value. At 200°C. this equilibrium was 62% while at 175°C. it was 57%.

The ratio of trans isomers at equilibrium was further verified by hydrogenation of samples of refined cottonseed oil to iodine values of 22 and 35. These samples were hydrogenated in a stainless steel hydrogenator under a pressure of 15 p.s.i.g., a temperature of 177°C., catalyst concentration of 0.1%, and mechanical agitation. The samples were found to contain 58-59% of trans components, calculated on the basis of total unsaturated constituents.

Summary

1. During the hydrogenation of methyl oleate, trans isomers are formed at a very rapid rate. As much as 38% of trans isomers formed while the first 10% of methyl stearate was formed.

2. The rate of formation of trans isomers in methyl oleate undergoing hydrogenation is increased by increasing the temperature, increasing the catalyst concentration, and decreasing the degree of dispersion of the hydrogen.

3. The hydrogenation of methyl oleate always resulted in the establishment of an equilibrium between cis and trans isomers, and irrespective of the conditions employed the concentration of trans isomers was always 67%, calculated on the basis of total unsaturated constituents.

4. It is concluded that all of the iso-oleic acids formed during the hydrogenation of methyl oleate adsorb hydrogen at the same rate as oleic acid and are adsorbed and desorbed from the nickel catalyst with equal ease.

5. Trans isomers are formed at a slightly lower rate during the hydrogenation of triolein than in the case of methyl oleate.

6. Partial hydrogenation of triolein also results in the establishment of an equilibrium between cis and trans isomers of oleic acid but at values of less than 67% of trans constituents (based on the total unsaturated constituents) observed with methyl oleate. The equilibrium concentration was found to vary with the conditions of hydrogenation and was found to be 62% at 200°C. and 57% at 175°C.

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Viscosity of Potassium Soap-Potassium Silicate Mixtures[1]

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IN 1949 Merrill and Getty (13) reported data on the solubility, pH's, and detergent properties of mixtures of potassium coconut oil soap with two potassium silicates. They concluded that the addition of potassium silicates to potassium soaps resulted in equivalent or better detergency and at appreciable savings in cost. The effect was particularly obvious in hard water. Since potassium soaps are commonly sold as liquids or pastes, it is important to know what effect silicate additives will have on the viscosity of the mixture. This paper is a report on that phase of the problem.

While there are many published references on the effects of additives on the viscosity of soap solutions (1-3, 5-9, 11, 12, 15-17, 19), no data have been found which are strictly comparable with the present work. Most of the published references are concerned with a) pure soaps, usually sodium soaps, b) low concentrations of soap and additives, c) higher working temperatures, and d) the effect of organic additives which were often used.

Thus in recent years Angelescu and co-workers have investigated the effects of cresols and other phenolic compounds on sodium and potassium stearate and palmitate and other pure soaps (1-3). Philippoff has studied the viscosity and elasticity of low concentrations of potassium laurate and other derivatives of dodecane (16, 17). Neiman in 1947 published viscosity data on the system potassium palmitate-water-isoamyl alcohol at 50°C. (15). Freundlich and Kores have also done work on the viscosity and elasticity of solutions of pure soaps (6, 7).

About 25 years ago King, and later McBain, Willavoys, and Heighington did work on the effect of NaCl and other sodium salts on the viscosity palmitate solutions (11, 12). They found that the addition of electrolytes increased the viscosity to a maximum value many hundred times greater than that of the original soap solution. Further additions decreased the viscosity almost as rapidly until the salting-out concentration was reached. In both of these studies viscosities were measured by falling ball method at a working temperature of 80°C.

Merrill (14) has shown that a liquid soap containing 33% soap corresponding to potassium laurate can be mixed in all proportions with a potassium silicate containing 38.7% solids with a silica-to-alkali mole ratio of 3.2:1.

In the present investigation commercial potassium paste soaps and commercial potassium silicates have been used. Thus the data have direct value for manufacturers and users of liquid potassium soaps.

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[1] Presented at the Meeting-in-Miniature of the Philadelphia Section of the American Chemical Society, January 18, 1951.

Experimental

Commercial potash soaps were obtained from the Davies-Young Soap Company and the New York Soap Company Inc. Properties of the soaps are summarized in Table I. The average equivalent weights of the fatty acids were determined by titration with standard NaOH solution, and the iodine numbers by the Hanus method (10). The coconut oil soap was yellow, the soya bean oil soap was brownish-orange, and the linseed oil soap was dark brown or black. Water solutions of these soaps were clear or slightly cloudy.

TABLE I

Analyses of Potassium Soaps

Soap	Fatty Acids		
	%	Av. Equiv. Weight	Iodine Number
Potassium coconut oil soap	44.5	220	8.9
Potassium soya bean oil soap	37.2	291	85.6
Potassium linseed oil soap	31.9	300	......

The analyses of the silicates are given in Table II. The more siliceous silicates are commercial products. The others were prepared from the $K_2O \cdot 4.0\ SiO_2$ and potassium hydroxide solution. The potassium hydroxide and the potassium chloride used in the comparison mixtures were reagent grade products. Distilled water was used in preparing all solutions.

TABLE II

Analyses of Potassium Silicate Solutions

Molecular Formula	% K_2O	% SiO_2	Molecular Weight	Specific Gravity	Viscosity Poises
$K_2O \cdot 4.0\ SiO_2$	7.78	19.77	333.58	1.245	0.14
$K_2O \cdot 3.3\ SiO_2$	12.81	26.69	290.42	1.394	13.30
$K_2O \cdot 2.0\ SiO_2$	13.34	16.95	213.71	......	......
$K_2O \cdot SiO_2$	29.45	19.02	155.03	......	......

Viscosities of the relatively fluid mixtures were measured on a Stormer viscometer (18). The more viscous mixtures were usually run in the Stormer and the results checked by the falling ball method. The latter, as developed by Bacon (4), gives the absolute viscosity in poises with an accuracy of ±1%. The Stormer viscometer is capable of accuracy of ±0.5%. Stormer seconds can, of course, be converted to poises by calibration against Arlex solutions, which are in turn standardized by a precise falling ball method. Both the Stormer and the falling ball methods were checked against the Bureau of Standard's viscosity standards.

Water from a thermostatically controlled water bath was circulated through the jacket around the viscometer cup, keeping the mixture in the cup at 19.95 ±0.05°C. The temperature of the mixtures in the falling ball tests was kept at 19.87 ±0.05°C.

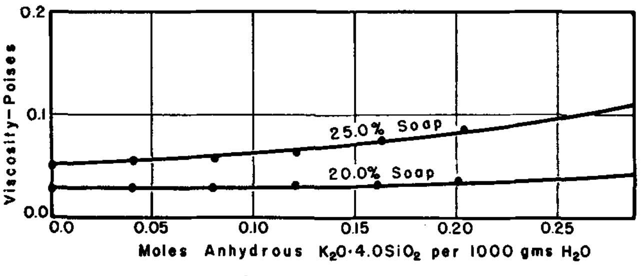

FIG. 1. Viscosities of potassium coconut oil soap-K_2O:4.0 SiO_2 mixtures at 20°C.

Results

Addition of silicates and potassium chloride had very little effect on the viscosity of the coconut oil soap solutions in the concentration range covered by this study. They had pronounced effects on the viscosities of the soya bean oil and linseed oil soaps.

Figure 1 shows the effect of additions of $K_2O \cdot 4.0\ SiO_2$ to coconut oil soap solutions. The results are typical of those obtained when silicates of any ratio were added to solutions of this soap. It is apparent that the addition of up to 0.3 moles silicate solids per 1,000 gms. water had very little effect. In fact, the silicate concentrations of these soap solutions were increased to about 0.4 molal (0.4 moles silicate per 1,000 gms. water present in the soap solution) without increasing the viscosity significantly. This concentration corresponds to about 8.5% silicate solids, or about 30% of the commercial $K_2O \cdot 4.0\ SiO_2$ solution.

Because of the small increases in viscosity caused by the added salts, less work was done on this soap than on the other two. In one series of tests KCl was added to solutions containing 20% and 30% of this coconut oil soap. Up to 1.2 moles KCl were added per kg. H_2O (about 6%) without raising the viscosity above that of the pure soap solutions, which had viscosities of 3 and 5 centipoises, respectively. Potassium metasilicate was added to a 20% soap solution to the extent of 0.3 mole per kg. H_2O (about 3% solids) with the same result.

The other two soaps gave results which were more varied. With these soaps the addition of a silicate or KCl to solutions of constant soap content yielded families of curves similar to the one seen in Figure 2. For these mixtures 0.1 mole per kg. water corresponds to about 2.2% silicate solids. Thus the highest silicate additions shown in Figure 2 are about 6.5% solids, which corresponds to the addition of 17% of the commercial silicate.

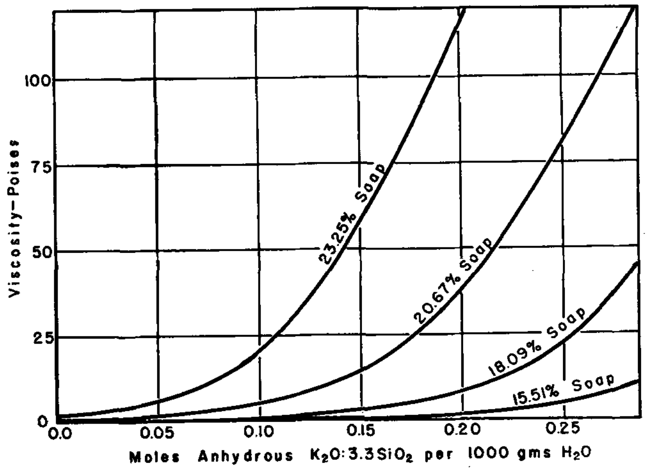

FIG. 2. Viscosities of potassium linseed oil soap-K_2O:3.3 SiO_2 mixtures at 20°C.

Having determined the viscosity curves for the various soap-silicate combinations, the effect of the various $K_2O:SiO_2$ ratios on the viscosities of the solutions could be compared. Such comparisons are shown in Figures 3 and 4 for the soya bean oil soap and the linseed oil soap mixtures, respectively. The order of silicates causing decreasing viscosities is the same for both soaps, but in the case of the soya soap

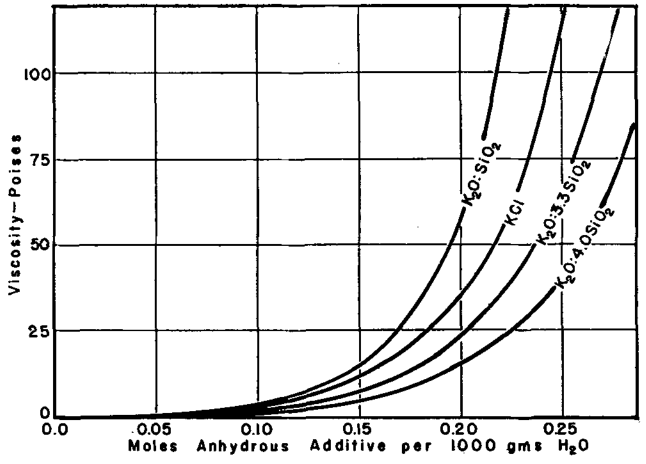

FIG. 3. Viscosities of potassium soya bean oil soap-potassium silicate mixtures at 20°C. Mixtures containing 20.0% anhydrous soap.

the soap-potassium chloride viscosities fall between those of the soap-metasilicate and soap-disilicate mixtures (the curve for the latter mixtures is not shown in Figure 3) while the addition of potassium chloride to the linseed oil soap caused smaller viscosity increases than any of the silicates.

It is obvious from these curves that the more alkaline silicates cause higher viscosities than the siliceous silicates when present in equal molal concentrations. It might seem that it was the alkali in the silicate which influenced the viscosities of the soap silicate mixtures, but, in mixtures containing different ratio silicates and having the same percentage of soap and molal concentration of the additive, the percentage of K_2O (alkali) will change very little.

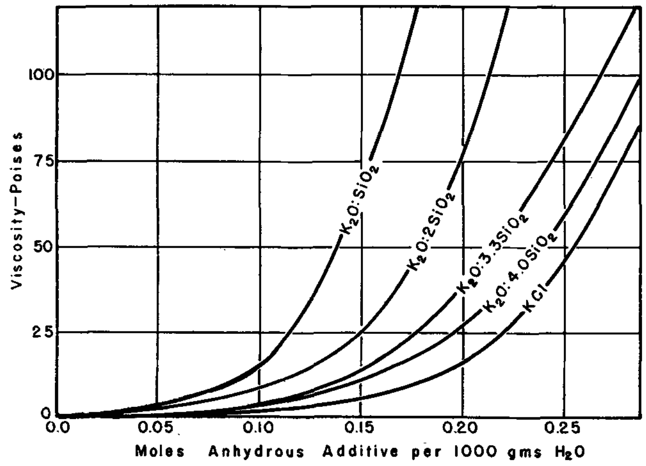

FIG. 4. Viscosities of potassium linseed oil soap-potassium silicate mixtures at 20°C. Mixtures containing 20.67% anhydrous soap.

In Figure 5 the viscosity is plotted as a function of the $SiO_2:K_2O$ ratio for the mixtures having constant soap and silicate concentrations (0.15 molal in K_2O). The curve for the linseed oil soap-silicate mixtures shows that increasing the amount of silica has the effect of decreasing the viscosity up to a ratio of about 4:1. A similar, but smaller effect is seen with the soya bean oil soap-silicate mixtures at these concentrations, but when the molal silicate concentrations are increased to 0.20 in 20% soap solutions, the resultant curve is almost identical to the linseed oil soap curve in Figure 5 over the range of ratios from 1:1 to 4:1.

The effect of excess alkali on the viscosity of soap solutions is well known, of course, and has sometimes been used commercially in salting-out operations. McBain, Willavoys, and Heighington (12) state that if one equivalent per cent excess NaOH was present in the sodium palmitate solution, the viscosity maximums were roughly 1.7 times greater. The effect of the soluble silicates in decreasing viscosity of built soap solutions from those obtained in soap-excess alkali mixtures is perhaps not so widely recognized. However this phenomenon does give the soap manufacturer another means of adjusting the viscosity of a soap-builder solution. Thus either the concentration or the ratio of the silicate could be varied to get a certain viscosity consistent with other desirable properties such as high pH, clarity of solution, etc.

As mentioned above, King (11) and McBain *et al.* (12) found maxima in the region 10 to 100 poises when working with sodium palmitate-sodium salt-H_2O systems at 80°C. These maxima came at 0.2 to 0.5 moles additive per 1,000 gms. H_2O. It is to be expected that the viscosity curves and maxima would be shifted upward as the temperature was decreased, and at the temperature of the present experiments the maxima have been shifted out of the range of interest. However in the present work the curve was followed out in a rough way for soya bean oil soap-KCl mixtures by simply laying on its side a bottle containing a standard amount of the combination and noting the time required for the mixture to reach the bottle top. The results are shown in Table III. Since this work was approximate, the soap concentration was not adjusted after each addition of the salt, which meant that it decreased somewhat. However this drop in soap concentration was insignificant compared with the viscosity changes.

The mixture having a viscosity of 4,900 poises looked about as solid and stiff as a gel, but it flowed slowly at room temperature. Although the falling ball method can be adapted to measure very high viscosities, as used in this project it was accurate only to about 1,000 poises so these higher ranges were not measured precisely.

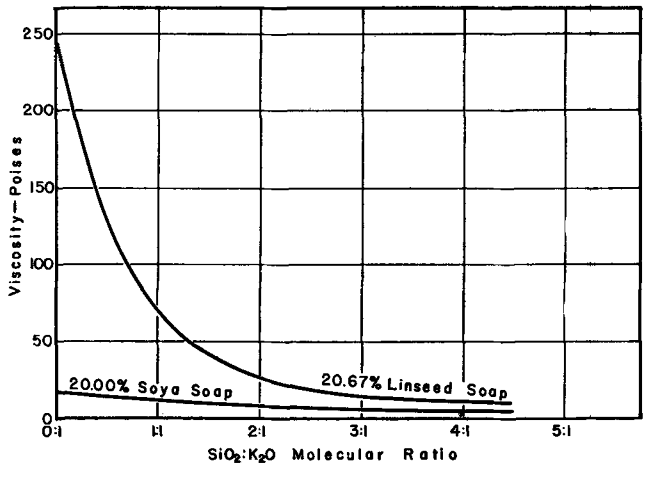

FIG. 5. Effect of $SiO_2:K_2O$ ratio upon viscosity for constant soap and silicate concentrations. (Each mixture contains 0.15 moles silicate solids per 1,000 gms. water.)

TABLE III

Effect of High KCl Concentrations on Viscosity of Soya Bean Oil Soap

% Soap	KCl		Approximate Viscosity Poises
	Molality	%	
24.0	.19	1.07	105
23.3	.76	4.12	4,900
22.7	1.21	6.41	1,470
22.2	1.63	8.45	79

One of the interesting questions raised by this work is why there is such a wide difference between the effect of the additives on the coconut oil soap on one hand, and on the soya bean oil and linseed oil soaps on the other hand. Merrill and Getty (13, 14) have shown that the solubility of potassium laurate and potassium coconut oil soap in the presence of $K_2O \cdot 3.3\, SiO_2$ is high. While similar data for the other soaps are not available, this is undoubtedly one of the reasons for the small viscosity changes in coconut oil soap solutions.

Summary

Viscosity measurements at 20°C. have been made on mixtures of three potassium soaps with four potassium silicates and potassium chloride in the range of 0 to 100 poises. It was found that the additives have a considerable effect on the viscosity of the potassium linseed oil and the soya bean oil soap solutions, but almost no effect on the viscosities of potassium coconut oil soap solutions in the concentration ranges studied. The alkaline silicates caused greater increases in viscosities than the siliceous silicates. Soap-KCl mixtures have viscosities of the same order of magnitude as equivalent soap-silicate mixtures in this viscosity range.

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Bleaching of Cottonseed Oil in Hexane[1]

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BLEACHING fats and oils by adsorption has become a standardized operation as a result of years of practical plant experience. There are however certain aspects of adsorption bleaching which offer possibilities of improving the process.

According to accepted theory (2), the quantity of color bodies removed from an oil by a bleaching clay or carbon should increase as the temperature decreases. In practice however it is preferable to bleach an oil at temperatures (5, 6) above atmospheric because increasing the temperature decreases the viscosity of the oil and permits it to penetrate the interstices of the adsorbent, thereby increasing the rate, and apparently the amount of adsorption. Theoretical considerations would lead one to predict that multiple or repeated bleachings should produce greater reduction in the color of an oil than would be accomplished with the same amount of adsorbent applied in one operation. Odeen and Slosson (6) and King and Wharton (4) did not find this to be true when oils were bleached at elevated temperatures with 2% of activated clay. They assumed that the extra heating and handling necessary to effect multiple bleaching produced new color bodies which offset the increased adsorption. Sanders (7) and Hassler and Hagberg (3) have reported data to show the savings in adsorbent which can be obtained by stepwise countercurrent bleaching, but the methods they described have seldom been applied.

The present investigation, which is concerned with bleaching refined cottonseed oil in commercial hexane, was prompted by several considerations as follows:

a) At a given temperature a solution of oil and hydrocarbon solvent has an appreciably lower viscosity than the oil alone.
b) Effective bleaching should be possible at atmospheric temperature.
c) At any given temperature less bleaching agent should be needed to effect a given reduction in color.
d) Countercurrent bleaching should be feasible.
e) The loss of oil during bleaching should be less than in current practice.
f) Solvent-extracted oil, if refined prior to removal of solvent, could also be bleached in the same solvent.

Experimental

Batch Bleaching. Commercially refined cottonseed oil (Lovibond color, 70 yellow and 8.1 red) was washed and dried to remove traces of soap and bleached in hexane with a commercial grade activated clay. Unless stated otherwise, the oil (designated as A) and the activated clay were the same in all of the following experiments.

All of the batchwise bleaching experiments were carried out with 30% solutions of the cottonseed oil in commercial hexane. The clay was added to each solution and the mixture agitated vigorously for 40 minutes at 25°C., after which the solution was filtered to remove the clay and the solvent removed by heating under vacuum at 100°C. For comparison, portions of the original oil were mixed with various amounts of clay and agitated vigorously for 40 minutes at 25°C. These conditions were found to be adequate for the adsorption to come to practical equilibrium. Another series of bleachings was made by a

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