

than the maximum permissible if sodium lauryl sulphate below the c.m.c. has no effect on the solubility.

Any theory of film stability, however sketchy, must be able to explain the difference between fast and slow draining films. Let us consider first a two-component system, one of which is surface-active. In a gravitational field the upper portion of a film must be under higher tension than the lower. Consequently in accordance with the general rule, a lower surface concentration will be required in the upper portion. Then some stretching of the upper portions of the film surface must take place to produce the decreased surface concentration and consequently elevated tension. If the film is of the gaseous type, quite a deal of stretching may be necessary to yield the appropriate increase in tension. Consequently the walls will descend and the film thinning will be accelerated. This film will be fast draining. If, on the other hand, the film is of the condensed type, this will, in general, mean that the surface active agent is but sparingly soluble and the film will behave toward any shocks of short period like a pure water film which is, of course, unstable. Thus it would seem that we could not obtain slow draining films in two-component systems.

In three-component systems the film will still have higher tension in its upper region, but we cannot say much about the surface concentrations except that a

surface concentration readjustment must take place on film stretching. If one of the two surface-active components is present in small amount and is able with the other surface-active component to form a condensed film, only a small extension may be necessary to provide the required vertical tension gradient. Consequently the walls will not descend rapidly. This film will be slow draining.

### Summary

It is believed that liquid films owe their stability to the Gibbs elasticity. How this elasticity may arise is discussed, and it is concluded that in some cases a nonequilibrium value may be the important concern. Some data on surface composition from radiochemical experiments and foam fractionation are presented. Finally an explanation of the origin of the slow and fast draining films of Ross, Miles, and Shedlovsky is offered.

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## Viscosities and Solubilities of Synthetic Detergent Mixtures Containing Soluble Silicates

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**S**OLUBLE silicates have long been used as builders for soaps, and their advantages are well known

(1). In synthetic detergents sodium silicate shows similar advantages and has recently assumed added importance, due to its inhibiting effect on corrosion. However attempts to incorporate silicate in synthetic detergents in many cases have resulted in difficulties due to increased viscosity of the slurries, with trouble in pumping and handling and in the formation of insoluble matter on drying, with subsequent formation of turbid solutions. The present investigation was undertaken to study this problem.

### Materials

The detergents used were: Sodium Oronite (Oronite Chemical Company), the sodium salt of an alkyl aryl sulfonate, received in the form of a paste containing 40.6% sodium alkyl aryl sulfonate, 49.6% water, and 9.7% sodium sulfate; Ultrawet 45 KX (Atlantic Refining Company), also the sodium salt of an alkyl aryl sulfonate, and containing 40.6% sodium alkyl aryl sulfonate, 5.1% sodium sulfate, and 54.3% water; Orvus WA Paste (Procter and Gamble), a sodium alcohol sulfate containing 29.6% sodium alcohol sulfate and 1.4% sodium sulfate. In order to produce mixtures comparable with those with the other detergents, the Orvus Paste was concentrated by evaporation to 52% solids and 2.5% sodium sulfate was added.

The phosphates used were: Tetrasodium pyrophosphate (TSPP) and sodium tripolyphosphate (STPP). In many cases a mixture of equal weights of the two phosphates (MP) was used. Compositions of the silicates used are:

	% Na <sub>2</sub> O	% Si <sub>2</sub> O	Wt. ratio Alkali: silica	Mole ratio
N.....	8.9	29.8	1:3.22	1:3.32
RU.....	13.8	33.1	1:2.40	1:2.48
BW.....	19.5	31.2	1:1.60	1:1.65
Metso Granular.....	30.0	28.7	1:1.02	1:1.04
Potassium silicate.....	19.0	30.8	1:1.62	1:2.53
	(K <sub>2</sub> O)			

### Experimental

The mixtures were prepared to contain 25% detergent (including sodium sulfate), 25% builder, and 50% water. The detergents and builders are reported on an anhydrous basis. Any water present in the original materials is included in the 50% water. In most cases the builder consisted of phosphate and silicate and sometimes other additives. Mixtures were prepared by adding the phosphate slowly, in small portions, to the warm (60°C.) detergent slurry, followed by the warm (60°C.) silicate solution, diluted with the remaining water. Other orders of mixing resulted in lumps or mixtures too thick to be used. The other additives were either added to the deter-

gent slurry before the phosphate or dissolved in the water used to dilute the silicate.

The viscosities of the mixtures were measured with a Stormer viscometer, in which a falling weight causes a cylinder to rotate inside a cup of the fluid (2). The temperature was maintained at 60°C. by water circulated from a constant temperature water bath. Rates of revolution were determined with the normal weight of 75 g. and with additional weights of 100 and 200 g. Measurements were made on the mixtures immediately after preparation, after they had stood for two hours at room temperature for about 24 hours. A portion of each mixture was spread on a glass plate and oven-dried at 105°C. for 24 hours, with occasional mixing if necessary to prevent separation. It was then ground to powder and added to distilled water to give a 0.5% solution. The solution was maintained at 70°C. for about three minutes, cooled to room temperature, and its turbidity measured with a Klett-Summerson Colorimeter. A yellow filter was used, and the colorimeter adjusted to read zero with distilled water alone.

The accompanying figures show the results of the viscosity measurements. The rates of rotation in revolutions per second are plotted as abscissa against the weights in grams producing the rotation. The solid lines indicate the initial viscosity, and the broken lines that after two hours. The values after 24 hours are also shown for some mixtures, for which they did not become too high to be conveniently plotted.

Very few of the mixtures give straight lines passing through the origin, as would a true Newtonian liquid. Most are plastic since a certain weight must be applied before any rotation begins. This weight will be called the yield value although it has not been calculated in the proper units of dynes per sq. cm., as only comparisons are desired. In most cases the lines decrease in slope as they rise, indicating that the "apparent viscosity" decreases as the flow rate increases.

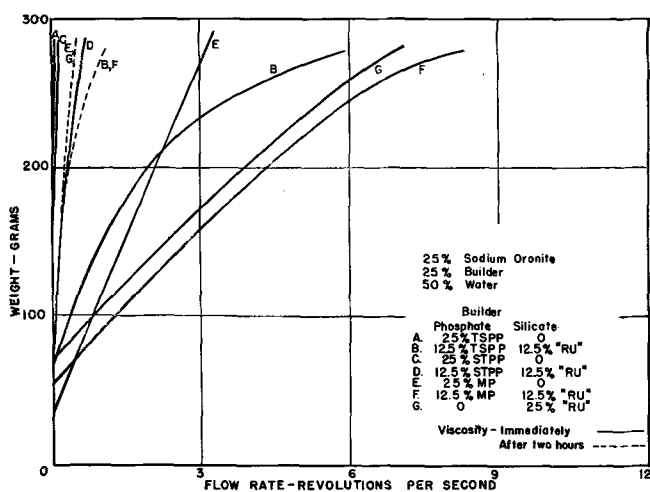


FIG. 1. Effect of sodium silicate and sodium phosphates on the viscosity of sodium Oronite slurry.

Figure 1 shows the effect of various phosphates and of RU silicate with sodium Oronite. In nearly every case the slurries increased in viscosity upon standing. Many of the resulting curves would lie so close to the vertical axis as to cause confusion and have been

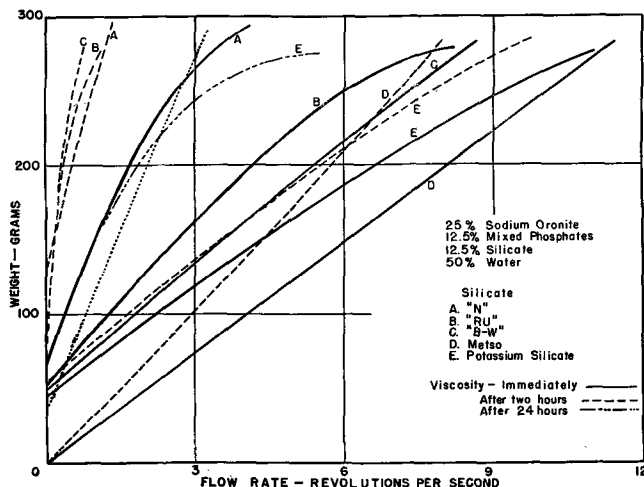


FIG. 2. Effect of different silicates on the viscosity of sodium Oronite slurry containing sodium phosphates.

omitted. In Figure 2 is shown the effect of several different silicates. The 24-hour viscosity has been plotted only for potassium silicate, where it remained fairly low. With N and RU the rate of revolution at

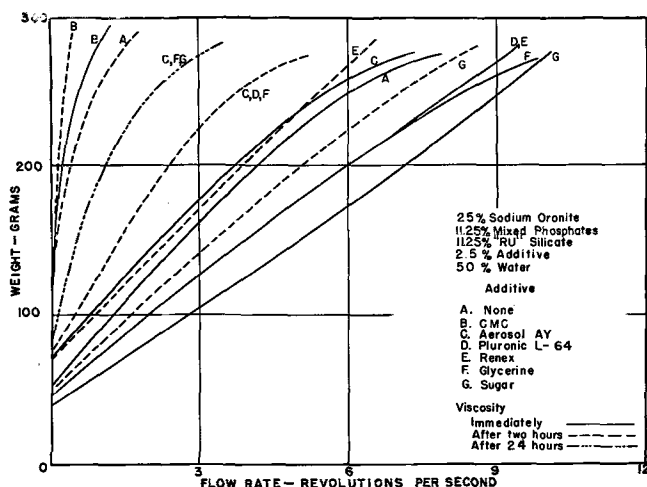


FIG. 3. Effect of various added materials on the viscosity of sodium Oronite slurry containing sodium silicate and sodium phosphates.

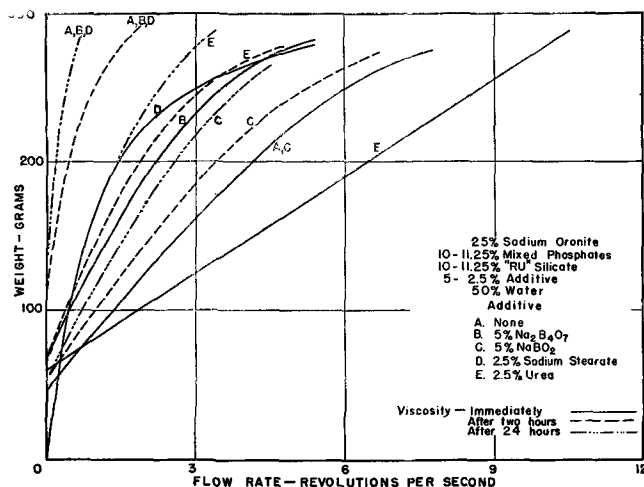


FIG. 4. Effect of various added materials on the viscosity of sodium Oronite slurry containing sodium silicate and sodium phosphates.

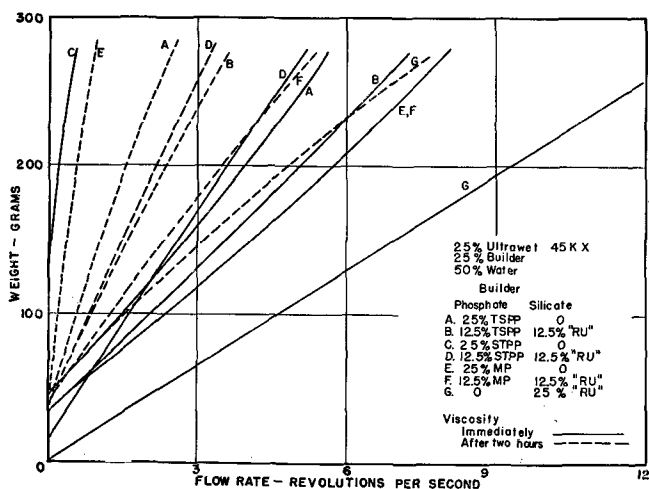


FIG. 5. Effect of sodium silicate and sodium phosphates on the viscosity of Ultrawet slurry.

24 hours was roughly half that at two hours with the same weight. With B-W very little change in viscosity occurred between 2 and 24 hours, whereas the mixture with Metso Granular increased to an extremely high value after 24 hours. The dotted line in Figure 2 is that for mixed phosphates and no silicate, line E of Figure 1. Figures 3 and 4 show the effect of various additives replacing equal weights of phosphate and silicate. In a few instances the 24-hour lines have been omitted to avoid complicating the graphs, and in each case the viscosity was increased considerably over the two-hour value. The effect of phosphates and RU silicate on Ultrawet slurries is shown in Figure 5. The lines for 24 hours have been omitted to avoid

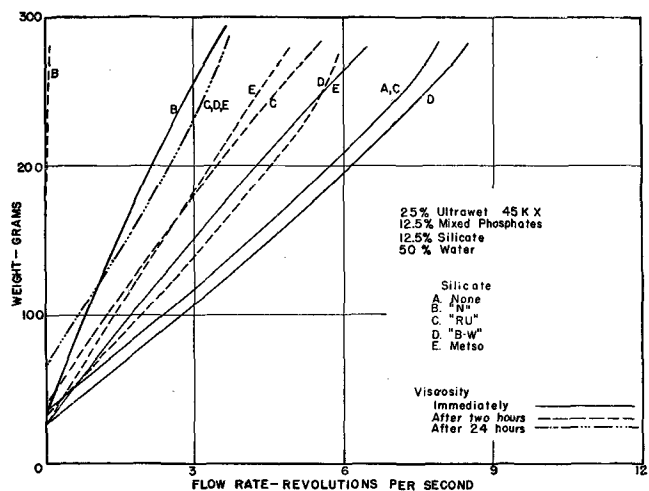


FIG. 6. Effect of different silicates on the viscosity of Ultrawet slurry containing sodium phosphates.

confusion. Except for mixtures containing sodium tripolyphosphate alone, where almost no change in viscosity upon aging occurred, RU silicate, where no change occurred between 2 and 24 hours, and the mixed phosphates, where the viscosity for 24 hours decreased slightly below the two-hour value, the viscosities after 24 hours were slightly higher than the two-hour values. In Figure 6 the effect of the ratio of silicate on the viscosity of mixtures with Ultrawet is shown. Figure 7 shows the results for Orvus with

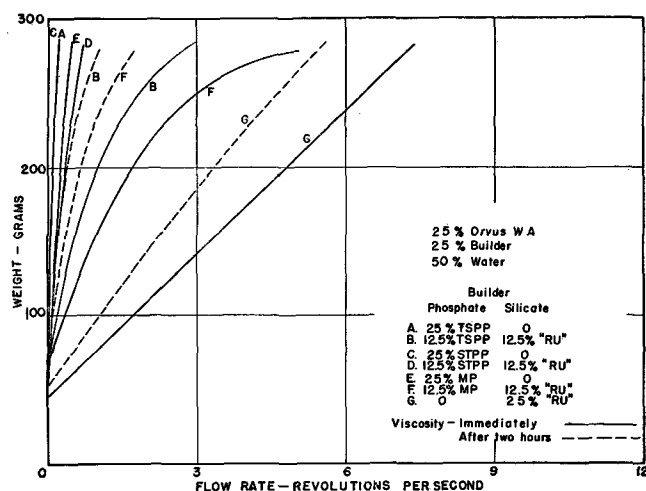


FIG. 7. Effect of sodium silicate and sodium phosphates on the viscosity of Orvus slurry.

phosphates and RU silicate. Many of the lines have been omitted from the graph to improve readability. The mixture containing tripolyphosphate alone was too viscous to measure even when fresh. Mixtures containing RU silicate and either tripolyphosphate or pyrophosphate increased in viscosity somewhat after two hours but showed very little further change after 24 hours. In Figure 8 the effect of the ratio of

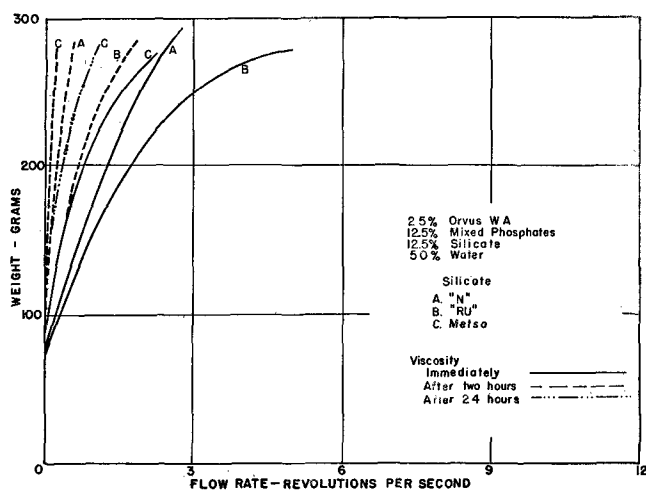


FIG. 8. Effect of different silicates on the viscosity of Orvus slurry containing sodium phosphates.

the silicate upon the viscosity of mixtures with Orvus is shown. Except for the mixture containing Metso Granular which showed a lower viscosity after 24 hours than after two hours, the viscosities increased on standing for 24 hours.

In Tables I, II, and III are listed the yield points, obtained from the graphs as the intersections of the viscosity lines with the vertical axis, and the turbidities and pH values of the 0.5% solutions of the dried detergents. The turbidities are given in arbitrary units, as read on the Klett-Summerson Colorimeter.

### Discussion

The viscosity phenomena are complicated by the considerable amount of solid material in the mixtures.

TABLE I  
 Properties of Slurries Containing Sodium Oronite

Phosphate	Silicate	Additive	Yield point, grams	Turbidity	pH
25.0% TSPP	.....	.....	200	4	9.6
12.5% TSPP	12.5% RU	.....	67	120	10.4
25.0% STPP	.....	.....	275	5	7.4
12.5% STPP	12.5% RU	.....	70	120	10.1
25.0% MP	.....	.....	41	10	8.7
.....	25.0% RU	.....	73	4	10.1
12.5% MP	12.5% N	.....	70	120	9.5
12.5% MP	12.5% RU	.....	55	82	10.2
12.5% MP	12.5% B-W	.....	52	0	10.7
12.5% MP	12.5% Metso Gran.	.....	0	4	11.5
12.5% MP	12.5% K Sil.	.....	44	70	9.8
11.25% MP	11.25% RU	2.5% CMC	70	30	10.1
11.25% MP	11.25% RU	2.5% Aersol AY	70	72	10.1
11.25% MP	11.25% RU	2.5% Pluronic L-64	44	36	10.1
11.25% MP	11.25% RU	2.5% Renex	40	35	10.1
11.25% MP	11.25% RU	2.5% Glycerine	44	22	10.1
11.25% MP	11.25% RU	2.5% Sugar	39	35	10.0
10.0% MP	10.0% RU	5.0% Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	70	10	9.6
10.0% MP	10.0% RU	5.0% NaBO <sub>2</sub>	38	5	10.1
11.25% MP	11.25% RU	2.5% Na Stearate	0	35	10.0
11.25% MP	11.25% RU	2.5% Urea	62	60	9.9

The original detergent slurries contained much undissolved detergent and, in the case of the Oronite, also sodium sulfate whose crystals tended to grow on long standing. The phosphates were added as fine powders and did not dissolve completely. The phosphates, especially sodium tripolyphosphate, hydrate and cake upon addition of water, but this hydration was largely avoided by holding the solutions at 63°C.

The increase in viscosity with increase in silica to alkali ratio is not surprising in view of the well-known increase in viscosity of sodium silicate solutions with increasing silica content at the same total solids. Perhaps the increase also found at a low silica to alkali ratio with Ultrawet and Orvus may be due to the decreased solubility of sodium silicate at low ratios (3) and the resulting increase in solids.

Potassium silicate solutions are generally more viscous than sodium silicate solutions of the same molar composition. Perhaps the lowering in viscosity upon substituting potassium silicate for sodium silicate of nearly the same molar ratio (RU) is due to higher solubility of some of the potassium compounds involved.

The effect of various additives on the viscosity is not easy to explain. That carboxymethyl cellulose increases the viscosity is not at all surprising. The non-ionic surface active agents, glycerine, sugar, and urea, which decrease the viscosity, have in common a large proportion of hydrophilic groups, hydroxyl, oxygen, and amine. Perhaps these groups tend to combine

 TABLE II  
 Properties of Slurries Containing Ultrawet 45 KX

Phosphate	Silicate	Yield point, grams	Turbidity	pH
25.0% TSPP	.....	47	0	9.6
12.5% TSPP	12.5% RU	22	6	9.8
25.0% STPP	.....	70	2	7.7
12.5% STPP	12.5% RU	17	80	9.9
25.0% MP	.....	37	0	.....
.....	25.0% RU	0	2	10.2
12.5% MP	12.5% N	30	73	9.9
12.5% MP	12.5% RU	40	22	9.9
12.5% MP	12.5% B-W	30	29	10.6
12.5% MP	12.5% Metso Gran.	27	0	11.2

 TABLE III  
 Properties of Slurries Containing Orvus WA Paste

Phosphate	Silicate	Yield point, grams	Turbidity	pH
25.0% TSPP	.....	70	0	10.0
12.5% TSPP	12.5% RU	70	2	10.0
25.0% TTP	.....	.....	0	.....
12.5% STPP	12.5% RU	70	100	10.3
25.0% MP	.....	70	0	8.6
.....	25.0% RU	45	24	10.4
12.5% MP	12.5% N	75	95	9.8
12.5% MP	12.5% RU	67	43	10.1
12.5% MP	12.5% Metso Gran.	75	2	11.5

with some constituent of the slurry and increase its solubility.

In general, there seems to be no correlation between viscosities of the slurries and the turbidities and pH values of their solutions. The use of pyrophosphate with silicate gave less viscous mixtures than did tripolyphosphate, but a combination of the two phosphates resulted in a still less viscous mixture. However turbidities with the mixed phosphates were intermediate, with the tripolyphosphate giving the highest value. Except with Oronite, the minimum viscosity was found at an intermediate ratio silicate, with the more alkaline and the more siliceous giving higher viscosities. The turbidity decreased as the alkalinity of the silicate increased, except for a few small deviations, which may be due to experimental error.

It is to be expected that the viscosity characteristics of detergent slurries, such as those included in this study, will be very sensitive to changes in composition and methods of preparation. It is unlikely that such slurries produced commercially would duplicate closely the values given here.

However the present results should indicate the direction and approximate magnitude of the effects produced by changes in composition. They should serve as guides to methods of altering the viscosity in a desired manner and in reducing the amount of insoluble material produced on drying.

### Summary

Slurries containing synthetic detergents, silicates, phosphates, and sometimes other additives, were prepared and their viscosities measured at several stresses. Portions of the mixtures were oven-dried and dilute solutions prepared. Their turbidities and pH values were determined.

Mixtures of silicate with pyrophosphate yielded lower viscosities and turbidities than with tripolyphosphate. A mixture of the two phosphates with silicate resulted in a still lower viscosity, but an intermediate turbidity. Increasing the alkalinity of the silicate decreased the turbidity, but the minimum viscosity occurred at an intermediate silicate ratio in most cases. A number of the additives tested lowered the viscosity, but all lowered the turbidity.

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