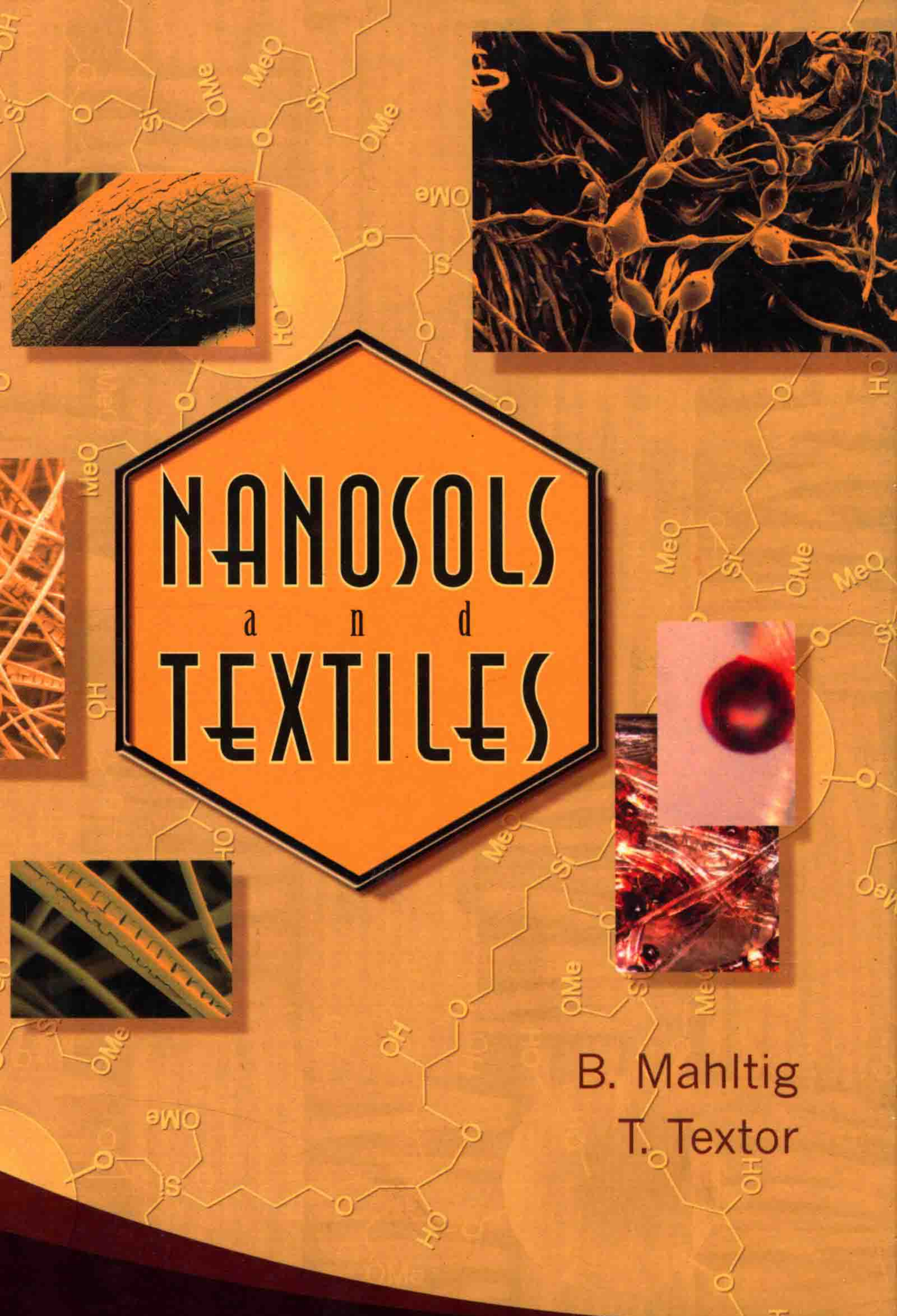

NANOSOLS and TEXTILES

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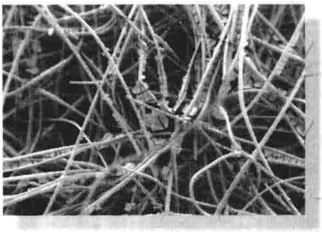

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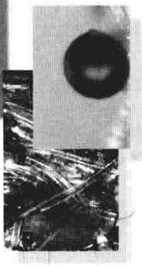

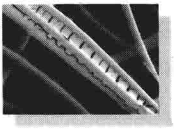

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I would like to dedicate this book to my academic teacher, Prof. Dr. Eckhard Schollmeyer, and thank for his guidance and support.

Torsten Textor

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
- …

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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

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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.

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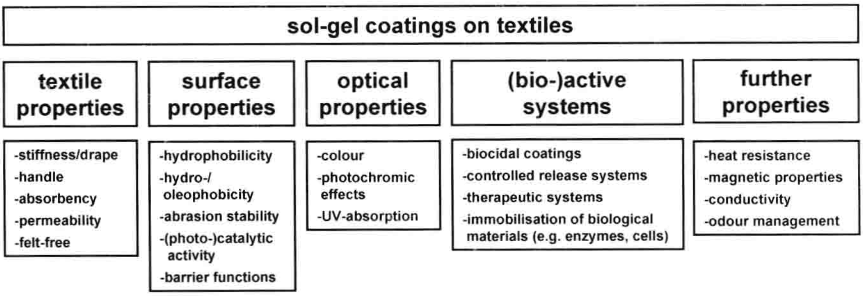


Figure 1.1 Selected examples for the improvement of textiles by application of sol-gel coatings.

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 semimetals 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.

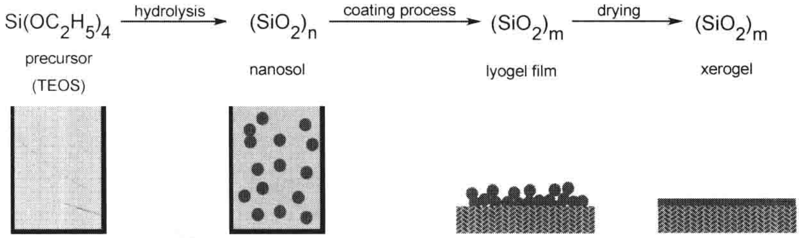


Figure 1.2 Main steps for the preparation of nanosol coatings (sol-gel process), here shown for a silica coating.

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)].

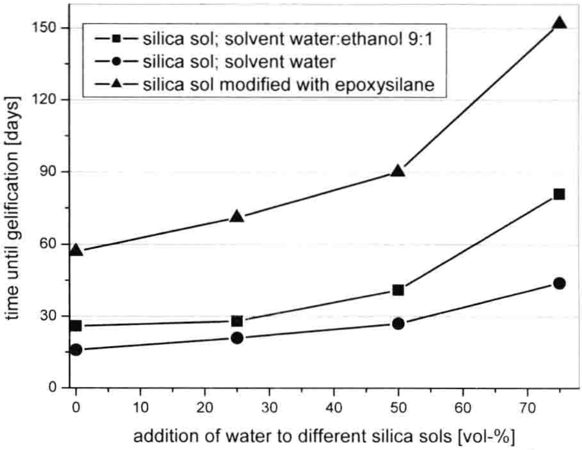


Figure 1.3 Enhancement of the stability of different silica sols with increasing dilution using water.

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.

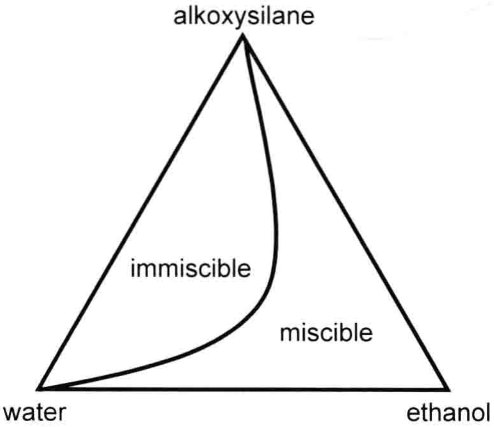
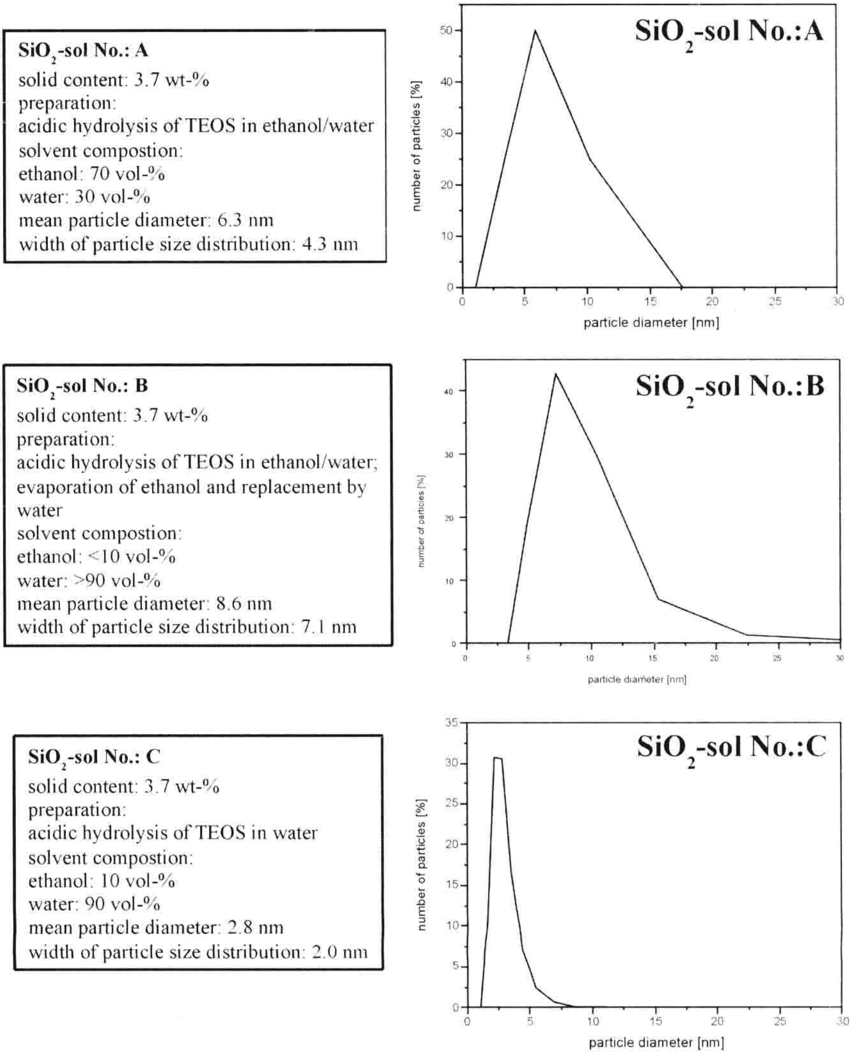


Figure 1.4 Schematic phase diagram of the system alkoxysilane, water and ethanol.

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

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