

Industrial Applications of the Sodium Silicates

SOME RECENT DEVELOPMENTS

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THE variety of useful properties shown by sodium silicates of different alkali, silica, and water contents and their low cost has led to utilization in many applications. According to the U. S. Bureau of the Census, the production of all forms of sodium silicate in this country during 1947 was 474,589 tons calculated on an anhydrous basis, corresponding to about 1,500,000 tons of the commercial solutions or "liquid" silicates. Each of the more than forty commercially available forms of silicate of soda has one or more uses not satisfactorily served by another grade. Vail (105) has reviewed the literature up to 1928. This paper discusses some more recent developments and a few interesting and important major applications.

ADHESIVES

One of the largest uses for colloidal silicates of soda having a silica to alkali ratio of 2.8 to 3.9 is as adhesives for many types of materials, particularly paperboard used in the manufacture of corrugated containers. The present annual consumption for this purpose is about 400,000 tons of the commercial silicate solutions containing 32 to 47% solids.

Although the largest amounts of silicate used as adhesive are for bonding paper, they are also used for wood, metals, and other materials. A 47° Bé., 2.9 ratio, and a 52° Bé. 2.4 ratio, silicate were used to attach sheet copper to the walls and ceiling of one of the rooms in Radio City, New York. Aluminum sheets coated with silicate may be bonded to cellulose (82). Acid-proof tanks are made by using silicate to hold fabric with a polyvinyl halide coating (which does not itself adhere well to metal) to a metal tank (11). Characteristics and a few applications of commercial grades of silicates at present most commonly used as adhesives are summarized in Table I.

TABLE I. CHARACTERISTICS OF SILICATES OF SODA USED AS ADHESIVES

%Na ₂ O	%SiO ₂	SiO ₂ / Na ₂ O Wt. Ratio	Sp. Gr. at 20° C., °Bé.	Viscosity at 20° C., Poises	Uses
11.0	31.9	2.9	47	9.6	Sealing cartons, shipping containers, metal foils, wall boards, flooring, and trunk making
8.9	28.7	3.2	41	1.8	Corrugated paper board, flooring, paper tubes
9.2	29.5	3.2	42	4.0	Combined board, (wall-board) plywood
8.3	28.2	3.4	39.7	3.3	Corrugated paper-board
6.7	25.3	3.7	35.0	2.2	Special uses

Recent developments in the commercial applications of silicates of soda as adhesives, soap builders, detergents, metal cleaners, cements, and binders for briquets and other bonded materials are summarized. Basic principles involved in the applications are stressed and variations of physical properties with silica to alkali ratio and water content are illustrated.

Viscosity - concentration - specific gravity relationships of three ratios used as adhesives are shown in Figure 1. Comparison of Table I with Figure 1 indicates that the loss of 1 or 2% of water from commercial adhesive silicates converts them from

a liquid to an essentially solid material. This loss of water, either by evaporation or by sorption through the porous materials to be bonded, is the mechanism by which silicate adhesives "set." The rate of set at an equivalent viscosity increases with ratio of silica to alkali. Tackiness is greater for the more alkaline ratios. This fast setting is of particular value on corrugating machines, which have been successfully operated at speeds as high as 500 feet per minute with a silicate adhesive and best modern techniques.

The advantages of a sodium silicate adhesive include good spreading and contact, a rate of set controllable over wide limits up to very fast, and formation of a permanent strong, rigid,

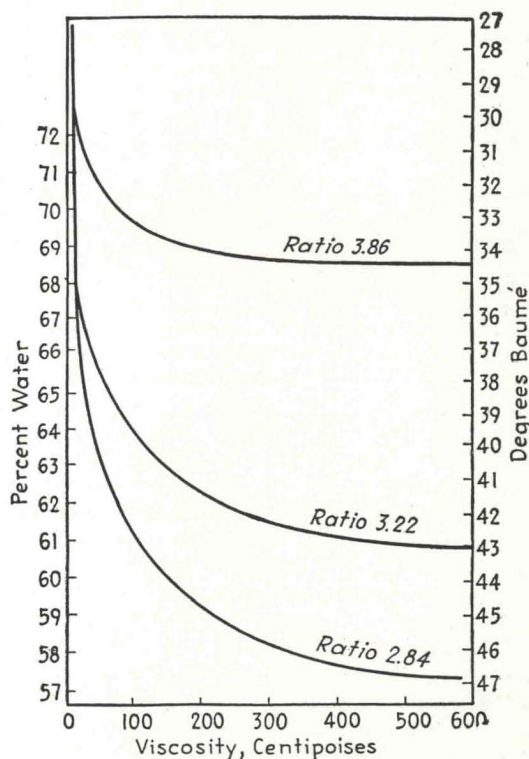


Figure 1. Viscosity - Specific Gravity - Water Content Relations of Silicate of Soda Adhesives (from 107)

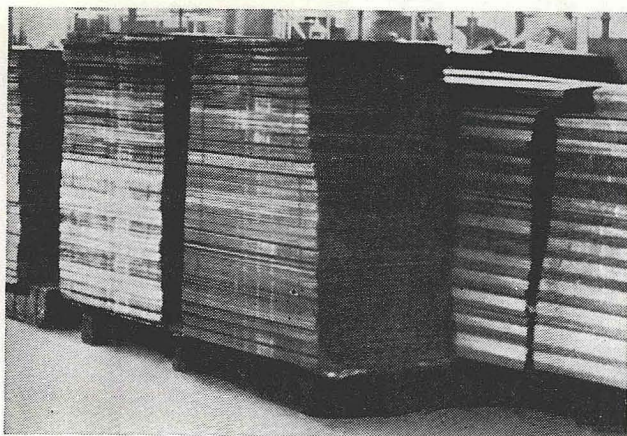


Figure 2. Paperboard Made with Silicate of Soda after Seasoning in Pile

water- and heat-resistant bond. The quality of a silicate bond is not ordinarily affected by storage and its strength is greater than that of paperboard and other materials with which it is frequently used. The low price, uniform quality, controllable characteristics, convenience, and unattractiveness to animal life are also advantages.

The strengthening and stiffening action of silicate adhesives in corrugated containers is due to the formation of a strong reinforcing shoulder at the point of contact between the corrugating medium and liners (85). The film at the point of contact is very thin and little penetration of the silicate into the paper occurs in a well made corrugated fiberboard box. The performance of sodium silicate adhesives in the manufacture of corrugated fiberboard is now fairly satisfactorily understood (14). From 16 to 30 pounds of silicate are commonly used per 1000 square feet of fiberboard. Setting may occur in less than 15 seconds.

Because of their alkalinity, silicate adhesives may attack the rosin size of paper and cause staining. This is frequently avoided by spreading a viscous silicate in a thin layer and drying rapidly. Another method is to pretreat the paper or other material with ammonium salts or metallic salts such as zinc sulfate or magnesium chloride (23). Pretreatment with aluminum chloride not only prevents staining and desizing but also gives a waterproof bond (25). A laminated board made from plies given this pretreatment after 2.5 hours' immersion in water adsorbed only 35% water and gave a Mullen test of 247 as compared with 57% and 223 for the untreated board. Paperboard containers made by this process have met federal specifications covering a waterproof box for export.

Although not completely waterproof, silicate bonds show considerable resistance to moisture, which increases with age and ratio of silica to alkali. The water resistance may be improved by the addition of fine powders such as zinc oxide, a silica gel-coated anhydrite (24), or whiting or other amorphous form of calcium carbonate, which react slowly with the silicate to form an insoluble mass. Up to 1.0% of zinc oxide may be dispersed in the silicate at 150° to 180° C. to form an apparently homogeneous product (112). The addition to silicates of complex ammine salts formed by adding aqueous ammonia or amines to a zinc or copper salt solution also improves their water resistance (54).

A property of silicate adhesives which, though frequently desirable, is sometimes objectionable is their tendency to adhere to and form deposits on metals. This tendency is reduced by coating the metal with graphite or a Bakelite varnish, or by spraying the hot metal with a solution containing 5% each of an aromatic monosodium sulfonate and aluminum sulfate. Surface active materials such as an aromatic monosodium sulfonate (53), ammonium laurate, potassium coconut oil soap, and triethanol-

amine, when incorporated in the silicate cause it to dry on hot metal as a friable, porous mass removable by scraping.

The wetting by silicate adhesives of metals, highly sized papers, or other materials on which silicate does not spread well is improved by the addition of surface active agents. Up to 2% of such materials as sulfonated castor oil, oleic or other fatty acids, bile acids, saponin, rosin soaps, naphthalenesulfonic acids (47), and sulfates of aliphatic compounds containing more than seven carbon atoms (58) has been used. Poor wetting of metals by a silicate adhesive may be due to dirt, grease, or an adsorbed gas film. When the gas film is removed by heating to 100° to 200° C. or by immersing in hot water, a strong bond is formed on heating a thin silicate of soda film to 55° (82).

The flexibility of films from silicate adhesives may be improved by the addition of a small amount of coumarone-indene resin (108), sugars, molasses, starch, water-soluble gums, glycerol, and rubber latex. Sorbitol and most other polyhydroxy derivatives are effective. Carboxymethylcellulose, sodium alginate, and a special oxidized cellulose have likewise proved satisfactory for this purpose.

The addition of up to 3% of acetate ion in a silicate adhesive increases its viscosity and gel point (57). The same amount of an alkali metal phosphate increased the bond strength (76).

Adhesives composed of mixtures of silicates of soda with starches, dextrin, glues, casein, blood, gum arabic and other water-soluble gums, borax, soybean meal, rosin, and rubber latex have been known and used for some time (32, 105). Usually such mixtures have properties not present to the desired degree in any of the constituents. Thus, the addition of silicate of soda to a casein- or vegetable protein-lime water-resistant adhesive increases working life and lowers cost. Typical examples of some recent patented mixtures are listed in Table II.

SILICATE-CLAY ADHESIVES

The addition of clay to a diluted silicate of soda increases viscosity but has a smaller effect on the rate of set. Mixtures containing large amounts of clay (up to 80%) have been used for many years in laminated paper products such as wallboard, because they have a lower setting time and a smaller alkali content than straight silicate adhesives (105). Such mixtures can not be used on modern high speed continuous pasting machines which require faster and more accurately controlled setting. Recent tendencies to use more water-resistant paper stock also made it desirable to use an adhesive with increased wetting action which retained the advantages of silicate-clay mixtures.

Modern silicate-clay adhesives which accomplish these results are prepared by adding a deflocculated clay slip prepared by mixing with a 0.1 to 0.5% solution of a dispersing agent, to a concentrated sodium silicate having a silica to alkali ratio of 2.5 to 4 (107). The finished adhesive has a content of well dispersed clay not exceeding 20%, a viscosity of 50 to 500 centipoises, and a controlled filterability. The aqueous phase should have a viscosity just less than that at the point of maximum curvature of the viscosity-concentration curve (Figure 1). A dilute sodium silicate

TABLE II. SOME ADHESIVE SILICATE MIXTURES

Added Material, Parts	Bonds	Use or Comments	Ref.
5 to 10 diglycerol	Plastic and glass	Manufacture laminated safety glass	(30)
1 blood albumin	Paper, wood, etc.	Dry mixture giving cold set	(28)
0.2 asphalt	Felt pads to metal panels	Inexpensive, tacky	(102)
0.5 clay	Nonporous surfaces	Rapid set without heating, strong flexible bond	(20)
2 rubber			
3 Fe ₂ O ₃ , CaO, Al ₂ O ₃	Wood, etc.	Dry powder for plywood uses Na ₂ SiO ₃	(18)
3 to 10 alkali-soluble phenolic resin	Paper	Laminated paper products	(101)
0.25 to 0.83 ungelatinized starch			

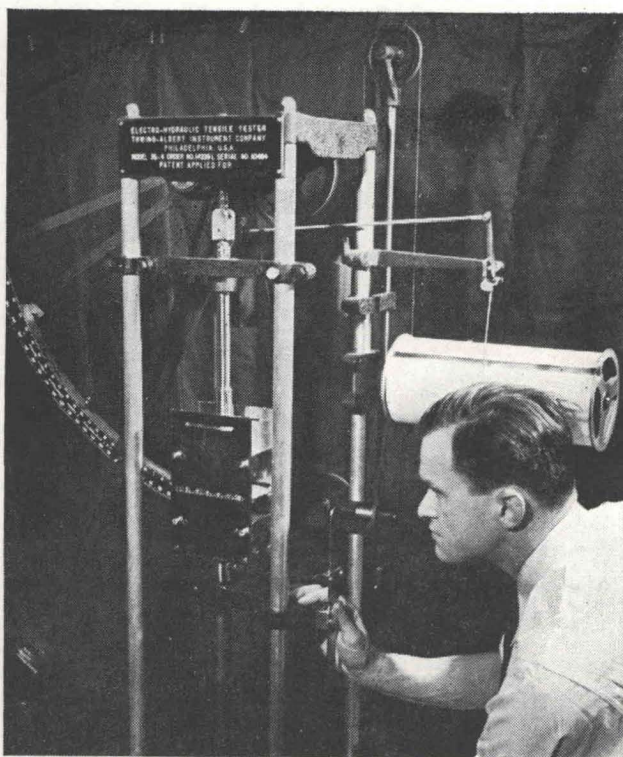


Figure 3. Tensile Strength Tester for Corrugated Board

solution is advantageously employed for dispersion. Other dispersing agents such as sodium ortho- or pyrophosphates, borax, sodium carbonate, or an organic peptizing agent such as tannic or gallic acid, and their salts or quebracho may also be used. Heating the adhesive above 50° for a short time stabilizes it to variations in temperature and brings about partial solution of the more reactive portions of the clay. Ball clays, China clays, and bentonites are satisfactory but the South Carolina kaolin type of clay is preferred. The usual clay content of a modern adhesive of this type is from 6 to 20%. The clay may also be dispersed by mixing with the silicate at 115° to 162° C. at 10 to 80 pounds per square inch pressure (15) or by passing the mixture through a colloid mill (13).

One main advantage of modern clay-silicate adhesives is that their controllable thixotropic character and lower water content per unit area of board give faster, readily controlled setting permitting increased machine speeds, and decreased heating and seasoning or storage times. They spread well even on highly sized or water-resistant boards and give a strong bond with little penetration into the paper. Under the same plant conditions, 11 to 12 pounds per square foot of a silicate-clay adhesive are used per 1000 square feet as compared with 17 pounds for the straight silicate.

Data of McCready and Katz (60, 61, cf. also 110) on the properties of corrugated fiberboards and boxes made with both normal and heavy applications of silicate, silicate-clay, and starch adhesives under similar practical conditions are given in Table III. Paperboard made with a silicate-clay adhesive had a higher Mullen test, greater breaking and column loads, and less deflection at constant load than that made with the straight silicate

adhesive. With one possible exception, which is probably within the experimental uncertainty of the data, the compression strength of the boxes was also greater with the silicate-clay adhesive. The column and breaking load was lower and the deflection at constant load higher for paperboard made with starch than for that made with either silicate or a silicate-clay adhesive. The Mullen test on paperboard made from starch was somewhat higher than that made with silicate. The compression strength for starch-made boxes was about 10% lower than for those made with either the silicate or silicate-clay adhesive. Heavy applications of the silicate adhesives increased the structural strength of the paperboard 10 to 22% above that with normal applications, whereas heavier applications of starch increased the column and breaking load only 5% and gave a 7% greater deflection at constant load.

SOAP BUILDERS

Although sodium silicates were added to soaps on a fairly extensive scale as early as 1837, only within the past 25 years has it become recognized and established by both laboratory studies and practical experience that silicates, as well as soaps, are good detergents and that a mixture of the two is often better for many cleaning purposes. The use of sodium silicates to produce a good soap mixture with a lower fat content than a pure soap is of particular importance during periods, such as the present, when fats and oils for soap making are scarce. It is reported (87) that just prior to the war the addition of 20% of silicate of soda to all soap manufactured in Germany was compulsory. Soaps made from siliceous silicates causticized with a mixture of sodium and potassium hydroxide have little, if any, tendency to effloresce or bloom and hold water more tenaciously than soda soaps; the finished curd soap undergoes no noteworthy change in weight or volume (88).

Mixtures of soaps and silicates have been shown to be as good as or better than either alone at preventing the deposition or redeposition on cotton of thirteen different types of soils under conditions closely approximating actual laundry practice (22). These included siliceous pigments such as ultramarine, burnt and raw umber, vermilion, ferric oxide, Philadelphia dust, ground mica, graphite, coal, and carbon black. Sodium hydroxide, sodium carbonate, and modified soda showed only slight power, or none at all to prevent the deposition of pigments. Trisodium phosphate is intermediate between these and the various silicates in preventing deposition. Except at great dilutions, silicates of highest ratio of silica to alkali were more effective for the more siliceous soils, illustrating the general principle of like to like. This prevention of deposition depends on the amount of soluble silica, rather than on the alkalinity.

The detergent action of sodium oleate on a soil containing wheat, starch, gum tragacanth, and various pigments is considerably reduced in hard waters, such as those containing calcium bicarbonate or carbon dioxide (26). The effect on mixtures of soap and silicate or the latter alone is much less, so that in hard water the mixtures become better than the soap both in removing pigments and in preventing their redeposition.

As much as 40% of soap can be replaced by sodium metasilicate or a silicate with a silica to alkali ratio of 2.0 before soil

TABLE III. PROPERTIES OF CORRUGATED FIBERBOARDS AND BOXES

Board	Mullen Test, Lb./Sq. In.	Structural Tests on Paperboard Beam Loading				
		Compression Strength of Boxes, Lb.		Column load, lb.	Breaking load, lb.	Deflection at constant load, 2.8 lb./inch
		Top to bottom	End to end			
Silicate, normal	226.8	1021	765	171	4.9	0.431
Silicate clay, normal	232.6	1082	777	194	5.2	0.413
Starch, normal	253.6	916	729	153	4.5	0.546
Silicate, heavy	210.2	1229	794	209	5.7	0.387
Silicate clay, heavy	219.2	1074	987	222	6.0	0.345
Starch, heavy	244.7	899	677	161	4.3	0.586

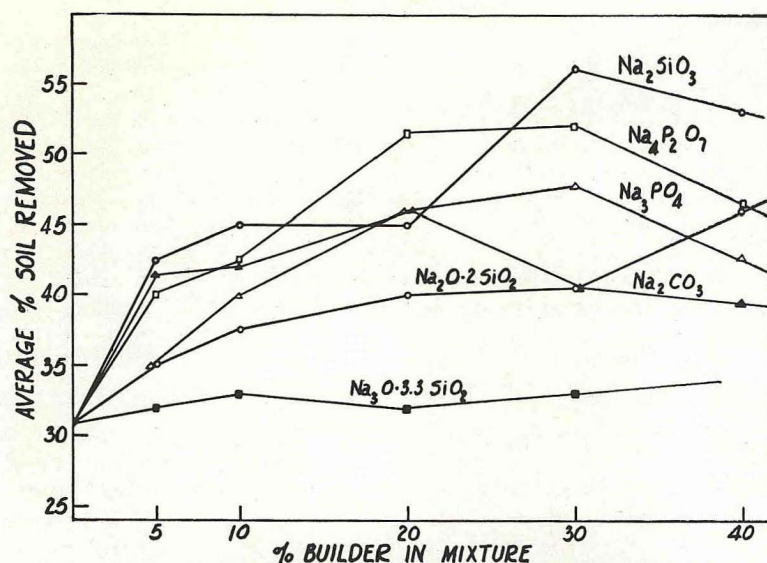


Figure 4. Removal of Carbon Black Soil by 0.27% Soap-BUILDER Mixtures at 140° F. in Water of 300 P.P.M. Hardness (Data from 29)

removal in soft water (50 p.p.m. hardness) is decreased at all soap-mixture concentrations (29, 41). Substituting for the soap a silicate with a silica to alkali ratio of 3.3 decreases removal of a graphite-vegetable oil soil, unless enough of the mixture is added for maximum detergent efficiency. Soil removal in hard water (300 p.p.m.) is considerably increased by replacing up to 40% of the soap by the metasilicate or 2.0 ratio silicate. At a concentration of 0.27% soap builder mixture the 3.3 ratio silicate could be substituted for 40% of the soap with a slight increase in soil removal, although at 0.32 and 0.37% decreases were observed. Some of these results are shown in Figures 4 and 5 which are replotted from the data of Cobbs, Harris, and Eck (29). Combinations of any of the three silicates with trisodium phosphate or tetrasodium pyrophosphate usually give better soil removal than with either builder alone. The effectiveness of the silicates both alone and in mixtures under their conditions increased in the order: 3.3 ratio, 2.0 ratio silicates, metasilicate.

Cotton, rayon, and wild silk are washed whiter in solutions of a silicated soap than in solutions of a pure olive oil soap or a sodium salt of a sulfated alcohol (27). With wool, the results for the two soaps are about the same. The wet strength of all fabrics except wild silk after as many as 50 washings is higher for the silicated soap than for the pure olive oil soap, even of wool, which is regarded as sensitive to alkalis.

Sodium metasilicate and 3.3 ratio silicate increase the detergency of fatty acid-rosin soap mixtures in sea water and the mixture can be produced in bar form (109).

The increased detergent action of synthetic detergents when silicates are added is often much greater than with the soaps. For example, in one case soil removal is more than doubled by replacing 60% of the dodecylbenzene sodium sulfonate with a mixture of sodium sulfate and metasilicate (41). Many synthetic surface active agents which are only poor or fair detergents become good cleansers in the presence of sufficient builder. This includes nonionic detergents as well as the more familiar anion and cation active compounds.

Silicates of soda reduce the amount of soap required to form suds in typical hard waters, which

results in a decreased consumption of soap under many practical conditions (17). The reduction varies considerably with different soaps, silicates, temperatures, and concentrations, and is greater if the silicate is added before the soap than if both are added together. The effectiveness of the various silicates increases with decreasing silica-sodium oxide ratio. Precipitates formed in hard water containing silicates or phosphates are so fine and so well dispersed as to be apparent only as a stable turbidity; precipitates formed in these waters by sodium hydroxide or sodium carbonate are large, adherent, and not easily broken up or dispersed.

The effects of sodium chloride and nine salts industrially important as soap builders on the phase behavior of aqueous systems of a commercial mixed soap have been studied at soap concentrations to 50%, electrolyte concentrations to 27%, and temperatures to 180° C. (66). The salts were sodium chloride, carbonate, and tetraborate, trisodium phosphate, tetrasodium pyrophosphate, Calgon "sodium hexametaphosphate," sodium metasilicate, sodium silicates of silica-sodium oxide ratios by weight of 2.46 and 3.93, and a potassium silicate

of silica-potassium oxide ratio by weight of 2.04. The solubility of the soap in solutions of these salts and their effect on the transition from crystalline to liquid crystalline soap vary widely on both a weight and a molecular basis. The order of increasing effect differs somewhat with concentration and temperature. In general it appears, however, that more of the siliceous silicates than any other builder tested can be added to soaps under conditions of commercial interest. A phase study of sodium palmitate-water systems with added silicates and phosphates gave similar results (68).

A detergent product may be produced by spraying a granular, powdered alkaline silicate with a saponifiable oil or fatty acid, forming a soap film on the surface (73, 93). Substantially homogeneous soap-silicate mixtures are obtained by reacting a fatty acid with an "expanded" or intumescent alkali metal silicate (106).

Soap made from rosin neutralized by an alkaline silicate is a better dispersing agent for crude or reclaimed rubber than that neutralized by an equivalent amount of sodium hydroxide (33).

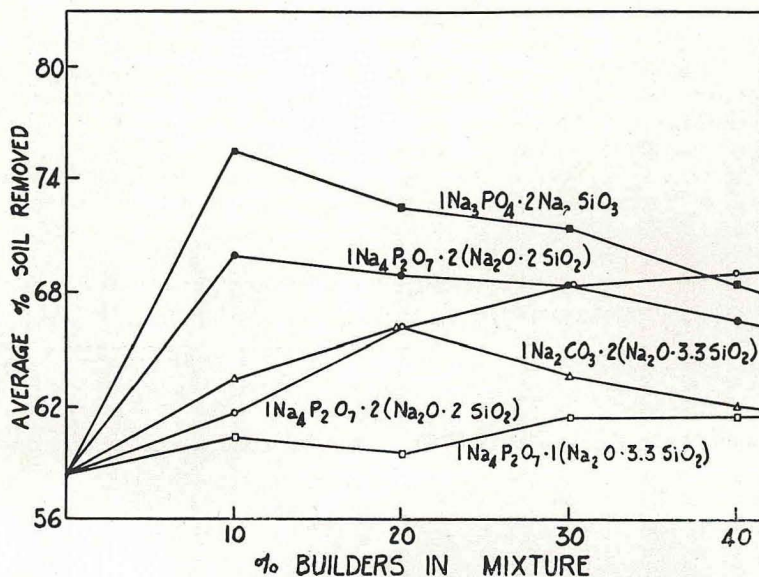


Figure 5. Removal of Carbon Black Soil by 0.15% Soap-BUILDER Mixtures at 140° F. in Water of 50 P.P.M. Hardness (Data from 29)

DETERGENTS

Although silicates of soda have been used in detergent operations for many years, it was largely the introduction of the stable, pure, white, free-flowing metasilicate pentahydrate about 1930 and of a stable hydrated sesquisilicate about 1934, that led to their present wide scale use for these purposes. These readily soluble alkaline silicates are successfully used in detergent operations varying from washing bottles, clothes, pigs, cans, and floors to locomotives and tank cars. Their value as detergents has been established by laboratory study of the factors involved (7, 59, 92) and of practical applications (35, 104).

The alkalinity of the silicates enables them to neutralize or saponify dirt such as fats, oils, paints, and some proteins which then become water-soluble or dispersible. Their high buffering capacity enables them to maintain approximately the same pH in the presence of acidic material or on dilution. Sodium metasilicate is more effective than sodium hydroxide, or carbonate or trisodium phosphate in wetting glass or displacing a petroleum oil from a glass surface (7). The data in Table IV show that the contact angle at 18° C. against a wax deposit and the surface tension of silicate solutions are lower than those of other alkalis. Both the wetting of wax and the lowering of surface tension increase with ratio of silica to alkali.

The interfacial tension against toluene of silicate solutions decreases with increasing silica to alkali ratio (59). Values for solutions of the 2.0 ratio silicate to which sodium hydroxide has been added are lower than for those of the same composition made from the crystalline silicates, since the reaction between siliceous silicates and strong bases is slow. Interfacial tensions of the more alkaline silicates against oils containing acidic or saponifiable material are only 2 or 3 dynes or less. Spontaneous emulsification is frequently observed in these systems. Solutions of sodium metasilicate and trisodium phosphate emulsify a light mineral oil better than those of sodium carbonate or hydroxide (7). The metasilicate is a good suspending agent, particularly for siliceous pigments, and is usually slightly superior to trisodium phosphate and definitely better than sodium hydroxide or carbonate. The silicate anion plays an important role in these cleaning processes (104).

TABLE IV. CONTACT ANGLE AGAINST WAX AND SURFACE TENSION OF VARIOUS ALKALI SOLUTIONS CONTAINING 1% SODIUM OXIDE

(Data from Liddiard, 59)		
Alkali	Contact Angle, °	Surface Tension, Dynes/Cm.
Sodium hydroxide	104	66.6
Sodium carbonate	102	...
Trisodium phosphate	70	...
Sodium orthosilicate	55.5	65.6
Sodium sesquisilicate	54.5	64.1
Sodium metasilicate	54.0	64.4
Sodium silicate, $\text{SiO}_2/\text{Na}_2\text{O} = 2$	40.5	62.2
Sodium silicate, $\text{SiO}_2/\text{Na}_2\text{O} = 3.3$	Less than 10	55.4

The sequestering action of sodium hexametaphosphate, sodium tetrphosphate, and tetrasodium pyrophosphate is greater for both calcium and magnesium hardness at 140° and 200° F. in the presence of metasilicate or sesquisilicate than with caustic soda, soda ash, or trisodium phosphate (63).

The laundry industry uses both meta- and sesquisilicates as detergents and soap builders, often in the same total quantity as the soap, beginning in the "break" and continuing through the various suds operations. Silicates are used in the textile industry in kier boiling, bleaching, back gray washing, soaping of prints, scouring rayon, wool, yarn, and other fabrics, and silk weighting. The sesquisilicate may also be used for the partial saponification of acetate rayons. The metasilicate may be used for wool scouring, but this requires careful control, since alkali tends to discolor the wool. A silicate with a silica to alkali ratio of 1.6 or

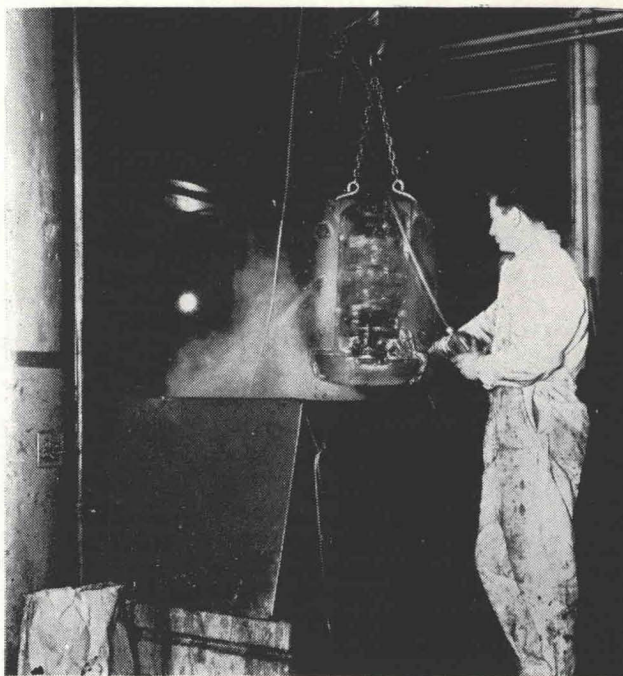


Figure 6. Cleaning Motors by Soaking in Sodium Sesquisilicate Solution

2.0 is recommended for this purpose. For degumming silk a combination of one of the organic wetting agents with silicates is preferable to soap alone or soap in combination with other alkalis, because the finished product is most satisfactory, particularly with respect to retaining pliability and elasticity (71). Waste paper is deinked with the aid of sodium metasilicate or the 1.6 ratio silicate, sometimes with the addition of a wetting agent.

Many detergent mixtures contain sodium silicate, a polyphosphate to sequester hardness, and a synthetic detergent to give rapid wetting. Machine dishwashing tests by Hughes and Bernstein show that a satisfactory detergent for that purpose should contain at least 8% of soluble silica and may include over 30% silica (45).

METAL CLEANING

Because of their detergent properties together with comparative freedom from attack on most metals, even those sensitive to alkalis (8), silicates are used in many metal cleaning operations. The protective action of the silica or silicate ions is apparently due to an invisible film of silica, or metal silicate which does not interfere with electroplating. The film formed on steel during cathodic cleaning in sodium metasilicate solutions is claimed on the basis of electron diffraction patterns to be a complex ferroferrisilicate ($9\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 8\text{H}_2\text{O}$) (91), but further evidence is needed.

Because the metasilicate attacks aluminum only below a concentration of 0.6% and silicates with a silica to alkali ratio greater than 2 do not attack the metal, a mixture of sodium metasilicate and a more siliceous silicate is used for aluminum cleaning. Such a mixture containing 25 to 50% of a spray-dried hydrated silicate (17.5% water) with a silica to alkali ratio by weight of 3.2 is used extensively for cleaning airplane parts. No attack has been noted by this mixture even after several hours' boiling. In order to prevent attack on aluminum utensils, the addition of about 25% sodium metasilicate to proprietary dishwashing compounds is recommended (100).

Several hundred immersion tests at 95° C. with various types of alkaline cleaners for metals indicated that those containing rosin soaps and silicates gave best results (80). One reason for



Figure 7. Scouring with Sodium Metasilicate Solution on Jig

the particular suitability of these mixtures for metal cleaning is their free rinsing properties (114). Oily deposits on the inside of locomotive boilers, difficult to remove by other methods, are satisfactorily cleaned with sodium metasilicate and a wetting agent in the proportions of 0.5 and 0.05 ounce per gallon and boiling under 100 pounds pressure (2). A mixture of 95 parts of sodium metasilicate and 5 parts of a commercial long-chain alkyl aryl sulfonate gives good results in removing mineral oil from steel, galvanized or tin-plated steel, aluminum, or brass (70). The rates of removal of soils from Dow metal under comparable conditions are given in Table V.

Sodium silicates, particularly the metasilicate, are satisfactorily used in electrolytic cleaning, including such familiar operations as cleaning brass, die castings, copper, or steel prior to the deposition of nickel and chromium (44). Hazel and Stericker (42) have recently shown that sodium silicates can be used safely for the electrolytic cleaning of zinc and zinc-base alloys over a wide range of conditions and are superior to most other alkalis for this purpose. When the correct silicates and proper conditions are used, no attack or deposit on the metal surface is observed.

CEMENTS

The somewhat arbitrary distinction between adhesives and cements is that the former are applied as a thin fluid film to unite

surfaces nearly in contact, whereas the latter are viscous or plastic mixes which occupy more space between the materials they bind. A variety of cements are made with powders and solutions of silicates of sodium and potassium of widely varying silica to alkali ratios. These are used for acidproof construction, digester linings, mending broken saggers in potteries, lining and coating refractories, and lining crucibles, brass furnaces, ladles, sulfite digesters for chemical wood pulp, and other similar units. Chimney, coke oven, stove, furnace, tunnel, spark plug, and patching cements are made with silicates of soda. Suitable mixtures have also been developed for binding porcelain and glass to metal, and china to glass.

The advantages of silicates as binders include resistance to acids (with the single exception of hydrofluoric acid and some of its derivatives), ability to withstand high temperature, ease of application, low price, resistance to water when dehydrated, and strong bonding action to many types of surfaces both by air drying and on heating. Setting may occur by loss of moisture, or by the formation of a silica gel or heavy metal silicate.

Silicate of soda refractory cements are made by mixing refractory fillers with silicate solutions to form plastic mixtures. Dry cements are made by mixing fillers with powdered silicates and adding water just before use. Filler materials in regular use include raw and burned fire clay, ground firebrick, various forms of silica (sand, ground quartz, and ganister), chromite, ground mica, asbestos, graphite, periclase, soapstone, and artificial refractory materials such as silicon carbide firesand (cf. 16). North Carolina pyrophyllite, forsterite, and crushed olivine are recommended as fillers for refractory cements (36-38).

Best results are obtained with mixtures of two or more of these ingredients, and several sizes of particles. The heat resistance of a silicate cement is much greater than that of the silicate itself. It depends on the fillers, and on the fluxing action of the

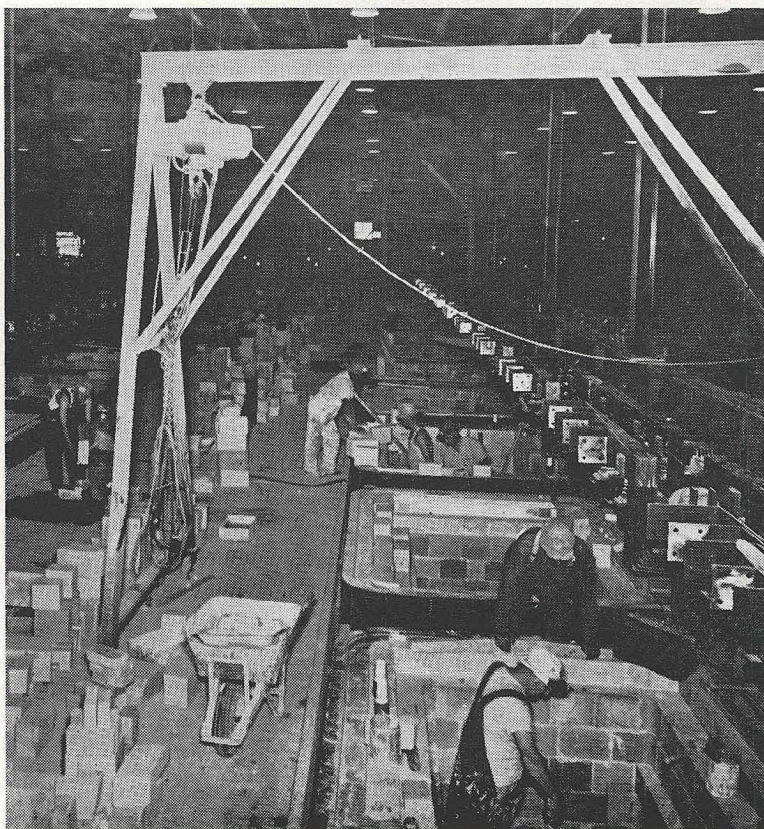


Figure 8. Laying Acid-Resistant Tile with Silicate Cement in Electrolytic Cells for Holding Molten Magnesium

TABLE V. RATE OF REMOVAL OF SOILS FROM DOW METAL BY ALKALINE SOLUTIONS CONTAINING 0.87% SODIUM OXIDE (0.28 N) (99)

Alkali	Time (Minutes) to Remove		
	Stearic acid soil	Paraffin soil	Red oxide buffing compound
NaOH	8	>20	>10
Na ₂ PO ₄	7	>10	3
Na ₂ HSiO ₄	3	0.5	1.5
Na ₂ SiO ₃	1	0.5	3

silicate which increases with alkalinity. A proper balance between plastic fire clays and mineral fillers minimizes the fluxing action of silicates. Sodium silicate cements have been used for at least 25 years at temperatures up to those of smelting furnaces and glass tanks. A periclase refractory bonded with a 3.2 ratio silicate is satisfactory up to 1800° C. and superior to those bonded with organic materials (77).

The addition of silicates to refractory cement mixes increases the tensile and shear strengths, and decreases porosity and shrinkage. For example, the addition of 5 and 12.5% by weight of a powdered 2.0 ratio silicate to a fire clay-ball clay-kaolin grog mix increased the strength from 100 to 600 and 2500 pounds per square inch, respectively (43). Additions up to 7.5% of the powdered 3.2 ratio silicate produced comparatively small increases in strength to about 500 pounds per square inch. Above 7.5% the mixes compared favorably in strength with those containing the more alkaline silicate. Compressive strengths of olivine and pyrophyllite refractory mixes containing 10% of a 41° Bé. 3.2 ratio silicate are higher than those bonded with sulfite pitch, a high alumina hydraulic cement, sodium aluminate, zinc phosphate, or bentonite (36, 38). The addition of 1 to 5% of zinc oxide (113), aluminum oxide (111), or calcium carbonate (56) to silicate-sand mixtures used in metal casting decreases adsorption of moisture, increases strength, and improves resistance to water and molten metals.

The hardening out of contact with air of some plastic cements containing certain clays is sometimes due to reaction with calcium, magnesium, and other heavy metal ions by base exchange. It may be avoided in these cases by a preliminary treatment of the clay to replace with sodium ions the ions precipitating silicate (72). Hardening due to reactions of other types is minimized by using a more alkaline silicate whose viscosity is not so greatly affected by slight reaction.

Acidproof cements have been made for many years by mixing a 33.5° Bé. 3.9 ratio silicate with several sizes of ground quartz. These set by drying which requires several days, although this can be speeded up by heating. Treatment with acid gives a quicker set but decreases the ultimate strength. Various mate-

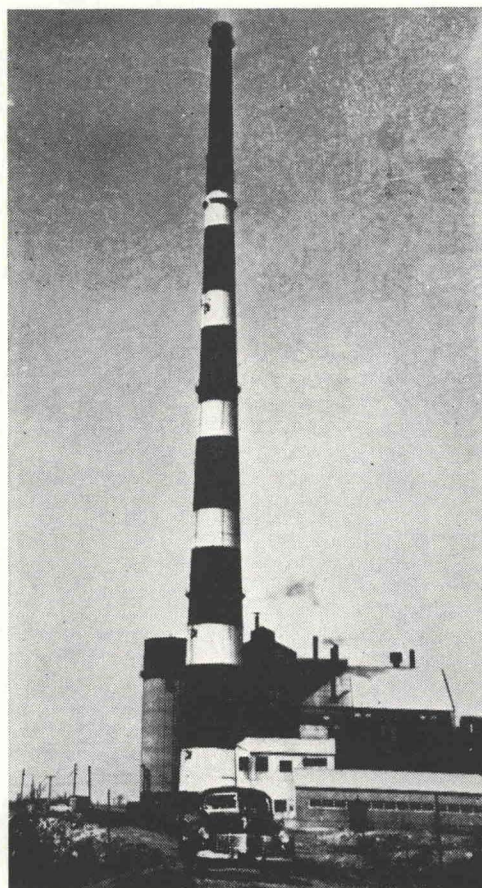
rials have been added which react with the silicate, forming a silica gel or insoluble silicate, and thus increasing the rate of set and decreasing the solubility of the cement (103).

The usual rapid-setting acid-resistant cements commercially available are those containing fluorides or fluosilicates. Although the exact mechanisms of the reactions are not known, a rapid, controlled rate of setting giving an insoluble acidproof cement is obtained. Widely used products of this type are made under the patents of Frank and Dietz assigned to the I. G. Farbenindustrie (34) and of Snell (94). Frequently they are sold as dry powders which are mixed with a 38° Bé. 3.2 ratio silicate before use. A product which is both water- and acidproof, and contains no alkali after setting is made from 100 parts of ground stoneware, 9.4 parts of sodium silicofluoride, and 70 parts of a 41° 3.2 ratio sodium silicate (94). It sets in 15 to 20 minutes. Numerous patents have been issued on acidproof cements of this type. The modulus of elasticity of these modern acidproof cements is around 800,000 pounds per square inch or about two thirds that of concrete. Their coefficient of thermal expansion is 6.3×10^{-6} per degree Fahrenheit between 70° and 500° F., which is of the same order of magnitude as that of steel (10).

Other materials added to accelerate the setting and decrease the solubility of silicate acid-resistant cements include barium hydroxide, calcium sulfate, phosphate, or carbonate, alkaline earth sulfides, zinc oxide, lead carbonate, ammonium salts, esters of fatty acids, acid anhydrides, and portland cement (4, 81, 103). Many of these greatly decrease the ultimate tensile strength. Silicon and its alloys accomplish these results by reacting with the alkali. The hydrogen liberated may make the cement porous

and prevent shrinking. Amorphous forms of silica, such as opal, chalcedony, and agate which react slowly with the alkali, may also be used. The silica available as a by-product in the manufacture of fertilizers from natural phosphate rock and aluminum salts from kaolin is satisfactory. The rate of reaction with silicate may be decreased by surrounding the added material with a water-resistant layer. According to a patent, a paraffin coating may be used or the surface of coarse granules may be coated with a water-resistant compound such as barium silicate (4).

The chemical reactivity of silicate-rubber latex cements may be decreased by heating the mixture with sulfur to cause vulcanization. Removal of the alkali from a silicate cement by electrolysis, usually in the presence of a small amount of silicon, hardens it and increases its acid resistance. Silicate of soda cements in contact only temporarily with sulfuric acid, with alternate exposure to air for long periods of time, may show mechanical spalling, although ordinarily this does not occur. This is due to the growth of sodium sulfate hepta- or decahydrate crystals in the joints or bricks. It can be eliminated by using potassium instead of sodium silicates. Recent patents cover



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Figure 9. Smoke Stack Constructed with Acidproof Cement Containing Silicate of Soda

acidproof cements containing aromatic sulfochlorides, acid-proof fillers, and potassium silicate (31), and a mixture of litharge with equal amounts of sodium and potassium silicates (116).

Preliminary unpublished data indicated that the addition of 3 to 5% of a 3.2 ratio powdered silicate composition to a mixture of 1 part of portland cement, 2 parts of sand, and 4 parts of gravel increased the compressive strength after 28 days by as much as 38% and decreased the water absorption 20 to 40%. A German patent claims that the addition of an alkaline silicate to a hydraulic cement increases its rate of set and improves the mechanical and water-resisting properties (48). Recently the use of a silicate cement for precoating investment castings has been publicized (3).

BRIQUETS AND BONDED MATERIALS

The adhesive character and low cost of silicates of soda cause their use in bonding a variety of materials including coal and the mixture used in making glass. Only recently has coal briquetting with silicate been successful on a commercial scale. Difficulties were that the silicate coating was partially water soluble and that the silicate acted as a flux for the ash, forming slag which deposited on the grates of the furnace. A method of overcoming this difficulty is to add a material such as calcium carbonate or some clay which reacts with silicate to form a product with a high fusion point. One patented process covers a binder comprising a dispersion of silicic acid gel in a 3.2 ratio sodium silicate solution (95, 96), while another adds an alumina-bearing material such as ground bauxite (74).

During the war three processes were developed in France for the production of coal-dust briquets, using silicate to replace and extend pitch (52). Two involved the preparation of an emulsion or paste of a 3.5 ratio silicate solution with pitch. The third method used a powdered disilicate glass. The silicate consumption for this purpose grew to 35,000 tons in three years, or 53.7% of the sodium silicates consumed in France that year. The amount used per ton of briquets decreased from 10.3% in 1941 to 4.4% in 1943.

The mixture of compounds used in manufacturing plate glass has been briquetted prior to melting with about 3 to 4% of both the 47° Bé. 2.9 ratio, and 41° Bé. 3.2 ratio silicates, although the more alkaline ratio gave a stronger briquet. Briquetting eliminated batch dust, reduced waste, gave greater uniformity of batch and easier melting, and reduced the heat required. The furnace life was increased. The 30% increase in melting rate reduced the fuel consumption per ton of glass (86, 89).

Abrasive wheels are made by bonding the abrasive grains with a 2.0 ratio silicate, usually in combination with clay and sometimes with a small amount of zinc oxide for water resistance. Similar mixtures are used for grinding and polishing wheel cements, although these frequently contain a less alkaline silicate and several additives. Some years ago the replacement of glues with a silicate base cement not only speeded up production of grinding wheels but often gave them a life several times longer than those obtainable with glue. The method now developed for spraying the abrasive and a silicate cement on grinding and polishing wheels so that the mixture sets almost instantly saves material and time (90).

During the war the amount of silicates of sodium and potassium used in welding rod coatings increased severalfold. These are complex mixtures, some of which contain as many as thirty ingredients. Titanium dioxide, various forms of silica, ferroalloys, carbides, cellulose, and asbestos fibers are common ingredients. Potassium silicates are used as binders where contamination of the metal with sodium would be undesirable or where the smoother arc obtained with potassium silicate is needed. Mixtures of sodium and potassium silicates are used.

Other types of materials bonded with silicates now commercially available are insulating materials from wood fiber and

TABLE VI. RECENT DEVELOPMENTS IN APPLICATIONS OF SODIUM SILICATES

Field	Development	Reference
Silica aerogels	Gel heated above critical temp. of solvent used as insulation, catalysts	(49, 50)
Silica gel	SiO ₂ gel in bead form for catalyst, desiccant	(64, 78)
Silica sols	Sols containing 20 to 30% SiO ₂ made by passing silicate solution through ion exchange resin	(12, 84)
Silica sols	Pptn. of salts in acid-silicate mixture by volatile organic liquid, distilling of liquid leaving salt-free aquasol	(65)
Silica sols	Active sols for coagulation made by aging acid-silicate mixtures, diluting	(67)
Organic silicates	Polysilic acid esters made by azeotropic distillation of acid-treated silicate-butyl alcohol mixtures	(46)
Calcium silicate	Silicate pptd. by soluble calcium salt gives particle size 0.3 to 30 microns. Used as rubber filler	(1)
Bleaching	Silicate used to stabilize peroxide, as detergent, buffering agent, to prevent corrosion in bleaching of groundwood and in continuous bleaching of textiles in J-boxes	(55)
Corrosion	Review of recent applications, developments	(98)
Water treatment	Potassium silicates recommended in boiler water treatment	(39)
Textiles	Impregnation of rayon tire cords with rosin-silicate mixture increases strength 16%	(21)
Pigments	Formation of silica or metasilicate coating on lithopone, titania, etc., improves heat, light weathering resistance, surface hiding power	(40, 75)
Soil stabilization	Silicates stabilize heaving shales met in oil well drilling	(9)

slag wool. Recent patents cover an absorbent of bauxite fines bonded with silicate (6), a hard, nondeliquescent detergent briquet which uses both the detergent and bonding properties of the silicate (62), and a foundry mold made of silica, a sodium silicate, and pitch (51). Iron oxide, brass chips, and metal shavings are bonded with silicate of soda (5, 69, 115, 116). Several patents cover molded products made from sand, silicate of soda, and a bitumen, fluosilicate, a boron compound, asphalt emulsion, or aluminum sulfate (83, 97). A wallboard composition from limestone, sandstone, and clay (19) and a coating for television tubes containing borates, phosphates, and colloidal carbon (79) illustrate additional materials bonded by silicates of soda.

OTHER USES

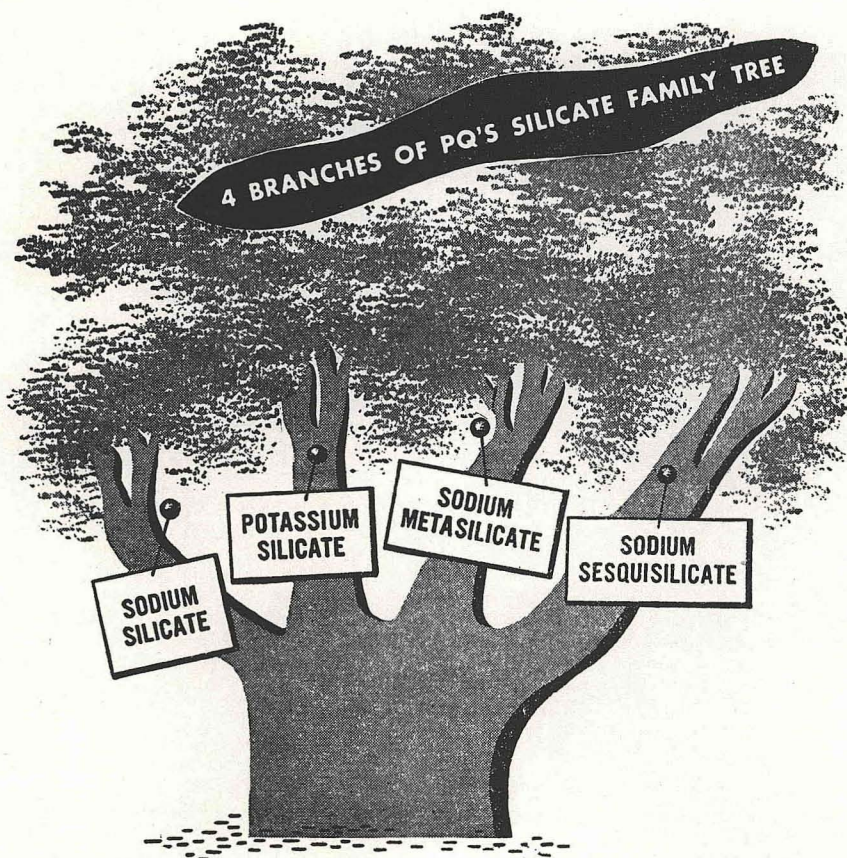
Although the above uses now consume a major share of the sodium silicates produced, these are not all of the commercial applications. Recent developments for other uses are summarized in Table VI. Another large group of uses involves the reaction of sodium silicates with acids, sodium aluminate, and other materials to form catalyst, desiccant, and base-exchange gels. Silicates of soda are used in roofing, granules, coatings, sizings, and paints, as deflocculants, and in flotation reagents; little scientific research has been done on these subjects.

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