

the less dilute solutions of the higher soaps, the upper limit is exceeded by several fold, and in the more dilute solutions the concentration may fall beneath the lower value. Solubilized hexane reduced the pH of potassium and sodium laurate but very slightly. Potassium or sodium chloride reduced the pH of soap solutions over a certain range but caused a slight increase in a narrow intermediate range.

Using the pH values obtained, the actual concentration of fatty acid in the soap solutions was calculated, and was found to be *less* than the saturation concentrations obtained by conductivity measurements through the entire range investigated. Free fatty acid therefore never separates as such from pure soap solutions unless acted upon by excess of acid such as carbon dioxide.

Percentage hydrolysis was calculated and curves were constructed. In general, the potassium soaps are hydrolyzed more than the corresponding sodium

soaps; the difference is slight for the laurates but is considerably greater for the myristates, palmitates, and stearates in higher concentrations at 25°C. The difference is appreciably smaller at 50° than at 25°. Percentage hydrolysis for the laurates is very much less than for the higher soaps.

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Silicates in Soaps

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SILICATES of soda were added to soaps before 1835. Soaps containing substantial quantities of silicate became popular in this country during the Civil War when the shortage of fats and rosin in the North caused manufacturers to add silicates to their soap in order to extend the supply. The war-time and present shortage of fats is reemphasizing the value of silicates for this purpose. It is estimated that the soap industry of the United States consumes more than 200,000 tons annually of silicates calculated to the 41° Baumé solution equivalent. Most commercial soaps now contain some silicate and some contain it in very large proportion.

At first silicates in soap were regarded simply as fillers which had little or no effect on the washing action of the soap. It is now well established both from careful laboratory studies and continued practical use under a wide variety of conditions over many years that silicates definitely improve the washing action of soaps under conditions of use. Silicates of soda are themselves detergents just as are soaps and the numerous types of new synthetic detergents. Mixtures of soap and silicates in the proper proportions are usually better than either alone.

Types of Silicate. Sodium silicates are composed of varying proportions of sodium oxide (Na_2O), silica (SiO_2), and water. More than 50 products varying in the ratio of these three components are commercially available as well as several potassium silicates. The characteristics of those of most interest to the soap and detergent manufacturer are summarized in Table I. The sesqui- and metasilicates are white crystalline, readily soluble, definite chemical compounds of fixed composition. "GC" has a silica to alkali ratio of 2.0 and is an amorphous hydrated powder. "SSC" is an essentially anhydrous solid of the same ratio. The "GC" silicate is spray dried and the "SSC" powder finely ground to provide rapid solubility. Commercially available silicates with a silica to alkali ratio greater than about two are glasses whose silica to alkali ratio may vary continuously from two to about four, which is now the practical

upper limit. Although quite soluble, these silicates can be dissolved satisfactorily only by steam under pressure so are sold as solutions as concentrated as practicable. The silicate now most commonly used by soapmakers has a specific gravity of 41° Baumé and a silica to alkali ratio of 3.2. The chemistry of the soluble silicates is discussed elsewhere (1, 10).

Detergency of Silicated Soaps

pH and Buffering Action. The phenomenon of detergency is complex and involves several factors whose relative importance varies with conditions. One important factor involves the neutralization of the organic acids, sweat, and other acidic materials in dirt and the saponification of fats, oil, and greases since these are a substantial fraction of many dirt. These materials are converted to water soluble sodium salts, which are readily removed by rinsing. Likewise, proteins and oil paints are usually more readily removed by alkaline solutions. This requires a high pH and high available alkalinity, which should be maintained over a wide range of concentrations and temperatures by effective buffering action. Both of these are obtained by using a suitable soluble silicate.

In addition to removing certain types of dirt by neutralization and saponification, the alkalinity of the silicates prevents the formation of acid soaps and/or free fatty acids by reaction of the soap with less alkaline materials. Such materials include bicarbonates in water softened by ion exchange methods, and carbon dioxide absorbed from the air as well as acidic dirt. Acid soaps are generally regarded as having little or no detergent action in aqueous systems.

Silicates, like other electrolytes, decrease the concentration at which micelles begin to form in soap solutions. This may be important for, as data presented by Preston (2) indicate, a marked increase in detergent action occurs at about the concentration at which micelles begin to form. Silicates by themselves do not solubilize water-insoluble dyes. This makes it possible to obtain good cleaning without fading dyed goods. The addition of silicates to a soap solution,

however, does increase its ability to solubilize water insoluble materials. This indicates that the proportion and size of the soap micelles are increased.

Several investigations have indicated that best detergent action is obtained with soap-builder mixtures having pH's at room temperature around 10 to 11 although the nature of the builder definitely has an effect [e.g. (3, 9)]. Since soaps containing no excess free alkali have pH's of around 10 or less at concentrations of detergent interest, these data indicate that it is necessary to add an alkali to obtain the optimum pH for washing. The variation of pH with concen-

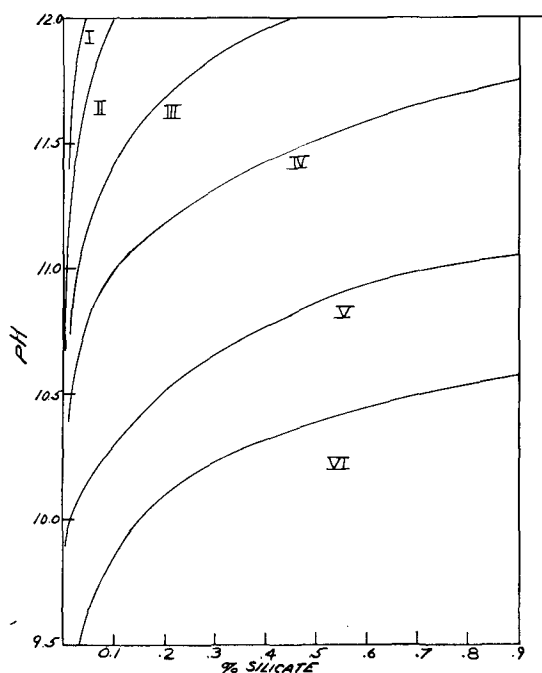


FIG. 1. pH vs. concentration for silicates of varying $\text{SiO}_2/\text{Na}_2\text{O}$ ratio at 20°C . Unpublished data from the laboratories of the Philadelphia Quartz Co.

Curve I— NaOH ; II— Na_2SiO_3 ; III— $\text{Na}_2\text{O}\cdot 1.6\text{SiO}_2$; IV— $\text{Na}_2\text{O}\cdot 2.0\text{SiO}_2$; V— $\text{Na}_2\text{O}\cdot 2.9\text{SiO}_2$; VI— $\text{Na}_2\text{O}\cdot 3.2\text{SiO}_2$.

tration and silica to alkali ratio makes it possible by using a suitable soluble silicate to reach and maintain over a wide range of concentrations, temperatures, and added acidic materials, any pH desired in cleaning applications with soap.

The increase in pH with concentration and decrease in pH with silica to alkali ratio are shown in Fig. 1 for various commercial silicates at 20°C . (68°F). The

buffering action due to the presence of soluble silica is also illustrated in this figure. Increasing the temperature lowers the pH of silicate solutions. For example, the pHs of 0.01% and 0.1% sodium sesquisilicate solutions decrease from 10.71 and 11.80 at 25°C . to 9.86 and 10.83 at 60° ; those of sodium metasilicate solutions of the same concentration from 10.55 and 11.55 at 25°C . to 9.71 and 10.64 at 60° (4). The change of pH with temperature for the more siliceous silicates is not accurately known, but is probably somewhat less. The pH's and hydroxyl ion concentrations at 25° and 60°C . of 0.01% and 0.1% solutions of alkalis commonly used as soap builders are given in Table II (4). The pH of soap solutions likewise decreases with increasing temperature.

A frequently raised objection to the use of alkaline silicates in soaps is that high pH's are hard on human skin. Some evidence indicates that silicate solutions are much less hard on human skin than other alkalis at the same pH. It appears that silicates in soaps tend to decrease some soaps' effect on the skin up to a certain concentration. The buffering action of the siliceous silicates prevents pH's from ever becoming high enough to irritate the skin. More work needs to be done on this subject.

Surface Activity. Another important factor in detergent action is the surface activity of the solution. The addition of silicates to a soap solution lowers its surface tension. For example, Richardson (5) showed that the addition of a silicate with a silica to alkali ratio of 2.83 markedly lowered the surface tension at 100°C . of 0.05 to 0.25% solutions of a commercial flake soap. The interfacial tensions of organic liquids against soap solutions are likewise lowered by the addition of silicates. Millard's data (6) show that one with a silica to alkali ratio of 1.6 was more effective than a 2.4 ratio silicate in reducing the interfacial tension of a soap solution at 40° against benzene. Snell's data (7) show that sodium metasilicate is more effective than trisodium phosphate, sodium carbonate, and modified soda in reducing the interfacial tensions of dilute soap solutions against benzene containing a small amount of acidic or saponifiable material. The surface tension, interfacial tension against toluene, and contact angles against wax of silicate solutions containing 1% Na_2O are lower than those of other alkalis. The surface tension and contact angle against wax decrease with silica to alkali ratio (8). The surface activity of a silicate-caustic soda mixture changes with time since the reaction between silicates and strong bases is slow under ordinary conditions.

TABLE I
Commercial Silicates of Interest to the Soap Manufacturer

Name	Formula	$\text{SiO}_2/\text{Na}_2\text{O}$ Wt. Ratio*	% Na_2O	% SiO_2	Anhyd. %Solids	Gravity		Approximate Viscosity Poises, 20°C .
						Sp. Gr. $20^\circ/20^\circ$	Bé 20°C .	
Sodium Sesquisilicate.....	$\text{Na}_2\text{HSiO}_4\cdot 5\text{H}_2\text{O}$ (or $3\text{Na}_2\text{O}\cdot 2\text{SiO}_2\cdot 11\text{H}_2\text{O}$)	0.69	36.6	24.4	61.0			
Sodium Metasilicate Pentahydrate.....	$\text{Na}_2\text{SiO}_3\cdot 5\text{H}_2\text{O}$	0.97	29.2	28.3	57.5			
GC.....	$\text{Na}_2\text{O}\cdot 2.1\text{SiO}_2$	2.00	27.5	55.0	82.5			
SSC Pwd.....	$\text{Na}_2\text{O}\cdot 2.1\text{SiO}_2$	2.00	32.7	65.4	98.1			
BW.....	$\text{Na}_2\text{O}\cdot 1.7\text{SiO}_2$	1.60	19.5	31.2	50.7	1.68	58.5	70
C.....	$\text{Na}_2\text{O}\cdot 2.1\text{SiO}_2$	2.00	18.0	36.0	54.0	1.69	59.3	700
D.....	$\text{Na}_2\text{O}\cdot 2.1\text{SiO}_2$	2.00	14.5	29.0	43.5	1.53	50.0	2.8
RU.....	$\text{Na}_2\text{O}\cdot 2.5\text{SiO}_2$	2.40	13.8	33.1	46.9	1.56	52.0	17
K.....	$\text{Na}_2\text{O}\cdot 3.0\text{SiO}_2$	2.90	11.0	31.9	42.9	1.48	47.0	9.6
N.....	$\text{Na}_2\text{O}\cdot 3.3\text{SiO}_2$	3.22	8.90	28.7	37.6	1.39	41.0	1.8
O.....	$\text{Na}_2\text{O}\cdot 3.3\text{SiO}_2$	3.22	9.16	29.5	38.7	1.41	42.2	4.0
Kasil No. 1.....	$\text{K}_2\text{O}\cdot 3.9\text{SiO}_2$	2.50	7.80	19.5	27.3	1.25	29.0	0.4
Kasil No. 6.....	$\text{K}_2\text{O}\cdot 3.3\text{SiO}_2$	2.10	12.6	26.8	39.4	1.39	40.7	17.5

* K_2O for potassium silicates.

TABLE II
 pH and Hydroxyl Ion Concentration of Various Alkali Solutions

Substance	0.01%				0.10%			
	25°		60°		25°		60°	
	pH	(OH ⁻) × 10 ⁴	pH	(OH ⁻) × 10 ⁴	pH	(OH ⁻) × 10 ⁴	pH	(OH ⁻) × 10 ⁴
NaOH.....	11.30	20	10.33	20	12.29	197	11.27	180
Na ₂ SiO ₃	10.55	3.6	9.71	4.9	11.55	36	10.64	42
Na ₂ P ₂ O ₇	10.29	2.0	9.65	4.3	11.31	21	10.63	41
Na ₂ CO ₃	10.40	2.5	9.74	5.3	10.94	8.8	10.30	48
Na ₄ P ₂ O ₇	9.50	0.32	9.23	1.6	10.0	1.0	9.64	4.2
NaHCO ₃	8.28	0.019	8.08	0.011	8.43	0.027	8.48	0.29

Interfacial tensions of the more alkaline silicates against oils containing acidic or saponifiable material are only 2 or 3 dynes or less, and spontaneous emulsification frequently occurs. Accurate data showing the effect of silicates on the wetting power of soaps against fabrics and glass are apparently not available, but it is a matter of observation and practical experience that wetting by silicated soaps is as good or better than by those containing no silicates. It has been demonstrated that the metasilicate is more effective than sodium hydroxide, carbonate, or trisodium phosphate in wetting glass or displacing a petroleum oil from a glass surface (9).

Foaming and Emulsification. Good foaming and emulsifying qualities are greatly desired in commercial soap products. That silicates increase the volume and stability of foam from a soap solution can be readily demonstrated by adding a little silicate to a soap solution so dilute that alone it produces only a trace of foam. The large resulting increase in lather volume has been shown and measured by Vail (10). The addition of 0.1% of a 40° Baumé 3.2 ratio silicate to a 0.1% sodium oleate solution increased the life of the foam more than tenfold (11). Baker (9) has demonstrated that the volume of foam formed by mixtures of alkalis with 0.0088% sodium stearate is greater with sodium metasilicate than with trisodium phosphate, sodium carbonate, or hydroxide. Stericker (12) observed that soap made by neutralizing fatty acids with silicate gave more suds than that produced by neutralization with caustic soda or soda ash. Likewise more suds were produced by adding various siliceous silicates to soap solution—kerosene emulsions than by adding sodium carbonate or by the soap solution alone. The addition of as much silicate as 60% of the total detergent minimized the tendency of the lather on a soap solution-oil emulsion to disappear on heating.

Stericker (12) has also shown that a mixture of soap and a siliceous silicate is a better emulsifying agent for mineral and saponifiable oils than soap alone or soap plus sodium carbonate. The ease of emulsification, volume of emulsion formed, and its stability vary with the type of oil, relative volumes of oil and soap-alkali solution, and temperature. Particularly stable, finely dispersed emulsions are formed with silicate-soap mixtures when the oil contains acidic or saponifiable material, as do many common dirt. Richardson concludes (5) "the quality of the emulsion formed by reaction of sodium silicate solutions with greasy materials containing free fatty acid is more significant than the quantity of soap produced." Another fact showing that the high efficiency of silicates is not entirely due to soap formation is that the emulsions formed with sodium carbonate or sodium hydroxide are much less stable. Vincent's investigations show (13) that a mixture containing

20% olive oil soap and 80% of a silicate with a silica to alkali ratio of around 3 is an excellent emulsifying agent. Mitchell found (13A) that at concentrations of detergent interest mixtures of sodium oleate with a silicate form a larger volume of emulsion with paraffin oil than does the same soap with caustic soda, soda ash, sesquicarbonate of soda, trisodium phosphate, sodium aluminate, or borax although the latter was equally effective at higher concentrations under his conditions.

Deflocculation and Suspending Action. A very important factor in detergent action is the ability of the detergent solution to keep dirt, which has been removed, dispersed in the solution so that it does not deposit or redeposit on the surface to be cleaned. This ability involves suspending, deflocculating, or peptizing action, and prevention of deposition or redeposition. Suspending action may be defined as the ability of an electrolyte to decrease the rate and amount of sedimentation of dispersed solid particles. McBain (14) has suggested that sedimentation is decreased by the free ions of opposite sign which are held in the neighborhood of a charged particle by electrostatic attraction. This means that suspending action is favored by the preferential sorption of one ion so that the suspended particle may have a large charge. The large preferential sorption of the various types of silicate ions as compared with sodium ion or other alkali anions may explain the observed superior qualities of silicates as suspending agents. This is particularly true for siliceous soils, exemplifying the general principle of "like to like." In addition to their suspending action silicates of soda, being colloidal, form mono- or polymolecular films around dirt particles and thus serve as protective agents.

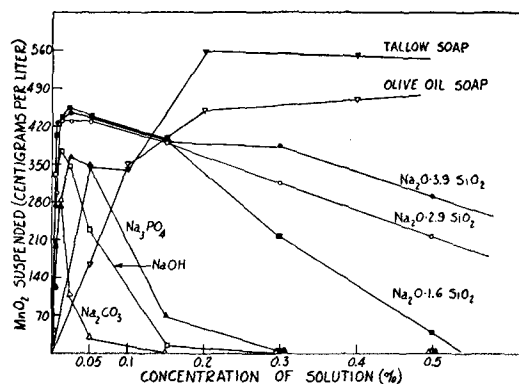


FIG. 2. Suspending action of soaps and alkalis for manganese dioxide at 40°C. Data from Fall (Ref. 15).

The suspending action of various soaps and alkalis on manganese dioxide at 40°C. is shown in Fig. 2, which has been plotted from the data of Fall (15). Similar relative results were obtained for 70° al-

though the maximum efficiency was about 22 to 25% greater at 40° than at 75°C. At room temperature the maximum efficiency of both silicates and soaps was 12 to 15% more than at 40°C. At low concentrations the silicates are more effective than soaps for suspending manganese dioxide and reach an optimum effectiveness around 0.04%. Their maximum efficiency compares favorably with that of soap at higher concentrations and is not much affected by the silica to alkali ratio. At higher concentrations the siliceous silicates are more effective. Qualitative tests showed that silicates are capable of suspending other dirt, clay, and lampblack as well as other forms of manganese dioxide. Experiments with coarse manganese dioxide particles using sodium carbonate, borax, sodium hydroxide, and trisodium phosphate led to the conclusion that "only silicate of soda and soap solutions produced stable suspensions" (15) although suspensions were obtained if the materials to be suspended were of smaller particle size.

Particularly stable suspensions are obtained with silicates when the material to be suspended contains acidic or saponifiable material. Richardson (5) states "when lampblack is mixed with oil or grease containing free fatty acid and the mixture shaken with a dilute solution of sodium silicate, we find that the suspension is characterized by unusual stability. This same stability does not result if sodium silicate is added to a suspension of lampblack previously produced by mixing it with a neutral hydrocarbon oil and shaking with a pure soap solution." Snell (16) found that sodium metasilicate was superior to sodium hydroxide, sodium carbonate, modified soda, and trisodium phosphate for deflocculating burnt umber coated with cottonseed oil, mineral oil, and oleic acid. Soap made from rosin neutralized by an alkaline silicate is a much better dispersing agent for crude or reclaimed rubber than that neutralized by an equivalent amount of caustic (17). These references and much practical experience show that the excellent suspending action of silicates on acidic or saponifiable materials is by no means entirely due to soap formation.

Of more practical importance in detergency than the effect of silicates in reducing the rate and amount of sedimentation is their ability to prevent the deposition or redeposition of dirt on a fabric or other material during agitation. Carter's studies (18) under conditions closely approximating actual laundry practice showed that mixtures of soaps and silicates are as good or better than either alone for preventing the deposition or redeposition of siliceous pigments on cotton. The 13 different types of pigments used included ferric oxide, Philadelphia dust, ground mica, graphite, coal, carbon black, and such siliceous pigments as vermilion, ultramarine, burnt, and raw umber. Sodium hydroxide, sodium carbonate, and modified soda showed only slight power or none at all to prevent the deposition of these pigments. The addition of protective colloids such as animal glue, gum arabic, colloidal clay, and wheat starch paste to these alkalis in some cases slightly increased their effect, but the mixtures were still not as effective as the silicates. Trisodium phosphate is intermediate between these and the silicates in preventing deposition. Silicates of all commercial ratios are effective, but, except at great dilutions, those of highest silica to alkali ratio seem to be more effective

for the more siliceous sols. This prevention of deposition depends on the soluble silica rather than on the alkalinity. Other experiments showed that silicates were excellent both in removing various types of soil from cotton and in preventing their redeposition. This was attributed in part to the formation of an exceedingly thin, invisible protective film on the cloth which is readily removed by rinsing.

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 (19). The effect on mixtures of soap and silicate, or the latter alone is much less so that in hard water the mixtures become more definitely better than the soap both in removing pigments and preventing their redeposition. This is apparently partly due to avoiding the formation of acid soaps and partially to selective precipitation of an amorphous, finely-dispersed, calcium silicate rather than sticky curds of calcium soaps.

Powney and Noad (20) have measured the deposition of ilmenite on cotton fabric under conditions of mechanical action such that sedimentation under gravity is not the predominating factor. Some of their results are replotted in Fig. 3. Comparison of

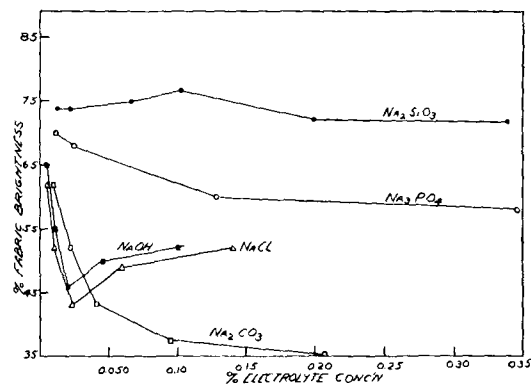


FIG. 3. Deposition of ilmenite on cotton fabric at 22°C. Data from Powney and Noad (20).

the five curves obtained under identical conditions shows metasilicate to be superior to trisodium phosphate in preventing the deposition of ilmenite on cotton and far superior to sodium hydroxide, carbonate, and chloride. The protective action of metasilicate was not affected by increase in temperature from 22° to 86°C. although deposition from water and sodium carbonate was increased. Increasing the concentration of the metasilicate and of silicates with a silica to alkali ratio of 2.0 and 3.8 gave an optimum suspending action approximately equal to that of 0.1% sodium oleate. Further increase in concentration of the silicates had little or no effect. This optimum suspending action is obtained at a concentration of 0.009% for the 3.8 ratio silicate, 0.012% for the 2.0 ratio silicate, and 0.02% for the metasilicate. The corresponding SiO₂ concentrations are 0.0071%, 0.0079%, and 0.0098%. This protective action is attributable to preferential adsorption of the silicate, either as simple anions or possible as aggregates. The increased negative charge on the fabric and on the dirt particles due to selective anion adsorption leads to an increased electrostatic repulsive force between

them and to a correspondingly decreased probability of adhesion. The hexametaphosphate and pyrophosphate exhibited a suspending action comparable to the silicates. The addition of sodium carbonate, hydroxide, or chloride to a soap solution decreased its ability to prevent deposition of ilmenite; the addition of silicate had no appreciable effect on the protective power of the soap but did exert its own effect.

Water Softening. Silicates of soda reduce the amount of soap required to form suds in typical hard waters. This results in a decreased consumption under many practical conditions. Their effectiveness as water softeners varies considerably with the type of soap, type of hardness, temperature, and presence of added materials. The reduction in soap consumption results mainly from the preferential reaction under some conditions of the silicate rather than the soap to form a fine, well dispersed calcium silicate. The reaction with hardness is not entirely stoichiometric for either soap or silicate. More sodium soap is lost than that required to react with hardness to form calcium or magnesium soaps. Likewise silicate may remove more hardness than the amount reacting to form calcium silicates (5). In most cases the water softening action of the silicate is somewhat greater if it is added before the soap rather than both being added together. The precipitate formed by hard waters with silicates and phosphates is of such small particle size and so well dispersed as to be apparent only as a quite stable turbidity which does not adhere to fabrics. This is in contrast with the large, rapidly settling, stable, adherent, precipitate formed in hard waters by sodium carbonates and hydroxide.

Richardson (5) showed that at room temperature a 2.83 ratio silicate had little effect in reducing the amount of sodium oleate needed to form stable suds in water containing calcium hardness but greatly decreased the amount for suds formation in water containing magnesium hardness. At 100°C. the silicate softened the water containing calcium hardness somewhat and softened that with magnesium hardness still more than at room temperature. In fact, at this temperature the silicate softened the water equally as well as an equivalent quantity of soap. Vincent's experiments (13) with an olive oil soap and a 3.2 ratio silicate in 0.001 molar salt solutions led him to conclude that under his conditions "at room temperature sodium silicate mixed with soap is of extreme value as a softener of water containing iron, of considerable value as a softener of water containing magnesium, and of very little worth as a softener of water containing calcium. At 100°C. its value as a softener of magnesium water is considerably enhanced while the increase in temperature increases the silicates effectiveness on waters containing calcium to only a very limited extent." The mixture containing 80% 3.2 ratio silicate and 20% olive oil soap was about twice as effective as pure soap for softening water containing iron.

Bolton (21) has reported an investigation of the ability of silicates of varying silica to alkali ratio, phosphates, borax, soda ash, and caustic soda to reduce the amount of sodium oleate or stearate required to form "permanent" suds in a synthetic hard water containing two-thirds calcium hardness and one-third magnesium hardness. All of these alkalies, with the exception of borax, decreased the amount of the soap required to form permanent suds. The silicates in-

creased in value with decreasing silica to alkali ratio although there was not much difference between ratios of 1.6, 2.0, and 2.4. The sesqui- and metasilicates were about as effective with sodium stearate at 60° as with sodium oleate at 20°; all the other alkalies were less so. Both silicates and phosphates formed well dispersed fine flocs with the hardness rather than hard lime-soap curds which were obtained with the caustic soda and soda ash. Results with sodium laurate, myristate, and palmitate are, in general, similar to those with the oleate and stearate although differences exist (22).

Effect on Fabrics. Thirty years ago Zanker and Schnable (23) showed that cotton washed in a silicated soap was stronger than that washed in soap containing no silicate. More recently, Castonguay, Leekley, and Edgar (24) found that the wet strength of cotton, wool, and various rayons after as many as 50 washings was higher when a silicated soap was used than with a pure olive oil soap. Their data also provide further evidence to show that silica does not deposit in the fabric when washing with a silicated soap as has been claimed. The ash content of all fabrics was about the same whether washed in a silicated or pure olive oil soap. Likewise the American Institute of Laundering states "the statement is occasionally encountered that when silicates are used as soap builders, an insoluble deposit of silica gradually is accumulated on the material being laundered. Under commercial laundry conditions wherein soft water is used with a multiple suds formula, this accumulation of insoluble silica has not been observed by the Department of Research. The ash content of a cotton fabric washed 150 times with a silicate-soap mixture is reported after ashing as 0.008%." The reported cases of increased ash content in fabrics washed with silicates are attributable to poor rinsing, either by rinsing in hard water or with insufficient agitation and volume of water to remove soluble and colloiddally dispersed impurities. The soluble silicates are readily rinsed from fabrics and are, in fact, added to caustic soda scouring baths to promote better rinsing, among other benefits. Experience has confirmed laboratory studies by showing that under usual conditions silicated soaps do not injure the common fabrics, are readily and easily rinsed, and do not leave deposits of silica in the cloth. Even if, due to failure to rinse properly, some silica were left it would not be in a hard abrasive form, as some writers have imagined.

Iron Stains. Although little quantitative work has been done on the ability of silicates to prevent iron rust stains, this effect is well established both experimentally and in actual washing practice. That silicate of soda prevents rust stains has been demonstrated by washing cloth in water containing 30 p.p.m. ferrous sulphate with soap both alone and in the presence of caustic soda, soda ash, and silicates. Only the clothes washed in solutions containing silicates did not show rust stains.

Germicidal Action. Silicates have little germicidal action except that due to their alkalinity. However, they appear to enhance this ability in other materials, possibly due to the improvement in wetting, penetrating, and bacteria or germ-removing capacity. Mixtures of caustic soda and metasilicate are better germicides than either alone, or a mixture of caustic with other alkalies (25). The addition of silicates

to a pyrethrum-sodium oleate mixture definitely increased its insecticidal action.

Wash Tests

The previous discussion has shown that the addition of silicates of soda to soaps affects favorably their colloidal and physical properties contributing to detergent action. Of possibly greater practical interest are the studies of the effect of silicates on actual washing operations under simulated practical conditions. Baker (9) found that the addition of metasilicate reduced the amount of soap required to wash soiled napkins to the same satisfactory degree of whiteness in a wash wheel using a standard commercial laundry washing formula. When sufficient metasilicate was added to raise the pH to 11.2, only 60% as much soap was needed as had been used at a pH of 9.9. Morgan's work (26) in a laundry wheel at 50° using 0.1% soap and a soap to builder ratio of 2 to 1 on cloth soiled with mineral oil, tallow, and lampblack gave the following decreasing order of efficiency: sodium metasilicate, soda ash, trisodium phosphate, and sodium hydroxide. Sodium metasilicate was likewise the best when each builder was compared at its concentration of maximum efficiency and notably increased the lathering power of the soap. Snell (27) found that 0.1% soap and sodium metasilicate was superior to soap alone or soap plus sodium carbonate, sodium hydroxide or modified soda for removing carbon black-mineral oil-cottonseed oil soil from cotton fabric at 40°C. in a laboratory washer. On the basis of his work and experience he concludes "an unbuilt soap cannot approach in effect a built soap" and "soap is not in the same class and not to be considered a competitor of built soaps." Oesterling and Mack (28) of the Pennsylvania Laundry Owners' Association stated that "the addition of varying amounts of sodium metasilicate to 0.1% low titre soap solution resulted in marked improvement in soil removal efficiency up to the point where the sum total of sodium oxide content of soap plus alkali reached 0.04%." From Germany came the report that in actual washing tests under household conditions metasilicate was rated as being twice as high in washing effect as soda ash (29). Vaughn and Vitton's data (30) on the removal of a carbon black-hydrogenated vegetable oil-mineral oil soil from fabric by 0.1% soap-0.05% builder solutions in a laundrometer at 60°C. show that up to a total washing time of one-half hour metasilicate was more effective than caustic soda, soda ash, sodium bicarbonate, modified soda, or trisodium phosphate. After one hour and 15 minutes caustic soda appeared more effective than metasilicate under their conditions. The metasilicate compared favorably with these other builders with respect to whiteness retention. The data of Castonguay, Leekley, and Edgar (24) show that solutions of a silicated soap washed cottons, rayons, and wild silk whiter than a pure olive oil soap or the sodium salt of a sulfated alcohol.

The most extensive published study of soil removal by soap-builder mixtures is that of Cobbs, Harris, and Eck. They report wash tests at 140°F. in both hard and soft waters using a medium titre soap with seven builders at three different detergent concentrations over a range of soap-builder ratios (31). Some of their data have been replotted in Figs. 4 and 5. As much as 40% of the soap could be replaced by

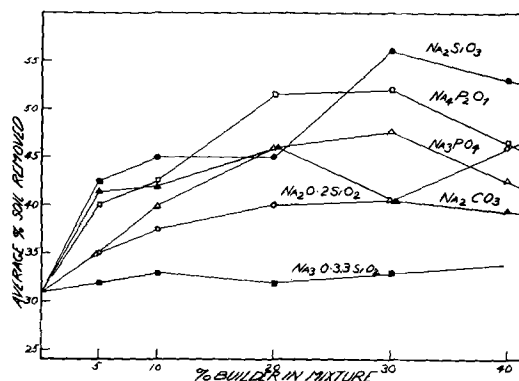


FIG. 4. Removal of carbon black soil by 0.27% soap-builder mixtures at 140°F. in water of 300 p.p.m. hardness. Data from Cobbs, Harris, and Eck (31).

sodium metasilicate or a silicate with a silica to alkali ratio of 2.0 before soil removal in soft water (50 p.p.m.) was decreased at all soap-mixture concentrations. Substituting for part of the soap a silicate with a silica to alkali ratio of 3.3 decreased removal of their soil unless enough of the mixture was added for maximum detergent efficiency. In all other cases

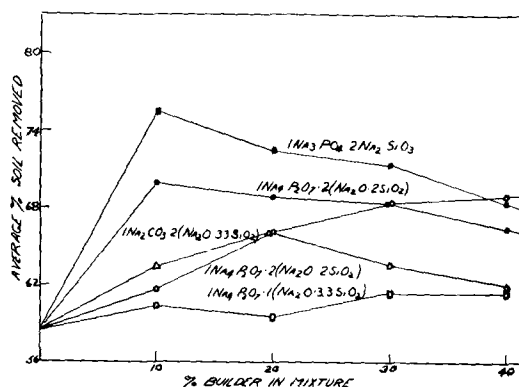


FIG. 5. Removal of carbon black soil by 0.15% soap-builder mixtures at 140°F. in water of 50 p.p.m. hardness. Data from Cobbs, Harris, and Eck (31).

replacing part of the soap by silicate increased soil removal. The amount of the increased efficiency was greater in hard than in soft water. For example, at a total soap plus builder concentration of 0.15% in soft water the soap removed 58.5% of the soil whereas a mixture of 20% of a 2.0 ratio silicate and 80% soap removed 66.7%. At a total soap plus builder concentration of 0.32% in hard water, soap alone removed 47.5% of the soil whereas a mixture of 40% of a 2.0 ratio silicate with 60% soap removed 66%. At the lowest concentrations studied the 3.3 ratio silicate could be substituted for about 40% of the soap with approximately the same detergent efficiency although at higher concentrations decreases were observed. Combinations of the metasilicate, and 2.0 and 3.3 ratio silicates with trisodium phosphate or tetrasodium pyrophosphate usually gave better soil removal than with either builder alone. The effectiveness of the silicates both alone and in mixtures appeared to increase with decreasing silica to alkali ratio. The soil used in this work was a mixture of oildag and vegetable oil. When siliceous pigments or a non-aponifiable oil is used as a dirt, the silicates show up

still more favorably and their effectiveness frequently increases with silica to alkali ratio.

Other Silicate Advantages

The benefits of adding silicates to soaps are not limited to increasing detergent efficiency and lowering cost. The siliceous silicates react with caustic soda to form a more alkaline silicate. This reaction can be used to prevent the occurrence of free alkali in soap, provided that the conditions are such that complete reaction occurs and the final silica to alkali ratio is not much below 2.0. The addition of the commercial "liquid" silicates to kettle soap, which may be coarse and grainy, produces a smooth mixture. Some soap companies therefore look upon silicate as a "smoothing agent." Silicates impart body and firmness to soaps, producing a bar which does not need drying to hold its shape and is not unduly softened or wasted in hot water. This is of particular value for soft soaps, such as those containing lower titre fats or rosin or in warm humid climates. The whiter, harder bar or flake soap thus produced may be attributed to better crystallization of the soap. Soaps containing up to about 15% silicates (anhydrous basis) as the only builder do not effloresce. Silicates also tend to prevent efflorescence or "blooming" in soaps containing sodium carbonate.

Another important advantage of adding silicates to soaps is their antioxidant qualities which are not possessed by most other alkalis. The use of approximately 1% (on an anhydrous basis) of a sodium silicate with a silica to alkali ratio greater than 2.0 prevents the development of rancidity in soaps (32). This ability is of particular importance in soap powders or spray dried soaps which have a large surface exposed to the oxygen of the air. The more siliceous silicates are often added to shaving soaps and cosmetics to prevent corrosion of the tin or aluminum containers. Probably this involves the formation of a film of a siliceous metal silicate. The cloudiness which results when liquid soaps are stored in glass containers from attack on the glass by the alkalinity of the soap solution may be prevented by adding 0.07 to 2% of a siliceous sodium silicate to the soap, heating to 70°C., allowing to stand for a week, cooling to 40°C., and filtering (33). The resulting liquid soap contains 0.022 to 0.016% of soluble silica which prevents solution of the glass container. The use of silicates to purify soaps by removing amino compounds during the salting out process has been suggested (34).

A recent patent (35) covers the process of spraying soap particles with a water-soluble silicate to reduce dust, to minimize their tendency to lump together when added to water, and to control the apparent density. Silicates tend to stabilize soap powders containing "active oxygen," such as those including perborates (36).

Manufacture of Silicated Soaps

Cold Process. The cold process for making a silicated soap involves mixing the carefully weighed or measured fats or grease, caustic soda, and silicate in a crutcher. Usually the silicate is added rapidly when the heat of reaction between the grease and caustic has lowered the viscosity of the mix. A formula successfully used for many years includes 75 lb. tallow, 25 lb. coconut oil, 75 lb. 35.5° Baumé (30%) caustic

soda lye, and 125 lb. of a 41° Baumé silicate with a silica to alkali (Na_2O) ratio of 3.2 ("N" Silicate).

Semi-Boiled Process. The semi-boiled method is similar to the cold process except that a longer period at a high temperature is provided. The tallow and grease is heated, usually to around 140°F., and the lye and silicate then added. Some soap makers prefer to mix the silicate and caustic and add them together. A successfully used formula for this type of soap includes 316 lb. tallow, 55 lb. coconut oil, 280 lb. 35° Baumé caustic soda lye, and 185 lb. 41° Baumé 3.2 ratio silicate ("N" Silicate).

Full-Boiled Process. In the full boiled process the silicate is added in a crutcher to the "kettle soap" resulting from the final salting out. The amount of silicate added varies. A usual proportion for the crutcher charge is 200 lb. of kettle soap to 100 lb. of silicate, but larger amounts are used, particularly in bar soaps. As much as 800 lb. of a 41° Baumé 3.2 ratio sodium silicate ("N" Silicate) can be added per 1,000 lb. of most kettle soaps (31% water) and a good soap produced without much difficulty. Since the commercial silicate of this composition contains 37.6% solids, the resulting product contains 38.3% anhydrous soap, 16.7% anhydrous sodium silicate solids, and 45% water. The water content will be lower if a more alkaline silicate is used which permits a higher solids content in the commercial silicate. More silicate than this can be added if suitable materials, good equipment, and technique or special methods are used. Semi-boiled or cold process soaps incorporate readily substantially larger quantities of silicate than do full-boiled.

When more than 800 lb. of the 41° Baumé, 3.2 ratio silicate, are added per 1,000 lb. of kettle soap, several difficulties may be encountered, but these can be overcome. The addition of large amounts of silicates or other electrolyte builders to kettle soap, if not properly incorporated in the soap, tends to cause separation into two layers—a layer of neat soap on lye. This results in the formation in the frame of a hollow area and free liquid encased by solid soap, commonly known as a soap "coffin." Recent research (37, 38) has indicated that much more of the siliceous silicates than of any other builder can be added to soap-water mixtures before tending to produce this separation. Soap products containing as much or more solid silicate than soap may effloresce or "bloom," particularly if soda ash is present. This makes a less attractive product and affects the solubility characteristics. The addition of sugars, long used to produce transparent soaps, tends to prevent efflorescence (39). Highly silicated soaps may become pasty or viscous but can be worked on the rolls to produce a smooth, white soap. The opaque rumpled flake produced under these conditions although not translucent or transparent, at least in some cases, is desirable. Although soaps containing moderate amounts of silicates are as good or better sudsing agents than pure soaps, those containing as much or more silicates than soap are poorer foaming agents. To some extent foaming power may be restored by adding other sudsing agents.

The presence of more than about 25% of an anhydrous siliceous silicate in a powdered, granular, chip, or spray dried soap, or other products having a large surface to weight ratio may result in the formation of some insoluble matter on prolonged exposure to

air. This rarely, if ever, occurs for mixtures of soap and silicate only but is much more likely to occur if other materials such as carbonates and phosphates are present.

The simultaneous use of silicates and carbonates in flaked soap may, under some conditions, result in the precipitation of an insoluble siliceous material (40). This is probably a hydrated amorphous silica or a sodium silicate with a silica to alkali (Na_2O) ratio greater than about 3.5. These can be formed by the sorption of carbon dioxide from the atmosphere and its reaction with the silicate to form sodium carbonate. Evaporation dehydrates both the silica and silicate. The formation of insoluble matter may be prevented by good packaging which reduces both contact with carbon dioxide and evaporation. More alkaline silicates should have less tendency to form insoluble matter.

Potassium silicates are said to have a decreased tendency to form insoluble matter on exposure to air. The addition of sucrose (cane or beet sugar), glucose, dextrin, corn syrup, honey, starch, and similar materials, as well as rosin, are reported to be helpful in reducing the formation of insolubles, and, in addition, produce clearer, smoother mixes in the crutcher. Compounds containing multiple hydroxyl groups, such as sorbitol, should behave similarly. Adding silicate to the crutcher in the form of a finely divided, soluble powder may, for a given silicate content, reduce the tendency to form insoluble matter on contact with carbon dioxide.

The addition of silicates to kettle soap produces a viscous mass which requires good mixing at elevated temperatures. The most effective crutching temperatures for silicate-soap mixtures vary with the type of soap stock, moisture content, efficiency of mixing, and nature of the silicate. The temperature must be just high enough that the mixture is sufficiently fluid to flow freely and permit good mixing to a smooth, homogenous product. Too high a temperature may cause separation into two layers. Soaps containing a large proportion of tallow or other high titre fats are satisfactorily crutched at 160° or 170°F . or above, grease and rosin soaps at 140°F . or even lower. Heating the silicate solution before mixing with the soap has been found to be helpful. When a smooth homogeneous dispersion has been obtained, the mixture should be gradually cooled and discharged from the crutcher at as low a temperature as is consistent with clearing the apparatus. A plastic mix is obtained at the lower temperature. In order to minimize the possibility of highly silicated soaps separating in the frames, they should be cooled as rapidly as practicable. Artificial cooling of the frames, or cooling by extrusion of the mixture through a water cooled orifice, such as that on plodders for making milled soaps, should be helpful. The mixture may also be cooled rapidly by passing it through a water-jacketed screw conveyor (e.g. a "Votator"). Usually special cooling is not necessary.

The type of soap stock is also an important factor in the production of a satisfactory silicated soap. Most soap makers have found it easier to incorporate silicates in soaps from tallow, palm, and other high titre fats than in soaps from greases, similar low titre fats, and rosins. At least part of the reason is that often soaps from these low titre fats are crutched at too high a temperature. Soaps from hydrogenated

oils incorporate silicate less readily than those from tallow. The addition of a coconut oil to tallow increases the ease of incorporating silicate in soaps made from the fat. However, coconut oil soaps do not incorporate silicate much, if any, more readily than a straight tallow soap, and considerably less readily than the mixture. Palm kernel oil soaps should behave similarly. Silicates are most readily incorporated in mixtures of high and low titre fats, which are miscible with the silicate at elevated temperatures and which solidify on cooling over a range of temperatures. Tallow-coconut oil mixtures containing approximately equal weights of each are good for making a highly silicated soap.

The addition of relatively small amounts of sodium hydroxide solutions aids in the incorporation of large amounts of silicates by lowering the viscosity of the mix and possibly also by increasing the stability of the dispersion or emulsion. Excess caustic may be added by finishing the soap "strong"—i.e., with an excess of lye. Another way is to add caustic to the usual 41° Baumé 3.2 ratio silicate. A common commercial practice is to causticize the silicate to a silica to alkali (Na_2O) ratio of around 2.4 to 2.5 before mixing with the kettle soap. In order that the reaction between the siliceous silicate and caustic may be essentially completed, they should be mixed and heated at least 24 hours before using. Otherwise the soap may contain free alkali which damages hands, fabrics, and some metals, and may cause carbonation. The purchase of a commercial silicate more alkaline than the usual 3.2 ratio, which contains a higher proportion of solids, has the advantage of obtaining a carefully controlled, completely reacted product at lower cost. The commercial alkaline silicates cannot be duplicated economically by causticizing a 3.2 ratio silicate and evaporating to a higher solids content.

The higher solids content of the commercial alkaline silicates makes it possible to substitute more anhydrous silicate solids for anhydrous soap at an equivalent moisture content. This is illustrated in Fig. 6. The lines on the graph show the maximum

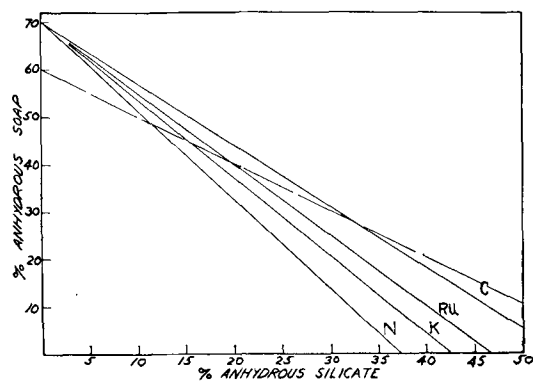


FIG. 6. Maximum solids contents of soaps obtainable by adding various commercial silicates to kettle soap.

solids content obtained by adding various commercial silicates to a kettle soap containing 70% anhydrous soap. Descriptions of the different silicates are given in Table I. It is apparent that the more alkaline the silicate (above a ratio of 2.0), the higher the possible solids content of the silicated soap, or the more soap can be replaced by silicate at a given water content. For example, a finished soap containing

60% solids made by adding various silicates to kettle soap containing 70% solids will have 33% anhydrous silicate solids if a 59.3° Baumé 2.0 ratio silicate is used, 20% if a 52° Baumé 2.4 ratio silicate is used, 16% for a 47°, 2.9 ratio, and only 12% for a 41°, 3.2 ratio. The corresponding values for anhydrous soaps are 29%, 40%, 44%, and 48%. Of course practical limitations on mixing may make it impossible to take full advantage of these differences. In addition to this advantage, a more alkaline silicate with a silica to alkali ratio of 2.0 can satisfactorily be used.

Efforts have been made, particularly in Germany, just prior to World War II, to increase the amount of silicate which can be readily incorporated in soaps by the addition of other materials. Lottermoser (41) has suggested that this be accomplished by using potash or potassium hydroxide. After partial saponification in one kettle, the mixture is transferred to a second pan or kettle where silicate solution and more soda and potash, or potassium hydroxide are added to complete saponification. He considers the potassium of importance for the production of a stable, highly silicated soap, which is a good detergent, does not effloresce or "bloom," and undergoes no noteworthy change in weight or volume on prolonged exposure of the finished bar to air. The addition of a mixed alkaline sodium and potassium silicate directly to kettle soap should accomplish the same result and make the extra step of saponification with a potassium alkali unnecessary.

Lorgus (42) reported that silicate-soap mixtures can be homogenized with the aid of a solution of sodium thiosulfate. The fatty acid content could be reduced to 30% without causing the soap to effloresce or lose its form.

Since the soap-silicate mixture in the crutcher can be considered an emulsion of a silicate solution in a soap solution saturated with silicate, attempts have been made to increase the stability of these mixtures by adding emulsifying agents. The long time use of starches with silicates is probably an example of this. Weissbein (43) has patented the use of saponin to increase the amount of salts which can be added to soap systems. Such emulsifying agents as balsam and other turpentine, sandalwood oil, terpene and other oils, turkey red oils, and synthetic detergents have been used recently (44). Curzon (45) found that colloidal substances such as hydrolyzed starch, flour, or other material containing a high proportion of starch, dextrin, gum arabic, gum ghatti, tragacanth, in fact all protective colloids, and even glucose increased the amount of silicate which could readily be added to soaps under practical conditions. Sudsing power of these products containing more silicate than soap was increased by adding such materials as tetrasodium pyrophosphate, sodium hexametaphosphate (Calgon), and soluble sodium aluminosilicates. His patent covers "a soap composition comprising kettle soap and sodium silicates, the ratio of sodium silicate to soap being at least 4 to 10, an organic water soluble colloidal dispersing agent in quantity sufficient to make the soap and silicate compatible, and a sudsing material selected from the group consisting of sodium pyrophosphate and sodium hexametaphosphate, said sudsing material being present in sufficient quantity to induce normal sudsing of said composition."

The sodium salt of cellulose glycolic acid used by the Germans during the war in amounts up to 25% of the total soap should assist emulsification of silicate-soap mixtures. Other materials of interest for this purpose are various types of oxidized and chlorinated starches, sodium alginate, sodium pectate or pectinate, carboxymethylcelluloses, sodium salts of polyacrylic acids, and the alkali metal salts of cellulose oxidized by nitrogen dioxide to a polyanhydroglucuronic acid. Various synthetic detergents, such as alkyl aryl sulfonates, should be helpful and at the same time promote sudsing.

Special Silicated Soaps. In addition to their use in the common types of soap such as laundry bars and chips, silicates are used in producing special types. A mechanics hand soap is made by preparing a paste from 100 parts soap chips made from stock containing coconut oil, 200 parts water, 25 parts 41° Baumé, 3.2 ratio silicate, 10 parts glycerine, and 5 parts perfume and then mixing with this 150 parts pumice or sand. The silicate forms a firm jelly which keeps the abrasive from falling out. Blue mottled soaps are also made by adding salt, soda ash, ultramarine blue and a 60° Baumé 2.0 ratio silicate to a suitable kettle soap (46).

Alkaline silicates have been used as saponifying agents in making soap mixtures. As early as 1909 Miss Hutchins (47) used a "homogeneous" (and therefore at least partially saponified) mixture of linseed oil, distilled water and silicate of soda as a cleansing fluid. More recently Leffer (48) has patented the use of a silicate causticized with sodium or potassium hydroxide to saponify fats or fatty oils at 260°F. and 2 to 6 atmospheres pressure to form a hard soap. Sesqui- or metasilicate have successfully been used to produce a good soap by saponification of fats and oils.

Fatty Acids and Silicates. At the present time there is a trend in the soap industry toward the manufacture of soaps from fatty acids rather than fats. The more alkaline silicates can be used without the addition of caustic to neutralize fatty acids with the formation of a silicated soap. Silicates with a silica to alkali (Na_2O) ratio of 2.5 or less should be used and care taken that the final ratio is below 3.9 and preferably below 3.0. Sesqui- and metasilicate should be particularly suitable. Although less alkaline than caustic soda, they are better wetting and emulsifying agents so that the rate of reaction in the two-phase system may not be very different. Mukai's Japanese patent (49) discloses a process of neutralizing fatty acids with sodium silicate, with or without additional alkali, in the presence of a large amount of water. A German patent issued to Bergell (50) covers the formation of soap from fatty acids by a concentrated metasilicate solution in the cold or luke-warm condition. A detergent has been prepared by Moss and Snell (51) by spraying fatty acids on metasilicate to form a coating of soap. Vail (52) produces substantially homogeneous soap-silicate mixtures by reacting fatty acids with "expanded" or intumescent metal silicates.

Theory. An understanding of the systems obtained by adding silicates to soaps is aided by a study of the ternary phase diagrams, soaps-silicates-water. A tentative diagram for the system commercial soap-2.46 ratio sodium silicate-water at 90°C. (194°F.) is shown in Fig. 7. The boundaries of the region of iso-

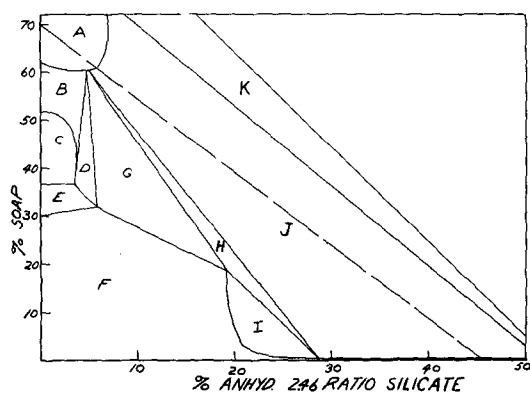


FIG. 7. Tentative phase diagram for a commercial soap—2.46 ratio sodium silicate-water system.

tropic solution (F) were determined experimentally (37) for a soap having the composition of a typical fitted and settled household soap made from fatty acids of average molecular weight 273 and an iodine value of 48.4. Its solubility in water corresponds approximately to that of a soap made from 75% tallow-25% coconut oil (53b). The remainder of the diagram is based by analogy on the previous work of other investigators with pure soaps, tallow-coconut oil soap mixtures, and sodium chloride (53). No attempt was made to depict equilibria in solutions more concentrated in soap and silicate than those above the upper right hand line of Fig. 7, i.e., those forming three phases consisting of curd fibre, neat soap, and the concentrated silicate solution corresponding to "lye" in the sodium hydroxide or chloride system. When the system is in equilibrium at 90°C., compositions enclosed within areas A, C, and F consist of single homogeneous phases, compositions in areas B, E, G, I, and J consist of two phases of varying composition and amount, and compositions enclosed within areas D, H, and K of three phases whose composition does not vary but whose relative proportion does. The phases in equilibrium in each are: A—neat soap, B—neat soap-middle soap, C—middle soap, D—middle soap-neat soap-nigre, E—middle soap-nigre, F—nigre (homogeneous isotropic solution), G—neat soap-nigre, H—neat soap-nigre—"lye," I—nigre—"lye," J—neat soap—"lye," K—neat soap-curd fibre or "crystallized" soap—"lye." The compositions of the mixtures formed, when to a kettle soap containing 70% anhydrous soap is added a sodium silicate solution containing 45.4% anhydrous solids of a silica to alkali ratio of 2.46, are shown by the dotted line. According to this tentative figure, at 90°C. an amount of the commercial "liquid" silicate equal to about 6% anhydrous silicate can be added to the liquid crystalline neat or kettle soap and the combination remains one homogeneous phase. The addition of larger amounts of silicate converts neat soap into two phases, neat soap and lye, and the mixture has a tendency to "open" or form two layers. Thus, the miscibility of kettle or neat soap with this silicate is limited and further amounts of silicate tend to cause separation.

However, this does *not* mean that the maximum amount of silicate or other builder which can be added to form an apparently homogeneous product is the maximum amount completely miscible with neat soap without tending to produce two phases. Much larger amounts of silicates can be added with

suitable mixing equipment to form stable dispersions or "emulsions" of the liquid crystalline neat or kettle soap saturated with silicate and the concentrated silicate. The microscopic structure of soaps containing a small proportion of builder is about the same as that of the original soap (54). MacLennan reports that the outstanding internal structure encountered with heavily built soaps was composed of numerous spherical, crystalline globules in various states of aggregation. These were presumably cemented together and held by a mixture of soap fibre and silicate. This observation indicates that the silicate is dispersed in the soap and comprises the internal phase in the crutcher. Possibly the highly silitated soaps MacLennan used were not thoroughly mixed.

On cooling from 90°C. to room temperature, the solubility of the silicate in neat soap is first reduced, and then the neat soap containing dissolved and dispersed or "emulsified" silicate crystallizes out into at least one and usually several of the multiplicity of crystalline soap phases now known to exist at room temperature. The temperature at which crystallization begins, identical with the T_c temperature of the phase studies by McBain and others (e.g. 53), is raised by the addition of silicates. Cooling converts the two-phase dispersion or "emulsion" of neat soap and lye into mixtures of crystalline soap or "curd fibres," neat soap and lye (region K), or crystalline soap and lye. These latter mixtures have a greater tendency to separate although this is avoided by agitating during cooling until the mixture solidifies sufficiently to prevent separation mechanically. Nothing appears to be known of the effect of silicates on the particular type or types of crystalline soap produced under different processing conditions. The position of the recently discovered "kettle wax" phase (55) has not been determined for silicate systems. The location and state of the silicate in the finished soap is not known with certainty. The silicate may form mixed crystals or solid solutions with the soap or remain as a concentrated solution or jelly around and between the crystalline soap fibres. It may be incorporated between the polar heads of the soap molecules and cause an increase in the long spacings revealed by X-rays.

These theoretical considerations provide an explanation of methods used to increase the amount of silicates or other builders which can be readily incorporated in soaps and suggest ways to attack the problem further. One way is to increase the solubility of the neat or kettle soap in silicate or other builder by raising the temperature, decreasing the average chain length, increasing the degree of unsaturation of the soap, or adding substituents such as chlorine or hydroxyl. Another is to choose the type of builder most miscible with soaps. Experimental studies (37, 38) indicate that the siliceous silicates are considerably more miscible with soap than any of the other common builders. Potassium silicates are much more miscible than sodium. The addition of some other materials is known to increase the solubility of soaps and thus should increase their miscibility with silicates. Sodium or ammonium sulfamates are claimed to prevent jelly formation and render soap solutions fluid at all temperatures (56). Ethyl acetate extends greatly the range of isotropic solutions, increases the concentration of salt required to

salt out soap, and greatly extends the region of existence of neat soap in the sodium oleate-water-sodium chloride system (57). Cyclohexanol, creosol, and pine oil are believed to increase the solubility of soaps in hard water although their action appears to be quite specific (58). Added materials which would serve as blending or coupling agents, or co-solvents for silicates and soaps should probably contain both non-polar portions to combine with the soap and polar portions to make this combination miscible with water and silicates.

Once a homogenous soap-silicate solution or dispersion is obtained by mixing at elevated temperatures, the problem is to maintain this on cooling to room temperature where the equilibrium state is at least two separate phases. Rapid cooling and crystallization to form a strong matrix or curd are necessary. Good agitation and the selection of a suitable soap stock are needed. The effectiveness of tallow-cocoonut oil mixtures is at least partly attributable to the relatively wide range of temperatures over which the mixture hardens. The effect of materials such as rosin soaps in increasing the ease of incorporating silicates in soaps containing them is attributable both to increasing the miscibility of soap-silicate mixtures and to widening the range over which the soap becomes firm (59). Possibly the addition of small amounts of soaps from fatty acids containing 20 or more carbonatoms, e.g., arachidic, behenic, cerotic, or mixed fatty acids from japan or other waxes may provide a strong "gel" or matrix to keep a uniform soap-silicate mixture without appreciably affecting the solubility characteristics. The addition of other good emulsifying and dispersing agents is helpful and further research on the newer materials of this type is warranted.

Another possible method of minimizing separation of soap-silicate mixtures is to add the builder in the form of a slowly soluble powder.

Potassium Silicates

Potassium silicates have been used to some extent as a builder, sometimes in conjunction with starch or flour as a builder for potash "figged" or paste soaps. The addition of potassium silicates to a sodium soap converts it partially into a potash soap. In this way, the rate and amount of solution can be increased without encountering the difficulties of salting out a potash soap. While there is apparently no data available on the detergent action of potassium silicates in the literature, they should resemble the sodium silicates closely in this respect. Another use for potassium silicates is in the preparation of liquid soap products. A commercial 30 to 40% potash cocoonut oil soap solution can be mixed in all proportions with a commercial potassium silicate containing 39.4% solids with a silica to potash (K_2O) ratio by weight of 2.10 (60). Mixing up to 25% of this silicate with a liquid soap may result in an improved detergent at lower cost.

Analysis of Silicated Soaps

Soluble silicates are obtained from a silicated soap in a form suitable for analysis in two ways. In one method the soap is first split with hydrochloric acid and the fatty acids extracted with ether. The aqueous layer is evaporated to dryness, filtered, and the silica determined gravimetrically in the usual manner. Probably a better way is to char the soap at a

low temperature until organic material has been burnt off. The residue is then fused with sodium carbonate, dissolved in water, and the silica determined gravimetrically. The portion of the total alkali needed to react with the fatty acids is subtracted, and the remainder is assumed to have been combined with the silicate. The usual analytical methods do not distinguish between free caustic soda and that which has reacted with the silicate.

As Edeler (61) has shown, the usual free alkali determination in silicated soaps gives results which are due to the extraction of alkali from the alkaline sodium silicate by the alcohol. Silicates with a silica to alkali (Na_2O) ratio by weight greater than of about 2 show no free alkali by the usual method. The exact ratio depends on the proportions of alcohol and moisture, and possibly also on the state of the silicate in the soap.

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Continuous Fat Splitting Plants Using the Colgate-Emery Process*

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A CONTINUOUS high temperature fat splitting process, employing countercurrent reaction in a pressure tower with internal heat exchange, has been developed and carried through pilot plant investigation to successful commercial operation. This method, known as the Colgate-Emery Fat Splitting Process, gives splitting efficiencies of about 98%, producing acids which can generally be bleached to a color equal to or better than that of the original fat. Because of savings in steam, since no catalyst is needed, the new process shows considerable economy over the old Twitchell method.

The earliest attempts to split fats were in soap making, where the fatty acids appear as sodium or potassium soaps and the glycerine is either left in the soap or is separated by salting-out. Fatty acids are readily made from soap by acidulation, but the overall process is indirect and costly in chemicals. Chevreul, in 1813, discovered that fat is a regular chemical compound of glycerine and one, two, or three fatty acids. He also discovered that fat can be separated into these parts by causing it to unite with water. In 1853 Tilghman (1) discovered that the reaction of fat and water, to form fatty acids and glycerine, can be carried out by mixing the fat with water and then subjecting the mixture to a high degree of heat while the pressure is maintained sufficiently high to prevent vaporization of the water. This inventor was in advance of his time, as materials of construction and techniques of operation for the required high temperature and high pressure conditions were then unknown. Twitchell, in 1890, took a forward stride when he devised a relatively simple method for producing fatty acids and glycerine directly from fats. This is an atmospheric pressure boiling method employing a reagent or catalyst to speed up the hydrolysis. Twitchell's method is widely used and will not be replaced entirely for many years because it is still a good process for certain types of splitting. Batch autoclave splitting at 100 to 150 psi with lime, magnesia, or zinc catalyst, has been widely used, especially in Europe, while the batch process at around 400 psi without catalyst has found limited popularity. Continuous countercurrent high temperature splitting, as carried out by Procter and Gamble (2, 3) and more recently in novel form by Colgate-Palmolive-Peet and Emery Industries (4, 5) constitutes a marked improvement over Twitchell and is

finding wide immediate acceptance, particularly for large scale operation. In the Colgate-Emery Process fat and water react countercurrently in a column at about 500 degrees Fahrenheit and about 725 psi. Heat exchange between fatty acid and water takes place in the top portion of the column and between fat and sweet water in the bottom part.

The fatty acid industry originated early in the last century and first produced stearic acid for candles. The present day stearic and oleic acid industry, based primarily on animal fats, has developed from this primitive origin and now produces materials which find their way into a wide variety of uses. Moreover the field for fatty acid from other sources such as vegetable oils and hydrogenated oils is steadily expanding. Because of the advantages of countercurrent fat splitting as a step in soap making, indications are that future expansion of the soap industry will continue in this direction.

Data on hydrolysis of many fats in a pilot countercurrent splitting plant built by Colgate-Palmolive-Peet have been published by Allen and coworkers (6). One of the present authors proposed an improvement of the original process consisting of the addition of internal heat exchange (5), of which the equipment details were reported in the last reference. A number of runs were made in the modified unit, and sufficient data were obtained to design a commercial plant.

The selection of the optimum temperature-pressure operating range called for a careful analysis of many factors. The higher the temperature (and therefore the pressure) the faster the reaction rate. The higher the temperature, the greater the solubility of water in fat, which is desirable until the amount becomes so great that the amount of water in the column cuts down on the tower capacity. The higher the pressure, the greater the cost of equipment per unit of volume but with increased reaction rate the volume of the splitting zone can be smaller. If the temperature is too high, it may have a deleterious effect on certain fats and may in fact make counterflow impossible by causing complete miscibility. A temperature of around 500°F. was selected as a practical compromise, and a maximum operating pressure of 725 lbs. was chosen to provide a suitable excess to prevent boiling (vapor pressure of water at 500°F. is 669 psi).

The first commercial plant, having a design capacity of 3,000 lbs. of feed per hour, intended primarily for low-grade fats, was built at Cincinnati, Ohio, by Emery Industries and has been in operation since

* Presented at the Twenty-First Annual Meeting of the American Oil Chemists' Society at the Edgewater Beach Hotel, Chicago, Illinois, Oct. 22, 1947.