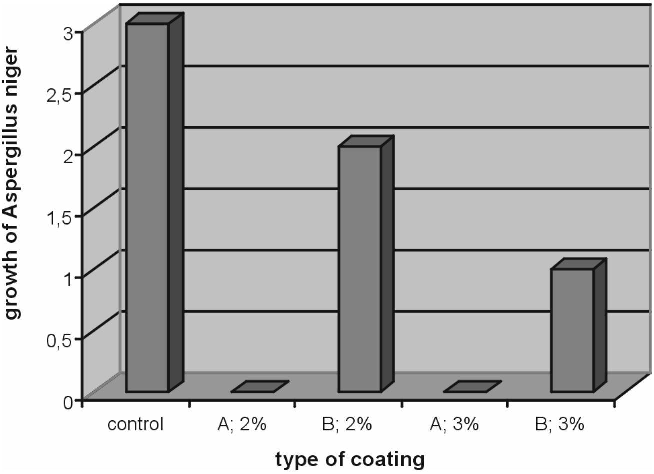


Figure 7.15 Antimicrobial activity – tested against *Aspergillus niger* – of silica sol coatings modified with different concentrations of substituted cinnamates. Cinnamates analogous to Figure 7.14 with A (R_1=Br) and B (R_1=OCH_3). The growth of *Aspergillus niger* is determined on a spatially separated agar plate.

7.2 Oil and flavour releasing coatings

Liquids and oils with boiling points of at least 150°C (but nevertheless having a certain vapour pressure) can be embedded into nanosol matrices and layers. As much as 30 wt.% of the oil (in proportion to the silica) were embedded into xerogels, nevertheless resulting in dry and non-sticky composite materials [Böttcher et al. (1999b)]. The embedding of liquids and oils into sol-gel matrices offers new opportunities for the development of release or delivery systems for flavours and fragrances [Quellet et al. (2001)]. As-prepared systems will delay the evaporation of the flavour due to the embedding of the corresponding oils within the nanosol coating.

In addition to the topic of Chapter 7.1, embedding of biocidal active oils such as perilla oil or manuka oil can also be used to implement antimicrobial coatings [Böttcher (2007); Haufe et al. (2008)]. As mentioned above, the release of entrapped liquids from silica films can be controlled by adjusting the mass ratio of active agent and silica, by chemical modification of the silica matrix or by addition of soluble or swelling pore-forming substances [Veith et al. (2005)].

A two-stage release has been suggested by [Böttcher et al. (1999b)] for the release of the physically immobilized liquids and flavours from nanosol matrices.

(1) A fast initial release, probably caused by the evaporation of the substances from open pores near the surface.
(2) A significantly slower process reflecting the diffusion of the remaining oils or liquids from inside the porous network to the surface.

The immobilisation of liquids within a modified silica sol coating and the controlled release during a possible application respectively use offers new opportunities for the development of highly functionalised textiles, such as:

- medical textiles used for therapeutic reasons such as wound dressings using immobilized highly viscous dexpanthenol for burns, oily α-tocopherol as an antioxidant, or liquid α-bisabolol for spasmolytic and antiphlogistic effects.
- insect repellent textiles: by immobilization of the widely used repellent liquid agents DETA (N,N-diethyl-m-toluamide) and citronella – either the single compounds or both in combination (cp. Figure 7.16 and Table 7.2) [Böttcher et al. (1999b); Tian (2006)].

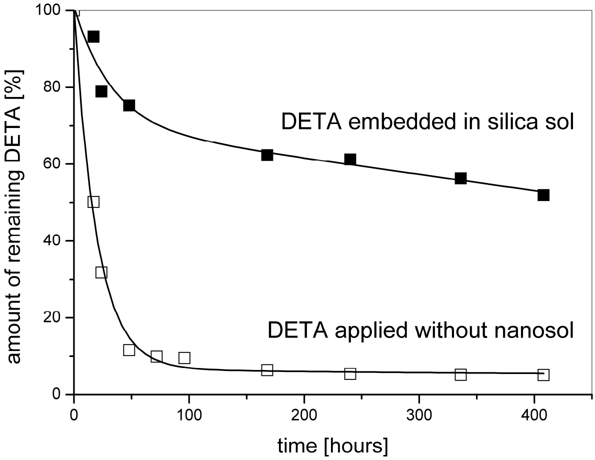


Figure 7.16 Release of diethyltoluamide (DETA) from cellulose fleece; DETA was as well applied as an additive to a silica sol as without the silica nanosol [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

- preparation of fragrance-releasing textiles: for home textiles that increase well-being or as medical textiles to reinforce the medicinal benefit. Essential oils are well known for their various wellness indications such as refreshing, relaxing and relief of congestion. The antimicrobial activity of essential oils and their major constituents have also been reported for the gaseous contact with pathogens [Inouye et al. (2001)]. Many of common ethereal oils, such as lavender, eucalyptus, rosemary or peppermint can be easily immobilized within silica nanosol coatings [Haufe et al. (2008)]. It is furthermore possible to combine different substances and control their release behaviour. For applications such as medical textiles it might be useful to apply the active agent containing nanosol coating only on one side of the substrate. The other side could be covered with a polymer foil, acting as a diffusion barrier. This assembly will guarantee that the release of the active substances can be directed to the skin only and the loss of active substances by evaporation to the surrounding is minimized by the abovementioned barrier [Neubauer (2005)].

Table 7.2 Release of insect repellents from cotton fabrics, either in an air stream or during washing. The fabrics were coated with certain nanosols modified with DETA or cintronella [Mahltig et al. (2005c)].

Remaining content [%]	Silica sol coating		Silica sol coating modified with PMMA	
	DETA	Citronella	DETA	Citronella
Air stream, 18 days	68	35	99	92
Washing, 1 hour at 40°C	9	10	99	97

The embedding and the release of fragrances from nanosol coatings can be improved by combination with certain host molecules co-embedded into the sol-gel matrix. Well investigated host molecules for fragrances are cyclodextrins that are able to form complexes with most of the hydrophobic fragrance molecules. The direct immobilization of these cyclodextrins on fibre materials is well known and meanwhile used commercially [Buschmann et al. (1991 & 2002)] (Figures 7.17 and 7.18). Cyclodextrins are – as the name implies – cyclic molecules based dextrin. Alpha-, beta-, and gamma-cyclodextrin are the known forms that are composed by condensation of six, seven respectively eight dextrin units. The interior spacing of the cyclic molecules (cp. Figure 7.17, 7.18) is comparably hydrophobic (while the exterior is comparably hydrophilic), which explains the complex formation in combination with hydrophobic molecules (in fact even partially hydrophobic molecules can form complexes if the hydrophobic part fits into the interior).

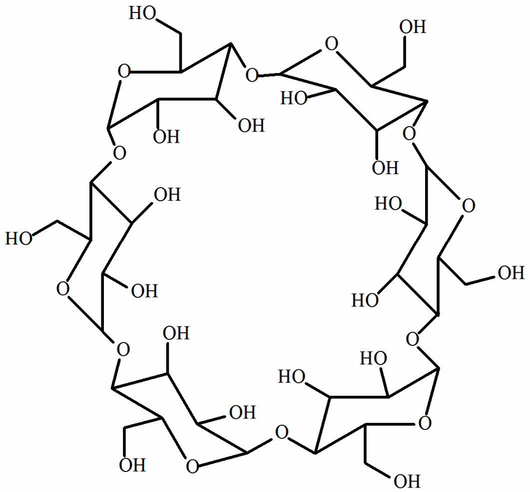


Figure 7.17 Structural formula of α-cyclodextrin.

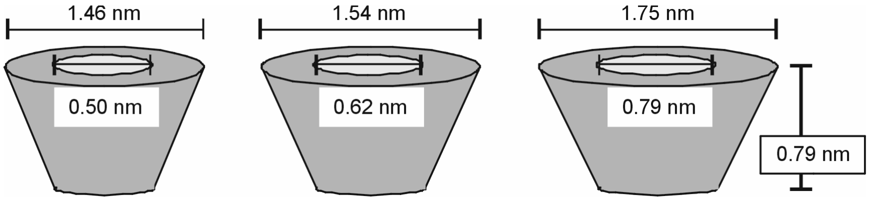


Figure 7.18 Dimensions of α-, β-, and γ-cyclodextrin.

When finishing textile materials with cyclodextrins derivatisation is necessary to achieve suitable durability. A useful alternative to the derivatisation is, among others, the incorporation of cyclodextrin into sol-gel derived matrices. Since the addition of cyclodextrins decreases the nanosol stability it is advantageous to combine the nanosol and the cyclodextrin shortly before the application is carried out [Wang et al. (2006)]. Fragrance molecules will form complexes with the cyclodextrin, thus the release of fragrance is less determined by interaction of fragrance and the sol-gel matrix, but more by the interaction with the co-embedded cyclodextrin – cyclodextrin complexes are very stable. In absence of humidity the fragrances can be immobilized for months or even years. In contact with humidity, for example, in contact with skin the complexes will be destabilized, initiating the release. In contrast with the release systems described above, the release is mainly controlled by the host molecule. An example is given for the release of orange oil in a complex with hydroxypropyl-substituted ß-cyclodextrin [Dreja et al. (2004)]. The combination of cyclodextrins and nanosol coatings could certainly be of interest for the preparation of release systems with improved long term behaviour. Furthermore, the complex formation of the cyclodextrins is reversible, a leached release system could therefore be simply reactivated by treatment of the textile with the corresponding active agent, for instance by spraying, dipping or even during washing by adding the substances during the rinsing process.

For application the fragrances can be either mixed with the nanosol and the cyclodextrins before carrying out the coating process or they can be applied to the already finished textile [Wang et al. (2006)]. For certain substances it could be useful to mix the cyclodextrins and fragrance before adding it to the nanosol. A complex formation before mixing with the sols could improve the solubility of the components. A hydrophobic substance that is insoluble in an aqueous solution can be dissolved in the same solvent if it forms a complex with cyclodextrin.

7.3 Embedding of enzymes and cells

Proteins, enzymes or even intact living cells can be physically embedded into a nanosol coating by simple mixing of the liquid nanosol and the biological component. During the following coating and drying process the biopolymers are incorporated into the developing inorganic matrix of the nanosol layer applied, for example, to a textile surface [Livage et al. (2001); Rodgers et al. (2006); Pastor et al. (2007)]. An interesting application is the use of textiles as substrates for cell growth employed for medical applications [Zolkov et al. (2004)] or *self-repairing* textile materials coated with nanosols containing the cellulose producing bacteria *Acetobacter-xylium* [Böttcher (2007)]. The high specific surface area of textile materials is advantageous for a sufficient yield of growing cells. In addition, the cell adhesion onto a textile could be improved by nanosol coatings leading to an enhanced wettability of the textile material [Zolkov et al. (2004)].

In process engineering the immobilization of enzymes can lead to several advantages compared to the use of free or dissolved enzymes. The immobilization or embedding of the sensitive enzymatic materials can lead to improved pH-stability, higher thermal stability and simpler reusability of the bio-catalysts [Li et al. (2007)]. Basically three different types of immobilization processes are employed for enzymes: adsorption onto a substrate, covalent bonding or embedding into certain matrices [Kuncova et al. (1997); Lin et al. (1997); Opwis et al. (2004 & 2005)]. Compared with adsorption or covalent bonding embedding is an advantageous method for several reasons, it also does not have some of the drawbacks of the concurrent methods. The advantages and drawbacks of the different methods are summarized in Table 7.3 [Raileanu et al. (2006)].

Table 7.3 Comparison of different methods for enzyme immobilization (adapted from [Raileanu et al. (2006)]).

	Adsorption	Covalent binding	Embedding
Preparation	simple	difficult	difficult
Binding force	weak	strong	intermediate
Enzyme activity	intermediate	high	low
Regeneration of carrier	possible	rare	impossible
Cost of immobilization	low	high	intermediate
Stability	low	high	high
General applicability	yes	no	yes
Protection of enzyme from microbial attack	no	no	yes

Attention should be paid to the interactions of the enzymes and the networks. Embedding might, for example, cause a steric hindrance for the enzymes. Since the basically inorganic sol-gel matrices are partially charged an electrostatic interaction between the matrix and the bio-catalaysts has to be taken in account. These electrostatic interactions are mainly determined by the net charge of the matrices determined by the isoelectric point (IEP) of the matrix material and the surrounding pH-value [Livage et al. (2001); Pastor et al. (2007)]. Various proposed interactions between network components and enzymes are schematically depicted in Figure 7.19.

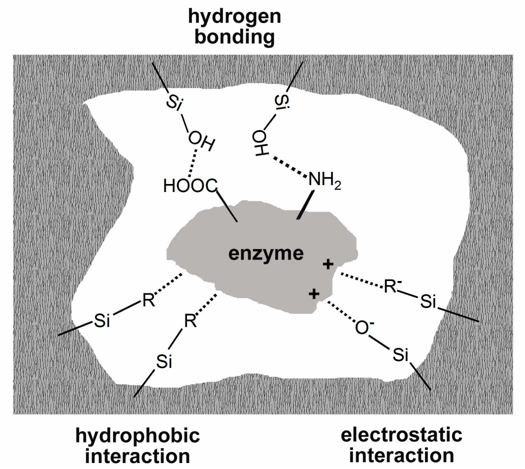


Figure 7.19 Proposed interactions of enzymes with organically modified silica sol coatings [Chong et al. (2004)].

In order to maintain the enzymatic properties after immobilization it is necessary to prevent the denaturation of the enzyme [Braun et al. (1990)]. The immobilization technique applied for soluble proteins has therefore to provide a hydrated environment at a pH-value that does not alter the charge state of the protein [Besanger et al. (2006)]. Thermal treatment after coating deposition should be only performed under moderate conditions. The denaturation of proteins in contact with the liquid nanosol can generally be avoided by a separate two stage application of inorganic nanosol coating and the protein leading to adsorption instead of embedding. An interesting example that has been reported are cellulose nanofibres modified with a titania nanosol coating which is able to bond the organic molecule biotin. Proteins such as *Strepavidin* that are able to bond to biotin can be easily attached to as-coated fibres in an additional treatment with aqueous protein solution [Huang et al. (2006)].

The activity of certain enzymes incorporated in a silica sol layer in appropriate composites was determined to be similar to that of the same enzymes in solution. This proves that highly effective bio-catalysed reactions can be carried out employing enzymes immobilized in a sol-gel layer [Künzelmann et al. (1997)]. Furthermore it was, for instance, demonstrated that the enzymatic activity of *Candida cylindracea* immobilized in co-hydrolysed propyltrimethoxysilane and TEOS coated to a polyester nonwoven is about 2.6 times greater than that of the free enzyme. In addition, the embedded enzyme exhibits higher thermostability [Chen et al. (2002)]. Furthermore, an increase of the lifetime of embedded enzymes has been reported [Rodgers et al. (2006)]. The above mentioned papers show that the activity of embedded enzymes can be optimized by modifying pure inorganic nanosols with appropriately modified organosilanes. The organosilanes also influence the porosity of the nanosol matrix and the enzyme interaction with the matrices (see Figure 7.19). For immobilization of *Penicillin acylase*, an improved enzyme uptake and a high initial activity of the biocatalyst has been reported if the enzyme was applied with a silica sol that was modified with vinyltriethoxysilane [Chong et al. (2004)].

There are several potential textile applications for nanosol coatings modified with enzymes:

(1) sensors, analytical systems for detection of organic compounds
(2) antimicrobial coatings by embedding of enzymes achieving corresponding properties
(3) enzymatic decomposition of biologic soils as soya cream, milk or blood
(4) Usage of (bio-)catalytic fabrics in industrial processes. The textile guarantees an optimal flow rate in a reactor, while the immobilization also guarantees a protein free product and frequent reusability.

Beside the immobilisation of enzymes, embedding of intact living cells, for instance, of bacteria and fungi has been reported [Coiffier et al. (2001); Böttcher et al. (2004)]. These biomaterials can be used as sensors for instance, in case of immobilisation of luminous *E. coli* [Premkumar et al. (2001)] or as catalytically active coatings [Fiedler et al. (2004)]. For successful preparation of such coatings it is necessary to maintain the cellular activity to a maximum extent, there are therefore some essential restrictions for the application of the sol-gel process to immobilize living cells.

The preparation of nanosol coatings modified with living cells is restricted to aqueous nanosols containing a minimal amount of organic solvents. The cells have to be added after the sol preparation is completed. A thermal treatment of the coatings with a temperature higher than 40°C will normally destroy the biological material, thus curing conditions cannot be compared with conventional application of sol-gel coatings. Curing at higher temperatures can only be carried out employing so-called extremophilic respectively thermophilic biomaterial. An overview in which thermophilic proteins are introduced is given by [Sterner et al. (2001)].

Besides observation of fundamental conditions such as an appropriate pH-value, moderate processing temperature and aqueous solvents, the use of several additives is helpful in preserving the viability of embedded bacteria cells. Additives such as glycerol [Nassif et al. (2003a)], polyvinylalcohol [Nassif et al. (2003a); Samuneva et al. (2004)] or gelatine [Nassif et al. (2003b)] can act as matrix softener, humidity preserver and as pore-forming agent – leaving certain pore structures after leaching. They furthermore suppress the cell lysis and therefore considerably prolong the viability of embedded cells.

In most air-dried biocers almost all vegetative cells are destroyed due to shrinkage of the inorganic silica gels occurring during evaporation of the solvent (compare Chapter 1.4). The addition of glycerol to the silica nanosol reduces the mechanical stress during the formation of the xerogels. Bacteria embedded in silica gels modified with glycerol remain viable for more than one month [Nassif et al. (2003a)]. A further improvement of the bioactivity can, for example, be achieved by co-embedding of nutrients.

As for the preparation certain restrictions have also to be fulfilled with respect to the storage conditions. Low temperature, sufficient humidity and the sufficient nutrients are most important to keep the cells embedded in a nanosol matrix alive [Premkumar et al. (2002)]. In case of embedded algae species sufficient light exposure is also necessary to keep the cells vital [Nguyen-Ngoc et al. (2007); Fiedler et al. (2007)].

Even though the preservation of the cells is mostly desired, damaged or dead cells can retain a certain activity, since, for instance, enzymes that are part of these microorganisms may maintain their activity. Embedding of cell extracts can therefore also be used to prepare enzymatically active coatings. This approach is often advantageous since it needs less effort with regard to the preparation and storage of the modified nanosols. For this reasons the use of cell extracts could be an advantageous alternative compared with embedding of the complete living cells.

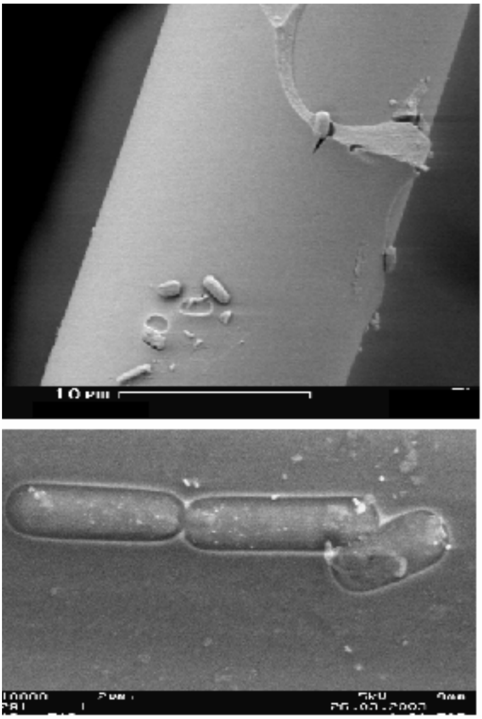


Figure 7.20 Nanosol coating containing the viable bacteria *Bacillus sphaericus NCTC 9602*. The coating was applied to a carbon fibre felt. Images prepared by scanning electron microscopy (images kindly supported by M. Mertig, Max Bergmann Center of Biomaterials, TU-Dresden, Germany).

The embedded cells are mutually separated with a small volume fraction and are randomly distributed [Fennouh et al. (2000)] within the coating. At higher cell concentration the cells will be in direct contact to a higher extent and can therefore interact and eventually form colonies of fibrous aggregates. A variation of the packing density of the microorganisms within the biocer layer could also influence the metabolic activity significantly.

Small bacteria as *Bacillus sphaericus* have been fully embedded in a comparably thick silica nanosol coating. A certain number of cells will be near the surface of the coating. These bacteria will therefore be observed as an elevation on the almost smooth nanosol coating. Mechanical treatments such as ultrasonic treatment can remove the surface near cells, leaving an imprint of the formerly embedded cell on the surface (Figures 7.20 and 7.21).

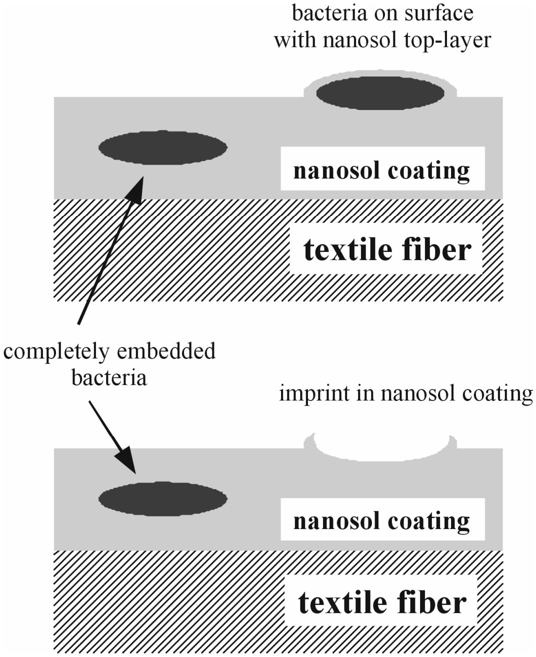


Figure 7.21 Schematic drawing of bacteria embedded in a nanosol coating, before and after mechanical treatment.

Larger cell species such as certain algae might be thicker than the nanosol coating itself or even thicker than the treated textile fibre. In this case the surface structure is determined by the algae, nevertheless the nanosol layer is responsible for the algae's immobilization (Figure 7.22).

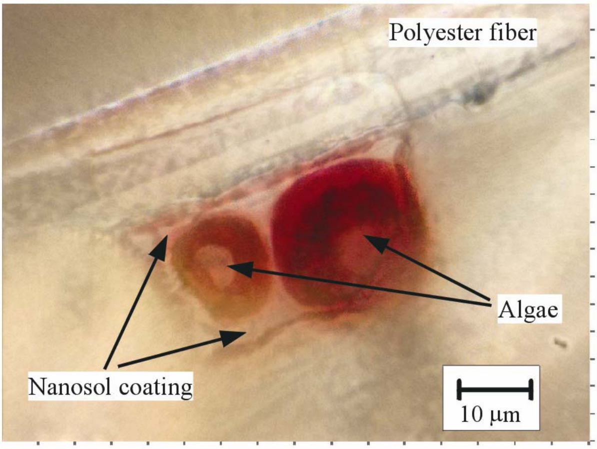


Figure 7.22 Light microscopy image of an algae containing nanosol layer applied to a polyester fibre felt.

The viability of embedded microorganisms allows transformation from a stage of metabolic rest (as a spore) to the active form (as bacteria germinating from a spore, or growing hyphae of fungi). For practical use of bioactive coated textiles it is useful if metabolic activity can be enabled after storing the material for a longer period of time (from some months up to several years). It has been shown that spores retain their metabolic functions after immobilization within sufficiently dried biocers This is either observed for bacteria such as *Rhodococcus rhodochrous* and for fungi such as *Aspergillus versicolor* [Fiedler et al. (2004)]. The cell growth usually occurs near the surface of a coating where the growing cells find additional space by escaping through pore channels to the surface or by partial buckling or delaminating of the covering silica nanosol material. The porosity of the material therefore plays an essential role for the (bio-)activity of the resulting coatings. The size and distribution of mesoscopic pores determine the velocity of the mass transport necessary. A sufficient macroscopic porosity is an essential requirement for germination of microorganisms within the biocer matrices. The pore size can – as mentioned several times above – be controlled by use of alkyltrialkoxysilanes, by co-embedding of leachable additives (for example, sorbitol or other saccharides [Künzelmann et al. (1997)], surfactants [Tan et al. (2006b)] or, for instance, polyethylene glycol [Conroy et al. 2000)]. These methods allow one to vary the mesoscopic as well as the macroscopic porosity of the biocer material sufficiently.

Chapter 8

Applications

Due to the manifold different types of modification of textile materials gained by nanosol finishing, there is a tremendously high number of potential applications. Great efforts have been made to develop nanosol treated textiles for commercial products. They are especially rewarding in fields where either new or particular textile products could be developed that were unrealizable with conventional finishing. Most innovative products are intended for medical applications. However, beside new biological properties also new material properties could lead to new products. This chapter presents two very interesting nanosol applications of textiles close to development as commercial products. One of these examples are medical textiles, the other example is a special technical textile for protective clothing, namely bulletproof vests.

8.1 Wound dressing

Textile wound dressings such as plasters or bandages are widely used for medical applications. In order to protect the wound from environmental influences it is necessary for the healing process to cover it.

Therefore, the first and the main task is the effective prevention of infection [Ovington (2001)] and on a longer time scale, the prevention of cronic wounds [Wollina et al. (2003)]. The prevention of infection is basically effected by the textile dressing itself working as barrier. Beside this an antimicrobial agent can be applied to the wound dressing to actively eliminate hazardous germs near to the wound. Many antimicrobial dressings based on inorganic and organic biocides have been recently developed. Two of the most important biocidal reagents are silver and silver containing compounds. There are fibres coated with metallic silver [Yin et al. (1999)] or polymer coatings filled with silver-releasing zeoliths [Schink et al. (1999)]. According to [Blaker et al. (2004)] silver doped coatings are helpful for tissue engineering and wound healing applications. Silver coated textiles for the therapy of atopic dermatitis have also been reported. Atopic dermatitis is a chronic inflammatory skin desease which is typically accompanied by a *Staphylococcus aureus* colonization of the skin. The antimicrobial properties of silver coated textiles can significantly reduce the burden of *Staphylococcus aureus*, results in a positive effect with respect to the atopic dermatitis [Haug et al. (2006)]. Due to the demands for repeated use in hospitals this silver textiles and their biocidal effect have to be stable not only against laundering at 90°C but also against water steam sterilisation at 121°C. These demands are also fulfilled by silver containing nanosol coatings (as described in Chapter 7) but in contrast to conventional silver textiles the nanosol systems can be easily applied on any kind of textile material. Costs could therefore be lower compared with products employing metallic silver fibres or those prepared by electrochemical deposition of silver.

Although silver modified textiles are of greatest commercial interest, the use of nanosols to create new medical wound dressings could in future be applied in other fields. One important topic is the acceleration of wound healing by embedding active substances in a nanosol coating applied to a wound dressing (Table 8.1). Active substances such as dexpanthenol can be released from the nanosol coating to the wound in a controlled manner and enhance rebuilding of the skin. The temporary immobilization of penicillin in nanoporous silica coatings is also possible. A controlled release of penicillin could prevent the infection of wounds. Furthermore compounds with higher molecular weight such as oligopeptides could be used as a growth factor or for deactivation of protease and would be useful in this way to support the wound healing process. Even the release of polymeric compounds such as dibutryrylchitin or chitin has been reported to accelerate wound healing [Pielka et al. (2003)].

Table 8.1 Potential substances for enhancement of the wound healing process.

Therapeutical aim	Active substances
Growth of edge of wounds	Dexpanthenol; dithranol
Acceleration of wound healing	Growth factor, e.g. insulin
Deactivation of surplus protease	Bromelain; inhibitors of trypsin
Prevention of infection	Penicillin; stryptomycin; chitin and its derivatives

It is unquestionable that wound dressings are necessary for wound protection and to support healing. However, the use of wound dressings leads also to certain disadvantages and a nanosol coating may compensate them. In general, textile wound dressings adhere to the healing wound, so during removing of the dressing the already healed wound might be damaged again and the healing process prolonged. This is a problem especially in case of chronic wounds such as *decubitus*. Appropriate materials for immediate pain control and easy replacement are wound dressings containing hydrogels [Cartmell et al. (1994); Kokabi et al. (2007)]. Hydrogel wound dressings are, however, more expensive compared with traditional dressings. In addition, one has to keep in mind that the use and storage of hydrogel-based systems is more critical since the hydrogel has to be kept wet permanently. An alternative, simple and less expensive dressing is realized by modification of conventional wound dressings with sol-gel coatings.

Ordinary textiles based on viscose or cotton can be easily modified by nanosol coatings to produce new wound dressings which do not adhere strongly to the healing wound [Mahltig et al. (2002); Höfer et al. (2003)]. For this application, silica nanosols are modified with hydrophobic alkyltrialkoxysilanes to generate the antiadhesive properties of the textile. The adhesion between an as-coated textile and the wound can be easily tested with a wound-model (developed at the Hohensteiner Institute, Germany) [Höfer et al. (2003)] (Figure 8.1). In this model the textile to be tested is placed on a fibrin layer (of approximately 5 mm thickness) on a glass substrate. During the removal of the dressing both the adhesive force and the amount of protein residue on the glass are determined. Optimal parameters for an antiadhesive wound dressing are low adhesive force and a high amount of protein left on the glass substrate. The adhesive force is determined by the type of textile material used, and by the hydrophobic component of the nanosol coating and, most important, by the concentration of the nanosol used. Some examples for the adhesive forces achieved by differently treated hydrophobic materials are given in Table 8.2.

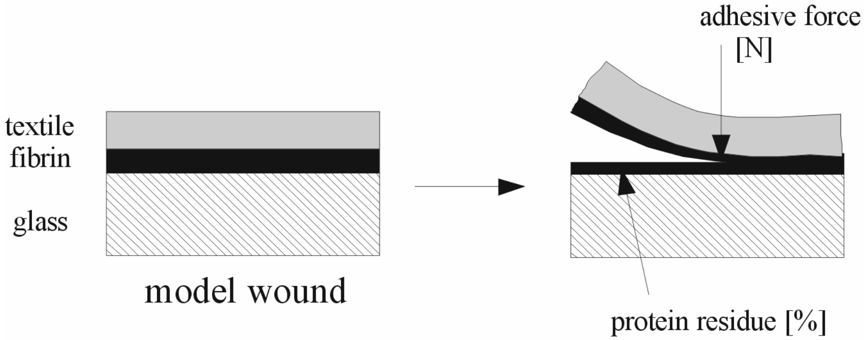


Figure 8.1 Schematic drawing of the setup for measuring the adhesive force between a wound dressing and a model wound (made of fibrin) (developed by Hohensteiner Institute – Germany) [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

Table 8.2 Examples for the adhesive force for typical textile materials used for wound bandages and hydrophobically modified silica sol coatings on them [Mahltig et al. (2002)].

Hydrophobic component of the sol	Fibre material	Adhesive force [N]
Grey fabric / viscose	Viscose	0.40
Butyltriethoxysilane	Viscose	0.12
Octyltriethoxysilane	Viscose	0.18
Hexadecyltriethoxysilane	Viscose	0.14
Perfluorooctyltriethoxysilane	Viscose	0.15
Grey fabric / cotton	Cotton	0.89
Phenyl/methyltriethoxysilane	Cotton	0.59
Perfluorooctyltriethoxysilane	Cotton	0.44

Beside the type of hydrophobic component in the nanosol the concentration of the nanosol employed is an important parameter for the antiadhesive improvement of wound bandages. One has to take in account that an increasing nanosol concentration will yield an increased stiffness of the dressing, which lowers the convenience considerably. One has to find a compromise between the antiadhesive properties and the tolerable stiffness. To evaluate the influence of the nanosol concentration, antiadhesive silica sol coatings modified with hexadecyltriethoxysilane were applied on viscose wound dressings with increasing nanosol concentrations (solid contents from 0.3 to 3.3 wt.%). Compared with the uncoated viscose textile, the adhesive force to the model wound is significantly decreased and a minimum is determined for a sol concentration of 0.9 wt.%. Compared with the uncoated viscose the protein residue on the glass substrate is also increased for the coated samples (Figure 8.2).

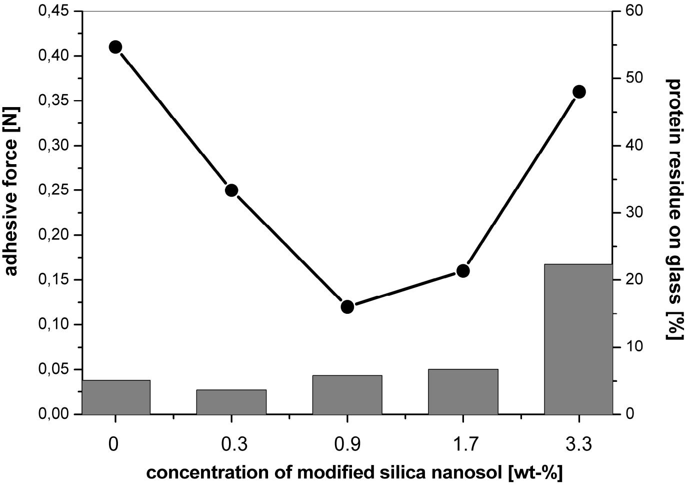


Figure 8.2 Adhesive force to a model wound (line) and the protein residue (bars) on the fibrin-coated glass substrate after removing of the viscose wound dressing coated with silica nanosols with increasing concentrations (Measurement performed by A. Kiel and M. Sverew, Hohensteiner Institute, Germany) [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

The water uptake was in addition determined for the nanosol coated viscose (Figure 8.3), resulting in a decreased water uptake with increasing sol concentration, which is in good agreement with the results presented in Chapter 2. It can nevertheless be guaranteed that even antiadhesive (hydrophobic) wound dressings can absorb at least a certain amount of liquid from the wound. This is of great interest for practical applications, because most common used antiadhesive dressings are not able to absorb the exudate of wounds. It seems that the sol-gel technique offers great opportunities to convert ordinary wound dressings such as viscose bandages into dressing with antiadhesive properties comparable with commercial antiadhesive products, but with improved absorption properties for the wound exudate.

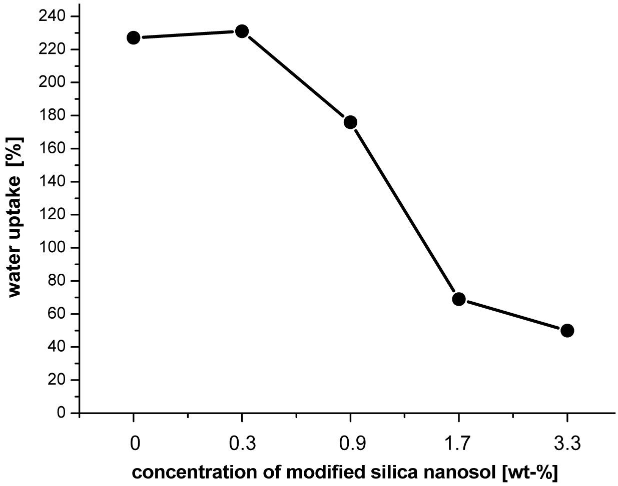


Figure 8.3 Water uptake of viscose wound dressings with modified silica nanosol with increasing concentrations [Mahltig et al. (2005c)] reproduced by permission of the Royal Society of Chemistry.

8.2 Protective textiles – bulletproof vests

Protective clothing is an important product group of technical textiles. High performance fibres based on materials as p-aramide (Kevlar® or Twaron®) or high density polyethylene (Dyneema®) are characterized by an enormous tensile strength. The tensile strength of, for example, p-aramide is about 2900N/mm^2. Due to this high strength the fibres are used for the production of bullet-proof vests. A stack of about 30 layers of p-aramide fabrics (mass of fabrics: ∼200 g/m^2) is able to stop a projectile from most conventional handguns.

While the vests protect against bullets, it will unfortunately not sufficiently protect against stab weapons like knifes. Statistically, the threat of being attacked with a knife is much higher than the risk of being shot, especially in Western Europe, since it is more difficult to obtain a gun. Several approaches are used to improve the stab resistance, such as the incorporation of metal foils, ceramic plates or chain mails.

A vest has a weight of typically 5–6 kg. A bullet-proof vest offers low clothing physiological comfort, it is stiff and it is comparably heavy. The acceptance of the vests is therefore limited. The incorporation of the above mentioned materials to improve the stab resistance will increase the weight significantly and it will usually also increase the stiffness. All these aspects lower the acceptance even more.

When a ballistic material is hit by a bullet the fibres will be mainly stressed in direction of the fibre axis and due to the enormous tensile strength the bundle of fabrics is able to stop the projectile. Interestingly, the fabrics will fail if soaked with water, but after drying it will recover its protective properties. A blade penetrating the fabric has two main effects. The first is that it is able to displace the fibres, the second is that it cuts fibres. (It is unfortunate that the p-aramide fibre exhibits only a comparably low strength perpendicular to the fibre axis.)

If the displacement is a problem one might think that it could be enough to fix the fibres, but a certain mobility of the fibres is necessary otherwise the ballistic properties are weakened dramatically.

Nanosols can be used to improve the stab resistance. [Textor et al. (2004, 2006)] developed a sol-gel based approach. They modified p-aramide fabrics with sols that were based on an organically modified alkoxysilane, an organic crosslinker and nano-sized alumina particles. Such coatings are known to be comparatively hard. Nanoparticles were embedded into the sol following different approaches. Commercially available alumina particles (Aluminiumoxide C®) were redispersed by simple ultrasonic treatment or by more complex reflux heating with an organically modified alkoxysilane before mixing. The other approach was based on the preparation of an alumina sol that was added to the above mentioned silane based sol. The fabrics were coated by a simple padding followed by curing for one hour at a temperature of about 130°C.

The German as well as the British police have similar specifications for testing the protection against stabbing. The modified fabrics were tested in a particular stab resistance test, slightly modified but generally according to the specifications. This test is carried out as follows: A standardized knife is connected to a missile, that is guided by a pipe. This missile falls down from a certain height, whereby the height is adjusted to a level guaranteeing a force of 25 N when hitting the fabrics. A stack of 20 fabrics is placed on a block of plasticine below the pipe. The setup of the test is depicted below for a better understanding (compare Figure 8.4).

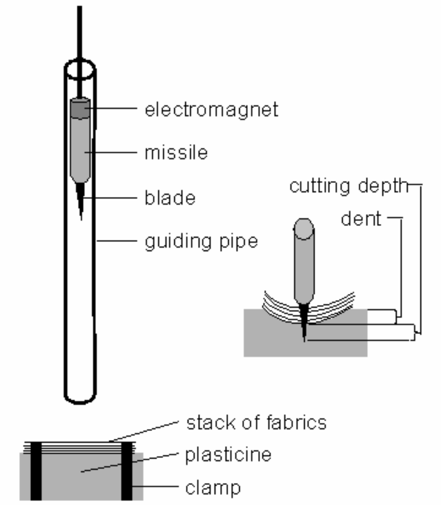


Figure 8.4 Setup for testing the stab-resistance of a bullet-proof vest according to the specification of the German and British police.

Two conditions are crucial for a stab resistant material. The first is that the blade may not cut into the body. The above mentioned specifications allow – maybe surprisingly – a penetration of the blade of 20 mm. From the medical point of view a cutting depth below this level will not cause life-threatening injuries. In addition, the specification investigates the deformation of the body during the attack. Since a temporary impression of the corpus of more than 20 mm might also cause deadly injuries, the dent in the plasticine measured in the test must not exceed 20 mm. To pass the stab-resistance test the dent as well as the cutting depth must be below 20 mm.

Table 8.3 Results of the stab-resistance test for differently coated p-aramide fabrics. The applied coatings differ in the way, the alumina nanoparticles are introduced into the coating sol.

	Layers	Cutting depth [mm]	Dent [mm]
Redispersed by ultrasonic treatment	20	27.0	1.2
Redispersed by reflux heating	19	15.0	19.5
Redispersed by reflux heating	23	14.9	3.7
Mixing with alumina nanosol	20	9.5	5.4
Mixing with alumina nanosol	19	13.7	5.9

The results presented in Table 8.3 show how complex the problem is, since both values have to be observed and changes improving one of the results might downgrade the other. If the fabrics become very stiff due to the coating, the dent is very small, but at the same time the cutting depth might be too high to meet the demands. This problem occurred for coatings that were prepared by a simple ultrasonic treatment for redispersing the alumina particles. The sols that were alumina modified by redispersing the particles by reflux heating lead to more flexible coatings, achieving better results. The dent and cutting depths met the required values, although the dent depth was only slightly below 20 mm. An increase in the number of p-aramide layers certainly improves both values but is not desired, since it would raise the costs and the weight, and lower the comfort still more. The best results were obtained by applying the sols that were prepared by mixing the sol based on the organically modified silane and the organic crosslinker with an alumina nanosol (another advantage using an alumina nanosol instead of nanopowders might be seen in the fact that no dispersion is necessary). Twenty layers of the modified fabrics pass the test with excellent results, and even after reducing the number of layers by one (which means saving 5 % in weight) the required values are met.

Ballistic tests had to be carried out following the stab resistance test, since an improved stab resistance is worthless if the ballistic properties can not be guaranteed. For testing the ballistic properties stacks of 30 layers of the ballistic fabrics are fixed on a block of plasticine and the stack is shot at from specified distances (10 m as well as point blank) and at specified angles (90° and 25°). Selected results of these tests are presented in Table 8.4. While the grey fabric passes the test without failure, the coated fabrics show different results. The coatings prepared with alumina particles that were redispersed by reflux heating showed promising results, while the other samples mostly failed the test.

Table 8.4 Results of the ballistic test for a differently coated p-aramide fabric. The applied coatings differ in the way that the alumina nanoparticles are introduced into the coating sol (all tests were carried out at distance of 10 m and at an angle of 90°).

	Sample	Number of tests	Number of failures	Number of intact layers (if test was passed)
Grey fabric	A	6	0	11–21
Mixing with alumina nanosol	B	6	4	7–8
Redispersed by ultrasonic treatment	C	4	3	9
Redispersed by reflux heating	D	6	1	15–23

An explanation for the failure of the samples can be given by changes in the force to pull out threads from the fabric due to the applied coating. Figure 8.5 shows the corresponding values. While the grey fabric has a very low pull-out force the samples B and C (compare sample names in Table 8.4) show an enormous increase of the force. Sample D also shows an increased value but much smaller compared with B and C. As mentioned at the beginning of this section the limitation of the mobility of the single fibres within the fabric leads to a decrease of the ballistic properties. When hit by the bullet the kinetic energy of the projectile is dissipated by stretching the fibre as well as by displacing it [Stein (1981)]. If the fibre is fixed against the displacement this will results in a decrease of the bulletproof properties. To guarantee a sufficient ballistic protection the number of p-aramide fabrics packed in the stacks would have to be increased. Since this would, as mentioned above, lead to an increase in weight (and certainly costs) further developments will still have to be carried to succeed with a transfer to commercial use.

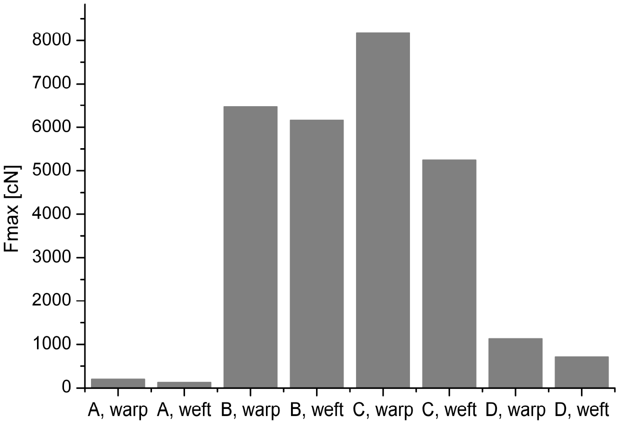


Figure 8.5 Force to pull out threads from the fabric measured for differently treated p-aramide fabrics (Sample names are corresponding to those given in Table 8.4).

[Tan et al. (2005)] reported about another approach. They impregnated a plain-woven fabric with silica colloids with an average particle size of approximately 100 nm in order to improve the ballistic limits of certain armour systems. They carried out ballistic tests, mainly with the moist fabrics immediately after impregnation. They reported an increase in the ballistic properties of the fabrics. Interestingly they observed comparatively strongly increased ballistic limits for two or four ply fabric systems after impregnation. The ballistic limits increase up to approximately 40 % compared with the untreated samples. Drying the impregnated samples decreased the ballistic limits but nevertheless silica dispersions of certain concentrations yield better results than the untreated fabrics. The results of [Tan et al. (2005)] show a strong dependency between the changes in the yarn pullout load caused by the impregnation and the ballistic limits. A certain increase of the load seems to correlate with better protection. Unfortunately the described improvements can not be detected for multiply samples with about 30 layers as necessary for a ballistic body wear with sufficient ballistic protection. Six ply systems show already decreased ballistic limits.

Beside the improved stab resistance other aspects might be of interest for p-aramide based systems. As described above, a fabric soaked with water looses its protective properties. The p-aramides are very hydrophilic, thus they quickly soak up high amounts of water. Hydrophobic finishes based on nanosols following the approaches explained in Chapter 4 allow one to increase the water repellence. Sufficient modifications of the coatings used to improve the stab resistance with small amounts of hydrophobic components as presented in Table 8.5 might yield better ballistic protection in wet conditions. The hydrophobic sols shown lead to a drop penetration time of more than one hour as well as excellent results in the DuPont tests. At present the p-aramide stacks used in bullet-proof vests are wrapped in waterproof foil, which is one of the reasons why a ballistic protection vest offers extremely poor clothing physiological comfort, since the vests are impermeable to air. A breathable vest that does not fail in contact with humidity would be an enormous technological advance.

Table 8.5 Drop penetration time (water) and results of the DuPont-Test for p-aramide fabrics treated with a basic hybrid polymer sol (based on glycidyloxypropyltrimethoxysilane) modified with certain amounts of hydrophobic compounds.

Hydrophobic component	Share referred to the basic sol [vol. %]	Drop-penetration time [s] TEGEWA-Test	DuPont-Test (8 is best)
Grey fabric	---	0	0
n-propyltrimethoxysilane	1.6	> 3600	4
Tridecafluoro-1,1,2,2-tetrahydrooctyl-triethoxysilan	0.7	~ 3600	8
n-Octyltriethoxysilan	9.0	> 3600	3–4

As with many other fibre materials the p-aramide fibre has comparatively bad UV-resistance. If the material is not stored in the dark it will change its color within a short time, indicating photochemical reactions which degrade the polymer. A longterm exposure to ultraviolet radiation would therefore most probably destroy the ballistic properties of a p-aramide fabric, since it would lead to a decrease of the tensile strength. Nanosols modified with UV-absorbing nanoparticles or with combinations of inorganic as well as organic absorbers could be useful to improve the UV-resistance of the fibres as described in Chapter 5.

A hybrid polymer based on 3-(glycidyloxypropyl) trimethoxysilane, Bisphenol A and ZnO was coated on a technical p-aramide fabric. Figure 8.6 summarizes the influence of UV-radiation treatment with conventional mercury lamps for several hours. As one can see the grey fabric tensile strength is reduced by more than 80 %. Due to this reduction the ballistic properties would be destroyed. The fabric coated with the sol modified with zinc oxide retains its tensile strength and will therefore retain its protecting properties. Analogously prepared coatings which were modified with the same proportion of titania (rutile) nanoparticles instead of zinc oxide showed comparable results.

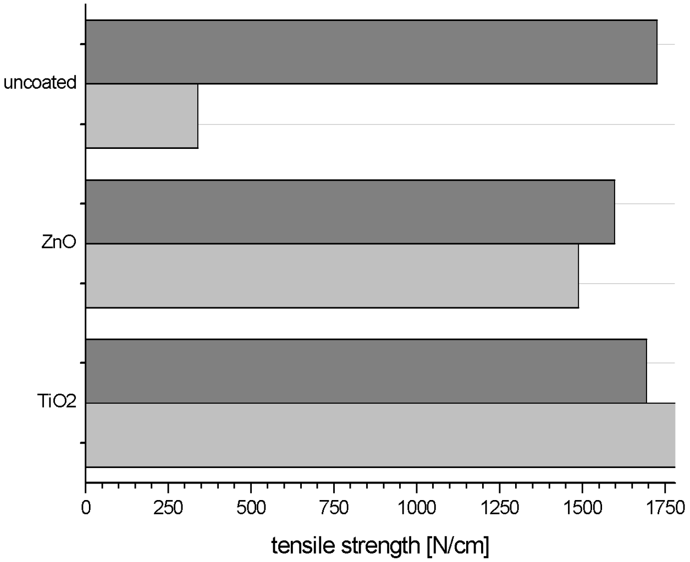


Figure 8.6 Tensile strength of differently modified p-aramide fabrics before and after a six hours treatment in an UV-reactor (in ambient conditions, therefore ozone developed during irradiation was not excluded).

Appendix

Glossary of Selected Methods

Since this book is not only addressed to those who are directly connected to textile industry, the following pages will give brief information about some testing methods that are largely specific to textile materials.

Air permeability

Air permeability is measured according to DIN EN ISO 9237, the samples are climatized for at least 24 h before the permeability is measured. The volume of air that passes through the fabric is evaluated at a pressure difference of 2 mbar.

Biocidal activity

The biocidal activity is a means to describe the ability of a textile to suppress the spreading of microorganisms. In the literature different testing procedures are described for testing the antimicrobial properties of textiles [Höfer (2006c)]. The degree of biocidal activity is measured by using the following procedure: Textile samples are impregnated with suspensions of different bacteria such as *E. coli*. After drying the textiles, the samples are incubated in a standard nutrient for 24 hours at 30°C. The colony forming units are counted after 2 days. Textiles without coatings are used as references. The biocidal activity BA is determined to be: $BA=100-(CFU_R/100 \cdot CFU_S)$, where CFU_R and CFU_S are the number of colony forming units of sample and reference, respectively. The BA is often also given as a logarithmic value: $BA(\log)=\log_{10}(CFU_R)-\log_{10}(CFU_S)$.

Capillary rise method

The capillary rise method is a method to evaluate the velocity with which a textile fabric soaks up water. This test is carried out according to DIN 53924. Textile fabrics are cut into stripes along the grain of fabric either in weft as or in warp direction (250 mm length, 30 mm width). The stripes are fixed, hanging in such a way that the lower edge is parallel to the surface of a basin filled with distilled water. The water basin is lifted up until the lower edge of the stripe dips into the water. From that moment on the capillary rise of the water is measured – in mm – after 10, 30, 60 and 300 s. For making the measurement a meter rule adjusted to the water level is mounted behind the sample.

Contact angle measurements

The deposition of a liquid drop on a solid substrate is an appropriate means to analyze the surface energy of a solid and by this to evaluate oleophobic or hydrophobic properties. The contact angle between the liquid and the solid is usually recorded by a camera after depositing the liquid on the given surface using a syringe [Marmur (2006)]. The lower the surface energy of the sample the larger the contact angle measured. Figure A1 illustrates the measurement of a contact angle θ. Since the surface roughness strongly influences the resulting contact angle a comparison between different surface modifications is only necessary if the roughness of the sample is the same.

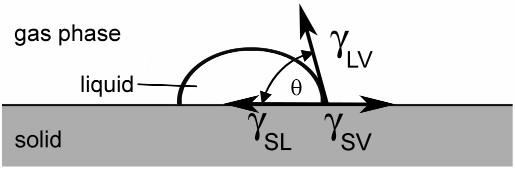


Figure A1 Scheme illustrating the measurement of the contact angle (θ). The contact angle is a result of the interface tensions between the solid and the liquid (γ_{SL}), the solid and the vapour (γ_{SV}) and the liquid and the vapour phase (γ_{LV}).

Crease recovery angle

The crease recovery angle (according to DIN53891) is a measure of the crease resistance. Climatized samples are cut in rectangular samples

(50 mm × 20 mm). The samples are folded and a weight of 1 kg is placed on the folded sample for five minutes. Afterwards the weight is removed and the folded sample is fixed with a clamp in a position allowing the creased leg to hang down vertically. The sample is allowed to recover for five minutes. During this time the clamp has to be turned clockwise to guarantee that the leg will hang down vertically permanently. The recovery angle is then measured. To illustrate the measurement Figure A2 depicts the setup employed.

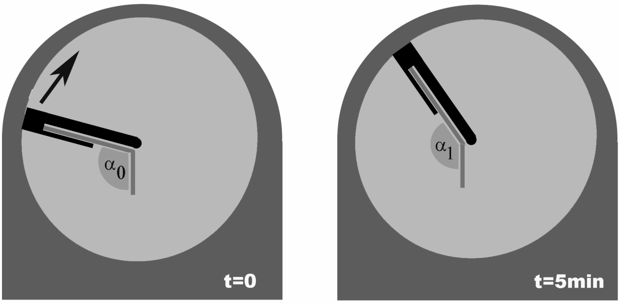


Figure A2 Illustration of the setup used for the measurement of the crease recovery angle. After the sample was folded and loaded with a weight of one kilogram, the sample is placed in a clamp and positioned as depicted allowing the leg of the sample to hang down vertically. The sample is turned clockwise during five minutes to permanently keep the free leg vertically. The resulting crease recovery angle (α_1) is then measured.

DuPont-Test

The DuPont Test is comparable to the TEGEWA drop test mentioned below. The test is carried out using eight different mixtures of water and isopropanol. The different mixtures are summarized in Table A1. A drop of each mixture is dripped onto the sample fixed in an embroidery hoop. Afterwards it is noted whether the different mixtures do not wet the fabric for at least 1 minute. The mixture with the highest proportion of isopropanol that does not wet the fabric within one minute determines the result of the DuPont test (compare Table A1).

The DuPont test is advantageous since it reduces the measuring time for hydrophobic samples in comparison with the TEGEWA test and simultaneously it gives certain information with regard to the repellence of less polar liquids.

Table A1 Different water/isopropanol mixtures used for the DuPont test.

Grading	Ratio water/isopropanol (v/v)
1	98 : 2
2	95 : 5
3	90 : 10
4	80 : 20
5	70 : 30
6	60 : 40
7	50 : 50
8	40 : 60

Laundry test I: ECE-washing

The washing process is performed in a domestic washing machine according to DIN EN ISO 6330. For this procedure an ECE-mixture is used as standard washing detergent – the composition of the detergent is determined by EN ISO 105-C06. The test is carried out at temperatures from 30 up to 95°C. Useful information concerning the ECE procedure is also given by [Phillips et al. (2001)].

Laundry test II: Lini-tester

Special testing equipment is used for this specific laundry test. The textile to be tested is placed in a vessel made of stainless steel. 10 steel balls are added to the textile before the vessel is partially filled with a standard wash detergent (according to DIN EN ISO 105, 4g/l ECE Colour Fastness Test Detergent 77 + 1 g/l Perborate). The closed vessel is fixed in a frame that allows it to rotate within a temperature-controlled bath. A single test is carried out for 30 min at 40, 60 or 95°C – depending on the requirements.

Martindale scrub-resistance test

The Martindale scrub resistance test is a useful test to evaluate the wear-resistance of fabrics. The test has to be carried out employing standardized testing equipment. A circular sample of the fabric to be tested is fixed in a stainless steel frame. The sample is placed on a standardized cotton fabric and loaded with a certain weight (the standard load is either 9 or 12 Pa). The samples to be tested are then scrubbed over the cotton surface. Depending on the requirements the sample surfaces are visually judged after a certain number of scrubbing circles has been carried out.

Oil repellence according to AATCC 118 (1992)

One test to determine the oil repellence is described in the AATCC 118 (1992). This test is carried out with eight different hydrocarbons (or mixtures) as summarized in Table A2. The test liquids are of varying surface tension in the range from 31.5 to 19.8 mN/m. A drop of each of the different liquids is placed on the surface of the textile to be tested.
The allocated result corresponds to the number of the oil with the lowest surface tension that did not wet the surface after 30s contact. The higher the grading, the better the oil-repellence.

Table A2 Different test liquids used for the oil repellence test according to AATCC 118 (1992).

Grading	Test liquid	Surface tension (mN/m), 25°C
1	Nujol	31.5
2	Nujol/n-hexadecane (65/35 v/v)	29.6
3	n-hexadecane	27.3
4	n-tetradecane	26.4
5	n-dodecane	24.7
6	n-decane	23.5
7	n-octane	21.4
8	n-heptane	19.8

Pull-out force of fibres

The pull-out force of fibres provides information about the force necessary to displace single weft or warp yarns (or fibres) of a fabric [Berndt (1983)]. Samples of a specified size are cut in weft as well in warp direction. The preparation of the samples is carried out as schematically depicted in Figure A3. A single yarn or fibre, as the case may be, sticking out of the fabric is pulled at a constant velocity. The maximum force necessary to pull the fibre is evaluated.

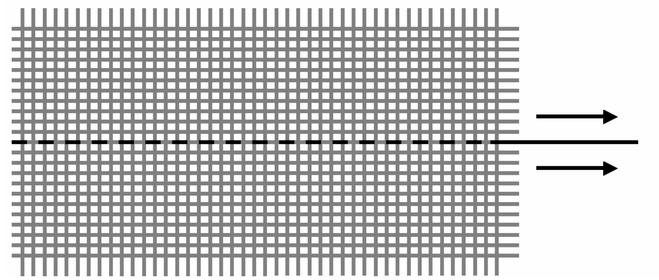


Figure A3 Sample preparation for measuring the pull-out force.

Stiffness in bending

The draping and the hand(le) of a textile are of particular importance for many applications but it is difficult to quantify these parameters objectively. The stiffness in bending gives at least a certain idea of these parameters. The general setup for evaluation of the mentioned values is schematically depicted in Figure A4 – according to DIN 53362. For measuring, samples are cut in stripes in weft as well as in warp direction. The sample to be measured is placed on a board, covered with a ruler and both are pushed simultaneously over an edge. The fabric bending downwards will be pushed over the edge until the stripe's edge will touch the dotted line (cp. Figure A4).

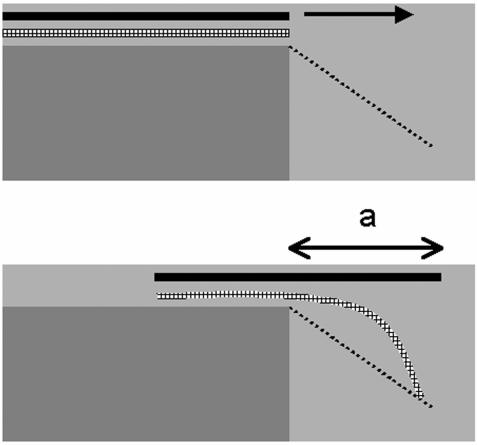


Figure A4 General setup for measuring the stiffness in bending.

The so-called bending length B (in cN/cm^2) will be calculated by using to the formula shown below.

$$B = F_l \times (a/2)^3, \text{ with } F_l = g_n \times m/l$$

(g_n = gravitational acceleration, $9.80665 m/s^2$; a = compare Figure A4; m = mass of the sample in g; l = length of the sample in cm)

Surface conductivity

An annular electrode is employed to evaluate the surface conductivity of textile materials. The textile material is climatized (T = 20°C, rel. humidity = 65 %) for at least 24 h before the surface conductivity is measured. The measurement itself is also carried out in a climatized room. The setup employed for this test is schematically depicted in Figure A5.

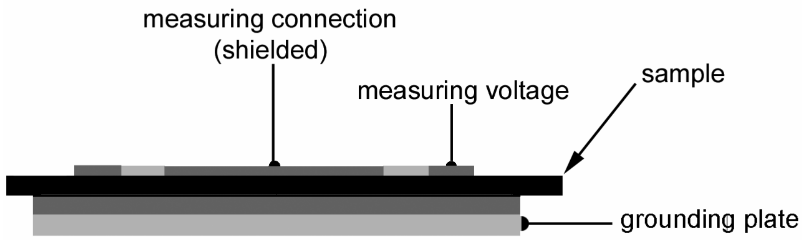


Figure A5 General set-up used for evaluation of the surface conductivity.

Tear propagation force

To measure the tear propagation force rectangular samples are prepared as well in weft as in warp direction. The samples are partially cut in the middle of a stripe parallel to the longer side (compare Figure A6). Each of these two legs is fixed with one of two clamps that are installed separated by a specified distance. By increasing the distance between the two clamps, the stripe will tear along the direction of the cut. The force that is necessary to tear the two legs apart is measured.

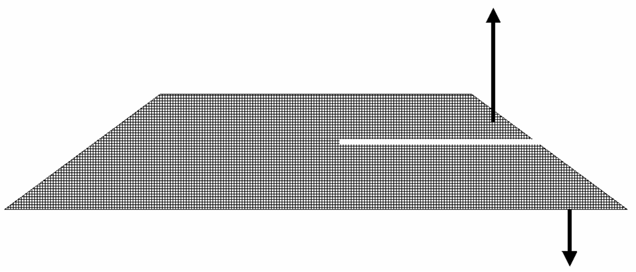


Figure A6 Illustration of the sample preparation and direction of the force applied to the two leg in the tear propagation force measurement.

Tensile strength and elongation at break

Textile fabrics are cut in stripes, in weft as well as in warp direction. To achieve useable results it is absolutely necessary to cut the samples exactly in the particular direction. A climatized sample is fixed between two vertically arranged clamps with a specified separation. The sample is stretched until it breaks. The important values are the force that is necessary to break the fabric and the elongation (in %) at break.

Water uptake, determination of water absorption of textile fabrics

The test quantifies the mass of water that is stored by a textile fabric after immersing it in water for a certain time. The storage occurs due to absorption as well to adsorption. To make the results reproducible the immersion process as well as the dripping off have to be carried out following a prescribed procedure. Climatized samples are cut in squares with an edge length of 120 mm and subsequently weighed. The edges of the samples are fixed on a strainer gauze (e.g., with needles at each edge) before it is placed on the bottom of a basin filled with water. The development of air bubbles below the sample must be prevented as much as possible, for example by slanting immersion of the samples. The sample is kept in the water for about one minute before it is removed (still fixed on the strainer gauze). Three of the needles holding the sample are removed and the strainer gauze is fixed horizontally, allowing the fabric to hang for three minutes before it is weighed again. The test is according to DIN 53923.

Xenotest

The Xenotest is a method for evaluation of the light fastness of a coloured textile. A xenon lamp is used for long-time illumination (120 h) of the textile samples under specific atmospheric conditions (temperature and rel. humidity) as described, e.g., in DIN 54004 or DIN 54003 [Wehlow (1988)].

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