# SILICA

## 1. Introduction

The earth' crust is almost exclusively made of siliceous minerals and silicon dioxide (~95%) in the form of approximately 800 crystalline minerals. In recorded history, there are numerous indications of the omnipresence of silicates in humanity's natural habitat. Siliceous minerals were either utilized by processing natural silicate deposits, eg, clay, porcelain, glass or enamel, or obtained by means of chemical conversion (silica, silicones, ceramics). The properties of pure elemental silicon are now of pivotal importance in the manufacture of integrated switching circuits and, therefore, also form the basis for the age of electronics. Silica and silicates in the form of amorphous white powders can also be made synthetically, using a thermal or pyrogenic process (fumed silica) or a wet process (precipitated silica, silica gels). Amorphous silica is used in various industries, such as food, feed, personal care, paper, tires, plant protection and many others, and is an essential part of many everyday products.

## 2. Structure of Siliceous Minerals

Although siliceous minerals (1–7) can appear in various structure types and stoichiometries, they can be classified using only a few relatively simple rules. The basic structural unit of most forms of silica and silicate minerals is a tetrahedral arrangement of four oxygen atoms surrounding a central silicon atom ($SiO_4$). The $SiO_4$ units can either be discrete and isolated or connected to each other via shared edges. The $SiO_2$ stoichiometry of silica requires that on the average each oxygen must be shared by silicons in two tetrahedral. Sharing of corners is the common mode of linkage of the coordination polyhedra; sharing of edges is rarely encountered; and sharing of faces never occurs because of the decrease in stability that would result from the close distance between silicon cations. Structurally, silica represents a limiting case in which an infinite three-dimensional network is formed by the sharing of all oxygen atoms of a given tetrahedron with neighboring groups. The possibility of linking tetrahedrons so that some corners remain unshared gives rise to a wide range of structural possibilities some of which are encountered in the silicates. Each unshared oxygen atom contributes a formal negative charge to the anionic groups thus formed, which is satisfied by the presence of other cations in the silicate structure. Six structural types are summarized in Table 1.

A more detailed treatment of silica and silicate structures can be found in Refs. 8,9.

## 3. Properties

Despite the fact that synthetic silica has been known for a long time, the question as to how they are best assigned characterization values has yet to be resolved. In a particular application, the behavior of products frequently differs from the expected on the basis of characterization values. There is, however, still hope that the accurate characterization of silica will allow conclusions to be drawn with respect to its mechanism of formation and its behavior in its intended application. Characterizing silica means describing its surface and structure, the morphology, as accurately as possible in an attempt to predict its behavior and performance in certain applications. Other analytical methods attempt to describe the surface chemistry; ie, they describe the number of silanol groups and their arrangement, surroundings and reactivity, the chemical composition and degradation behavior of the silica structure. Furthermore, there are a number of methods that can collectively be termed bulk chemical analysis.

This article attempts to summarize physical and chemical analytical methods for characterizing silica (10,11), but does not lay claim to completeness. Moreover, some methods are of scientific interest and in most cases not very useful for practitioners and are therefore not described in detail either. An extensive bibliography provides interested parties with the opportunity to pursue the methods in detail.

## 4. Manufacture

Amorphous, synthetic silica and silicates can be manufactured using a “thermal” or “pyrogenic” or a “wet” process. The thermal process leads to fumed silica, the wet process to either precipitated silica or silica gels.

**4.1. Fumed or Pyrogenic Silica.** The technical synthesis or production of fumed silica can fundamentally be described as continuous flame hydrolysis of silicon tetrachloride, $SiCl_4$. Hereby, $SiCl_4$ will be converted into the gas phase (“evaporated”) and then reacted with hydrogen and oxygen (“hydrocarbon flame”). The “intermediate” water, $H_2O$, will spontaneously react with the silicon tetrachloride to form silicon dioxide quantatively according to equations 1–3.

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \tag{1}$$

$$SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4\,HCl \tag{2}$$

or

$$2\,H_2 + O_2 + SiCl_4 \rightarrow SiO_2 + 4\,HCl \tag{3}$$

The chemical reaction is exothermic and therefore generates a lot of heat requiring cooling of the reaction products. The only by product of the reaction is hydrochloric acid, which needs to be separated from the fumed silica powder and can be recycled and used for the manufacture of silicon tetrachloride according to equation 4.

$$Si + 4\,HCl \rightarrow SiCl_4 + 2\,H_2 \tag{4}$$

Ferrosilicon (FeSi), which is widely used in the steel manufacturing process, is usually the source of silicon. The generated hydrogen is recycled and used in the burner to create the flame, so that the overall process is very environmentally friendly.

The physical-chemical properties, eg, surface area, particle size distribution and structure, of the fumed or thermal silica can be controlled through variation of the concentration of the reactants, the flame temperature and reaction time. Instead of silicon tetrachloride or other silanes, eg, methyltrichlorosilane, trichlorosilane etc, can be used for the formation of fumed silica. The use of the above mentioned silanes instead of silicon tetrachloirde requires an adjustment of the process conditions to get the same final product. Figure 1 shows a block diagram of the fumed silica manufacturing process.

The obtained fumed silica is of hydrophilic nature, which means it can be dispersed in water. In an after treatment step, hydrophilic fumed silica can be converted into hydrophobic fumed using, eg, silanes, chlorosilanes, alcoxysilanes or silazanes. In the process, a chemical reaction between the silanol groups of the hydrophilic fumed silica and the silanes occurs, turning them into hydrophobic products which can no longer be dispersed in water.

**4.2. Precipitated Silica.** The raw materials used for the production of precipitated silica are alkali silicate solutions, preferably sodium silicate and acid. The various steps of manufacturing silica are displayed in Figure 2.

In the first step (precipitation), the raw materials consisting of water glass (sodium silicate solution) and mineral acid, normally sulfuric acid is used, are dosed into a stirred vessel containing water. In many cases, once a defined pH value has been set, the components are fed continuously into the reactor, this process taking place simultaneously over a certain time interval. Typically, precipitated silica is manufactured at pH values $>7$, whereas silica gels are manufactured at pH values $<7$. Another possibility is to first supply a particular quantity of water glass and initially (first stage) dose just sulfuric acid followed by a second stage in which water glass and sulfuric acid are added simultaneously under defined reaction conditions. The chemical reaction is described in equation 5.

$$\mathrm{Na_2O} \times 3.3\,\mathrm{SiO_2} + \mathrm{H_2SO_4} \rightarrow 3.3\,\mathrm{SiO_2} + \mathrm{Na_2SO_4} + \mathrm{H_2O} \qquad (5)$$

After the chemical reaction (precipitation) has been completed, the obtained suspension is filtered, and the filter cake is washed to remove the sodium sulfate. The filter cake can then be resuspended and spray dried or directly fed to a term drying process. Depending on the drying technology and the required particle size of the silica, the product can be optionally milled to obtain a finer particle size or granulated to convert the powder into a low dust form. Precipitated silica too can be converted from hydrophilic to hydrophobic using a chemical after treatment.

**4.3. Silica Gels.** Silica gels are generally being manufactured using the same feedstock that is used for precipitated silica: an alkali silicate solution, preferably sodium silicate (“water glass”) and acids, mostly sulfuric acid. The same chemical reaction as shown in equation 5 is followed. Different from precipitated silica in the process of making silica gels, the two raw materials are not reacted and precipitated in huge vessels for up to several hours, but are brought together in relatively small mixers. The raw materials are passed through the mixers within a couple of seconds and are intensively mixed forming silica hydrosols. The silica hydrosol is then collected in containers where rapid gelation of the mixture occurs. Silica hydrosols are typically formed at $\mathrm{pH} < 7$. At a given silica concentration and temperature, the rate of gelation strongly depends upon pH. As pH of formation increases, the surface area of silica gels becomes lower. The gelation of the silica gels is usually followed by an aging step to further modify the performance of gels. The resultant gel block must be crushed before further processing. After gelation and aging, the silica gel is washed to remove the soluble salts. The conditions of washing affect the gel properties as well. If the product is dried only enough to remove excess surface water, the product is called a hydrogel. If the washed gel is further dried, xerogels are obtained. Milling may accompany drying to achieve a desired particle size distribution. The drying of hydrogels and xerogels usually causes a partial collapse of the silica gels structure and a loss of pore volume and porosity.

The final category of silica gels of commercial importance is the aerogels, first reported by Kistler in the 1930s (12,13). Aerogels, like xerogels, are dry gels, but they are made in such a way as to prevent pore collapse upon drying. In order to do so, the water in the hydrogel is replaced with a liquid of lower surface tension, eg, alcohol or acetone. The liquid is then removed by heating the silica gel to above the critical point and then releasing the pressure. This way a liquid-vapor interface never forms, so surface tension forces never have the opportunity to collapse the pore structure (14). Figure 3 shows the production process for silica gels.

## 5. Analytical Methods

### 5.1. Methods to Characterize the Morphology of Silica.

*Specific Surface.* The specific surface of silica is generally determined using the Brunauer-Emmett-Teller (BET) adsorption method (15) or a modification thereof (16,17). For measurement, the silica sample is cooled to the temperature of liquid nitrogen. At low temperature, nitrogen is adsorbed on the silica surface. The quantity of adsorbed nitrogen gas is a measure of the size of the silica surface. When performed under defined conditions, the BET method yields perfectly reproducible results. The BET surface always provides the sum of the so-called outer geometrical surface and the inner surface, ie, the surface within the porous structure of the silica. If it is ensured that not only the surface of a sample is covered with nitrogen but also the pores are filled, then the distribution of mesopores (pores between 2–30 nm in size) can also be determined using the Barrett-Joyner-Halendar method (BJH) (18).

*CTAB Surface Area.* The CTAB method originated from carbon black technology, but has been adapted to silica. The method is based on the adsorption of surface active molecules from aqueous solutions. The adsorbed molecule is cetyltrimethylammonium bromide (CTAB) (19). The preferred adsorption site for these large CTAB molecules is the outer, geometrical surface. Comparison with the BET surface, which is the sum of the outer and inner surface of a silica, provides an indication, with a certain margin of error, of the ratio between outer and total surface. The CTAB surface often coincides very closely with the surface determined from transmission electron microscopy (TEM).

*Pore Volume and Pore Size Distribution.* The term "pore volume" and a specific evaluation method have not been described explicitly (20,21). The pore volume of synthetic silica can be understood as (a) surface roughness, (b) the micro- or submicropore volume within particles or aggregates, (c) the void volume. The most common methods of determining the pore volume of silica are mercury porosimetry (22,23) and the BJH method described earlier in this chapter. The mercury porosimetry uses the measured pressure, p, as quantity required to force the mercury into the pores of the silica sample. The necessary pressure is inversely proportional to the pore diameter. If the volume of mercury is known at a given pressure, the pore volume can be calculated.

*DBP Number, Oil Absorption.* The assessment of the liquid-absorbing capacity of silica may involve the absorption of dibutylphthalate (DBP) (24–26). This largely automated measurement technique provides an indication of the total volume of liquid that can be absorbed by a silica sample. Because of the toxicity of DBP oil, attempts are being made to replace it with paraffin oil (27).

*Microscopic Methods.* The only method allowing direct insight into the dimensions of interest in case of silica is electron microscopy, which provides information on the size of primary particles and aggregates or agglomerates and, with certain limitations, on the particle size distribution of an examined sample. Electron microscopic surfaces can be calculated from various particle size distributions, and these can be compared with those from BET measurements or other investigations.

Transmission Electron Microcopy (TEM) (28) works in much the same manner as light microscopy: Electrons are passed through a thin object and, following their interaction with the prepared sample, are used to produce an image. However, the resolution exceeds that of a light microscope by a factor of 1000; for TEM the resolution is 0.2−0.3 nanometers (nm), for a light microscope it is $\sim$ 200 nm. TEM images with high resolution provide valuable information on the composition of the structure of different silica samples. With a suitable imaging technique, even the crystalline short-range order of silica can be detected. The structure of the silica can also be recognized, as can the manner in which the primary particles unite with one another. Figure 4 shows some examples of TEM images for different types of silica.

Scanning Electron Microscopy (SEM) (29) is not actually a microscope technique, in the sense that it uses electromagnetic lenses in order to magnify images, similar to the case with light optics (this comparison also applies to the transmission electron microscope). It merits the name "electron microscope" only because it produces a strongly magnified image with the help of electrons. The extremely sharply focused beam of electrons produces very good resolutions and depth of focus. It is the great depth of focus in particular that makes SEM superior to TEM for certain applications.

**5.2. Characterization of Surface Chemistry.** In the literature, a variety of methods are described that are suitable for determining silanol groups and their chemical reactivity on the surface of silica (30–32). All of these methods are based on applying the experience gathered in small molecule and low molecular weight chemistry to surface chemistry. However, the fact that this analogy is flawed can be demonstrated by the following simple consideration. On the surface of solids, particularly in the interior of micropores, spatial inhibition, other equilibrium conditions, and other chemical reaction possibilities may prevail. Chemical reactions are, nonetheless, an important tool for characterizing solid surfaces. The reactions generally yield easily reproducible characteristic values allowing different products to be compared. A small selection of the reactions described in the literature is presented here.

In the determination of silanol groups with lithiumaluminumhydride ($LiAlH_4$), a silica sample is first degassed in a vacuum and then allowed to react with $LiAlH_4$ at room temperature, and the resultant hydrogen is determined volumetrically (33,34). Another method is the reaction of a sample with an alkyllithium or alkylmagnesium reagent (35) followed by a volumetric determination of the resulting alkane. Further reactions may be performed with alcohols (36), chlorosilanes (37,38), hexamethylendisilazane; $BCl_3$, $AlCl_3$ (39) or boroethane (40–42).

*Spectroscopy.* With $Si^{29}$ nmr (20,43–46) examinations of solids, it is possible to detect different surroundings of the silicon atom on the basis of oxygen atoms and hydroxyl groups in the silica sample. The ratios of the detected signal intensities correspond to the proportion of the various Si surroundings in the sample. With the solid NMR method, it is possible to distinguish between three main groups around the silicon atom in silica: (*1*) Siloxane bridges (bulk) with a chemical shift of approximately $-110$ ppm; (*2*) isolated, terminal SiOH groups with a chemical shift of approximately $-100$ ppm; (*3*) geminal SiOH with a chemical shift of approximately $-90$ ppm; The relative content of isolated or geminal silanol groups and siloxane bridges is quantifiable, and the different silanol groups are assigned different reactivities.

Infrared spectroscopy (ir) is another method of differentiating between various silanol groups (47). The following groups can be detected with their respective ir bands in the spectrum: (*1*) Isolated SiOH at approximately $3745\,cm^{-1}$; (*2*) vicinal SiOH at approximately $3640\ cm^{-1}$; and (*3*) water bridges at approximately $3420\,cm^{-1}$.

*Thermoanalytical Methods.* Thermal analysis (48) is the term given to a group of methods that measure a physical property of a substance (and/or) its reaction products as a function of temperature or time while subjecting the substance to a controlled temperature program. With differential thermal analysis (DTA) it is possible to monitor the changes in enthalpy of a sample during the course of a temperature program. The pre-conditions is that the corresponding process (chemical reaction or phase change) is sufficiently short to allow a thermal effect to be observed. DTA is often combined with thermogravimetry (TG), which records the weight loss of the sample as a function of the temperature. From the weight loss, information can be obtained on resulting products and on the possible course of degradation (49). In the case of silica, rational information can be obtained only by means of a combined DTA-TG measurement, because the thermal effects observed in DTA are generally negligible on their own (50). Although it is difficult to draw conclusions regarding the structure of a silica surface from the combination of DTA and TG alone, the results obtained can nonetheless be compared to those from other investigations.

*Atomic Force Microscopy.* Since the beginning of the 1990s, atomic force microscopy (AFM) (51–54) has been used to characterize surfaces of crystalline and amorphous, biological and synthetic products including crystals and films. AFM can be used to characterize the microstructure of silica or to determine the dispersion of silica in a rubber matrix.

**5.3. Chemical Bulk Analysis.** *X-ray Diffraction.* Synthetic silica is amorphous. That is, unlike crystalline solids, silica does not possess an infinite three-dimensional long-range order. Consequently, use of classic X-ray diffraction method is not possible. Silica, however, like glass, does have areas of short-range order that can be determined by appropriate evaluation of diffuse X-ray diffraction bands. When the sample is tempered, changes in short-range order can be detected at temperatures as low as 200 degree centigrade using X-ray diffraction (20).

*Loss on Drying and on Ignition.* Loss in drying (55) and loss on ignition (56) are significant characteristic parameters that can be used to characterize the differences between synthetic silica. Precipitated silica and silica gels typically exhibit a loss on ignition of more than 3% (typically in the region of 5%), provided they have not received special after treatment. In the case of fumed silica, the loss on ignition is less than 3%.

A comparison of selected typical product characteristics for fumed and precipitated silica and silica gel is shown in Table 2.

## 6. Health and Safety Factors

Silica, produced in a thermal (fumed silica) or precipitation process (precipitated silica, silica gels), is characterized by the absence of any sharp peaks in X-ray powder diffraction scans, and considered totally amorphous. Exposure to synthetic silica is most likely to occur due to dust ingestion, dermal contact or inhalation, with inhalation being by far the most important route of contact. When handling synthetic amorphous silica and observing the TLV (Threshold Limit Value) for total dust, no negative or harmful effects were detected. If the TLV is exceeded, the respiratory tract may be mechanically overloaded as with other nuisance dusts. After contact with skin and mucous membrane (eye, respiratory tract) no symptoms of irritation have been noticed up to now. Synthetic amorphous silica is essentially non-toxic when ingested. Always consult the manufacturers Material Safety Data Sheet (MSDS) for details prior to using the silica. A good summary of health and safety data for synthetic amorphous silica is provided in (57).

## 7. Uses

Silica is widely used in various products of daily life such as food, feed, plant protection, coatings, toothpaste, tires, and mechanical rubber goods, and unsaturated polyester resins, etc. Some of the most important applications and products containing silica are discussed in this section, but the list is not complete.

**7.1. Food.** Powdered ingredients play an increasingly important role in the food industry due to the customer's need for convenient, easy to handle products with a consistent quality. Fruit powders, sea salt, dairy products, or vegetable powders as well as ground spices or spice mixtures are only a few of many examples. Many of those ingredients tend to pick up moisture, become sticky over time and start to cake or loose there ability to flow freely. Tailor made silica products have a very high absorption capacity for water or oil, thus are capable of drying the surface of the food ingredients, preventing them from sticking together and help to keep them as free flowing powders.

**7.2. Feed.** Animal feeds and premixes are blends of many ingredients needed by a particular species for good nutrition. Generally included are grains, fats, proteins, sugars, amino acids, vitamins and minerals. Many of these ingredients flow poorly, or cake during storage. Some are in liquid form, therefore are difficult to add accurately to a dry blend. Due to its unique absorption capacity, silica is used as a carrier medium for, eg, Vitamin E. Silica helps turning liquids into free flowing powders and facilitates dosing feed additives for livestock. Some silica can absorb liquids up to three times their own weight and still remain free flowing powders. Many feed ingredients are hygroscopic, that is possess a high affinity to absorb moisture from air. This causes them to change chemical state during processing or storage. An ingredient which begins as a free flowing powder can quickly become caked depending on the ambient temperature and humidity and the quality of packaging. Silica is very effective in solving these problems and assuring, the powder ingredients remain free flowing over extended periods of time.

**7.3. Agriculture.** The food stuffs produced worldwide is 97% of agricultural origin, only 2% come from fishing and 1% from pasture farming. The world's supply depends on the crop yields. More than one third of the potential crop yields throughout the world are lost as a result of diseases and pests. A well balanced pest control is required in order to protect nature and life cycles. Synthetic silica greatly contributes towards optimizing the formulations for plant protection and pest control. Silica, fumed and precipitated, is widely used in different formulation types, powder or granulated formulations and liquid formulations. Silica, mainly precipitated, in powder formulations regulates and maintains the flow properties during storage, is used as a grinding additive or carrier to absorb and carry the active ingredient of the formulation. Silica, mainly fumed, is used in liquid formulations to stabilize the suspension containing a variety of liquid and solid ingredients. Due to its unique structure, fumed silica forms a three-dimensional network when suspended in a liquid system, thus preventing any solid components from settling. Solid substances can be "stored" within the three dimensional network enhancing the shelf life of the formulation significantly.

**7.4. Coatings.** The increasing demand for matt-finish paint systems, either as a fashionable trend or as means of increasing safety by preventing glare or in course of general product improvements, led to an increasing demand for silica. Changing trends in coatings technology have forced many formulators to re-examine their requirements for matting agents' performance. As the industry moves from conventional solvent-based systems to high solid and water based technology, the matting agent's performance becomes more critical for uniform and consistently matted finishes. Fumed, precipitated silica and silica gel, vary in average particle size, particle size distribution, oil absorption, moisture content and surface treatment. All of these characteristics play an important role in how well the matting agent will perform in each system. The formation of a coating film surface with defined roughness and hence, the degree of matting, can be influenced by changing the characteristics of the silica. To improve settling characteristics, especially to eliminate hard settling, matting agents can be given a variety of surface treatments without sacrificing matting efficiency.

**7.5. Defoamers.** Foam occurs in many natural and industrial processes as well as in everyday life. Food products like ice cream, whipped cream of cappuccino are some examples. On the opposite, the formation of stable foams can cause major problems in industrial processes such as in the manufacturing of paints and coatings, textiles, paper, detergents, and in the chemical industry. Here, foam can either affect the quality of the final product or impede the manufacturing process by reducing the capacity of tanks or containers or by causing pumping problems. For this reason, foam control processes have been developed. Highly effective foam control systems, with no negative impact on the manufacturing process or final product, are dispersions made of oils and hydrophobic, pre-treated, silica with a great variety of silica being used. In addition to their use as highly effective active component in foam control systems, silica also finds use as anti-settling agent in the manufacture of defoamers thus stabilizing the defoamer system providing a longer shelf life and consistent quality.

**7.6. Personal Care.** Oral care and oral health is continuing to gain importance globally. This fact can be attributed to intensified research, improved technologies and growing public awareness of the importance of good oral hygiene. Synthetic silica as a major component in toothpaste significantly contributed to the progress in personnel oral hygiene. Silica in toothpaste serves one of two functions – they provide abrasivity and therewith cleaning, and they act as rheology modifier or thickening agent. Abrasive silica grades in toothpaste provide efficient cleaning of the teeth when brushing without causing damage to the teeth surface. Different grades of abrasive products have been developed covering a wide range of abrasiveness from very mild in toothpaste for children, to medium in adults' everyday toothpaste, to very strong abrasivity for use in whitening or smoker toothpastes. Rheology plays an important role in toothpaste formulations. It is controlled by the appropriate thickening silica – binder ratio. Silica serves the following functions: structuring toothpastes of gels and stabilizing dentifrices against separation through adding thixotropy and viscosity. Silica is also used in personal care products such as shampoos, body washes, creams, and lotions and sun lotions. Silica in these products helps to control viscosity and thixotropy and to stabilize the formulations improving storage stability and shelf life.

**7.7. Paper Coatings.** The world of printing is changing dramatically and is becoming more and more digital. Digital data sources, digital transfer, and certainly digital printing. The past decades have already seen tremendous technological advances especially in non-impact printing technologies. This is particularly true for ink jet systems in which the development of hardware has paralleled the advanced made in computerized image-processing systems. High speed and low cost availability are now driving the so-called SOHO (small office home office) markets, while the professionals have learned to use inkjet for a great variety of applications. However, to get the best possible quality levels, specialized inkjet media have to be developed.

The majority of ink used in ink jet printing contains water soluble organic dyes and dispersed pigments with the overwhelming majority of the typical ink formulation containing water. Once deposited on the substrate, the ink must dry quickly to avoid spreading through the paper fibers adjacent to the printing pixel. Otherwise, wicking and a subsequent loss in resolution occur. With the drive to accelerate print speed and reduce drop size, fast drying becomes crucial. A key to meeting these requirements is coating the surface of the substrate with silica-based materials. These coatings allow for rapid ink absorption, thereby promoting sharp edge acuity, spheric and defined spreading of the ink drop, no shine-through or strike-through of the inks, and an excellent image density.

**7.8. Silicone Rubber.** Silicone rubber parts are typically used in the automotive industry in, ie, ignition cables, spark plugs, membranes, and bellows. In electrical and electronics applications, silicone rubber is used in key pads, housing seals, in insulating hoses and high voltage insulators. Swimming goggles, snorkels and mouth pieces are usually made of silicone rubber too. Even in hospitals and pharmacies seals for medical appliances, baby nipples, catheters and inflating bellows are made of silicone rubber.

In the silicone industry, synthetic silica is used predominantly as a reinforcing agent in order to give the silicone rubber sufficient mechanical strength. In principle, both fumed and precipitated silica can be used. Precipitated silica can give advantages to silicone rubber applications which can not be obtained with fumed silica and vice versa. The vulcanization temperature is the distinguishing feature of the different silicone systems. HTV silicone rubber (High Temperature Vulcanizing) and LSR (Liquid Silicone Rubber) are vulcanized at temperatures exceeding 100°C. In the case of RTV silicone rubber (Room Temperature Vulcanizing), the cross-linking takes place as the name suggests at room temperature. Precipitated silica has its advantages in HTV systems such as easy compounding, good dynamic properties (compression set) which are needed in HTV silicone rubber. Fumed silica is generally preferred in RTV and LSR silicone rubber systems.

**7.9. Unsaturated Polyester Resins (UPE).** The main area of application for unsaturated polyester and vinyl ester resins (70%) are fiber-reinforced plastics used in the construction industry (tanks, containers, pipes), in boatbuilding, transportation, electrical engineering, and the automotive industry. The remaining amount is used in nonreinforced applications such as in molded parts (buttons), adhesives or surface finishes (putties, cast surfaces). Compared to precipitated silica and silica gels, fumed silica is by far the largest product in the UPE industry having the following advantages: very efficient viscosity modifier, efficient in adding thixotropy, and better clarity of the formulation. Fumed silica contributes significantly to the stability of the formulation and prevents segregation. Precipitated silica has found a niche in UPE gel coats. Gelcoats are a high performance UPE resin that is applied to the outside of a composite part for aesthetics and to provide resistance to weathering. Other advantages of precipitated silica are fast dispersion, lower costs, better leveling of the coating or casting and, in some cases, less viscosity drift (change of the formulation viscosity over time).

### 7.10. Rubber Applications: Mechanical Rubber Goods and Tires.

Silica, in conjunction with organosilanes as coupling agents, is widely used in the manufacture of mechanical rubber goods such as seals, cables, profiles, belts, and hoses. The silica–silane system is needed for industrial rubber goods that require high reinforcement combined with the possibility to manufacture white or colored products. The silica is used to improve tear resistance, and in some dynamic applications the silica–silane systems are needed to reduce heat buildup. Another important field for silica–silane systems is the segment of non-marking colored shoes, which require good abrasion resistance, high stiffness, and high elasticity.

Since the introduction of the "green tire concept" in 1992, precipitated silica in conjunction with special solution polymers and functional organosilanes acting as coupling agents, has been used in passenger car tire treads. The latest generation of silica, highly dispersible silica, makes it possible to achieve considerable improvements in wet-skidding properties and rolling resistance of car tires, but also to improve their wearing characteristics.

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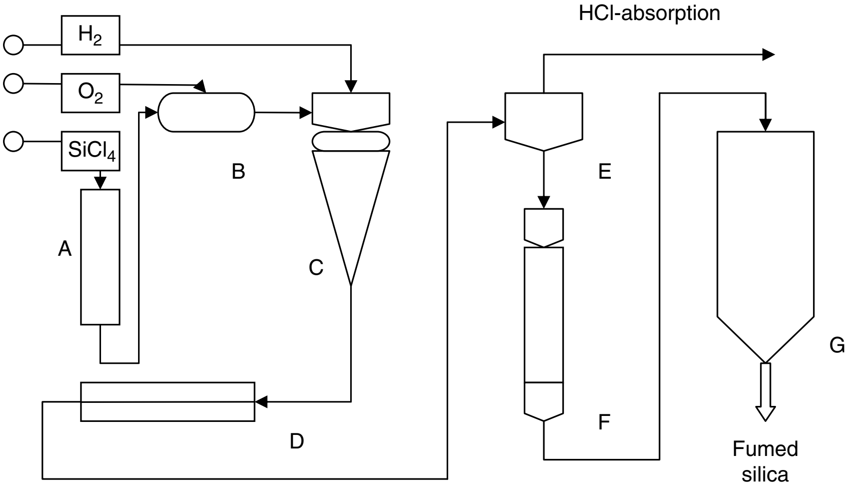

**Fig. 1.** Flow diagram of the manufacturing process for fumed silica A = Evaporator; B = mixing chamber; C = burner; D = cooler; E = filter; F = de-acidifier; and G = silo.

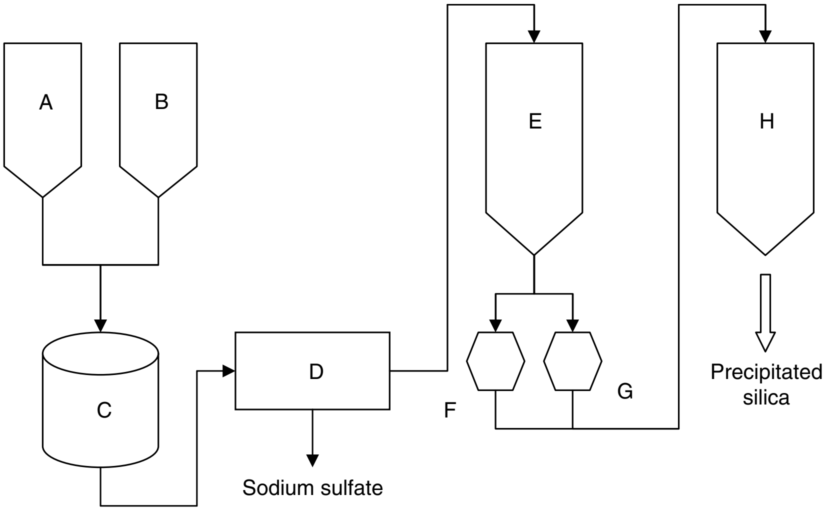

**Fig. 2.** Flow diagram of manufacturing of Precipitated Silica A = Sulfuric acid; B = Sodium silicate solution; C = precipitation tank; D = filtration; E = drying; F = optional milling; G = optional granulation; and H = silo.

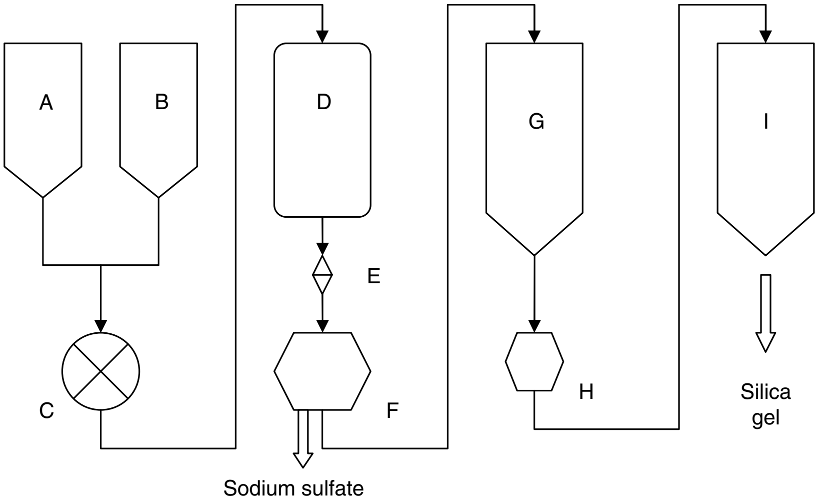

**Fig. 3.** Manufacturing of silica gels – flow diagram A = Sulfuric acid; B = Sodium silicate solution; C = Mixer; D = aging; E = crushing; F = washing; G = drying; H = milling; and I = silo.

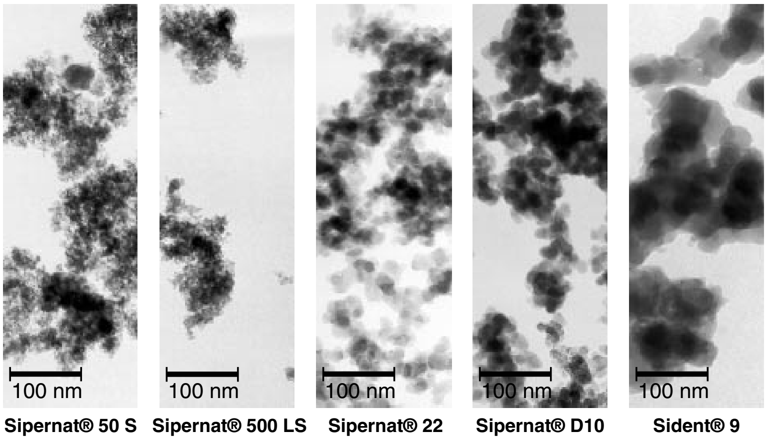

**Fig. 4.** TEM images of different Sipernat® (Degussa AG) and Sident® (Degussa AG) silica grades. TEM Total scale: 200000:1.

Table 1. **Structural Types of Silica and Silicates**

| Name | Structure | Number of shared O-atoms |
|---|---|---|
| *neso*-silicate | discrete {$SiO_4$} units | no shared O-atom |
| *soro*-silicate | discrete {$Si_2O_7$} units | one shared O-atom |
| *cyclo*-silicate | closed rings | two shared O-atoms |
| *ino*-silicates | chains | two shared O-atoms |
| *phyllo*-silicates | layers | three shared O-atoms |
| *tecto*-silicates | three-dimensional networks | four shared O-atoms |

Table 2. **Comparison of Selected Typical Product Characteristics for Fumed and Precipitated Silica and Silica gels**

| Silica gels | Precipitated Silica | Fumed Silica |
|---|---|---|
| narrow pore size distribution<br>mesopores<br>limited micropores | wide pore size distribution<br>macropores<br>limited mesopores<br>no micropores | nonporous |
| pore size is adjustable during manufacturing | pore size can be influenced during manufacturing | not applicable, nonporous |
| silica gels are hard, particles more angular | precipitated silica is softer, particles more spherical | fumed silica is tentatively harder than precipitated silica, but softer than gels |
| refractive index: 1.4620 | refractive index: 1.4540 | refractive index: 1.4600 |
| surface area: 200–1200 $m^2/g$ | surface area: 50–750 $m^2/g$ | surface area: 80–350 $m^2/g$ |