# **Potassium Silicates in Soaps**

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THAT potassium silicates would be useful additives to soaps is not a new idea. Henry Gathman's book, "American Soaps," published in 1893, recommends the addition of 25 lb. of 18° Baumé potassium silicates per 100 lb. of soft soap stock. For making figged soaps potassium silicates were recommended because the sodium silicates interfered with proper crystallization of this particular type of soap. However, little information has appeared in the literature on the detergent properties of potassium silicates or on their use in soaps. Seiden (1) reported in 1937 that in Germany potassiumsodium silicate mixtures were added to soaps since the potassium salts have little if any tendency to effloresce or bloom and hold water more tenaciously; and the finished soap undergoes no noteworthy change in weight or volume.

Sarin and Uppal's data (2) on the suspending action of various alkaline electrolytes and detergent products (Table I) show that a potassium silicate of unspecified silica to potassium oxide ratio suspends umber almost as well as either sodium oleate or a "standard" soap, 13 times better than sodium hydroxide, and 16 times better than carbonate.

The present paper reports some solubility, pH, and detergent properties of potassium silicates of interest in connection with their use in soaps.

					TABLE I					
Mgs.	of	Umber Alkalin	Remaining e Electrolyt Hour	in es s S	Suspension and Deterge Standing (cf.	in ent R	0.1% Produ ef. 2)	Solutions acts After	of 24	Various

Substance	Mgs. Umber per 100 cc. Solution
NaOH	5
$Na_2CO_3$	6
Potassium silicate	81
Standard soap	91
Sodium oleate	89
Saponin	100
Soap nut powder	62

## Materials

Properties of the commercially available potassium silicates used in this work are summarized in Table II. The potassium coconut oil soap was made by neutralizing an alcoholic solution of coconut oil fatty acids to the phenolphthalein end point with alcoholic potassium hydroxide and evaporating to dryness. The distilled coconut oil fatty acids had an average equivalent weight of 214.6 determined by titration and an iodine value of 8.6 as determined by the Hanus method. The potassium hydroxide and carbonate were C. P. The ilmenite was "Air Floated Ilmenite Black" made by British Titan Products Company, Billingham, Stockton on Tees, England. The iron oxide was Merck's red, ignited ferric oxide *(crocus martis)*. The raw umber was obtained from the E. E. Nice Company and, like the iron oxide, is the same sample used by Carter and Stericker (3).

## Experimental Data

Solubility. The synthetic method was used to study the solubility relations of the potassium coconut oil soap-3.3 ratio potassium silicate-water system at concentrations of practical interest. Sealed glass tubes, 13 x 50 mm., containing known amounts of soap, water, and silicate were heated until the contents became homogenous and isotropic. They were then cooled very slowly in a well stirred oil bath and the temperature, T<sub>i</sub>, recorded at which a birefringent phase first appeared. All of the soap systems observed in this work were either liquid crystalline or isotropic solution; no crystalline or "curd fiber" phases were detected. The  $T_i$  values were determined with calibrated thermometers and are precise and reproducible to  $\pm 2^{\circ}$ C. The same equilibrium values are obtainable on heating with continued agitation although the liquid crystalline phase is difficult to redissolve. Anhydrous potassium coconut oil soap particles when wet with water form a coating of liquid crystalline material which greatly hinders solution. This makes it more difficult to approach equilibrium from undersaturation although equilibrium is attainable from both super- and undersaturation.

The solubilities of the potassium coconut oil soap in water and varying concentrations of the 3.3 ratio potassium silicate are given in Table III and illustrated in Fig. 1. The isotherms at 0, 100, and 150°C. were deduced by linear interpolation from the experimental data (circles) representing T<sub>i</sub> values of systems of known compositions. The solubility of the potassium coconut oil soap in water at 0°C. is about 40% as compared with the corresponding solubility of 34% for potassium laurate (4). The addition of the 3.3 ratio potassium silicate reduces the solubility only slightly: the solubility of the potassium coconut oil soap is still about 30% at 0°C. in the presence of 15% potassium silicate on an anhydrous basis. Compositions of mixtures obtainable by adding the commercial 3.3 ratio potassium silicate (which contains 39.6% solids) to a 40% soap solution are given by the dotted line of Fig. 1. As indicated by the figure, a 40% potassium coconut oil soap is miscible in all proportions with the commercial potassium silicate of this ratio even at 0°C.

pH. The pH values at room temperature (~25°C.) of solutions of the 3.3 and 3.9 ratio potassium silicates, the potassium coconut oil soap, and a mixture containing 80% by weight potassium coconut oil soap

TABLE II Properties of Potassium Silicates Mean Gravity 20°C. Weight Ratio SiO<sub>2</sub>/K<sub>2</sub>O Viscosity Poises 20°C. Mol. Formula C SiO. Trade Name C K OSp. Gr. Baumé 1.2529 0.4 Kasil No. 1 ..... K<sub>2</sub>O·3.9 SiO<sub>2</sub> 2.57.80 19.5Kasil No. 6.....  $K_2O \cdot 3.3 \operatorname{SiO}_2$ 12.826.81.3940.817.52.1

and 20% of the 3.3 ratio potassium silicate were determined with a Model G Beckman pH meter. The data are given in Tables IV and V and shown in Fig. 2. As expected, the pH's of the potassium silicate solutions are about the same at an equivalent normality as those of sodium silicates of the same molecular silica to alkali ratio. Solutions of the 3.9 ratio potassium silicate have pH's about the same as those of the same weight concentration of the 3.3 ratio silicate

TABLE III Ti Values for Potassium Coconut Oil Soap-3.3 Ratio Potassium Silicate-Water Systems

% Soap	% Anhyd. Silicate	<b>T</b> <sub>i</sub> (°C.)
39.7	0	< 0
40.6	0	95
41.7	0	122
42.4	0	142
44.2	0	159
46.0	0	170
50.2	0	>180
39.0	3.00	110
39.4	7.64	157
35.5	13.9	157
30.4	20.9	152
34.6	3.13	< 0
41.9	3.45	160
41.4	7.54	170
37.0	7.18	109
31.8	13.7	80
27.0	19.6	42
35.0	6.33	< 0
40.5	4.95	152
36.6	10.6	152
31.3	16.9	127
32.4	9.94	< 0
35.9	2.37	< 0
35.3	17.0	168
37.2	4.40	< 0
34.0	7.93	< 0

except at concentrations greater than  $\frac{1}{2}\%$ . Above this concentration solutions of the 3.3 ratio silicate have higher pH's. The potassium coconut oil soap solutions show a maximum in pH with increasing concentration, as do solutions of most other soaps. pH's of solutions of the mixture of four parts by weight of the soap to one of the silicate are higher than those of the soap solutions and their pH's increase consistently with concentration.



FIG. 1. Solubility of a potassium coconut oil soap in varying concentrations of  $K_2O\cdot 3.3 \, \mathrm{SiO}_2$  at different temperatures. O systems form liquid crystal on cooling from isotropic liquid, • systems remaining isotropic at 0°C. Lines represent isotherms at 0, 100, and 150°C. deduced by linear interpolation from the experimental measurements (circles) representing  $T_1$  values (various temperatures). Dotted line gives compositions obtainable by adding commercial  $K_2O\cdot 3.3 \, \mathrm{SiO}_2$  solution to a 40% soap solution.

TABLE IV pH's of Potassium Silicate Solutions

K <sub>2</sub> O ·	$3.3  { m SiO}_2$		K20.	$3.9  { m SiO}_2$	
Wght. % Anhyd. K <sub>2</sub> O·3.3 SiO <sub>2</sub>	Norm.	рН	$\begin{array}{c} \text{Wght. \% Anhyd.} \\ \text{K}_2\text{O}{\cdot}3.9\text{SiO}_2 \end{array}$	Norm.	pH
$\begin{array}{c} 39.56\\ 23.17\\ 17.24\\ 9.18\\ 5.75\\ 2.82\\ 1.53\\ 0.98\\ 0.70\\ 0.52\\ 0.32\\ 0.25\end{array}$	$\begin{array}{c} 3.80\\ 1.91\\ 1.35\\ 0.676\\ 0.412\\ 0.198\\ 0.106\\ 0.068\\ 0.049\\ 0.036\\ 0.022\\ 0.017\\ \end{array}$	$\begin{array}{c} 11.58\\ 11.40\\ 11.37\\ 11.30\\ 11.16\\ 11.00\\ 10.90\\ 10.73\\ 10.63\\ 10.42\\ 10.29 \end{array}$	$\begin{array}{c} 28.83 \\ 18.40 \\ 11.22 \\ 8.16 \\ 6.57 \\ 3.44 \\ 2.12 \\ 1.07 \\ 0.74 \\ 0.33 \\ 0.22 \\ 0.11 \end{array}$	$\begin{array}{c} 2.19\\ 1.28\\ 0.737\\ 0.524\\ 0.416\\ 0.213\\ 0.130\\ 0.065\\ 0.045\\ 0.020\\ 0.013\\ 0.0065 \end{array}$	$\begin{array}{c} 11.17\\ 11.13\\ 11.11\\ 11.10\\ 11.02\\ 10.99\\ 10.85\\ 10.67\\ 10.45\\ 10.30\\ 9.93 \end{array}$
$0.20 \\ 0.13 \\ 0.045 \\ 0.022$	$0.014 \\ 0.0089 \\ 0.0031 \\ 0.0015$	$ \begin{array}{c c} 10.22 \\ 10.03 \\ 9.71 \\ 9.48 \end{array} $	$\begin{array}{c} 0.033\\ 0.018\end{array}$	$0.0020 \\ 0.0011$	9.69 9.51

TABLE V pH's of Solutions of a Potassium Coconut Oil Soap and a Mixture of 80% Potassium Coconut Oil Soap—20% K<sub>2</sub>O·3.3 SiO<sub>2</sub>

Total % Solids	pH K Soap	pH { 80% K Soap { 20% K <sub>2</sub> O·3.3 SiO <sub>2</sub>
20.0	9.70	11.40
10.0	9.78	11.20
6.0	9.83	11.00
3.0	9.89	10.75
1.0	10.07	10.36
0.60	10.00	10.17
0.30	9.88	10.01
0.10	9.10	9.00

Foaming. Fig. 3 shows the volume of foam formed by shaking solutions containing 0.015% of a potassium coconut oil soap, and the same concentration of soap plus 0.010% K<sub>2</sub>O as potassium carbonate and as the 3.3 ratio potassium silicate. A liter of the freshly prepared solution was placed in a 2-liter stoppered graduated cylinder and shaken vigorously for two minutes. The photograph was taken one-half minute after shaking. The volume of foam was about three times as much when the soap was dissolved in a 0.031% K<sub>2</sub>O·3.3SiO<sub>2</sub> solution as when dissolved in the same molecular concentration of potassium carbonate; only a trace of foam was formed when the soap was dissolved in pure water.

Suspending Action. Quantitative measurements of suspending action were obtained with an apparatus



FIG. 2. pH's of potassium silicate and potassium coconut oil soap solutions as a function of concentration. Note semi-log scale.

 $\bigcirc$ —K<sub>2</sub>O·3.3 SiO<sub>2</sub>;  $\blacksquare$ —K<sub>2</sub>O·3.9 SiO<sub>2</sub>;  $\square$ —potassium coconut oil soap;  $\blacksquare$ —80% potassium coconut oil soap, 20% K<sub>2</sub>O· 3.3 SiO<sub>2</sub>.

	rotassium Sil	icate anxitre."	
% 80 K Soap   20 K <sub>2</sub> O·3.3 SiO <sub>2</sub>	Mgs./100 ml. After 3 hrs.	$\% \mathrm{K}_2\mathrm{O}{\cdot}3.9\mathrm{SiO}_2$	Mgs./100 ml. After 3 hrs.
$\begin{array}{c} 3.0\\ 2.25\\ 1.5\\ 0.75\\ 0.375\\ 0.187\\ 0.050\\ 0.025\\ 0.010\\ 0.0025\\ 0.0025\\ 0.0010\\ 0.0025\\ 0.0001\\ 0.0005\\ 0.0001\\ \end{array}$	$     \begin{array}{r}       14 \\       18 \\       46 \\       78 \\       67 \\       76 \\       76 \\       76 \\       64 \\       60 \\       52 \\       43 \\       16 \\       \end{array} $	$\begin{array}{c} 2.45\\ 1.05\\ 0.17\\ 0.087\\ 0.035\\ 0.017\\ 0.0035\\ 0.0010\\ 0.00050\\ 0.00010\\ 0.00005\end{array}$	$     \begin{array}{r}       11 \\       21 \\       64 \\       73 \\       83 \\       82 \\       82 \\       82 \\       74 \\       66 \\       38 \\       6     \end{array} $
% K <sub>2</sub> CO <sub>3</sub>	Mgs./100 ml. After 3 hrs.	% K Soap	Mgs./100 ml. After 3 hrs.
$\begin{array}{c} 1.03\\ 0.73\\ 0.44\\ 0.15\\ 0.073\\ 0.014\\ 0.0073\\ 0.0014\\ 0.00073\\ 0.00014\\ 0.00014\end{array}$	$\begin{array}{c} 4.4 \\ 6.7 \\ 6.3 \\ 23 \\ 60 \\ 58 \\ 40 \\ 10 \\ 4.7 \end{array}$	$\begin{array}{c} 3.72\\ 2.13\\ 0.53\\ 0.27\\ 0.053\\ 0.027\\ 0.0053\\ 0.0027\\ 0.00053\\ 0.00053\\ \end{array}$	29 42 82 93 52 41 25 26 20
$\% K_2O(3.3 \mathrm{SiO}_2)$	Mgs. '100 ml. After 3 hrs.		
$\begin{array}{c} 2.16\\ 1.54\\ 0.92\\ 0.31\\ 0.15\\ 0.031\\ 0.015\\ 0.0031\\ 0.00081\\ 0.00098\\ 0.00031 \end{array}$	$     \begin{array}{r}       10 \\       17 \\       26 \\       42 \\       60 \\       83 \\       82 \\       76 \\       64 \\       16 \\       \end{array} $		•
*Amount susper	nded in distilled v	water after 3 hrs. i	s 2.7 mg./100 ml.

TABLE VI Suspending Action on Ilmenite Black of 3.3 and 3.9 Ratio Potassium Silicates, Potassium Carbonate, a Potassium Coconut Oil Soap, and an 80% Potassium Coconut Oil Soap—20% 3.3 Potassium Silicata Mixtura \*

FIG. 3. Volume of foam produced by 0.015% potassium coconut oil soap (left side), 0.015% soap + 0.015%  $K_2CO_3$  (0.010%  $K_2O)$  (center), and 0.015% soap + 0.031%  $K_2O\cdot 3.3\,SiO_2$  (0.010%  $K_2O)$  (right side).

similar to that described by Poliakoff (5). It consisted of a glass stoppered 250-ml. Pyrex glass cylinder to which was attached an outlet tube with stopcock at the 75-ml. mark. The outlet tube was inclined up at an angle of about 20° from the horizontal in order to prevent solid from settling out in it. In making measurements, 200 ml. of a 0.1% suspension of ilmenite were placed in the cylinder and vigorously shaken for one minute. After 3 hours settling at 25°C., a 50.0-ml. sample was withdrawn through the stopcock. The sample was analyzed by measuring its light absorption in a photoelectric colorimeter and comparing this with the calibration curve obtained from suspensions of known concentration.

The average numbers of milligrams of ilmenite suspended per 100 ml. of various concentrations of the 3.3 and 3.9 ratio potassium silicates, potassium carbonate, and the potassium coconut oil soap are given in Table VI and illustrated in Fig. 4. Both potassium silicates suspend ilmenite about equally well above 0.03%; below this concentration the 3.9 ratio silicate is the better. Potassium carbonate suspends at the maximum, about 78% of the amount of ilmenite suspended by silicates. Below 0.03% the silicates and carbonate suspended more ilmenite than did the potassium coconut oil soap; above 0.1% the soap was better than either under these conditions. All four suspending agents had an optimum concentration for best suspending action; that for the silicates and carbonate was around 0.02 to 0.03%, whereas that of the soap was at about 0.3%.

*Prevention of Deposition.* The ability of the potassium silicates, carbonate, hydroxide, coconut oil soap, and their mixtures to prevent the deposition of suspended soils on cotton fabric was studied, using raw umber and ferric oxide as soils. One gram of either of these soils and 100 ml. of the solution of the detergent in distilled water were placed with a 3-inch square of desized Indianhead cloth and 10  $\frac{1}{4}$ -inch steel balls in a pint jar. The jars were sealed, placed in a Launderometer (6), and rotated at about 48 r.p.m. for 20 minutes at 60°C. The soil suspension was then removed and replaced by 200 ml. of distilled water before rotating for 5 minutes at 60°C. in the Launderometer. This rinsing with distilled water was repeated and the cloth allowed to air dry



FIG. 4. Suspending of ilmenite by potassium silicates, carbonate and coconut oil soap at 25 °C.

 $\bigcirc$ —K<sub>2</sub>O·3.3 SiO<sub>2</sub>;  $\bigcirc$ — $\overline{K}_2$ O·3.9 SiO<sub>2</sub>;  $\bigcirc$ —potassium coconut oil soap;  $\blacksquare$ —K<sub>2</sub>CO<sub>3</sub>;  $\bigtriangleup$ —80% potassium coconut oil soap— 20% K<sub>2</sub>O·3.3 SiO<sub>2</sub>. before being ironed. The reflectances of the various pieces of cloth were compared to that of the original unsoiled cloth with a Lumetron photoelectric colorimeter equipped with a device for measuring reflectances. Three measurements of the reflectance were made, which usually differed by less than  $\pm 0.5$  from the average. The data on prevention of deposition are summarized in Tables VII and VIII and illustrated in Figs. 5 and 6.

Comparison of Figs. 5 and 6 shows that the efficiencies of materials preventing deposition varies



FIG. 5. Prevention of deposition of ferric oxide pigment on cotton fabric by detergent solutions at  $60^{\circ}$ C.  $\bigcirc -K_2O \cdot 3.3 \operatorname{SiO}_2$ ;  $\bigcirc -K_2O \cdot 3.9 \operatorname{SiO}_2$ ;  $\bigtriangleup -KOH$ ;  $\blacktriangle -K_2CO_3$ ;

 $\square$ -K coconut oil soap;  $\blacksquare$ -80% K coconut oil soap-20% K<sub>2</sub>0·3.3 SiO<sub>2</sub>.

somewhat with the nature of the soil. The mixture of soap and 3.3 ratio potassium silicate prevents the deposition of ferric oxide about as well as soap alone; this mixture is more effective than soap alone in preventing the deposition of raw umber. For preventing the deposition of ferric oxide the potassium silicate with a silica to alkali ( $K_2O$ ) molecular ratio of 3.9 is better than that with a ratio of 3.3; with raw umber the 3.9 ratio potassium silicate is the better at concentrations above 0.1% but less effective



FIG. 6. Prevention of deposition of raw umber on cotton fabric by detergent solutions at 60°C.

 $\begin{array}{c} \bigcirc -\mathbf{K}_{2} \odot \cdot \mathbf{3.3} \operatorname{SiO}_{2}; \quad \bigoplus -\mathbf{K}_{2} \odot \cdot \mathbf{3.9} \operatorname{SiO}_{2}; \quad \bigtriangleup -\mathbf{K} \operatorname{OH}; \quad \blacktriangle -\mathbf{K}_{2} \operatorname{CO}_{3}; \\ \square -\mathbf{K} \text{ coconut oil soap}; \quad \blacksquare -80\% \text{ K coconut oil soap} -20\% \\ \mathbf{K}_{2} \odot \cdot \mathbf{3.3} \operatorname{SiO}_{2}. \end{array}$ 

TABLE VII

Prevention of Deposition of Ferric Oxide Pigment on Cotton Cloth by Various Detergents at 60°C.

	Average % Reflection									
Conc'n. Wght.%	кон	K <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> O· 3.3 S <sup>2</sup> O <sub>2</sub>	K <sub>2</sub> O 3.9 SiO <sub>2</sub>	Soap	80% Soap 20% K <sub>2</sub> O 3.3 SiO <sub>2</sub>				
0.005	69.6 55.1		$50.2 \\ 51.1$	59.0 53.8	$91.2 \\ 90.7$	83.9 91.5				
0.05 0.10	$29.3 \\ 27.2$	$     44.0 \\     40.0 $	$\begin{array}{c} 58.9\\61.0\end{array}$	$69.9 \\ 68.1$	$\begin{array}{c} 91.1 \\ \pm 0.3 \end{array}$	88.7 79.2				

at lower concentrations. Both silicates prevent the deposition of raw umber more effectively than does soap alone or the soap-silicate mixture below 0.1% and are not much less effective above this concentration. Potassium carbonate usually prevents the deposition of both soils more than the hydroxide; these alkalies are considerably less effective than the silicates and soaps. The ability of silicates at low concentrations to prevent the deposition of soils is of particular importance in rinsing.

Soil Removal. The ability of the potassium coconut oil soap and soap-builder solutions to remove soil from cloth was measured by a method similar to that suggested by Harris (7). Indianhead (permanent finish) cloth was desized by boiling 10 minutes in 0.1 N sodium hydroxide, then rinsing in warm water, and boiling 10 minutes longer in a 0.45% solution of a commercial soap containing no builder, and finally rinsing in first warm then cold water until soap free. This cloth was heavily soiled by passing five times through a mixture of 2.25 gms. refined cottonseed

 TABLE VIII

 Prevention of Deposition of Raw Umber on Cotton Cloth by Various Detergents at 60°C.

	Average % Reflection									
Conc'n, Wght.%	кон	K <sub>2</sub> CO <sub>3</sub>	$\frac{\mathbf{K}_2\mathbf{O}\cdot}{3_13\mathbf{SiO}_2}$	$rac{\mathrm{K}_{2}\mathrm{O}\cdot}{\mathrm{3.9~SiO}_{2}}$	Soap	80% Soap 20% K <sub>2</sub> O 3,3 SiO <sub>2</sub>				
0.005	50.7	47.6	52.6 56.2	56.0 53.8	50,5 18.9	48.1				
0.01 0.05 0.10	$53.5 \\ 51.1$	53 7 55.9	70.4 69.6		$\begin{array}{c} 61.2 \\ 65.7 \end{array}$	$62.7 \\ 69.7$				
0.25	46.8	53.1	67.9	72.3	74.1	78.2				

(Wesson) oil, 10.0 gms. Oildag (Acheson graphite), and 1 liter of carbon tetrachloride. The soiled cloth was dried in air, ironed, and cut into 6" x 7" pieces. The reflectance of each piece was measured in a photoelectric colorimeter at 8 different locations, each <sup>3</sup>/<sub>4</sub> inch in diameter, to establish uniformity of soiling. A 6" x 7" piece of soiled cloth and 100 ml. of a solution of the detergent undistilled water solution were sealed with 10  $\frac{1}{4}$ -inch steel balls in a pint jar and placed in a Launderometer (6). The jars were rotated at about 48 r.p.m. and 60°C. (140°F.) for 10 minutes. A  $1\frac{1}{2}$ " strip was then cut from the cloth and the remainder washed for another 10 minutes under the same conditions with 100 ml. of a fresh detergent solution. This was repeated at the end of a total washing time of 20, 30, and 40 minutes. Each 10-minute washing was made with a fresh detergent solution. The washed strips were rinsed first in warm and then in cold water, dried, and ironed. The reflectance at four positions along each strip was measured and an average taken. The height of the suds in the pint jars, 5 minutes after the last wash, was measured. The pH of each solution was deter-

Conc'n		80% K Soap-20% K <sub>2</sub> CO <sub>3</sub>							80% K Soap-20% K <sub>2</sub> O·3.3 SiO <sub>2</sub>						
	Ind	crease in Re	eflectance At	iter	Suds		Increase in Reflectance After				Suds				
(70)	10 min.	20 min.	30 min.	40 min.	(Inches)	рн	10 min.	20 min.	30 min.	40 min.	(Inches)	P11			
$\begin{array}{c} 0.05 \\ 0.20 \\ 0.35 \\ 0.50 \\ 0.65 \end{array}$	5.3 12.0 18.4 14.2 18.0	12.3 18.7 28.1 30.9 35.0	11.5 24.4 32.6 50.9 54.8	14.4 36.1 52.6 58.2 53.3	0 1 1/4 3/8 1/4 1/8	$9.98 \\10.17 \\10.23 \\10.40$	$     \begin{array}{r}       10.8 \\       23.1 \\       13.6 \\       20.4 \\       26.1     \end{array} $	$     \begin{array}{r}       14.7 \\       28.3 \\       25.3 \\       32.5 \\       36.3     \end{array} $	22.7 35.0 37.2 38.0 56.4	29.7 39.8 50.5 51.0 67.0	$\begin{matrix} 0 \\ 4 \\ 2 \frac{1}{2} \\ 1 \frac{1}{2} \\ 0 \end{matrix}$	9.3710.4010.4010.4210.63			
Conc'n	In	crease in Re	eflectance A	fter	Suds		Increase in Reflectance After Suds								
(%)	10 min.	20 min.	30 min.	40 min.	Hght. (Inches)	$_{\rm pH}$	10 min.	20 min.	30 min.	40 min.	Hght. (Inches)	$_{\rm pH}$			
0.05 0.20 0.35 0.50 0.65	$ \begin{array}{r} 12.3 \\ 14.3 \\ 15.8 \\ 23.3 \\ 28.0 \\ \end{array} $	$     \begin{array}{r}       16.0 \\       22.3 \\       28.3 \\       38.6 \\       52.3 \\     \end{array} $	$ \begin{array}{r} 23.5 \\ 25.8 \\ 42.4 \\ 46.3 \\ 59.3 \\ \end{array} $	$     \begin{array}{r}       17.2 \\       30.1 \\       54.4 \\       60.4 \\       65.0 \\     \end{array} $	0 4 4 5%	9.72 10.13 10.20 10.30	$ \begin{array}{r} 21.7 \\ 27.9 \\ 25.1 \\ 24.0 \\ 17.2 \\ \end{array} $	19.8 35.8 32.4 36.7 30.6	$ \begin{array}{r} 27.6 \\ 42.6 \\ 43.5 \\ 44.9 \\ 39.8 \\ \end{array} $	27.5 47.5 47.7 59.8 55.7	$0 \\ 4 \\ 4 \\ 3 \\ 1^{1/2}$	9.30 9.72 9.88 9.90			

TABLE IX Soil Removal by Potassium Soap and Builder Mixtures in Distilled Water

mined at room temperature ( $\sim 25^{\circ}$ C.) with a Beckman pH meter after the last wash. These data are summarized in Table IX.

Table IX and Fig. 7 show that the mixture of potassium coconut oil soap and 3.3 ratio potassium silicate was somewhat less effective at low concentrations and more effective at high concentrations than the soap alone at removing this soil under the conditions of our test. The mixtures of the soap with the 3.9 ratio silicate and the carbonate were not so effective as soap alone below 0.3% detergent but above this concentration gave about as good results. The most soil was removed by the soap-3.3 ratio silicate mixture at a concentration of 0.65%.

Soil removal by these detergent mixtures was also studied with the same technique in a hard water equivalent to 300 p.p.m.  $CaCO_3$ . Two-thirds of the



FIG. 7. Soil removal at 60°C. by detergent solutions. A-0.35% detergent in distilled water; B-0.65% detergent in distilled water; C-0.35% detergent in hard water (300 p.p.m. CaCO<sub>3</sub> equivalent); D-0.65% detergent in hard water;  $\Box$ --K coconut oil soap;  $\blacksquare$ -80% K soap-20% K<sub>2</sub>O·3.3 SiO<sub>2</sub>;  $\Delta$ --80% K soap-20% K<sub>2</sub>CO<sub>3</sub>;  $\blacktriangle$ -80% K soap-20% K<sub>2</sub>O· 3.9 SiO<sub>2</sub>.

hardness came from calcium chloride; the remainder from magnesium sulfate. The cloth for this series of measurements was soiled with a cottonseed oil, Oildag mixture similar to that described above, but the soil did not adhere quite so firmly. The average increase in reflectance during the four washing periods is given in Table X and illustrated in Fig. 7. Table X also includes the pH at room temperature ( $\sim 25^{\circ}$ C.) of the solutions after the last washing. Only the 0.5% potassium coconut oil soap solution showed any permanent suds after the last washing.

In 300 p.p.m. hard water acceptable cleaning was obtained only at 0.5% and above. The soap-3.3 ratio silicate-mixture was generally more efficient than the potassium coconut oil soap alone or the mixture of soap with the 3.9 ratio silicate or potassium carbonate at concentrations above 0.3%.

Measurements of the solubilization of the water insoluble dye Orange OT by aqueous potassium coconut oil soap solution (Table XI) show a marked change

TABLE XI Solubilization of Orange OT by Aqueous Solutions of Potassium Coconut Oil Soap at 60°C.

Soap Conc'n (N)	Mgs. Dye/110 ml. Sol'n
0.0090	0.78
0.0085	0.74
0.0080	0.67
0.0074	0.60
0.0070	0.52
0.0060	0.39
0.0050	0.32
0,0040	0.25
0.0030	0.21
0.0020	0.15
0.0010	0.12

in the effectiveness of the soap at around 0.005 N (0.11%) indicating that the "critical concentration for micelle formation" occurs around this normality. This is in contrast to the value of 0.023 N (0.5%) for potassium laurate (8). Our results suggest rather large differences between commercial mixtures and pure soaps in the concentration at which micelle formation becomes apparent and their solubilizing action.

The data in this paper show no relation between micelle formation and the ability of the soap to suspend solids or prevent their deposition. These latter properties appear to be due to the ability of the soil particles to become charged by preferential sorption of one ion from the detergent solution. In agreement with data assembled by Preston (9) there appears TABLE X

Conc'n (%)		80% I	K Soap20%	$K_2CO_3$	ļ	80% K Soap-20% K <sub>2</sub> O·3.3 SiO <sub>2</sub>					
	Increase in Reflectance After						Increas	e in Reflectan	ce After		
(707	10 min.	20 min.	30 min.	40 min.	pH	10 min.	20 min.	30 min.	40 min.	pH	
$\begin{array}{c} 0.05 \\ 0.20 \\ 0.35 \\ 0.50 \\ 0.65 \end{array}$	14.1 10.4 9.2 12.0 20.3	$     \begin{array}{r}       11.2 \\       18.7 \\       16.8 \\       23.9 \\       49.4     \end{array} $	$\begin{array}{r} 32.7 \\ 24.0 \\ 25.8 \\ 27.6 \\ 61.5 \end{array}$	$     \begin{array}{r} 37.8 \\       40.2 \\       34.7 \\       41.0 \\       65.6 \\     \end{array} $	8.68 9.83 10.22 10.34* 10.39	9.66.625.117.746.0	$     18.9 \\     12.3 \\     28.9 \\     28.9 \\     61.0   $	26.5 21.0 40.8 39.3 63.3	29.9 27.7 44.0 53.3 64.0	8.91 9.31 9.99 10.02 10.17	
		80% K S	0ap—20% K <sub>2</sub> (	) • 3.9 SiO <sub>2</sub>	K Coconut Oil Soap						
Cone'n		Increas	e in Reflectan	ce After		Increase in Reflectance After					
(70)	10 min.	20 min.	30 min.	40 min.	pH	10 min.	20 min.	30 min.	40 min.	pH	
0.05 0.20 0.35 0.50 0.65	$8.2 \\ 5.7 \\ 4.3 \\ 13.2 \\ 26.3$	$     \begin{array}{r}         11.6 \\         11.5 \\         10.0 \\         20.7 \\         47.9     \end{array} $	$     \begin{array}{r}       12.8 \\       13.3 \\       7.0 \\       29.2 \\       60.7     \end{array} $	$ \begin{array}{r} 22.3 \\ 16.9 \\ 14.5 \\ 40.4 \\ 64.1 \end{array} $	$8.79 \\ 9.22 \\ 9.71 \\ 9.93 \\ 10.10$	$   \begin{array}{r}     3.3 \\     2.0 \\     5.2 \\     15.8 \\     35.3   \end{array} $	9.9 7.5 3.2 24.2 46.4	10.2 8.6 6.8 30.9 59.1	$     \begin{array}{r}       17.2 \\       18.3 \\       15.8 \\       49.5 \\       60.1 \\     \end{array} $	7.30 7.52 8.21 8.42 8.77	

to be a definite increase in the ability to remove soil in distilled water over the concentration range in which micelle formation becomes apparent; more data would be needed to establish a direct correlation.

## Discussion

The above data indicate that, like the sodium silicate (10), the potassium silicates by themselves and mixed with soaps possess detergent properties and are a useful builder for soaps. By using them alone or mixed with other detergents, it should be possible to obtain equivalent or better detergency at lower cost than with the pure detergent alone, particularly in hard waters. Their precise value for a particular application must await evaluation under the exact practical conditions.

Since potassium silicates are more expensive than the corresponding sodium silicates, they will be used only where their special properties justify the additional cost. Their high solubility and miscibility with soap systems justifies their use in liquid, figged, and paste potash soaps. They may be added to soda soaps to increase the solubility and rates of solution and sudsing without encountering the difficulty of salting out a mixed soda-potash soap. Other physical characteristics imparted to the soap mixture may justify their use.

### Summary

Properties of potassium silicates of interest in regard to their use as a detergent with soaps have been studied. A 40% potassium coconut oil soap can be mixed in all proportions with the commercial 3.3 ratio potassium silicate containing 39.6% solids. The pH's of the silicate solutions vary from 9.6 to 11 at concentrations of most practical interest. The 3.3 ratio silicate increases the pH of a potassium coconut oil soap solution. More suds form when the soap is dissolved in a 0.031% K<sub>2</sub>O·3.3SiO<sub>2</sub> solution than in the same molality of a potassium carbonate solution or in pure water.

Quantitative measurements of their suspending action on ilmenite shows that at their optimum concentrations both silicates are more effective than potassium carbonate and almost as good as soap. The maximum effect of soap occurs at a higher concentration than that for the silicates. A mixture of soap and  $K_2O \cdot 3.3 \operatorname{SiO}_2$  prevents the deposition of ferric oxide pigment on cotton cloth about equally as well as soap alone; this mixture is more effective than soap alone for preventing the deposition of raw umber. Both silicates prevented the deposition of raw umber more effectively than soap alone or soap-alkali mixtures below 0.1% and are not much less effective above this concentration.

Soil removal experiments with a cottonseed oil-Oildag soil showed that a mixture of K<sub>2</sub>O·3.3SiO<sub>2</sub> and potassium coconut oil soap was about equally as efficient in distilled water and more efficient in 300 p.p.m. hard water than soap alone.

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