SILICA, AMORPHOUS

1. Introduction

Amorphous silica, ie, silicon dioxide [7631-86-9], SiO_2, does not have a crystalline structure as defined by X-ray diffraction measurements. Amorphous silica, which can be naturally occurring or synthetic, can be either surface-hydrated or anhydrous. Synthetic amorphous silica can be broadly divided into two categories of stable materials (1): vitreous silica or glass (qv), which is made by fusing quartz at temperatures greater than ~1700°C (see SILICA, VITREOUS SILICA), and microamorphous silica, which is discussed herein.

Microamorphous silica includes silica sols, gels, powders, and porous glasses. These consist of ultimate particles of the inorganic polymer $(SiO_2)_n$, where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms. Each of the four oxygen atoms is covalently bonded to at least one silicon atom to form either a siloxane, $-Si-O-Si-$, or a silanol, $-Si-O-H$, functionality. The bond distances and bond angles in amorphous silica are similar to those of cristobalite [14464-46-1] (2): Si−O bond distances are ~ 0.16 nm, and Si−O−Si bond angles are ~ 148°. Surface silanol groups can be isolated from one another, so that intramolecular hydrogen bonding does not occur (Fig. 1**a**); vicinal to one another, thus promoting the formation of intramolecular hydrogen bonding (Fig. 1**b**); or geminal to one another, whereby two silanol groups are bonded to the same silicon atom (Fig. 1**c**). Initially formed low molecular weight species condense to form ring structures so as to maximize siloxane and minimize silanol bonds (Fig. 2).

A random arrangement of rings leads to the formation of complex structures of generally spherical particles less than ~100 nm in diameter (3) (Fig. 3). These particles have high surface area values, generally greater than ~3 m^2/g. Crystallinity is usually determined spectroscopically by using X-ray diffraction (4) to establish the absence or presence of definitive lines in the diffraction pattern of silicas. For example, Fig. 4 shows X-ray diffraction patterns of crystalline quartz sand (Fig. 4**a**) and of cristobalite (Fig. 4**b**). Both exhibit distinct reflections that can be used for identification. The X-ray diffraction patterns of four commercial synthetic amorphous silicas are shown in Fig. 5. The colloidal silica (Fig. 5**a**) is a sol or stable dispersion of discrete particles. There is a general absence of definitive reflections in these curves. Studies of radial distribution function curves of a vitreous silica have indicated that regions of local atomic order can exist that approximate the cristobalite structure. Whereas amorphous silica is closely related to the cristobalite structure, this local order is believed to be limited to crystalline domains of up to 2 nm in diameter that have completely random orientations and that are thus statistically distributed (5). Sharp X-ray diffraction patterns (lines) would therefore not be obtained.

Chemical methods to determine the crystalline content in silica have been reviewed (6). These are based on the solubility of amorphous silica in a variety of solvents, acids, or bases, with respect to relatively inert crystalline silica, and include differences in reactivity in high temperature fusions with strong bases. These methods are qualitative, however, and fail to satisfy regulatory requirements to determine crystallinity at 0.1% concentration in bulk materials.

Microamorphous silica can be divided into microparticulate silica, ie, microscopic sheets and fibers, and highly hydrated silica (1). The microparticulate silicas are the most important group commercially. These include silicas precipitated from aqueous solution and silicas formed in the vapor phase, called pyrogenic or fumed silica. Several synthetic routes exist to prepare any form of microporous silica, where microporous often refers to the ability of the silica to adsorb gases or liquids. For example, pyrogenic silica can be prepared by either (*1*) vaporizing silicon dioxide in an arc or in a plasma jet, and condensing it in an inert gas; (*2*) oxidizing the more volatile silicon monoxide, SiO, in the vapor phase with air, and condensing it; or (*3*) oxidizing silicon compounds (qv), eg, SiH_4, $SiCl_4$, or $HSiCl_3$, in the vapor phase in a hydrocarbon flame, and then condensing to produce branched-chain aggregates of silica up to ~1 μm in length (Fig. 6). Pyrogenic silica is collected as a finely divided powder.

Amorphous silica formed in aqueous solution can occur as sols, gels, or particles. A silica sol can either consist of polysilicic acid having a molecular weight of SiO_2 up to ~100,000, or be a stable dispersion of fine colloidal particles of diameters >5 nm (Fig. 7). A silica gel has a three-dimensional, continuous structure (Fig. 8). Macroscopic particles formed by aggregation of a sol or very small particles of a gel to afford bunched aggregates of silica up to approximately 1 μm in diameter are called precipitated silica (Fig. 9). This is collected as a powder by physically agglomerating these aggregates and evaporating the water.

Microscopic sheets of amorphous silica have been prepared in the laboratory by either (*1*) hydrolysis of gaseous $SiCl_4$ or SiF_4 to form monosilicic acid [10193-36-9] (orthosilicic acid), $Si(OH)_4$, with simultaneous polymerization in water of the monosilicic acid that is formed (7); (*2*) freezing of colloidal silica or polysilicic acid (8–10); (*3*) hydrolysis of $HSiCl_3$ in ether, followed by solvent evaporation (11); or (*4*) coagulation of silica in the presence of cationic surfactants (12). Amorphous silica fibers are prepared by drying thin films of sols or oxidizing silicon monoxide (13). Hydrated amorphous silica differs in solubility from anhydrous or surface-hydrated amorphous silica forms (1) in that the former is generally stable up to 60°C, and water is not lost by evaporation at room temperature. Hydrated silica gel can be prepared by reaction of hydrated sodium silicate crystals and anhydrous acid, followed by polymerization of the monosilicic acid that is formed into a dense state (14). This process can result in a water content of approximately one molecule of H_2O for each silanol group present.

2. Characterization

Amorphous silica is distinguished by chemical composition, physical properties, and characteristics of the particles. Exact analytical procedures depend on the type and intended application of the amorphous silica. The most important chemical information is the amount of silica, % SiO_2; percentage of associated water, determined by weight loss at 105°C; total solids content of nonoxidizable materials, determined by weight loss upon ignition at ~1200°C; presence of stabilizers, eg, formaldehyde (1); carbon content, such as carbon dioxide, carbonate, and organic carbon, determined by combustion to carbon dioxide; level of soluble salts, eg, chloride and sulfate, determined by X-ray fluorescence spectroscopy (15) or by chemical methods, eg, extraction; level of nonsiliceous ash; level of metal impurities, determined by X-ray fluorescence, eg, aluminum, sodium, calcium, manganese, and iron, or by atomic absorption, eg, copper and chromium; and silanol group density, determined by infrared (ir) spectroscopy (16) or chemical titration.

Physical characteristics include measurements of pH determined as a 5% aqueous slurry, density and tamped density, viscosity, turbidity, refractive index, light-scattering properties, and/or sedimentation rate by ultracentrifugation. Silica particles are characterized by specific surface area as determined by the adsorption of nitrogen gas by the BET method (17) or by the adsorption of cetyltrimethylammonium bromide (CTAB) (18); average particle size and size distribution; sieve residue; porosity such as average pore diameter and pore volume as determined by intrusion of mercury or adsorption of nitrogen gas (19); degree of aggregation as determined by mean projected area (MPA) measured using transmission electron microscopy (20); oil absorption, eg, dibutylphthalate, dioctylphthalate, or linseed oil; and rate of dissolution. Particle size is measured by transmission electron microscopy (21), light scattering, absorbance of visible light, low angle X-ray scattering, centrifugation, rate of reaction with molybdic acid, or surface area measurement of dried particles. Table 1 is a summary of standard test methods used to characterize amorphous silica follows:

The typical range of properties for commercial colloidal silicas, silica gels, precipitated silicas, and pyrogenic silicas is given in Table 2.

3. Commercial Production

In 2004, ~36% of synthetic amorphous silica production capacity is in Europe, followed by North America at 26%, China at 25% (estimated), and Japan at 13%. Worldwide production is ~80% of capacity. Table 3 is a summary. Although deposits of naturally occurring amorphous silicas are found in all areas of the world, the most significant commercial exploitation is of diatomaceous earth in industrialized countries (see DIATOMITE). This is because of the high cost of transportation relative to the cost of the material. Worldwide manufacturers of amorphous silica products are listed in Table 4.

4. Heterogeneous Reactions

4.1. Dissolution. Amorphous silica dissolves or depolymerizes in water according to equation 1:

$$SiO_2\,(s) + 2\,H_2O\;(l) \longrightarrow H_4SiO_4\;(aq) \qquad (1)$$

H_4SiO_4 (aq), which is either a monosilicic or an orthosilicic acid, is also expressed as $Si(OH)_4$ (aq) or H_2SiO_3 (aq). This material has not been isolated (1).

The solubility of amorphous silica in water at 25°C ranges from 70 to 150 ppm SiO_2 (1.2–2.2 mmol/kg). The variation results from differences in particle size, degree of hydration, and level of trace impurities. Areas having a small positive radius of curvature (convex) dissolve most extensively, and areas having a small negative radius of curvature (concave) dissolve least extensively (22). Particles having a diameter of less than $\sim$5 nm have a progressively greater solubility than do particles of continually increasing diameters. Particles $<$3 nm in diameter are very soluble (1). The solubility of amorphous silica in water increases with increasing temperature and pressure (23). For example, the solubility at 101.3 kPa (1 atm) and 0°C is $\sim$ 50 ppm of SiO_2 (0.8 mmol/kg), increasing to 100 ppm (1.7 mmol/kg) at 25°C, and 750 ppm (12.5 mmol/kg) at 100°C. The solubility increases by $\sim$ 50% as pressure is increased from 101.3 kPa to 101 MPa (1 to 1000 atm) at temperatures between 0 and 25°C.

Hydrated amorphous silica dissolves more rapidly than the anhydrous amorphous silica. The solubility in neutral dilute aqueous salt solutions is only slightly less than in pure water. The presence of dissolved salts increases the rate of dissolution in neutral solution. Trace amounts of impurities, especially aluminum or iron (24,25), cause a decrease in solubility. Acid cleaning of impure silica to remove metal ions increases its solubility. The dissolution of amorphous silica is significantly accelerated by hydroxyl ion at high pH values and by hydrofluoric acid at low pH values (1). Dissolution follows first-order kinetic behavior and is dependent on the equilibria shown in equations 2 and 3. Below a pH value of 9, the solubility of amorphous silica is independent of pH. Above pH 9, the solubility of amorphous silica increases because of increased ionization of monosilicic acid.

$$\mathrm{H_2SiO_3\ (aq) \rightleftharpoons H^+\ (aq) + HSiO_3^-\ (aq)} \quad K_1 = 1.6 \times 10^{-10} \tag{2}$$

$$\mathrm{HSiO_3^-\ (aq) \rightleftharpoons H^+\ (aq) + SiO_3^{2-}\ (aq)} \quad K_2 = 7.4 \times 10^{-13} \tag{3}$$

Amorphous silica is essentially insoluble in methanol, thus solubility in methanol–water mixtures decreases with increasing percentages of methanol. Natural biogenic silica often has an organic coating that inhibits dissolution. The coating can be removed by acid washing. The point of zero charge for the silica surface is between pH 2.5 and 3 (26).

4.2. Polymerization. Dissolved silica undergoes polymerization to give discrete particles that can further react. The three stages of reaction are polymerization of monomers to form particles, growth of particles, and linking of particles to give chains and then networks. In basic solution, the particles grow in size and decrease in number. In acid solution or in the presence of flocculating salts, particles aggregate into three-dimensional (3D) networks and form gels (Fig. 10) (27).

At concentrations below $\sim$ 100 ppm of SiO_2, the solubility of amorphous silica in water is such that monosilicic acid is in a true solution in water. Polymerization occurs only when solubility is exceeded and there is no solid phase present on which the silica can be deposited. The polymerization is an ionic reaction proportional to the concentration of hydroxyl ion at pH $>$ 2. Because of the thermodynamic tendency to maximize siloxane, –Si–O–Si–, and to minimize silanol (−Si−O−H) bonds, initially formed low molecular weight species are condensed, forming ring structures, such as cyclic tetramer, hexamer (see Fig. 2**a**), and octamer (see Fig. 2**b**). These species continue to react with additional monomer and become linked to one another (see Fig. 3). Internal condensation reactions continue to occur that lead to formation of a small particle. At temperatures >80°C and pH values >7, the particle is anhydrous. The silanol groups generally only form on the surface. These particles serve as nuclei on which 3D particle growth occurs. Because of the solubility difference, small particles dissolve and the silica is deposited on larger particles that grow in average size. This process is known as Ostwald ripening. Increasing temperature either increases the growth of sol particles or causes gel formation. The presence of dissolved salts assists in neutralizing particle surface charges to enhance aggregation of the particles into 3D gels. The rate of aggregation also increases with dissolved silica concentration in solution. As polymerization occurs, the solution still contains dissolved silica at a concentration equivalent to the solubility of amorphous silica (1,27–29).

5. Silica Sols and Colloidal Silica

5.1. Properties. Colloidal silica is a stable aqueous dispersion or sol of discrete amorphous silica particles having diameters of 1−100 nm. It is derived from sodium silicate. Silica sols do not gel or settle out of solution for at least several years of storage. Aqueous sols that contain up to 50% silica have been developed (30,31). Particle sizes of ∼ 130 nm in diameter are possible (32), but slowly settle out of solution.

In the absence of a suitable solid phase for deposition and in supersaturated solutions of pH values from 7 to 10, monosilicic acid polymerizes to form discrete particles. Electrostatic repulsion of the particles prevents aggregation if the concentration of electrolyte is below ∼ 0.2 N. The particle size that can be attained is dependent on the temperature. Particle size increases significantly with increasing temperature. For example, particles of 4−8 nm in diameter are obtained at 50−100°C, whereas particles of up to 150 nm in diameter are formed at 350°C in an autoclave. However, the size of the particles obtained in an autoclave is limited by the conversion of amorphous silica to quartz at high temperatures. Particle size influences the stability of the sol because particles <7 nm in diameter tend to grow spontaneously in storage, which may affect the sol properties. However, sols can be stabilized by the addition of sufficient alkali (1,33).

The stability of a silica sol depends on several factors (Fig. 11) and can be controlled by the surface properties of the silica (1). The pH value should be >7 to maintain sufficient negative charge on the silica particle surface to prevent aggregation. This surface charge is neutralized by soluble salts that ionize and reduce the size of the double layer around the silica surface (Fig. 12), allowing aggregation. Therefore, sols are only stable at low salt concentrations. In the low pH value region sols are metastable, and gelling and aggregation are catalyzed by even very small amounts of fluoride ion. In this low pH value region, water-miscible organic solvents, like alcohol, retard gelling. Gelling occurs more rapidly at higher temperatures and is facilitated by a high silica concentration in the sol.

Silica sols can be destabilized by aggregation, gelation, crystallization, or particle growth plus settling. Aggregation occurs by coagulation in which particles collide or by flocculation in which particles become linked by bridges of flocculating agent (see FLOCCULATION AGENTS). Aggregation is prevented at neutral or lower pH values by the presence of an adsorbed layer of inert material, such as a surfactant, on the silica surface, thus preventing the direct contact of silanol groups with one another. Aggregation, as well as particle growth, is minimized by maintaining either a low silica concentration, a low reaction temperature, and/or a pH value of 9–10. Destabilization of a sol by crystallization of silica rarely occurs because this is a slow process at ambient temperatures (1).

5.2. Preparation. To produce sols that are stable at relatively high silica concentrations, particles must be grown to a certain size in weakly alkaline aqueous dispersion. Sols can be prepared by (*1*) neutralizing a dilute solution of sodium silicate with acid to a pH value of 8–9. A sol is produced if the sodium salt concentration is less than ~0.3 *N* and the neutralization reaction is performed at elevated temperatures to promote rapid particle growth. Rapid mixing prevents formation of low pH regions where gelation might occur; (*2*) washing sodium ions from the sodium silicate solution by electrodialysis or using an ion-exchange resin to form active silica, ie, low molecular weight polysilicic acid (1), which is stored at 82–100°C. Additional active silica is added to grow the sol particles, which can then be concentrated by evaporation or ultrafiltration; (*3*) washing out the salt from a freshly formed silica gel and peptizing at elevated temperature and pressure; (*4*) hydrolyzing $SiCl_4$ or organosilicates, such as ethyl silicate plus isopropyl alcohol. However, such sols are generally not stable and gel quickly; (*5*) cleaning pulverized silicon metal with hydrofluoric acid to remove the oxide coating, which causes a reaction with water in an alkaline medium to produce hydrogen gas and colloidal silica, which can be stabilized as a sol with alkali; and (*6*) oxidizing $SiCl_4$ or ethyl silicate at high temperature, or vaporizing silica in the presence of a reducing agent to give pyrogenic silica powder. Particles are partly coalesced, have a low concentration of surface silanol groups, and are difficult to disperse in water to form sols without the addition of a wetting or other dispersing agent, or such treatment as grinding. The resultant sols contain aggregates. A detailed review of silica sol preparation methods is available (1).

Silica sols can be purified with the aid of an ion-exchange resin, dialysis, electrodialysis, or washing. Washing is usually affected by centrifugation, flocculation, ultrafiltration, or electrodecanting, followed by redilution and reconcentration. A preservative, such as formaldehyde is sometimes added to prevent the growth of microorganisms. Sols are concentrated by evaporation using forced circulation evaporators. If the sol becomes too concentrated, a hard layer of silica is deposited on the equipment walls, especially on heat-exchanger surfaces, so evaporation must be carefully monitored. Sols having particle size >30 nm in diameter are concentrated by centrifugation. Ultrafiltration (qv), where the sol collects near the impermeable filter, can be used to remove water and salts. Sols that are low in soluble salts are concentrated by electrodecantation (1).

5.3. Modifications. Coagulation, flocculation, or gelation of silica sols and their subsequent drying produce amorphous silica powders. Gelation is rapid at pH values of 4–6. It is effected by increasing the silica content, such as by evaporation (qv). Further drying of the resulting gel yields colloidal aggregates. Coagulation of a sol is prevented by surface charge and surface hydration; conversely, neutralizing the surface charge by lowering the pH value or by adding salt causes coagulation. Addition of salts also causes surface adsorption of cations that reduce surface hydration. Polyvalent cations, eg, Al^{3+}, are strongly adsorbed by silica surfaces and neutralize the surface charge. Hydrated metal cations act as bridging compounds or flocculating agents (qv) for silica particles. Flocculating agents used with silica sols are cationic surfactants (qv), eg, octadecyltrimethylammonium bromide, or organic polymers, eg, polyethyleneimine or polyacrylamide (1).

Sol particles are extremely small, and particulate silica obtained from sols is composed of aggregates or porous particles that have a much higher specific surface area than estimated from apparent size. Aggregates are also called secondary particles. Once silica particles have been formed as a sol, the surface can be modified by the attachment of different atoms or groups to obtain specific properties. Addition of aluminate ions gives an aluminosilicate surface that is much less soluble than is the silica surface and much more stable toward gelling, even at pH values of 4–6 and in the presence of salts. Addition of polyvalent metal oxides reverses the surface charge of silica and prevents bridging by siloxane bond formation. Organic groups can be added to silica surfaces in the form of organic ions through the formation of Si–O–C bonds as in esters or Si–C bonds as in organosilicon compounds. These surface alterations make silica easily dispersible in organic solvents, including nonpolar hydrocarbons. Some of these processes may cause the silica surface to become hydrophobic. Even a small change in particle surface characteristics may change the chemical behavior of the particle. Thus, a silica particle covered with alumina behaves in many ways as an alumina particle, and a silica particle covered with a hydrocarbon coating acts in many ways as a large hydrocarbon molecule (1,34–37).

5.4. Applications. In 2002, >83,000 metric tons of colloidal silica (38) were manufactured by DuPont, Eka Chemical, Kemira, Nalco, Precision Colloids, and Nyacol Nano Technologies in the United States; by Azem (France), Bayer (Germany), Chemiewerk Bad Kostritz (Germany), Eka Chemicals (Germany, Sweden), and DuPont AirProducts NanoTechnologies (United Kingdom) in Europe; and by Catalysts & Chemicals, Fuso, and Nissan Chemical in Japan. Colloidal silicas are typically used for making silica gels having uniform pore sizes and pore volumes; as binders in molds for precision casting of superalloys; for increasing the friction properties of surfaces, such as paper, floors, fibers, and films; as antisoiling finishes on paper, textiles, and painted surfaces; for hydrophobizing surfaces and increasing their wettability by water; for strengthening polymer and latex goods; for polishing silicon wafers used in electronics industry; for improving performance of agents used for wetting and dispersing; as photographic emulsions; and for clarifying wines (see WINE), beers (see BEER), and gelatin (qv) (39).

6. Silica Gel

6.1. Properties. Silica gel (see Fig. 8) is a coherent, rigid, continuous 3D network of spherical particles of colloidal silica. Both siloxane, −Si−O−Si−, and silanol, −Si−O−H, bonds are present in the gel structure. The pores are interconnected and filled with water and/or alcohol from the hydrolysis and condensation reactions (40). A hydrogel is a gel in which the pores are filled with water. A xerogel is a gel from which the liquid medium has been removed, causing the structure to collapse, thus decreasing porosity. If the liquid medium is removed in a manner such that shrinkage and collapse of the gel structure do not occur, an aerogel is formed. Porous glass is similar to a silica gel. Silica powder can be made from xerogels by grinding or micronizing, which decreases the size of the gel fragments but leaves the ultimate gel structure unchanged. Gels and powders are characterized by the density, size, and shape of the particles, particle distribution, and aggregate strength or coalescence (1,27–29,41–44).

Silica gels are classified into three types: regular, intermediate, and low density gels. Regular density silica gel is made in an acid medium, which gives high (eg, 750 m^2/g) surface area, small ultimate (or primary) particles having average pore diameters of 2.2−2.6 nm, and a pore volume of 0.37−0.40 mL/g. This regular density silica gel contains ~ 6 wt % water as surface hydroxyl groups, which imparts a high capacity for adsorption of water and other polar molecules (see Desiccants). The gel exhibits a high selectivity for polar molecules and has a large percentage of small pores. Intermediate density silica gel consists of larger ultimate particles having a lower (300−350 m^2/g) surface area, larger (0.9−1.1 mL/g) pore volumes, and larger (12−16 nm) average pore diameters. Because of the large pore size, intermediate density silica gel has a high capacity for water adsorption at high humidities. It is often used as a fine powder because aggregate (or secondary) particle size and porosity can be controlled. Low density silica gel (eg, an aerogel) has lower (100−200 m^2/g) surface areas, larger (18−22 nm) average pore diameters, and larger (1.4−2.0 mL/g) pore volumes. It is usually prepared as a very fine powder of extremely low density. Shrinkage of the gel during drying is minimized.

6.2. Preparation. Silica gels can be prepared by several methods (1,40,43). Most commonly, a sodium silicate solution is acidified to a pH value of <10−11. The gelling time varies, as shown in Fig. 10. Syntheses include the bulk-set, slurry, and hydrolysis processes. The bulk-set process consists of preparing a silica hydrosol (gel) by mixing sodium silicate and a strong mineral acid, followed by mechanically breaking, washing the hydrogel particles free of electrolytes, drying, and activating. In the slurry process, sodium silicate solution and acid are mixed, either in batch or semicontinuously, to produce a gelatinous precipitate that is washed and dried, often by spray drying. These gels usually have a small particle size and the salts must be washed away before use. Gels can also be made directly from salt-free colloidal silica, which provides larger ultimate particle sizes, and hence greater stability, along with low salt contents. Such gels may also have lower specific surface areas and larger pore diameters. Hydrolysis of pure silicon compounds, such as ethyl silicate, silicon tetrachloride, and other volatile hydrolyzable silicic esters, is another method of preparing gels. Although more expensive, this process produces dense gels of high purity and very small pore size.

The properties of a finished gel are determined by the size of the primary particles at the moment they aggregate into the gel network, called the gelation point (or gelation time). It is usually defined as the point at which aggregation in the sol forms a 3D network that can support a stress elastically. The sol-to-gel transformation is not well defined because it occurs as a continuous increase in viscosity (40). The concentration of the primary particles in solution affects the physical properties of the gel, including the compactness of the gel network, the pH, salt concentration, temperature, and time during which the gel is aged while wet, and the mechanical pressure or shear forces applied to the gel before or during drying. Additionally, the physical properties are influenced by the temperature, pressure, pH, salt content, and surface tension of the liquid medium as it is being evaporated from the pores of the gel, and the temperature, time, and type of atmosphere in which the gel is heated after being dried (1). The type of catalyst used in gelation can have significant effects on the kinetics of the process and the structure of the silica gels formed (45,46). For some applications, silica gel is converted to pelletized or granular form by extruding pulverized gel with a binder or by shaping the hydrogel during drying. Silica can be gelled in spherical form by spray-drying, or by spraying droplets into an immiscible liquid (emulsion polymerization). Freezing of a silica sol produces silica gel particles of nonspherical shapes.

6.3. Characterization. When silica gel is used as an adsorbent, the pore structure determines the gel adsorption capacity. Pores are characterized by specific surface area, specific pore volume (total volume of pores per gram of solid), average pore diameter, pore size distribution, and the degree to which entrance to larger pores is restricted by smaller pores. These parameters are derived from measuring vapor adsorption isotherms, mercury intrusion, low angle X-ray scattering, electron microscopy, gas permeability, ion or molecule exclusion, or the volume of imbibed liquid (1).

Surfaces can be categorized as fully hydroxylated, in which the surface consists solely of silanol, −Si−O−H, groups, a siloxane, −Si−O−Si−, or an organic surface. Silanol surfaces are formed by drying silica gels or precipitates from water at temperatures below 150°C. These surfaces are readily wetted by water. Hydroxylated surfaces heated from 300 to 1000°C progressively develop a siloxane surface by dehydration, such as that found on pyrogenic silica surfaces. The behavior of particles having organic surfaces depends on the coating material. The particles may become dispersible in water, oil, or other organic solvents. If fluorocarbons are the surface group, the silica becomes both hydrophobic and oleophobic. The nature of the surface can be determined by measuring the heat of nitrogen adsorption, dye adsorption, ir adsorption, or chemical analysis (1,28,33–37).

6.4. Modifications. Once a gel structure is formed, it can be modified in the wet state to strengthen the structure or enlarge the pore size and reduce surface area, through a process called aging (1,40,47). Silica gel reinforcement can be carried out in several ways: (*1*) active silica, ie, low molecular weight polysilicic acids (1), can be added to a broken-up gel in order to deposit it at a uniform rate on the gel; (*2*) active silica can be added to a sol as the gel is growing, causing strong gel bridges to form between particles; (*3*) wet gel can be heat-aged to increase coalescence of the particles.

In this aging process, silica is dissolved from smaller particles and deposited at the points of contact between larger particles. Condensation reactions in the gels continue to occur because of the presence of the silanol, −Si−O−H, groups (48,49). Because of the formation of new siloxane bonds that bridge the particles, the continued polymerization reactions strengthen and stiffen the network (47). Washing can also be an aging step because aging a wet gel can increase interparticle bonding, which leads to less shrinkage of the gel during drying. Low density silica gels are made by minimizing shrinkage during drying by reinforcing the gel by aging, or by replacing the water with a liquid of lower surface tension, eg, an alcohol. The gel is then heated to a temperature above the critical point of the liquid, thereby releasing the liquid as a vapor. Supercritical drying is often used in aerogel processing (1).

Sintering, or heating to convert a powder into a continuous mass, a dried silica surface in air, or in a vacuum causes shrinkage that decreases the surface area, whereas sintering in steam increases pore size. For example, micropores are obtained by heating a hydrated gel at 1000°C for 10 h. The presence of impurities, such as aluminum tends to minimize changes caused by heating. At temperatures >1000°C, however, and in the presence of impurities, silica gel is converted to cristobalite or nonporous silica glass. Gels having extremely small pores can be made. Such gels include impervious silica, porous glass, and adsorbents for which the applications are tailored to surface properties and pore size.

6.5. Applications. Approximately 175,000 metric tons of silica gels were manufactured in 2002 (38), primarily by Grace, INEOS, Multisorb, and PQ in the United States; by CECA (France), Chemie-Werke Bad Kostriz (Germany), Grace (Germany), and INEOS (United Kingdom) in Europe; and by Dohkai, Mizusawa, Tokai and Tosoh in Japan. However, the largest manufacturing base is in China where 60−80 thousand metric tons of silica gels were produced in 2004, with 30,000 metric tons exported. The largest application areas for silica gels include healthcare products as thixotropic agents in cosmetics (qv) and dentrifices (qv); selective absorbents to maintain clarity during the brewing of beer; desiccants; thixotrope and flatting agents in coatings (50–52); and supports for polymerization catalysts. Specialized silica gels that have uniform pore structure, and that are often surface treated, are used in the production of chromatography (qv) columns for gas- and liquid-phase separations. Amorphous silica gels (53) and aerogels (54) are also used as insulating materials and sol−gel coatings for optical applications (55).

7. Precipitated Silica

Particulate silica is composed of aggregates (or secondary particles) of ultimate (or primary) particles of colloidal-size silica that have not become chemically linked in a massive gel network during the preparation process. Particulate silicas are either made from the vapor phase to form pyrogenic (or fumed) silicas, or by precipitation from solution, generally aqueous, to form precipitated silicas.

Particulate silica powders have a more open structure with higher pore volume than do dried pulverized gels, as can be seen by comparing Figs. 6 and 9 to Fig. 8.

7.1. Properties. The physical and chemical properties of precipitated silicas can vary according to the manufacturing process. Ultimate particle and aggregate sizes of silicas precipitated from solution can be varied by reinforcement and control of suspension pH, temperature, and salt content value. The surface area, as determined by nitrogen (17) or CTAB (18) adsorption, is a function of the ultimate particle size, which can range from 5 to 50 nm in diameter. Aggregates are three-dimensional clusters of ultimate particles (see Fig. 9), which range in size up to ~ 500 nm in diameter. Ultimate particles in aggregates are covalently bonded to one another via siloxane bond formation. Aggregate particles can be physically agglomerated through hydrogen bonding of surface silanol groups to one another, thus affording structures that can range up to ~ 100 μm in diameter. The median agglomerate particle size is generally 20–50 μm in diameter, but can be reduced in size by milling, eg, to ~ 1 μm.

7.2. Preparation. Precipitated silica is formed from an alkaline metal silicate solution, eg, sodium silicate, in a ratio of ~ 2.5–3.3 SiO_2/Na. Lower concentrations of silicate are used in silica gel preparation. In the absence of a coagulant, silica is not precipitated from solution at any pH value (1). Silica is precipitated by adding acid to sodium silicate to reduce the pH value of the hot suspension to a pH value of 9–10, where the concentration of sodium ion exceeds ~ 0.3 *N*. Sulfuric acid, hydrochloric acid, and carbon dioxide are examples of acids used commercially to neutralize sodium silicate and precipitate silica. Figure 13 shows a schematic of this process. Precipitation proceeds in three basic steps: forming colloidal particles through nucleation and particle growth to the desired ultimate particle size; coagulating colloids into aggregates to form a suspended precipitate, where the control of pH and sodium ion concentration is critical; and reinforcement of the aggregate particle to the desired degree without further nucleation (1) so that the structure is not altered.

Coagulation can also be induced by using polyvalent metal cations, eg, calcium ions, as well as by using ammonium and fluoride ions, and certain organic compounds. Reinforcement can be carried out by adding active silica, low molecular weight polysilicic acids, to the aggregate suspension under alkaline conditions $>60^{\circ}C$, or by adding acid and metal silicate at a controlled rate so that active silica forms and is polymerized on the suspended silica without forming new particles. To obtain a dry precipitate by water removal, the ultimate particles should be larger than ~ 10 nm, typically >20 nm, and the aggregates should be reinforced so that the pore structure does not collapse upon drying as a result of capillary forces. This reinforcement of the silica aggregate is characterized by the buildup ratio, which is the ratio of the final weight of silica in the system to the weight of the aggregated silica. Buildup ratios of $<4:1$ are usually preferred in order to achieve, eg, dispersibility in rubber. For each type of precipitated silica there is an optimum degree of reinforcement for maximum dispersibility (1).

7.3. Modifications. Precipitated silicas are hydrophilic and may contain up to ~ 10% water as surface silanol, –Si–O–H, groups that remain after drying at 150°C. The interaction of the surface of amorphous silicas with organic molecules is strongly affected by the degree of hydroxylation of the silica surface. Thus, modification to hydrophobize the surface of a precipitated silica can be an important step toward increasing its compatibility with substrates such as nonpolar polymers. The choice of appropriate modifying substance and the method of surface modification are important. Surfactant (57–59), organosilane (60), and organotitanate (61) coupling agents and polymeric films (62,63) may be employed.

7.4. Applications. In 2002, ~ 840,000 metric tons of amorphous precipitated silica were manufactured for sale (38). Degussa, J. M. Huber, PPG, and Rhodia in the United States, Degussa (Germany), Grace (Germany), J. M. Huber (Finland), PQ (Netherlands), Rhodia (France), and Silquimica (Spain) in Europe, and Degussa (DSL jv), Tokuyama, and Tosoh in Japan, Oriental (China, Taiwan), Rhodia (Korea) are the primary producers. In addition, a large number of local maunfacturers are present in China (>100) and in India, which manufacture ~25% of global production, see Table 3.

Additionally, precipitated silica is manufactured and utilized internally for such uses as extenders for detergents and cleaners. Because of the small particle size and complex aggregate structure (see Fig. 9), precipitated silica imparts the highest degree of reinforcement to elastomer compounds, eg, natural rubber, among all of the mineral fillers (see RUBBER, NATURAL). This superior reinforcement is employed in a variety of rubber compounds for shoe soles, industrial rubber goods, and tires (64–66). Precipitated silica is used in shoe soles for its resistance to wear and tearing, for its nonscuffing characteristics, and in order to obtain compounds having light color, or even a transparent material. In addition, precipitated silica is used to improve the tear strength and resistance to flex fatigue, ie, cracking and cut growth, and heat aging in a wide variety of manufactured rubber goods, including conveyor and power transmission belts, hoses, motor and dock mounts, and bumper pads. Rubber rolls that utilize the abrasion resistance, stiffness, and nonmarking characteristics of precipitated silica are important for use in paper processing and the dehulling of grains, particularly rice (see WHEAT AND OTHER CEREAL GRAINS) (67).

Precipitated silica is used in a variety of tire applications (Fig. 14). The reinforcement of rubber compounds by precipitated silica has been found to be directly related to the surface area of the silica (68), which is a function of the ultimate particle size (68–70), and of efficiency to the silane coupling reaction (70–76). The use of precipitated silica at very high levels in tire treads has been shown to impart outstanding wet traction and rolling resistance to passenger tires, which improve vehicle handling and fuel economy (77).

Additional uses of amorphous precipitated silica include reinforcement of specialty elastomers, especially those based on polydimethylsiloxane (78); defoamer in paper processing (79), and an ingredient for good ink retention; production of polyethylene/silica membranes used as separators for plates in lead–acid batteries (qv) (80,81); control of viscosity in dentrifice (82) and coating formulations (83); abrasive ingredient in toothpaste (82) and polishing formulations; absorbent of liquids in food applications (84), animal feedstocks, and fire extinguishers; starting material for high purity zeolite manufacture; gloss control agent in coatings and plastics; carrier for active ingredients, eg, pesticides (85); and extender for detergents, papers, and coatings (56).

8. Pyrogenic Silica

8.1. Properties. Amorphous pyrogenic (fumed) silicas are fluffy white powders that are generally less dense and of higher purity than are silicas precipitated from solution. Pyrogenic silicas have a much lower hydrated surface and are sometimes completely anhydrous. Surface silanol density normally ranges from 2–4/nm^2 of surface area. The particle size is controlled by combustion conditions during the flame hydrolysis. Pyrogenic silicas having surface areas $<300\ m^2/g$ are essentially nonporous, whereas those having higher surface areas can have some porosity. They generally can contain a few hundred ultimate particles fused into branched-chain, 3D aggregates (56) (eg, see Fig. 6). Pyrogenic silicas in the 100-nm to 2-μm diameter particle size range are common (86).

8.2. Preparation. Pyrogenic silica can be prepared in several ways, including vaporizing silica and oxidizing organic or inorganic silicon compounds. Vaporizing silica at high temperatures of $\sim 2000°C$ forms anhydrous amorphous silica particles upon cooling. In the presence of a reducing agent, eg, coke, silica sublimes at $\sim 1500°C$ to produce the volatile silicon monoxide, SiO, which can then be oxidized to produce particulate fumed silica, SiO_2. Oxidation of silicon tetrachloride, $SiCl_4$, vapor at high temperatures produces fumed silica and Cl_2. Alternatively, silicon tetrachloride can be burned in the presence of methane, CH_4, or hydrogen, H_2, gases to produce fumed silica, H_2O, and HCl. The latter process is an important commercial method (Fig. 15) (56). Silicon ester vapors can be oxidized and hydrolyzed to produce particulate silica of high purity, though at high cost. Silicon tetrafluoride, SiF_4, a by-product of the phosphate fertilizer industry, can also be used to produce pyrogenic silica by hydrolysis of the vapor at 1600–2200°C. HF is a by-product that can then react with sand to produce more SiF_4 (1,87).

8.3. Applications. Pyrogenic or fumed silica production in 2002 was estimated to be 120,000 metric tons (38). Cabot and Degussa in the United States and in Europe, General Electric (United States), Wacker-Chemie (Germany), Nippon Aerosil (Japan), and Tokuyama Soda (Japan) were the largest manufacturers. Pyrogenic silica is used in rubber applications that require a low level of surface water per unit surface area of the silica, primarily as a reinforcement in adhesives, sealants (88), and elastomer compounds based on silicone polymers (89,90). Pyrogenic silica also has a variety of other uses. It serves as a thixotropic agent in plastics, eg, in polyester casting resins; gel coats (91); sealants and adhesives (92); cosmetics in ointments and lotions (93); toothpastes; coatings (91); printing inks (94); free flow, antistatic agent in animal feedstuffs and hygroscopic powders; carrier for active ingredients, eg, pharmaceuticals (qv), catalysts, and liquid spice extracts (95); gloss control agent in coatings and foils (56); coating additive to improve the mechanical reliability of fused silica optical fibers (96); and antifoaming or defoaming agent in the manufacture of paper, decaffeinated coffee and tea, poultry and seafood processing, and oil refining (97).

9. Fused Silica

Transparent fused silica can be formed at a temperature of 1200°C and a pressure of 13.8 MPa (2000 psi) from silica powder consisting of 15-nm ultimate particles (98) or by electric arc fusion of pure silica sand having low iron and alkali metal contents. The cooled product is ground to the desired particle size, usually powders >8 μ in diameter. Fused silica is primarily manufactured by C-E Minerals, MINCO, and Precision Electro Minerals in the United States; by Didier-Werke (Germany), Frank and Schulte (Germany), Saint-Gobain Quartz (United Kingdom), Sico (Austria), and Vesuvius (France) in Europe; by Denki Kagaku Kogyo, Kinsei Matec, Micron, Tatsumori, Tokuyama, and Toshiba Ceramics in Japan. Based on 2002 data, an estimated 170,000 metric tons of fused silica were used as a sacrificial component or investment casting in the manufacture of metals and as a component in refractory materials (99) and in the lithography industry (100).

10. Naturally Occurring Amorphous Silica

10.1. Formation.

Most naturally occurring amorphous silica deposits are biogenic forms deposited from the exoskeleton, plates, or spines of aquatic organisms, eg, diatoms, radiolarians, silicoflagellates, and certain sponges. These organisms extract silica from very dilute solutions, eg, 0.1 ppm of SiO_2 or 2 mmol/kg, and are found in both marine and freshwater environments. Large deposits of these materials are found as loosely coherent chalk-like sediments in the equatorial Pacific area, ie, radiolarians, and in high latitude areas of all oceans, ie, diatoms. All biogenic silicas are noncrystalline because the kinetic barrier to crystallization is high [$\sim$ 800 kJ/mol (191 kcal/mol)] in neutral aqueous environments. In all these structures, the mineral exists as a hydrated, covalent inorganic polymer having the general structure $(SiO_{n/2}(OH)_{4-n})_m$, where m is a large integer representing the degree of polymerization and n ranges from 0 to 4 to indicate the degree of hydration (101).

The silica structure has a close relationship to the cellular structure of the organism. Silica is deposited as gels, sheets, fibers, tubes, and globular assemblies. It has been found that the macroscopic geometric structure of the deposited silica is replicated in the short-order (two–three siloxane unit) structure (101). Although the dissolution of silica is inhibited by inclusion of various metal ions in the structure and often an organic coating, these deposits are converted over millions of years to opal-CT and opal-C, which are well-crystallized cristobalite (102). These siliceous materials are also transformed by dissolution, precipitation, recystallization, and compaction over geological time to form a less soluble, denser material, which is called chert if granular, chalcedony if fibrous, or flint if dark gray. Amorphous silica can be formed by the alteration of sand to a colloidally subdivided high surface area, amorphous silica volcanic ash (1). Amorphous silica is sometimes precipitated from the hot supersaturated waters of hot springs (siliceous sinter) and geysers (geyserite) where it is often found along with calcareous sinter (103,104).

10.2. Applications. The most significant commercial material from the biogenic silicas is diatomaceous earth [7631-86-9], also called kieselguhr or diatomite (qv). These deposits are the sediment of fragments and shells of one-celled algae, which form very fine particles having high surface area and as high as 94% silica content. Initially, silica in diatomite is amorphous, but portions of these deposits have been converted to cryptocrystalline quartz (103). Approximately 1,500,000 metric tons of diatomaceous earth were used in 1994 as absorbents, fillers, insulating materials, and polishing agents, primarily in China, France, Germany, Italy, Korea, Mexico, and the United States. Tripoli, a white-to-gray, soft, porous material used as an abrasive or a filler, is mined from the Devonian deposits in southern Illinois. It is sold as amorphous silica, although it is actually a microcrystalline quartz ($<10\,\mu m$ dia) formed by leaching of carbonates from calcite- or dolomite-bearing chert (see FILLERS).

11. Health and Safety Factors

Amorphous silica is classified as nontoxic by ingestion. Soluble silica is present in most drinking water. It has been observed that silica passes through the body in soluble form being excreted with the water (39).

Unlike crystalline silica, amorphous silica has not been shown to cause silicosis (105), even in workers having long exposure to the product. This is presumed to be a result of the differing surface chemistry and solubility between crystalline and amorphous silica (106). The biological effects in animals of inhaled amorphous precipitated, fumed, and gelled silicas have been studied (107). After 12–18 months exposure to an environment containing an average daily respirable dust concentration of 6.9–9.9 mg/m^3, rats, guinea pigs, and Cynomolgus monkeys were tested for pulmonary function and by microscopic examination of internal organ tissue sections. Respiratory function was impaired for all animals and the presence of macrophage and cell aggregate lesions in the lungs of the monkeys were reported. It has been reported that these lesions regress after exposure to the dust is stopped (108). Monkeys exposed to fumed silica show the presence of reticulin fibers in the lungs as well.

Amorphous silica is classified by the Occupational Safety and Health Administration as a nuisance dust. The principal reported health reaction is contact dermatitis resulting from the absorption of protective oils from the skin (1). Effective May 15, 2002, the Environmental Protection Agency regulated an exemption from the requirement of a tolerance for residues of silica, amorphous, fumed (crystalline free), also known as silicon dioxide fumed amorphous, when used as an inert ingredient when applied to animals (109).

BIBLIOGRAPHY

“Silica and Silicates (Silica Gel)” in *ECT* 1st ed., Vol. 12, pp. 345–360, by S. S. Hubbard, The Davison Chemical Corp.; “Silica (Amorphous)” in *ECT* 2nd ed., Vol. 18, pp. 61–72, by R. K. Maher, Davison Chemical Division, W. R. Grace & Co.; in *ECT* 3rd ed., Vol. 20, pp. 766–781, by J. D. Willey, University of North Carolina at Wilmington; in *ECT*

4th ed., Vol. 21, pp. 1005–1032, by W. H. Waddell, Exxon Chemical Co., and L. R. Evans, J. M. Huber Corp.; “Silica, Amorphous Silica” in *ECT* (online), posting date: December 4, 2000, by W. H. Waddell, Exxon Chemical Co., and L. R. Evans, J. M. Huber Corp.

CITED PUBLICATIONS

1. R. K. Iler, *The Chemistry of Silica*, John Wiley & Sons, New York, 1979.
2. W. Nieuwenkamp, *Z. Krist.* **96**, 454 (1937).
3. F. Ordway, *Science* **143**, 800 (1964).
4. H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed., John Wiley & Sons, New York, 1974.
5. E. Gorlich, *Ceramics Int.* **8**, 3 (1982).
6. W. J. Miles and R. D. Hamilton, *Anal. Chim. Acta* **286**, 3 (1994).
7. R. Schwartz and O. Liede, *Chem. Ber.* **53B**, 1680 (1920).
8. H. Kautsky and R. Irnich, *Z. Anorg. Allg. Chem.* **295**, 193, 206 (1958).
9. H. Kautsky, W. Otto, and H. Pfleger, *Z. Naturforsh* **19**, 102 (1964).
10. H. Kautsky and R. Reise, *Z. Naturforsh* **20b**, 93 (1965).
11. E. Wiberg and W. Simmler, *Z. Anorg. Allg. Chem.* **283**, 401 (1956).
12. U.S. Pat. 2,801,902 (Aug. 6, 1957), G. B. Alexander and R. K. Iler (to E. I. du Pont de Nemours & Co., Inc.).
13. T. Nemetshek and U. Hofmann, *Z. Naturforsh* **8b**, 410 (1953).
14. A. Simon and P. Rath, *Z. Anorg. Allg. Chem.* **202**, 191 (1931).
15. E. P. Bertin, *Principles and Practices of X-ray Spectrometric Analysis*, 2nd ed., Plenum Press, New York, 1975.
16. A. T. Bell and M. L. Hair, eds., *Vibrational Spectroscopies for Adsorbed Species*, American Chemical Society, Washington, D.C., 1980.
17. S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).
18. National French Test Method, T 45-007 (1987).
19. S. J. Gregg and W. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed., Academic Press, London, U.K., 1982.
20. ASTM D3849, *Primary Aggregate Dimensions from Electron Microscopic Image Analysis*, ASTM, Philadelphia, Pa., 1980.
21. D. B. Williams, *Practical Analytical Electron Microscopy in Materials Science*, Electron Optics Publishing Group, Mahwah, N.J., 1987.
22. G. Hulett, in J. Alexander, ed., *Colloid Chemistry*, Chemical Catalog Co., New York, 1926.
23. J. V. Walther and H. C. Helgeson, *Am. J. Sci.* **277**, 1315 (1977).
24. C. M. Jephcott and J. H. Johnston, *Arch. Ind. Hyg. Occup. Med.* **1**, 323 (1950).
25. J. J. Denny, W. D. Robeson, and D. A. Irwin, *Can. Med. Assoc. J.* **40**, 213 (1939).
26. S. G. DeBussetti, M. Tschapek, and A. K. Helmy, *J. Electroanalyt. Chem.* **36**, 507 (1972).
27. R. K. Iler, in E. Matijevic, ed., *Surface and Colloid Science*, Vol. 6, John Wiley & Sons, New York, 1973.
28. Z. Z. Vysotskii and co-workers, in D. N. Strazhesko, ed., *Adsorption and Adsorbents*, No. 1, John Wiley & Sons, New York, 1973.
29. R. K. Iler, *J. Colloid Interface Sci.* **75**, 138 (1980).
30. U.S. Pat. 3,012,973 (Dec. 12, 1961), R. C. Atkins (to E. I. du Pont de Nemours & Co., Inc.).
31. U.S. Pat. 3,440,176 (Apr. 22, 1969), R. Sippel (to E. I. du Pont de Nemours & Co., Inc.).

32. U.S. Pat. 2,574,902 (Nov. 13, 1951), M. F. Bechtold and O. E. Snyder (to E. I. du Pont de Nemours & Co., Inc.).
33. D. H. Napper and R. J. Hunter, *Med. Technol. Publ. Int. Rev. Sci. London* **7**, 241 (1971).
34. J. A. Hockey, *Chem. Ind. London* **2**, 57 (1965).
35. L. C. F. Blackman and R. Harrop, *J. Appl. Chem.* **18**, 37 (1968).
36. A. Snoeyink and W. Weber, in J. F. Danielli, M. D. Rosenberg, and D. A. Cadenhead, eds., *Progress in Surface and Membrane Science*, Vol. 5, Academic Press, Inc., New York, 1972.
37. D. Barby, in G. D. Parfitt, and K. S. W. Sing, eds., *Characterization of Powder Surfaces*, Academic Press, Inc., New York, 1976.
38. D. H. Lauriente and K. Yokose, CEH Marketing Research Report, *Silicates and Silicas*, Chemical Economics Handbook-SRI Consulting, 2005.
39. R. K. Iler, *Chem. Aust.* **53**, 355 (1986).
40. L. L. Hench and W. Vasconcelos, *Annu. Rev. Mater. Sci.* **20**, 269 (1990).
41. C. Okkerse, in B. G. Linsen, ed., *Physical and Chemical Aspects of Adsorbents and Catalysts*, Academic Press, Inc., New York, 1970.
42. S. Kondo, *Hyomen* **10**, 321 (1972).
43. I. E. Neimark and R. Y. Sheinfain, *Silica Gel: Preparation, Properties and Uses*, Nauk Dumka, Kiev, CIS, 1973.
44. H. Teicher, in T. C. Patton, ed., *Pigment Handbook*, Vol. 1, John Wiley & Sons, New York, 1973.
45. C. J. Brinker and co-workers, *J. Non-Cryst. Solids* **48**, 47 (1982).
46. M. W. Colby, A. Osaka, and J. D. MacKenzie, *J. Non-Cryst. Solids* **99**, 129 (1988).
47. C. J. Brinker and G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, Inc., Boston, 1990.
48. T. W. Zerda, I. Artaki, and J. Jonas, *J. Non-Cryst. Solids* **81**, 365 (1986).
49. L. W. Ketls, N. J. Effinger, and S. M. Melpolder, *J. Non-Cryst. Solids* **83**, 353 (1986).
50. L. Kutik, *J. Coat. Technol.* **58**, 91 (1986).
51. D. J. Kent, T. E. Fletcher, and N. Wings, *Asia Pacific Coatings J.* 20 (Oct. 2004).
52. D. J. Kent, T. E. Fletcher, and N. Wings, *Paint Coatings Ind. J.* 64 (Sept. 2005).
53. C. J. Brinker and co-workers, *Mater. Res. Soc. Symp. Proc.* **284**, 469 (1993).
54. J. Fricke and A. Emmerling, *Adv. Materials* **3**, 504 (1991).
55. L. L. Hench, *Ceram. Trans.* **29**, 591 (1993).
56. P. Kleinschmit, *Spec. Inorg. Chem.* **40**, 196 (1981).
57. A. W. Kiselew, *J. Colloid Interface Sci.* **28**, 430 (1968).
58. H. Ferch, *Chem. Ing. Technol.* **48**, 922 (1976).
59. G. Taylor and J. H. Adkins, *J. Phys. Chem.* **70**, 1678 (1989).
60. E. P. Plueddermann, *Silane Coupling Agents*, Plenum Press, New York, 1982.
61. S. J. Monte and G. Sugerman, *Proceedings from the 33rd Technology Conference*, Reinforced Plastics/Composite Institute, Washington, D.C., 1978.
62. W. H. Waddell and co-workers, *J. Appl. Polymer Sci.* **55**, 1627 (1995).
63. J. H. O'Haver and co-workers, *J. Appl. Polymer Sci.* **59**, 1427 (1996).
64. M. P. Wagner, *Rubber Chem. Technol.* **49**, 703 (1976).
65. W. H. Waddell and L. R. Evans, *Rubber Chem. Technol., Rubber Reviews* **69**, 377 (1996).
66. W. H. Waddell and L. R. Evans, in J. Dick, ed., *Rubber Compounding and Testing for Performance*, Hanser, Munich, 2000.
67. R. F. Wolf and C. Stueber, *Rubber Age* **87**, 1001 (1960).
68. L. R. Evans and W. H. Waddell, *Rubber Plast. News* 15 (Apr. 25, 1994).
69. T. A. Okel and W. H. Waddell, *Rubber Chem. Technol.* **67**, 217 (1994).
70. W. H. Waddell and L. R. Evans, *Rubber Chem. Technol.* **69** (Aug. 1996).

71. M.-J. Wang and S. Wolf, *Rubber Chem. Technol.* **64**, 559 (1991).
72. M.-J. Wang, S. Wolf, and J.-B. Donnet, *Rubber Chem. Technol.* **64**, 714 (1991).
73. M.-J. Wang and S. Wolf, *Rubber Chem. Technol.* **65**, 329 (1992).
74. M.-J. Wang and S. Wolf, *Rubber Chem. Technol.* **65**, 715 (1992).
75. H.-D. Luginsland, J. Frohlich, and A. Wehmeier, *Rubber Chem. Technol.* **75**, 563 (2002).
76. O. Taikum and H.-D. Luginsland, *Rubber World* **230**, 30 (2004).
77. U.S. Pat. 5,227,425 (July 13, 1993), R. Rauline (to Michelin).
78. T. A. Okel and W. H. Waddell, *Rubber Chem. Technol.* **68**, 59 (1995).
79. R. A. Crawford and G. E. Alderfer, *Neut./Alkal. Papermaking* 125 (1990).
80. M. J. Weighall, *J. Power Sources* **34**, 257 (1991).
81. J. L. Boyer, *Batteries Int.* 60 (Oct. 1994).
82. M. Pader, *Cosmetic Toiletries* **103**, 84 (1988).
83. S. K. Wason and J. W. Maisel, *Plast. Compound.* **3**, 21 (May/June 1981).
84. FAO/WHO Joint Expert Committee on Food Additives, 17th Meeting, *World Health Org. Tech. Report Ser.* **539**, 16 (1974).
85. R. Oelmueller and H. Ferch, *ASTM Spec. Tech. Publ.* **1036**, 85 (1989).
86. R. D. Kulkarni, E. D. Goddard, and B. Kanner, *Ind. Eng. Chem. Fundam.* **16**, 472 (1977).
87. G. D. Ulrich, *Combust. Sci. Technol.* **4**, 47 (1971).
88. H. Cochrane and C. S. Lin, *Rubber World* **192**, 29 (1985).
89. B. B. Boonstra, H. Cochrane, and E. M. Dannenberg, *Rubber Chem. Technol.* **48**, 558 (1975).
90. J. C. Saam, *Mat. Res. Soc. Symp. Proc.* **274**, 91 (1992).
91. D. G. Miller, W. F. Moll, and V. W. Taylor, *Mod. Paint Coat.* **73**, 53 (1983).
92. H. Cochrane and D. G. Miller, *Mod. Paint Coat.* **73**, 159 (1983).
93. *Cosmetic Chemicals: Worldwide Specialty Chemicals*, SRI International, Menlo Park, Calif., 1989.
94. D. Riffel, *Pigm. Resin Technol.* **15**, 13 (1986).
95. T. A. Bolton and G. A. Geineccius, *Perfumer Flavor.* **17**, 2 (Mar./Apr. 1992).
96. V. V. Rondinella, M. J. Matthewson, and C. R. Kurkjian, *J. Am. Ceram. Soc.* **77**, 73 (1994).
97. *Chemical Economics Handbook Marketing Research Report, Silicas and Silicates*, SRI International, Menlo Park, Calif., 1993.
98. H. E. Bargna, *Ind. Quim.* **28**, 123 (1970).
99. B. M. Cooper, *Ind. Mineral.* **258**, 43 (Mar. 1989).
100. G. P. Callahan, E. Kubacki, and L. Abbott, *Laser Focus World* 151 (June, 2005).
101. S. Mann and C. C. Perry, *Structural Aspects of Biogenic Silica*, Ciba Foundation Symposium 121, John Wiley & Sons, Inc., New York, 1986, pp. 40–58.
102. J. B. Jones and E. R. Sequit, *J. Geol. Soc. Aust.* **18**, 57 (1971).
103. R. V. Dietrich and B. J. Skinner, *Rocks and Rock Minerals*, John Wiley & Sons, New York, 1979.
104. R. O. Fournier, *Proceedings of the Symposium on Hydrogeochemistry and Biogeochemistry*, Clarke Co., Washington, D.C., 1973.
105. R. H. Wilson and D. H. Groth, *ASTM Spec. Tech. Publ.* **732**, 143 (1981).
106. R. K. Iler, *ASTM Spec. Tech. Publ.* **732**, 9 (1981).
107. D. H. Groth and co-workers, *ASTM Spec. Tech. Publ.* **732**, 118 (1981).
108. G. W. H. Schepers and co-workers, *Arch. Ind. Health* **16**, 125 (1957).
109. *Fed. Reg.* **67**(94), 34616 (May 15, 2002).

GENERAL REFERENCES

R. K. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*, John Wiley & Sons, New York, 1979.

P. Kleinschmit, *Special. Inorg. Chem.* **40**, 196 (1981).

H. D. Gesser and P. C. Goswami, *Chem. Rev.* **89**, 765 (1989).

L. L. Hench and W. Vasconcelos, *Ann. Rev. Mater. Sci.* **20**, 269 (1990).

WALTER H. WADDELL
ExxonMobil Chemical Company

Table 1. **Test Methods for Characterizing Amorphous Silica**

Property tested	Test methods
color	ISO 787, Parts I, XII; ISO 5794, Part I
average particle size	ASTM C721, D1366, E20, E523, and F660; ISO 787, Part XVIII
SiO_2 content	ASTM C575 and D297; ISO 5794, Part I
coarse, insoluble material	ASTM C117 and D185; ISO 787, Parts III, VI, VII, and VIII; ISO 5794, Part I
volatile matter (water)	ISO 787, Part II
specific surface area	ASTM D1993 and D5604; ISO 5794, Part I; NF T 45-007
bulk density	ASTM D604; ISO 787, Parts X, XI
mean projected area of aggregates	ASTM D3894
metal ion and salt content	ASTM C575 and D719; ISO 5794, Part I, Annexes A, B, C, D
absorption of oil	ASTM D2414; ISO 787, Part V
pH	ASTM D1512; ISO 787, Parts IV, IX
porosimetry	ASTM D4284
occupational exposure	ASTM E1156

Table 2. **Properties of Commercial Amorphous Silica**

Property	Colloidal silica	Silica gels[a]	Precipitated silica	Pyrogenic silica
SiO_2, %	15–50	96.5–99.6	85–95	98.3–99.8
surface area, m^2/g	50–750	200–800	25–700	35–410
oil absorption, g/g	0.9–3	1.5	1.5–3.5	0.5–3
pH, aqueous	3–5, 8–11	2.3–7.4	5–9	3.5–5
weight loss, %				
at 105°C	50–80		4–7	0.5–2.5
at 1200°C	50–90	2–17.5	10–14	1–4
density, g/cm^3	2.2–2.3	2.22	1.9–2.1	2.16
bulk density, g/cm^3	1.2–1.4	0.1–0.9	0.03–3	0.03–0.12
particle size				
ultimate, nm	4–60	1–100	5–50	5–50
aggregate, nm			100–500	100–1000
agglomerate, μm		3–25	1–50	1–3
refractive index, n_D	1.35–1.45	1.35–1.45	1.45	1.45
Na_2O, maximum %	1	1	2	0.2

[a] Dry.

Table 3. **Worldwide Amorphous Silica Capacity and Production**

	Capacity[a]					
	U.S. + Mexico	Europe	Japan	China	Korea	Total capacity
precipitated silica	229	421	66	250[b]	45	1011
silica gel	62	39	12	100[b]	11	224
fused silica	75	60	90[b]			225
fumed silica	50	83	27			160
colloidal silica	37	26	35[b]			98
Totals	453	629	230	350	56	1718
% capacity	26.4	36.6	13.4	20.4	3.3	100.0

	Production[a]					
	U.S. + Mexico	Europe	Japan	China	Korea	Total production
precipitated silica	191	308	45	250[b]	45	839
silica gel	41	25	11	100[b]	11	188
fused silica	54	45	69			168
fumed silica	37	61	21			119
colloidal silica		17	10			53
Totals	349	456	156	350	56	1367
% production	25.5	33.4	11.4	25.6	4.1	100.0 79.57%

[a] Thousands of metric tons, % SiO_2 dry weight.

[b] Estimated.

Table 4. **Major Manufacturers of Amorphous Silicas**

Producer[a]	Silica products	Manufacturing locations[b]
Cabot	fumed	Germany, United Kingdom, United States
C-E Minerals	fused	United States
Denki Kagaku Kogyo	fused	Japan
Degussa	fumed, precipitated	Belgium, France, Germany, India, Japan, Taiwan, Thailand, United States
Didier-Werke	fused	Germany
DuPont	colloidal	United Kingdom, United States
Eka Chemicals	colloidal	Germany, Sweden, United States
Frank and Schulte	fused	Germany
Fuso	colloidal	Japan
Grace	gel, precipitated	Germany, United States
INEOS	gel, precipitated	Indonesia, United States
Huber	precipitated	Finland, India, United States
MINCO	fused	United States
Nissan Chemical	colloidal	Japan, United States
Oriental	precipitated	China, Taiwan
PPG	precipitated	Mexico, United States
PQ Corporation	colloidal, gel, precipitated	Netherlands, United States
Precision Electro Minerals	fused	United States
Rhodia	gel, precipitated	China, France, India, Korea, United States
Saint-Gobain Quartz	fused	United Kingdom
Sico Technology	fused	Austria
Silquimica	precipitated	Spain
Tokuyama Soda	fumed, precipitated	Japan, Thailand
Tosoh	fumed, precipitated	Japan
Vesuvius	fused	France
Wacker-Chemie	fumed	Germany

[a] Includes joint venture companies.

[b] Does not include local manufacturers in China and India.

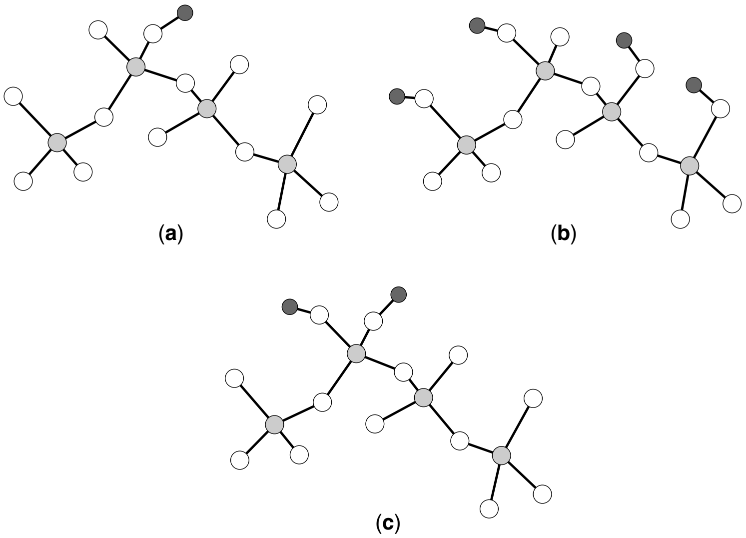


Fig. 1. Silanol groups of amorphous silica surface, where ◍ = Si; ○ = O; and ● = H: (**a**) isolated, (**b**) vicinal, and (**c**) geminal.

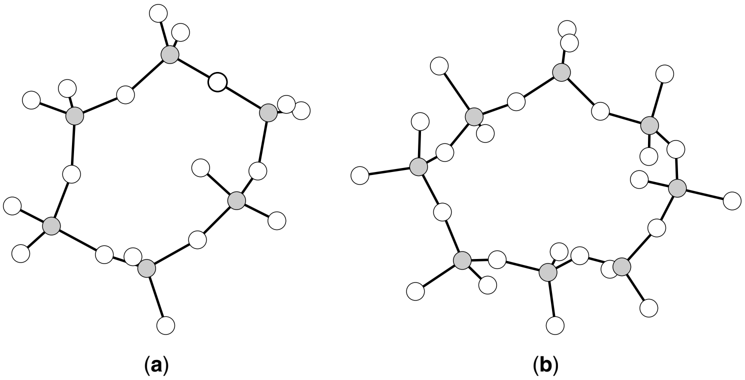


Fig. 2. Silica ring structures, where ◍ = Si; ○ = O: (**a**) 12-membered SiO_2 hexamer, and (**b**) 16-membered SiO_2 octamer.

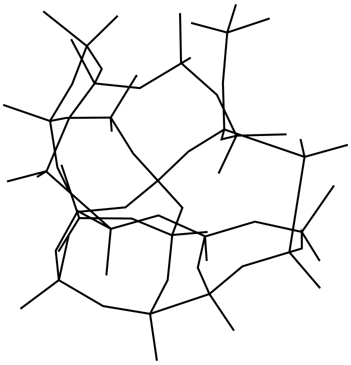
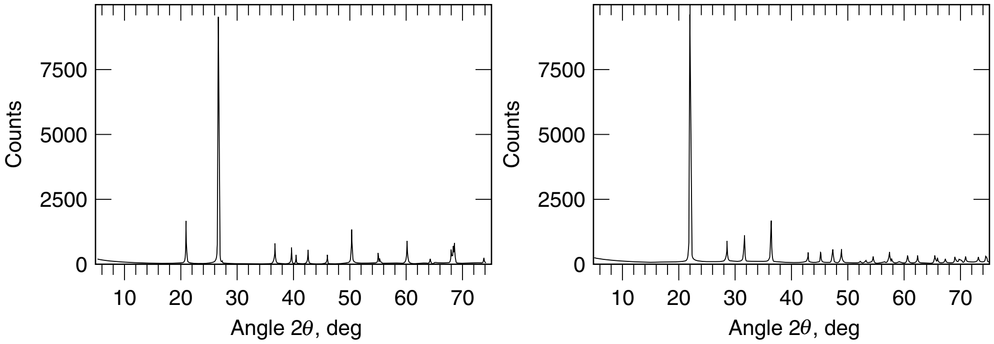


Fig. 3. Complex ring structures in SiO_2 polymer.



(**a**) (**b**)

Fig. 4. X-ray diffraction patterns using a Cu anode: (**a**) crystalline quartz sand and (**b**) cristobalite.

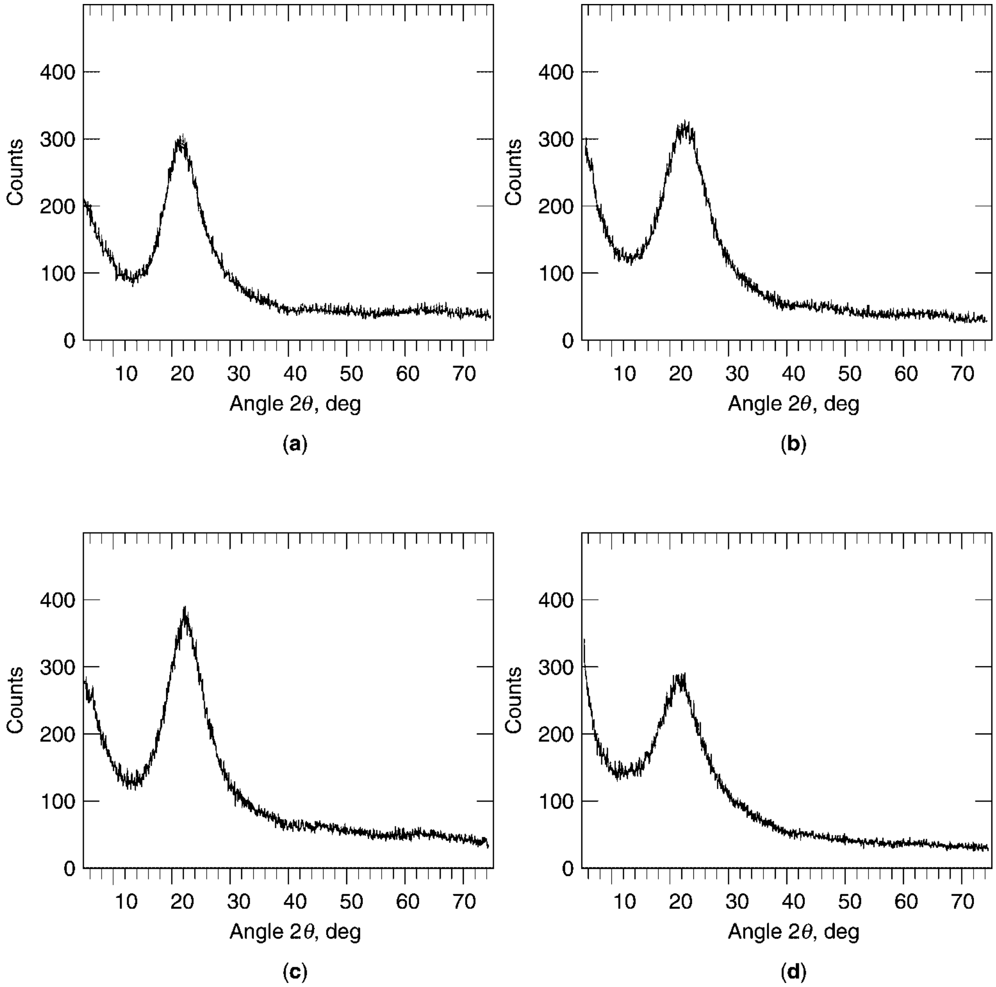


Fig. 5. X-ray diffraction pattern of commercial samples: (**a**) colloidal silica, DuPont Ludox TM50; (**b**) silica gel, Sylodent 700; (**c**) precipitated silica, PPG Hi-Sil 190; and (**d**) pyrogenic (fumed) silica, Wacker HDK.

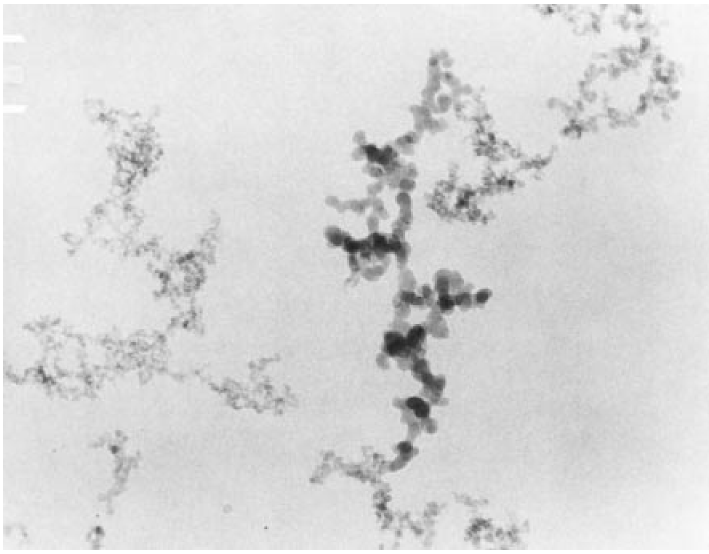


Fig. 6. Transmission electron micrograph of a commercial pyrogenic silica, Wacker HDK. Magnification of 225,000×.

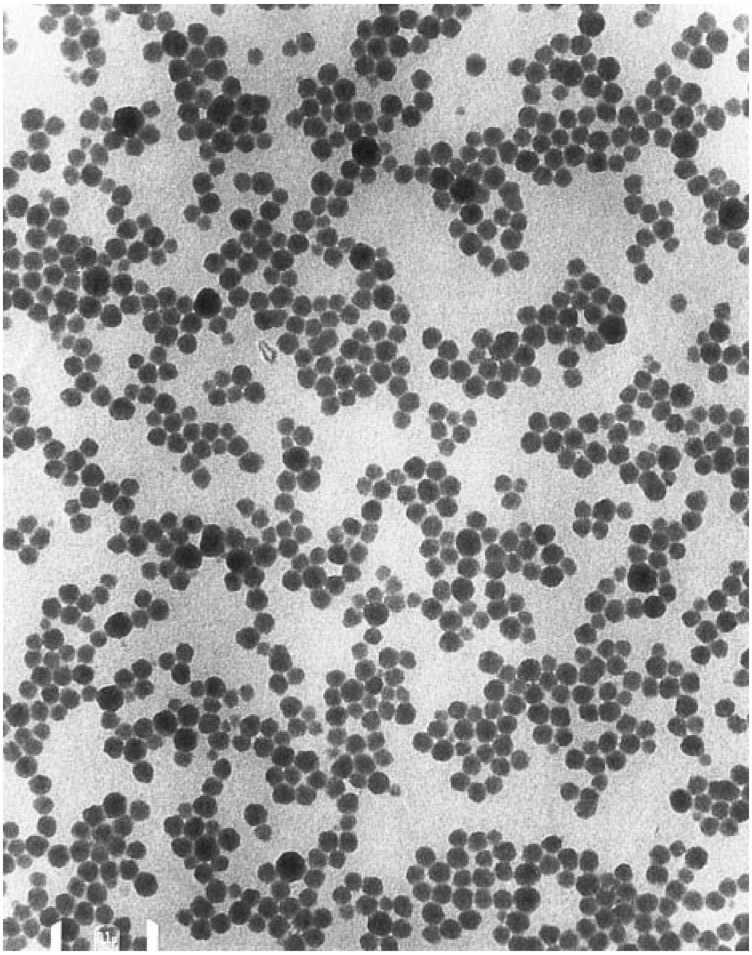


Fig. 7. Transmission electron micrograph of a commercial colloidal silica, DuPont Ludox TM50. Magnification of 225,000×.

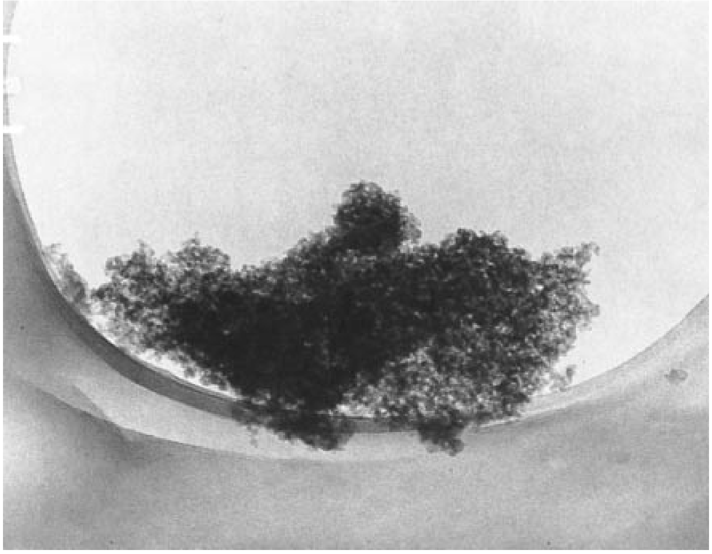


Fig. 8. Transmission electron micrograph of a commercial silica gel. Magnification of 300,000×.

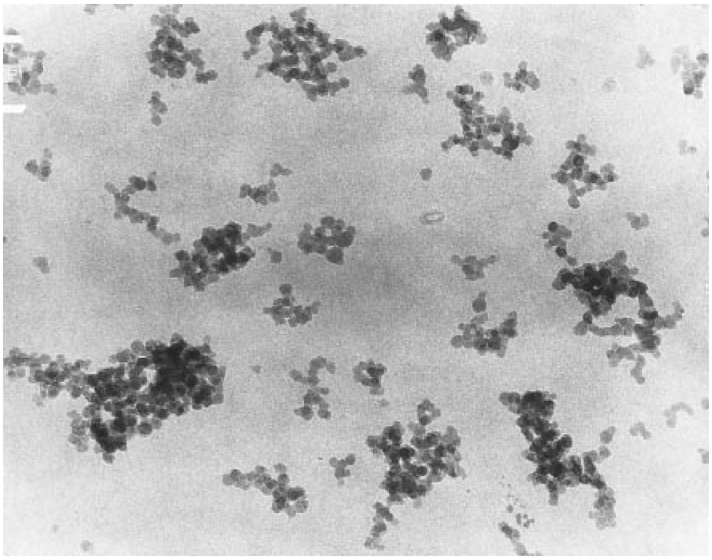


Fig. 9. Transmission electron micrograph of a commercial precipitated silica, PPG Hi-Sil 190. Magnification of 225,000×.

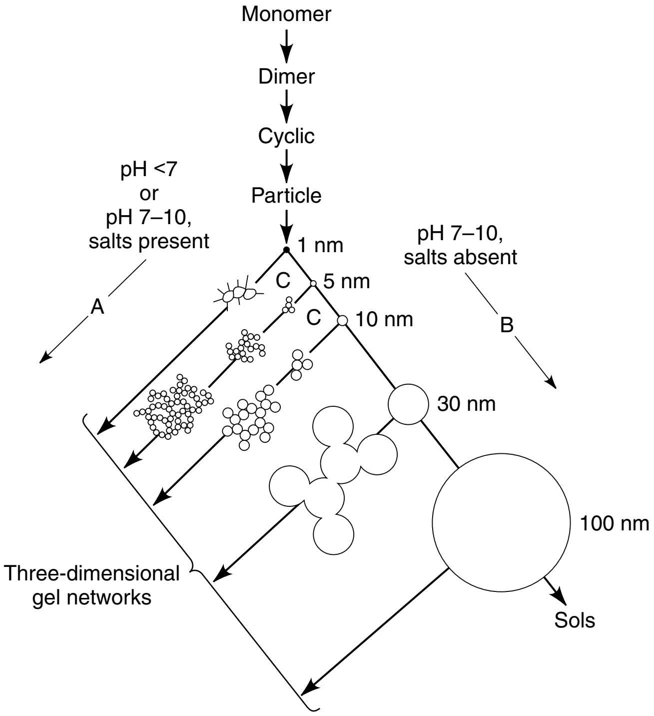


Fig. 10. Polymerization behavior of silica. In basic solution (B), particles grow in size and decrease in number; in acidic solution or in the presence of flocculating salts (A), particles aggregate into 3D networks and form gels (1).

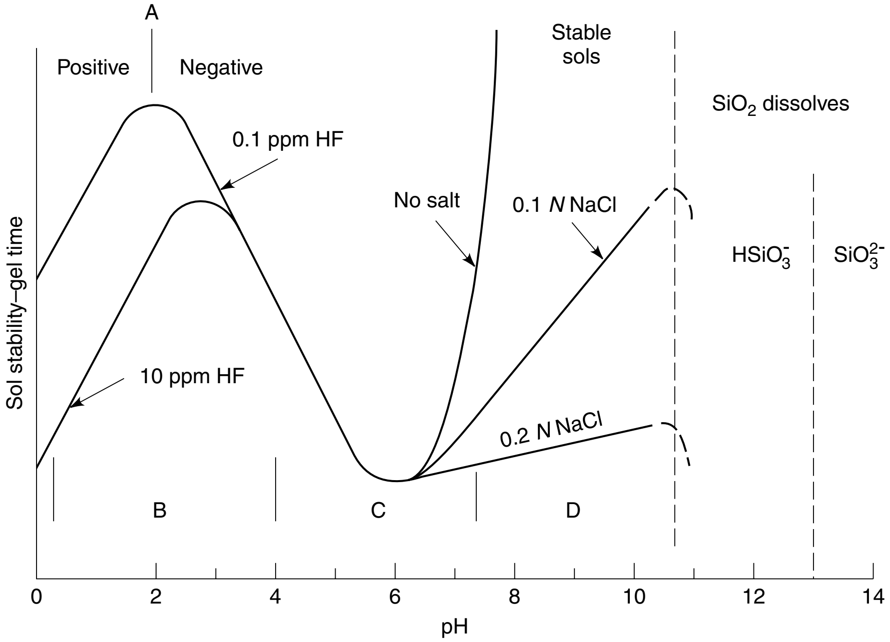


Fig. 11. Effects of pH in the colloidal silica–water system (1), where A represents the point of zero charge; regions B, C, and D correspond to metastable gels, rapid aggregation, and particle growth, respectively. Positive and negative correspond to the charges on the surface of the silica particle.

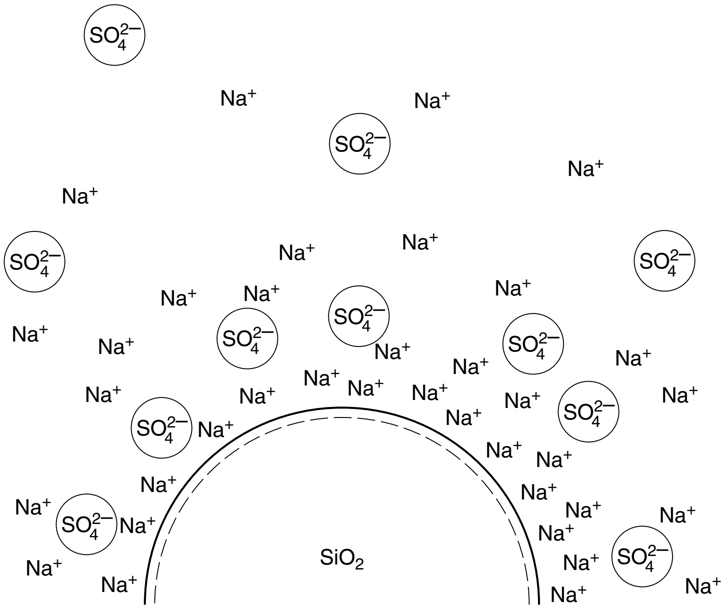


Fig. 12. Salt retention by colloidal particles. The curved dashed and solid lines represent the surface of a negatively charged silica particle. Around this there is a layer of counter sodium cations; outside there is a layer in which sulfate anions (○) are more concentrated than in the bulk solution.

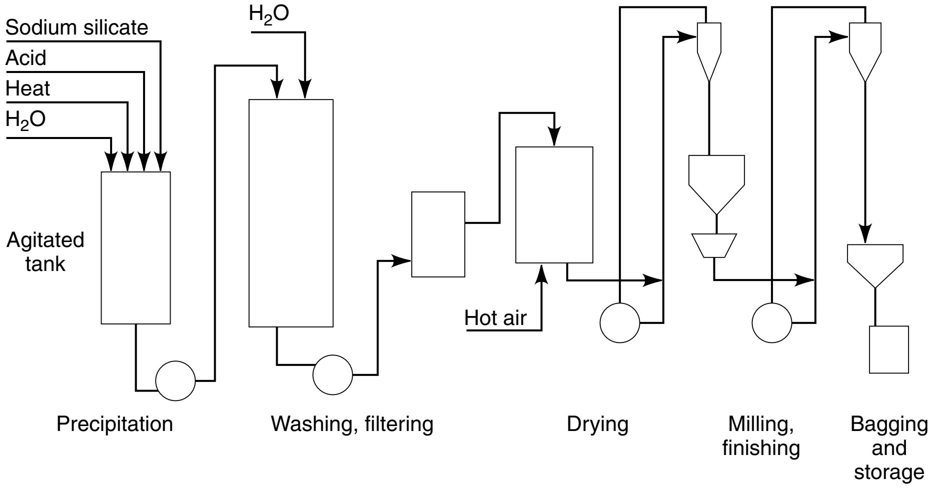


Fig. 13. Schematic of precipitated silica production (56), where ▯ =, eg, reactor, washer, filter, and dryer; ○ = pump or transfer device, eg, bucket elevator and air conveyor; ▽ = storage bin; ▽ = optional size modifier, eg, mill and granulator.

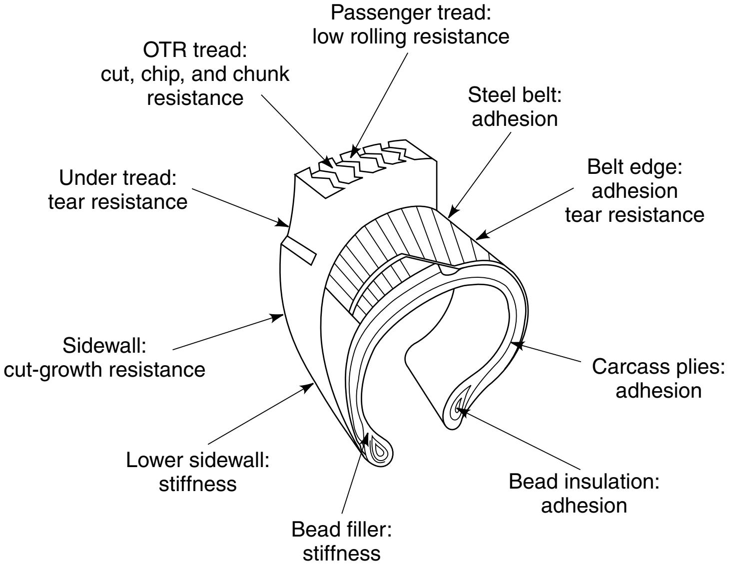


Fig. 14. Schematic of a passenger tire showing individual components and use of precipitated silica to improve rubber compound performance. OTR = off-the-road.

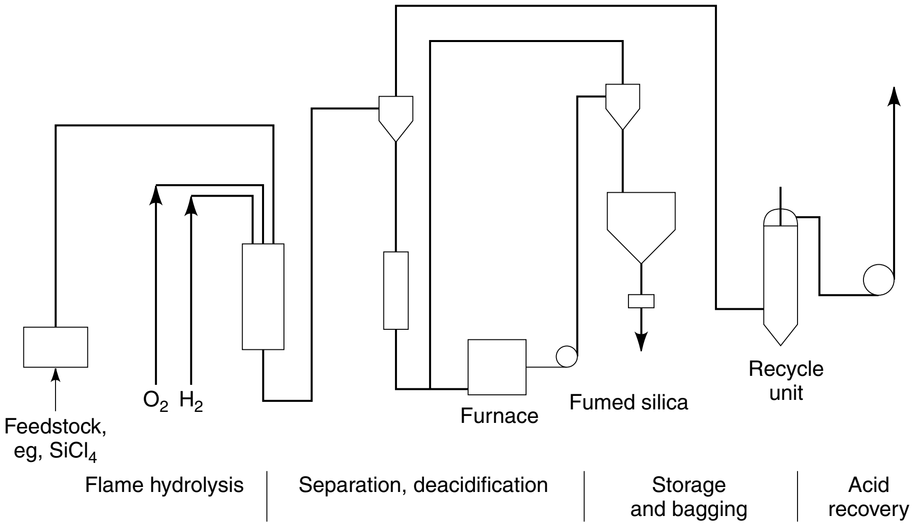


Fig. 15. Schematic of pyrogenic silica production (56). See Fig. 13 for definitions.