

THE HALOGENS AND THE NONMETALS BORON AND SILICON

3011

TABLE 40.9. Some Commercial Silicon Alloys

Name	Composition
Standard 50% ferrosilicon	47-51% Si, remainder mainly Fe
Standard 65% ferrosilicon	65-70% Si, remainder mainly Fe
Standard 75% ferrosilicon	73-78% Si, remainder mainly Fe
Standard 85% ferrosilicon	83-88% Si, remainder mainly Fe
Silicon metal	97.75% Si min, 0.07% Ca max, 0.51-1.00% Fe max
Calcium-silicon	30-33% Ca, 60-65% Si, 1.50-3.00% Fe
Calcium-manganese-silicon	16-20% Ca, 14-18% Mn, 54-59% Si
Ferrochrome silicon	38-42% Cr, 38-42% Si, 0.05% C max
Magnesium ferrosilicon	44-48% Si, 8-10% Mg, 1.00-1.50% Ca, 0.50% Ce
Simanal	approx. 20% each of Si, Mn, Al, balance mainly Fe
Silicomanganese	65-68% Mn, 12.5-18.5% Si, 1.50-3.00% C, balance mainly Fe
SMZ alloy	60-65% Si, 5-7% Zr, 5-7% Mn, 3-4% Ca, balance mainly Fe

iron and steel industry, silicon alloys, often referred to as silicides, are used for alloying, deoxidizing, and reducing other alloying agents such as Mn, Cr, W, and Mo. In the nonferrous metal industry, silicon is used primarily as an alloying agent for Cu, Al, Mg, and Ni. In the form of 75 percent ferrosilicon, it is used as a reducing agent in the production of magnesium by the Pidgeon process. The reaction between ferrosilicon and caustic soda can be used to make hydrogen.

Table 40.9 lists some of the more important commercial silicon alloys.

U.S. Domestic production of ferrosilicon in 1973 was 447,000 short tons of a total world production of 1.543 million tons, European countries contributing 55 percent of the total (36).

For further details on the types, production and uses of these alloys, see the chapter on silicon in Reference 53.

3.7.2 Silicon Dioxide, SiO_2

Silicon dioxide exists in two varieties, amorphous and crystalline. A number of natural noncrystalline varieties of SiO_2 exist, such as the hydrated form, opal, and an unhydrated form, flint. In recent years, synthetic amorphous silicas have come on the market, in three forms according to their method of preparation, SiO_2 gel (silica G), precipitated SiO_2 (silica P), and fumed SiO_2 (silica F).

The chief representative of crystalline SiO_2 is quartz. Three other forms of crystalline SiO_2 are cristobalite, tridymite, and tripoli, which, though identical chemically, differ from quartz in crystalline form. They occur naturally and synthetically.

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Amorphous Silica. By definition (117) synthetic amorphous SiO_2 is silica produced either by vapor-phase hydrolysis, precipitation, or other processes which assure the absence of crystalline particles. The fumed variety is derived from the vapor-phase hydrolysis of a silicon-bearing halide, silicon chloride; silica gels by reacting sodium silicate and an acid in solution; and precipitated silica by destabilizing sodium silicate in solution, causing precipitation of very fine silica particles.

Because of the many and varied special use requirements, these three varieties have proliferated into numerous types, presently 64, each with company-designated trade names such as Hi-Sils, Aerosils, Cab-O-Sils, Silcrons, and Syloids. These types have been further grouped into five classes according to their physiological effects when inhaled by human subjects, based on a few standard test procedures that identify dusts having similar origins or methods of manufacture.

The most striking property of these silica powders is their enormous surface areas, which in turn determine their applications; precipitated SiO_2 has a surface area (B.E.T.) of 125 to 150 m^2/g ; fumed SiO_2 , 175 to 225; silica gels, from 275 to 325 m^2/g , for a mean particle diameter of 0.014 to 0.022 to 0.010 to 0.018 μm , respectively. Their density varies around 2 g/ml . Oil absorption is high, from 170 to 190 $\text{g}/100 \text{ g}$ for precipitated SiO_2 to 275 to 325 $\text{g}/100 \text{ g}$ for the gels. Their pH at 5 $\text{g}/15 \text{ g H}_2\text{O}$ is between 6.5 and 7.5 for precipitated gels, but considerably lower for the fumed, 3.5 to 4.2 (117).

These amorphous silicas have as many as 20 applications in rubber and rubber goods, 25 in paper and paper products, 31 in anticaking, conditioning, and carriers in food, feeds, and chemicals, and 14 in paints, varnishes, and protective coatings. Their diversity of uses results in the rubber industry from their reinforcement qualities, giving increased tensile strength and hardness, abrasion resistance, increased stiffness, and better color. In the paper industry, the qualities of increased opacity and brightness allow better printability and improved smoothness and bulk. In their anticaking and conditioning qualities, improved flowability and dispersion of mixes commend them for such use, and their faster wetting of chemicals, foods, and feeds gives an outlet for these silicas in this area. They also provide controlled polishing and cleaning as well as acting as carrier for encapsulating catalysts and antifoams and defoamers. In their applications in paints, varnishes, and protective coatings, they provide higher hiding power, efficient flattening and extension of prime colors, improved thixotropy, and protection from the elements and corrosion.

Pathologic Effects. The newer methods of producing ultrafine amorphous SiO₂ particles with their enormous surface areas (SA) gave cause for reinvestigating their toxic potential. (The comparison of the SA of 55 m²/g of the fluorescent grade of BeO dust, which is highly injurious when inhaled, with the SA of the newer silicas of 2.5- to sixfold greater, is sufficient reason to prompt

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a reinvestigation.) Such an investigation was made by a team of researchers in inhalation toxicology, particle size and electron probe analysis, animal pulmonary function studies, and animal pathology in the Division of Biomedical Science, NIOSH, Cincinnati, during 1978 and 1979 (118a). Because of the great health significance of the results, and their present unpublished form, they are given in some detail.

An animal inhalation toxicity study was performed on 80 to 90 rats, 20 guinea pigs, and 10 monkeys for daily periods of 5.5 to 6 hr for up to 18 months at 7 to 10 mg/m³ respirable dust (15 mg/m³, total SiO₂ dust). Exposures were to the three types of synthetic amorphous silicas, precipitated (P), gelled (G), and fumed (F) (pyrolyzed). All three dusts were analyzed by proton-induced, X-ray fluorescence. Some of the rat lungs were analyzed for silicon by plasma emission spectroscopy. Anderson impactor studies revealed that 46 percent of silica P, 62 percent silica G, and 65 percent silica F were less than 4.7 μ m in diameter, and therefore to these extents were respirable. Autopsies were performed on rats at 3, 6, and 12 months and on guinea pigs and monkeys at 10 to 18 months after the start of exposures.

The most significant morphological alterations from all three silicas were confined to the lungs of the monkeys, which contained large numbers of macrophage and mononuclear cell aggregates, and which, in the respiratory bronchioles, appeared to reduce the size of their lumina significantly.

In the cellular aggregates, there was a difference in type and quantity of extracellular components. Reticulin fibers were uniformly present in the aggregates from all three silica types, but collagen was present in significant amounts only in those monkeys exposed to silica F; none were seen in the aggregates of lungs of monkeys exposed to silica G, and very few in those exposed to silica P. Histopathological examination of the lungs of rats and guinea pigs showed far fewer and smaller aggregates than those of the monkeys. A probable reason was the estimate made from light microscopy that less than 10 percent silica was in the lungs of these animals than in the monkeys. Microprobe analysis revealed the presence of silicon in all the aggregates examined (116c).

The great significance of the presence of collagen fibers in the cellular aggregates in the monkey lungs exposed to amorphous silica F is that it is *fibrogenic*. The much smaller amounts of collagen in the monkey lungs exposed to silica P indicate that it is much less fibrogenic than silica F. The reticulin fibers found in all aggregates is not without toxicologic significance also, for its potential for producing collagen in silica-containing aggregates is greater than in those areas without it. The full potential effect of the presence of reticulin and collagen fibers from exposure to these silicas is probably not expressed in these studies of 10 to 18 months duration, which is relatively brief for monkeys.

The silicon content of the freeze-dried lungs of the exposed animals, as analyzed, was, as expected, considerably greater than those of controls, which

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in the case of the rats were six, three, and two times greater for silica P, G, and F, respectively. In view of the fact that silica F was the most fibrogenic, the finding of the lowest amounts of the three provides further evidence for the far greater fibrogenic potential of silica F.

Pulmonary Function. Eleven tests of pulmonary function were made to determine the degree of respiratory impairment in the monkeys exposed separately for 1 year to the three amorphous silicas in an apparatus uniquely designed for the purpose (118b). Of the functions that were statistically significantly different from controls at the end of 1 year were the lung volume measurements of forced vital capacity (FVC), inspiratory capacity (IC), and total lung capacity (TLC) in those exposed to silica F and P. In the measurements of lung ventilatory mechanisms, resistance, compliance, forced expiratory flow at the last 10 percent ($FEF_{10\%}$), and closing volume were statistically different from controls in the F and G groups; the greatest differences from controls occurred in compliance, $FEF_{10\%}$, and in residual volume/total lung capacity, the magnitude of the differences again being greatest in the silica F group. These significant decrements in lung function after an exposure of only 1 year further demonstrate the injurious effects of these amorphous silicas. Heretofore, amorphous silicas previously encountered were considered to produce a benign pneumoconiosis. Whether effects of greater severity would result from long-term exposure must be left for future study. Another intriguing question from these studies is, why is silica F restrictive of lung size, yet obstructive in getting respiratory flow expired?

Although no proven explanation is forthcoming on the greater, early fibrogenic action of silica F, the explanation may be in its far greater surface area than its counterparts, silicas P and G, its greater solubility resulting in a far lower pH value (see above), thus providing greater degree of tissue irritation, and the greater content of aluminum (67- and elevenfold) in silicas P and G. Aluminum is recognized as an abettor of silicosis and thus conceivably reduces the fibrogenic action of these two silicas.

A pathological study of rats inhaling Degussa dust, a submicron, high surface area, amorphous SiO_2 by Schepers (118c) 20 years before, showed that at about 50 mg/m^3 (1.5 mg/ft^3) the majority of the rats died from pulmonary, vascular obstruction coupled with pulmonary insufficiency due to emphysema at three to five months. Progressive increases of SiO_2 in the lungs accompanied the pulmonary lesions. Surprisingly, the majority of the surviving rats rapidly recovered on removal from the dust exposure, the silica was largely eliminated, and the cellular nodules, perivascular infiltrations, and emphysema were almost completely resolved.

It is clear from the above findings that the TLV for these amorphous silicas must be reduced in accordance with their relative fibrogenicity from the TLV of 6 mg/m^3 for total, and 3 mg/m^3 for respirable dust.

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Crystalline Silica, SiO_2 . *Source and Production.* The chief source of crystalline SiO_2 is quartz, a mineral found ubiquitously in most classes of rock, and an important constituent of those igneous rocks such as granite and pegmatite which contain an excess of SiO_2 . Quartz also occurs in large amounts as sand in stream beds, seashores, and deserts, and as a constituent of soils. In rocks, quartz is associated chiefly with feldspar, a potassium aluminum silicate, KAlSi_3O_8 , and its hydrous form, $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ muscovite.

Two other minerals chemically identical to quartz are cristobalite and tridymite, differing from quartz in crystalline form and recognized by microscopic examinations, X-ray diffraction, and infrared spectrophotometry. Cristobalite and tridymite usually occur together as high temperature silicate minerals in the volcanic rocks of California, Colorado, and Mexico. Cristobalite also forms in the calcining of diatomaceous earth, the amount depending on the time and temperature of calcining. Under usual operating conditions, cristobalite may form to the extent of 60 percent of the original diatomaceous earth.

Apart from the usual mining operations of dredging and mechanical crushing to obtain impure quartz, pure crystals of quartz are prepared by mass production methods under carefully controlled conditions of temperature and concentration.

Uses and Industrial Exposures. Impure quartz, as silica sand, is used in the manufacture of glass and silica brick, in mortar, and as an abrasive. In powdered form, as silica flour, it is used in paints, porcelain, scouring soaps, and as a wood filler. The clear rock crystals of the colored varieties are valued as gems and used ornamentally (amethyst, onyx, rose quartz, agate). Pure, synthetic quartz is used in electronic components, for piezoelectric control in filters, oscillators, frequency standards, wave filters, and for radio and TV components.

The sources of industrial exposures are many. Probably the most common source of SiO_2 dust exposures leading to silicosis is the drilling of free silica-bearing rock. Presenting even more extreme hazards is abrasive blasting. Pottery workers come under significant SiO_2 exposure if dust-dirty work clothes are not properly cleaned. Likewise, dust generated from handling and transporting SiO_2 -containing dust from crushed rock, sand, gravel, clay, or other minerals can pose a hazard. Similarly the handling of carloads and bags of SiO_2 flour has an associated exposure hazard. Finally, flux-calcined diatomaceous earth containing substantial amounts of cristobalite and/or tridymite can generate very hazardous dust, as does the dust associated with maintenance and repair of equipment.

Physical and Chemical Properties. The physical and chemical properties of three forms of crystalline SiO_2 are given in Table 40.8, but the physical properties of quartz are far more complex than can be presented in such a table. Twenty-two different phases of silica have been identified. At 573°C the ordinary α -quartz changes over reversibly to β -quartz, which has a lower density,

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and at 86°C, β -quartz changes to a different crystal modification, β -tridymite. At a still higher temperature, 1470°C, β -tridymite becomes a third modification called β -cristobalite. Both β -tridymite and β -cristobalite have lower temperature α modifications which have lower optical symmetry, and all the forms can be maintained at room temperature if chilled rapidly from the stable equilibria. Each appears to have its own melting point, but the usual melting point for silica is that of β -cristobalite, about 1723°C. Rapid chilling of the liquid produces silica glass, often incorrectly called quartz glass, a vitreous modification of SiO_2 which has a very low coefficient of expansion.

Analytic Determination—Sampling and Analysis. The National Institute for Occupational Safety and Health (NIOSH) endorses the sampling and analysis procedures for evaluating worker exposure to crystalline SiO_2 (quartz, tridymite, cristobalite) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) (119a, b).

The dust is collected with a size-selective personal sampler positioned in the breathing zone of the worker. Dust penetrating the precollector is collected on a low-ashing polyvinyl chloride (PVC) filter and the free SiO_2 content is determined by X-ray diffraction, after the dust is redeposited on a silver membrane filter.

The procedures are also given in detail with regard to principle of the method, range and sensitivity, interferences, precision and accuracy, advantages and disadvantages, and apparatus (120a, b).

Physiologic Response. The pulmonary effects on workers exposed to crystalline SiO_2 are to be found in Vol. 1 of this edition (121). Accordingly, only those aspects of exposure relating to these effects are summarized here in an attempt to demonstrate the basis on which the control of SiO_2 exposure was made for the prevention of the disease in the many industries and occupations, where varying types and percentages of SiO_2 dust and associated nonsiliceous dusts and personal habits (smoking) interact.

Silicosis, a dust disease (pneumoconiosis) of the lungs resulting from over-exposure to free SiO_2 dust, usually begins insidiously, with symptoms of coughing, dyspnea, wheezing, and repeated, nonspecific chest illnesses. Impairment of pulmonary function may be progressive. In individual cases, there may be little or no decrement when simple, discrete, nodular silicosis is present, but when nodulations become larger, or when conglomeration occurs, cardiopulmonary impairment tends to develop.

The various stages of progression of the silicotic lesions are related to the degree of exposure of free SiO_2 , the duration of exposure, and the time during which the retained dust is permitted to react with the lung tissue. Epidemiologic studies show that the higher the SiO_2 dust exposure, the more rapid the development of silicosis and its prevalence. As dust is controlled, however, the

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frequency of occurrence of silicosis decreases, the severity of the disease lessens, and the length of time for the disease to become manifest increases. As a consequence of this extended time, it becomes increasingly difficult to establish a relation between dose and response.

To illustrate the complexities facing early investigators in attempts to find a "safe" exposure limit for free SiO_2 -containing dusts, one has only to note that there were six major classes of industries which presented different degrees of exposure and differing percentages and sizes of SiO_2 dusts. To cope with this situation, early (1930) investigators assigned different "maximal, permissible, safe, dust limits" which were reported at a National Conference on Silicosis, held in Washington, D.C. in 1936 (Table 40.10) (122). Not considered at the conference were the exposures presented in the iron and steel industries, the nonferrous foundries, and the amorphous SiO_2 -producing industry (cf. Section 6.7.2), which also has its individual and varied types of exposure.

Hygienic Standards of Exposure. Hygienic standards of exposure to free SiO_2 -containing dusts are based on the concept that the degree of toxicity is proportional to the concentration of free SiO_2 in the dust. When represented as a threshold limit, it is expressed as

$$\text{Threshold limit} = \frac{K}{\% \text{SiO}_2} \text{ mppcf}$$

where K is a constant related to the incidence of silicosis as determined from epidemiologic studies.

To make the threshold limit consistent with the nuisance dust TLV, adopted

TABLE 40.10 Industries with Potential Exposure to Free Silica and Permissible Limits^a

Industry	Location	Percent SiO_2 in Dust	Permissible Safe Dust Concn. (mppcf)
Metal mining	South African gold mines	80	4.5
	Ontario gold mines	~35 (in rock)	8.5
Coal mining	Pennsylvania anthracite	35	5-10
Nonmetal minerals (except fuels)	Broken Hill, Australia	10-17	14
Stone, clay, and glass products	Barre, Vt. granite	31-38	10-20
	Australia sandstone	90 (in rock)	6

^a From National (U.S.) Silicosis Conference, 1937 (122).

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in 1970, K was placed at 300 and a constant of 10 added in the denominator:

$$TLV = \frac{300}{\%SiO_2 + 10} \text{ mppcf} \quad (a)$$

Hosey et al. (123) reported in 1957 that no cases of silicosis occurred in Vermont granite workers whose exposure to dust had been subsequent to dust control in 1937 and where dust exposures had averaged less than 5 mppcf. The airborne dust averaged 25 percent quartz, so the revised TLV formula, $300/(\% \text{ quartz} + 10)$, would have given a TLV of 9 mppcf. This was identical with the upper limit of exposure of the group of granite workers found without silicosis by Russell in 1929 (124). The count formula is also reasonably consistent with results from studies in the anthracite region of Pennsylvania (125a), an early nonferrous metal mine study (125b), and studies of pegmatite workers (125c). Studies of foundry workers (125d), pottery workers (125e), and metal miners (125f) showed chest roentgenograms consistent with silicosis in workers who were at the time of the surveys exposed below the TLV, but it was believed that previous exposures may have been considerably higher. Early limits for count concentration of dust from South Africa, Australia, and Ontario (Table 40.10) were reasonably consistent with the count formula, even though sampling methods and counting procedures were somewhat different from U.S. practice.

With the development of devices for size sampling of dusts, it became possible to express the TLV in terms of mass for respirable and total dust, which has considerable, obvious advantages over the counting procedure. Comparisons of impinger-count concentration and respirable-mass concentrations show that 9 to 10 mppcf of granite dust, suggested as a limit by Russell, contains 0.1 mg/m^3 of respirable quartz (126a). The formula $TLV = (10/\% \text{ respirable quartz}) \text{ mg/m}^3$ generalizes this relationship to all percentages of quartz in respirable dust. If the TLV were used only for dust containing at least 5 percent quartz, the above TLV formula would be satisfactory, but to prevent excessively high permissible respirable dust concentrations when the fraction of quartz in the dust is less than 5 percent, a constant has been added in the denominator, as with the count TLV (a), giving the formula

$$TLV = \frac{10}{\% \text{ respirable quartz} + 2} \text{ mg/m}^3 \quad (b)$$

The additive constant "2" limits the concentration of respirable dust with 1 percent quartz to 5 mg/m^3 . The above TLV has been demonstrated to give hazard evaluations comparable to the impinger method in foundry dust exposures (128b). Where agglomerates are a factor, the results by the respirable mass method are more closely related to the hazard.

Percent quartz in respirable dust is often quite different from the percentages in settled dust or total airborne dust, and the percent quartz for use in the

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respirable-mass TLV formula must be determined in a sample of respirable dust.

The concentration of respirable dust must be determined by an instrument which gives a size separation equivalent to that specified in the ACGIH criteria for size selection (126c). The ACGIH criteria are as follows:

Aerodynamic Diameter (μm) (Unit Density Sphere)	% Passing Selector
<2	90
2.5	75
3.5	50
5.0	25
10	0

For low concentrations of dust, especially where quartz percentages are high, respirable quartz may be determined directly from air samples and concentrations of quartz compared with the basic value of 0.1 mg/m^3 quartz. In the use of 0.1 mg/m^3 respirable quartz as a limit, care must be taken that other limits ("nuisance" dust, coal mine dust, etc.) are not exceeded.

A formula for total dust concentration expressed as mass has also been recommended by the TLV Committee:

$$\text{TLV (total dust)} = \frac{30}{\% \text{ quartz} + 3} \text{ mg/m}^3 \quad (\text{c})$$

It is based on the limitation of "nuisance" dust to 10 mg/m^3 and the fact that respirable quartz usually averages less than one-third of the total quartz. Limited data from foundries and coal mines suggest that the formula for the TLV for total dust will usually give a result on the safe side, when compared with the respirable dust TLV formula. However, respirable quartz must not average more than 0.1 mg/m^3 , and in those instances where respirable dust is more than one-third the total dust, the respirable dust TLV formula must be used. Thus three formulas, (a), (b), and (c), for controlling free crystalline SiO_2 in workroom air are recommended by ACGIH.

NIOSH, however, in recommending a standard exposure to crystalline SiO_2 to OSHA, took a different tack. Instead of adopting formulas that allow differences in dust concentration according to its SiO_2 content, NIOSH made a blanket recommendation of 0.05 mg/m^3 as the standard of permissible exposure for all situations, the standard to be applied as a TWA concentration, "as determined by a full-shift sample for up to a 10-hour workday, 40-hour workweek" as a breathing zone sample (120b).

The reason for this choice is not made clear in the criteria document (120b). As stated, however, the basis was the 50-year study of the Vermont granite

sheds by the USPHS, in which effective control was gained at 5 mppcf, which in mass is equivalent to 0.05 mg/m³. Accordingly, "it seemed appropriate to apply this limit, in terms of respirable mass, to other operations producing dusts containing free silica."

The present federal standard for free SiO₂ is an 8-hr, TWA based on the 1968 ACGIH TLV formulas of 250/(%SiO₂ + 5) mppcf or 10/(%SiO₂ + 2) mg/m³ for respirable quartz, one-half this limit for cristobalite and tridymite.

The allowable level of airborne quartz in coal mines is 0.10 mg/m³, twice the limit recommended by the criteria document.

Silicosis Therapy. For a discussion of aluminum in the prevention and treatment of silicosis, see Section 5.9 in the chapter "Metals," Vol. 2A of this edition.

Cristobalite, Tridymite, Tripoli, and Fused Silica. Of the four crystalline forms, three, cristobalite, tridymite, and tripoli, exist naturally. Cristobalite, tridymite, and fused silica (quartz) can be produced by heating quartz or amorphous SiO₂ to elevated temperatures. The industrial source of cristobalite and tridymite, however, is from flux-calcining diatomaceous earth at regulated temperatures and times. These two minerals are used extensively as filtering and insulating media, and as siliceous refractory materials for furnace linings and silica bricks.

Cristobalite and Tridymite. These two minerals are treated together because of their common natural (volcanic rock) and synthetic association, their common industrial applications, and toxicologic response.

Physiologic Response. The pneumoconiosis-producing effects of these two minerals have been much studied both in industry (127a-c) and in the laboratory (128a-d) since the early (1941) report of Fulton and associates in the burned silica brick industry (129). This study drew attention to the greater capacity of cristobalite and tridymite to induce silicosis than quartz, a finding later confirmed by animal studies (128b, c) and suggested by epidemiologic studies of the diatomite industry (127b, c) and which led to a *threshold limit value* of one-half that calculated from the count or mass formulas for both silica forms (130).

Tripoli, as encountered in industry, refers to a *group* of highly porous, microcrystalline minerals with free silica contents ranging from 90 to 98 percent, found in Missouri, Oklahoma, Arkansas, and Georgia, in the United States. It is not to be confused with tripolite, a diatomaceous earth, found in Tripoli, North Africa. Rottenstone and microcrystalline silica are similar to tripoli. These minerals are used in buffing compounds, on buffing wheels, in scouring soaps and powders, and in polishes; a very finely sized white grade, "white rouge," is used for polishing optical lenses. About 35,000 tons of tripoli, including rottenstone and microcrystalline silica, was used for abrasives in the United States in 1960.

Early (1943) physiological response studies by McCord et al. showed that

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direct implantation of tripoli in animals led to tissue proliferation similar to that from quartz (131a), but later (1962) investigation of tripoli workers by McCord (131b) failed to find any clinical evidence of silicosis among the workers. He attributed this lack of response to a relative lack of exposure brought about by the dielectric properties of tripoli particles, which, because of rapid agglomeration and settling of the airborne particles, reduced exposure to a minimum. Gardner had similarly suggested particle flocculation as a reason for the absence of serious lung pathology in diatomaceous earth workers, whereas animal studies showed that this substance produced progressive nodular fibrosis (131c).

Because of particle agglomeration, conventional counting procedures by light-field microscopy are of questionable value, and the *threshold limit* is based on *respirable mass* and is the same as that for quartz.

Fused silica is quartz that has been melted to a glass-like substance on cooling. According to Gross (132), although fused silica may appear amorphous, when submitted to X-ray diffraction it is actually shown to consist of microcrystals of quartz too small to be detected by direct X-ray. Although King et al. (128b) found fused silica considerably less active than quartz when injected intratracheally in rats, his particle size of 87 percent $<2.6 \mu\text{m}$ may account in some part for his results. Be that as it may, the lack of sufficient industrial experience with fused silica handling and use moved the TLV Committee to recommend the same *threshold limit* as that for quartz.

Fused silica finds use in apparatus and equipment, such as vacuum tubes, where its high melting point, ability to withstand large and rapid temperature changes, chemical inertness, and transparency including to UV light are requirements. It is produced as fibers and fabrics where heat resistance, low expansion coefficient, and high dielectric strength are needed.

3.7.3 Silicates

Silicates can be grouped into two great classes, natural and synthetic. Of major industrial importance in the natural group are asbestos, mica, mineral wool, perlite, portland cement, soapstone, talcs, and tremolite, all of which have recommended threshold limits. The synthetic, inorganic group comprises for the most part the soluble silicates formed with the alkali metal and quaternary ammonium base such as the sodium silicates (Table 40.8). Insoluble silicates such as lead silicates are formed from the alkali metal silicates. Insoluble silicates also exist in nature, for example, beryllium aluminum silicate, beryl.

Insoluble, Inorganic Silicates. Asbestos. Limitations of space confine the treatment of these silicates, particularly asbestos, to brief summaries and references to the literature for further details.

Asbestos is a generic term that applies to a group of naturally occurring,

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hydrated mineral silicates that are separable into fibers. Chrysotile, with the theoretical formula $3 \text{MgO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$, is the variety wanted by more than 95 percent of the world's consumers. Other types include amosite, $(\text{FeMg})\text{SiO}_3$, crocidolite, $\text{NaFe}(\text{SiO}_3)_2 \cdot \text{FeSiO}_3 \cdot \text{H}_2\text{O}$, anthophyllite, $(\text{MgFe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$, and tremolite, $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$.

Total world production in 1974 was 4.5 million tons of all grades and varieties (36). Of this, Canada's output was 40 percent, the Soviet Union, an estimated 33 percent, South Africa 8 percent, Republic of China 5 percent, Italy 4 percent, and the United States 2 percent.

Asbestos is adaptable to more than 2000 uses, all as processed fiber. Chrysotile is graded and grouped according to fiber length, the longest fibers being in groups 1 to 3, whose major uses include textiles, different types of packings, woven brake linings to clutch facings, and electric insulation. The major use of fibers in group 4 is in asbestos cement pipe for transporting water, and in group 5, for asbestos cement sheets, low pressure cement pipes, and molded products; the main consumption of fibers in groups 6 and 7 is in asbestos cement mixes such as gaskets, vinyl sheet backing, joint and insulation cements, roof coatings, plastics, and caulking compounds.

Amosite is used mainly for felted insulation for high temperature service up to 900°F and as covering for marine turbines and jet engines; long fiber crocidolite (blue asbestos) is woven into fabrics for locomotive boiler lagging and is used for acid-resistant packings and gaskets, shorter fibers being used for asbestos cement pipe; anthophyllite and tremolite are used for chemical-resistant filters, as welding-rod castings, and as fillers in various products.

It can be seen from these many and varied uses that potential industrial (and environmental) exposures are almost ubiquitous.

Analytic Determination. Because fibers, not the motes, are generally, but not completely, agreed to be the injurious agent, fiber counting is the approved way of estimating exposure to airborne asbestos (133). The preferred index of asbestos exposure is the concentration of fibers longer than $5 \mu\text{m}$ counted on a membrane filter at $430\times$ with phase contrast illumination.

The recommended method for taking airborne samples and counting fibers is collection on a 37-mm Millipore type AA filter mounted in an open-face filter holder fastened to the worker's lapel, with air drawn through at a flow rate of from 1 to about 2.5 liter/min.

Details of counting procedure may be found in References 133 or 134.

Physiologic Response. The pulmonary aspects of fibrogenesis (asbestosis) and bronchogenesis, as well as mesothelioma, have been discussed by Wright in Vol. 1 (121). The aspects treated are under the following headings: (1) fiber aerodynamic behavior and pulmonary penetration, (2) fate of fibers in respiratory tract, (3) development of fibrogenesis and its organization relative to fibers and motes, (4) role of immunologic processes in pulmonary tissue

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