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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TABLE I

Effect of Bleaching Refined Cottonseed Oils With Activated Clay With and Without Addition of Hexane[a]

Activated clay used,[b] %	Color of oil bleached as shown, Lovibond red units[c]					
	Oil A in hexane at 25°C.	Oil B in hexane at 60°C.	Without hexane at 25°C.		Modified A.O.C.S. method[d]	
			Oil A	Oil B	Oil A	Oil B
0.0	8.1	10.5	8.1	10.5	8.1	10.5
0.5	4.9	7.9	6.7	9.4	5.7	8.7
1.0	4.4	7.0	6.1	....	5.1	....
2.0	3.9	6.0	5.7	8.5	4.0	6.6
3.0	3.6	4.7	5.3	....	3.6	....
6.0	3.3	3.5	....	7.5	2.9	4.9
8.0	....	....	4.5	....	....	....

[a] 30% cottonseed oil in hexane.

[b] Calculated on oil basis.

[c] Measured in 5.25-in. tube using the ratios of yellow to red according to the official A.O.C.S. method.

[d] Modified by using various percentages of activated clay in place of A.O.C.S. standard clay.

slight modification of the official A.O.C.S. bleach test for cottonseed oil (1). It differed only in the type of activated clay used and the fact that other quantities were used in addition to that prescribed by the official method. The results obtained in the three series of experiments are given in Table I.

Comparison of the bleachings for oil A at 25°C. shows that in each case greater reduction in the color of refined cottonseed oil was obtained by bleaching in the presence of solvent regardless of the quantity of clay used. Also the amount of color reduction was in all cases, save one, the same or greater than that obtained with the modified A.O.C.S. bleach method at 110°C. To effect small reductions in color, bleaching in hexane solution requires the least amount of clay, but for larger reductions the modified A.O.C.S. procedure uses the smaller amounts.

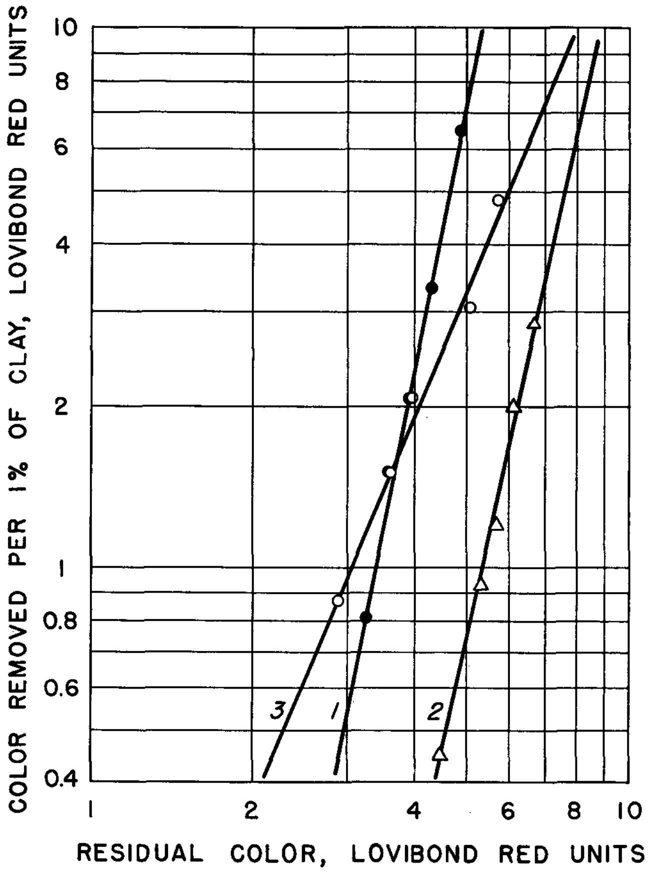

FIG. 1. Adsorption isotherms of (1) refined cottonseed oil bleached in hexane at 25°C., (2) the same oil bleached alone at 25°C., and (3) the same oil bleached at 105-120°C. (See Table II). *K* and *n* values (in the order mentioned) for the three curves are: (1) 0.002, 5.10; (2) 0.0006, 4.55; (3) 0.07, 2.39.

The three bleaching methods can be compared better in graphic form by plotting the data for oil A in Table I as Freundlich adsorption isotherms on log-log coordinates as shown in Figure 1.

The Freundlich equation is $x/m = Kc^n$ where x is the amount of substance adsorbed, m the amount of adsorbent, and c the amount of residual substance after adsorption. K, which in Figure 1 is the value of the intercept at unit residual color, and n, which in the same figure is equal to the slope of the adsorption curve, characterize the adsorption and are the important values in these experiments.

The approximately equal values of n for curves 1 and 2 show that at 25°C. the addition of hexane to the oil does not greatly change the manner in which the bleaching clay acts. The value of K for curve 1 is 3.3 times as great as that for curve 2, i.e., the addition of hexane increased the decolorizing power of the adsorbent approximately 3.3 times. The fact that the value of n for curve 1 is greater than that for curve 3 indicates that the bleaching procedure represented by curve 1 is relatively more effective in removing the first portions of color. The manner in which a bleaching clay functions in hexane solution, that is, the value of n, can be controlled to some extent by varying the temperature. Increasing the temperature tends to decrease the value of n.

Table I also records data obtained with a laboratory-refined cottonseed oil, B, subjected to bleachings similar to those reported for oil A, except that the bleaching temperature in hexane was 60°C. instead of 25°C. The calculated value of n for bleaching in hexane at 60°C. is practically identical with that obtained for the modified A.O.C.S. bleach method at 110°C. Except for the bleachings in hexane, the values of n for the corresponding bleachings shown for the two oils are almost identical.

The effect of oil concentration on the degree of bleaching obtained in oil-hexane solutions was determined by another series of tests in which oil A was diluted to form solutions of different concentrations, each of which was bleached with 3% (on an oil basis) of activated clay, the procedure otherwise being the same as that used with the hexane solutions of oil A, described in Table I.

The bleached oil colors for 10, 30, 50, and 100% concentrations of original refined oil were 2.7, 3.5, 4.0, and 5.4 red Lovibond units, respectively. When plotted on rectangular coordinates, these values show a linear relationship, i.e., the color of the bleached oil decreases linearly with the concentration of the oil in the solution in which it was bleached.

The three series of bleachings represented by the data for Oil A, Table I, were repeated with a laboratory refined, washed, and dried cottonseed oil (designated as C) and a commercial activated carbon in place of the activated clay of the previous experiments. The results of these tests are given in Table II, from which it is evident that bleaching at 25°C. in the presence of hexane was best at all concentrations of carbon used except at 6%. At this concentration the modified A.O.C.S. procedure was equally effective. The failure of the carbon to reduce the

TABLE II

Effect of Bleaching Refined Cottonseed Oil With Activated Carbon With and Without Addition of Hexane[a]

Activated carbon used,[b] %	Color of bleached oil, Lovibond red units[c]		
	Bleached in hexane at 25°C.	Bleached without hexane at 25°C.	Bleached by modified A.O.C.S. procedure[d]
0.0	11.6	11.6	11.6
0.5	6.2	8.1	9.5
1.0	5.7	7.9	7.8
2.0	4.7	7.7	7.2
3.0	4.1	7.5	5.6
6.0	3.2	6.7	3.2

[a] *30% cottonseed oil C in hexane.*

[b] Calculated on oil basis.

[c] Measured in 5.25-in. tube using the ratios of yellow to red according to the official A.O.C.S. method.

[d] Modified by using various percentages of activated carbon in place of A.O.C.S. standard clay.

color to a low value in any of the tests is in agreement with general experience that carbon alone is not an effective decolorizing agent for cottonseed oil. The data obtained by bleaching with carbon do not follow Freundlich's adsorption isotherm and hence are not amenable to analysis by this method. It can only be said that the final colors of the solvent bleached oils are as good or better than those obtainable by bleaching in the absence of solvent.

Countercurrent Bleaching

Countercurrent adsorption is used in the petroleum industry for decolorizing and degumming mineral oils and should be of value in bleaching vegetable oils. In the present investigation cottonseed oil-hexane solutions were usually bleached in columns packed with commercial activated clay or carbon mixed with five parts of a coarse diatomaceous earth. However columns consisting of granular clay and of powdered clay and sand were tested and found to perform satisfactorily.

An adsorption column loses its ability to decolorize quite slowly, especially when solutions such as cottonseed oil A and hexane are passed through the type of activated clay similar to that used in these experiments. The high value of n (Figure 1) for such a combination of clay, oil, and hexane indicates it is particularly suited for countercurrent bleaching at temperatures of about 25°C.

When a 30% solution of cottonseed oil A in hexane was passed through a short column (ratio of height to diameter, 4.5:1) containing 6% of activated clay on an oil weight basis, the color of the oil was reduced from 8.1 to 2.6 Lovibond red units. As additional fresh batches of solution, containing the same amount of oil as the first, were passed successively through the column, the colors of the bleached oil increased to 3.3, 3.7, 3.8, and 4.1 Lovibond red units. The average color of the six batches of bleached oil was 3.6 Lovibond red units, and the average amount of clay used was 1%. On the basis of the data in Table I, 3% or three times as much clay would have been required to bleach this oil to the same extent by normal methods.

Since the regeneration of a spent bleaching clay *in situ* is desirable for maximum efficiency, the elutriating power of different solvents was determined. For these tests a solvent-extracted cottonseed oil was refined with a 0.3% excess of sodium hydroxide and the refined oil bleached with activated clay. The spent clay was mixed with diatomaceous earth, a specified portion of the mixture placed in the column, and a specified quantity of the selected solvent passed through the clay. The exit oil-solvent mixture was thoroughly mixed and its color determined.

TABLE III

Elutriating Power of Various Solvents for Spent Bleaching Earth

Solvent	Lovibond color of wash solutions	
	Yellow	Red
Skellysolve "F"[a]	1	0.14
Skellysolve "H"[a]	1	0.14
Skellysolve "B"[a]	1	0.20
Benzene	2	0.29
Toluene	2	0.29
Trichloroethylene	1	0.29
Ethyl ether	5	0.60
Methanol	5	1.19
1,4-Dioxane	15	1.48
Isopropanol	15	1.66
Ethanol	10	1.75
Butanol	10	1.92
Acetic acid	20	2.09
Amyl acetate	15	2.91
Ethyl methyl ketone	35	3.93
Acetone	35	4.86

[a] These solvents are named as part of the specification of the exact experimental conditions and does not imply that these products are particularly endorsed or recommended by the Department of Agriculture over other solvents having the same or similar properties.

The data which are summarized in Table III show that the low molecular weight ketones are the most effective solvents for regenerating spent bleaching clays. It is also apparent that petroleum naphthas are the best solvents for oils to be bleached.

Little acetone is needed to regenerate a column which has been used in bleaching cottonseed oil. When this solvent is percolated through a spent column, the adsorbed pigments are concentrated in the first portions of acetone which emerge from the column.

A column, 11.5 cm. in height and 2.5 cm. in diameter and containing 7.2 g. of clay mixed with diatomaceous earth, was used to bleach 400 g. of a 30% solution of cottonseed oil A in hexane. After washing the column with 100 g. of hexane, acetone was added at the top and when the color bodies began to emerge, a single, 40-ml. batch of wash solution was collected. It contained over 96% of the total color bodies which could be elutriated with this solvent.

The quantity of pigments and fatty material adsorbed during countercurrent bleaching is approximately 0.3% (on an oil weight basis) when the clay in the column amounts to 6% of the cottonseed oil treated. It increases to about 0.6% when the clay equals 18% of the weight of oil treated.

The mixture of pigments and fatty material recovered from the acetone wash solutions is a viscous, dark red liquid containing approximately 4% of free fatty acids and possessing an iodine value approximately 10 units below that of the original oil.

A series of bleachings using a solution of cottonseed oil in hexane was made to determine the number of times a clay could be reused when regenerated with acetone. Bleachings were made in a column 2.5 cm. in diameter and 11.5 cm. high and containing 3.6 g. of activated clay mixed with diatomaceous earth. Batches containing 60 g. of cottonseed oil A in the form of 30% solutions in hexane were passed through the column. After each bleaching the column was washed with 60 g. of hexane, regenerated with 60 g. of acetone, and again washed with 60 g. of hexane. The colors of the bleached oils obtained from successive batches are shown in Table IV. It is apparent that the regeneration of the bleaching clay was effective. Results similar to those shown in Table IV were obtained when other refined cottonseed oils were bleached with activated carbon or official A.O.C.S. bleaching earth.

TABLE IV

Effect of Repeated Use of Clay on the Color of Cottonseed Oil Bleached in Hexane[a] at 25°C.

Times clay reused	Lovibond red color[b] of bleached oil	Times clay reused	Lovibond red color[b] of bleached oil
0	2.8	11	3.6
1	3.0	12	3.4
2	3.0	13	3.7
3	3.2	14	3.6
4	3.5	15	4.1
5	3.5	16	4.0
6	3.4	17	4.3
7	3.5	18	3.9
8	3.6	19	3.8
9	3.9	20	4.1
10	3.6	....	....

[a] 30% solution cottonseed oil A (Lovibond color, 70 yellow and 8.1 red), 6% clay on oil weight basis.

[b] Measured in 5.25-in. tube using the ratio of yellow to red according to the official A.O.C.S method.

Absorption spectra were determined in iso-octane solution for three of the products involved in the bleachings represented in Table IV, namely, the unbleached oil, the first bleached oil, and the bleached oil obtained after regenerating the clay 20 times with acetone. These spectra, which are reproduced in Figure 2, reveal two facts: a) bleaching cottonseed oil in hexane produces a product entirely similar to that obtained by usual methods, and b) regeneration of the spent clay with acetone does not markedly affect the characteristic color of the bleached oil.

In the experiments shown in Table IV the contact times between the oil-solvent solution and the clay-diatomaceous earth mixture was approximately 12 minutes, a period in excess of the required minimum.

When similar experiments were carried out at 66°C. and 25°C., the colors of the oils bleached at the higher temperature were about 0.5 Lovibond red unit lower than those of the oils bleached at the lower temperature.

Bleaching experiments using columns packed with granular clay (prepared by wetting, drying, and grinding the activated clay) showed that marked reductions of color could be obtained with short contact times. A column prepared with clay, which passed a 20-mesh sieve but was retained on a 60-mesh sieve, showed that the color of cottonseed oil A could be reduced to 0.7 Lovibond red unit when bleached in a 30% solution of hexane with a contact time of 3.5 minutes. This time was sufficient for the adsorption to attain equilibrium. The columns prepared with granular clay were also readily regenerated by washing with acetone.

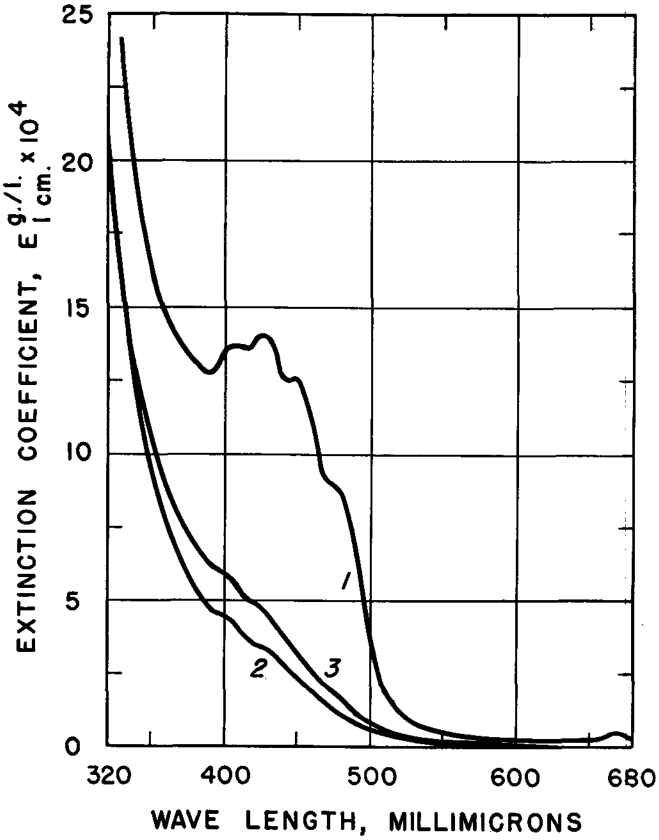

FIG. 2. Absorption spectra of (1) refined cottonseed oil, (2) the same oil after bleaching in hexane solution by passing through a column of activated clay, and (3) the same oil after passing through the same column after regeneration 20 times with acetone.

Summary

1. Cottonseed oil dissolved in commercial hexane was not only bleached readily by activated clay and carbon, but the reduction in color was greater than that obtained in the absence of a solvent, other conditions being similar.

2. At 25°C. the addition of solvent did not significantly change the manner in which the clay acted, but it did increase its capacity to adsorb pigments about three-fold. For a fixed proportion of clay to oil, the amount of color reduction in cottonseed oil-hexane solutions was dependent upon the concentration of the oil. The color decreased as the concentration of the oil decreased.

3. Countercurrent bleaching of cottonseed oil-hexane solutions in columns packed with adsorbents proved to be highly efficient with respect to the utilization of the adsorptive capacity of a given quantity of clay and also with respect to the amount of oil lost by adsorption.

4. Columns of spent bleaching clay could be regenerated easily with acetone. The Lovibond red color of the first batch of oil bleached in one such column was 2.8 while that of the twentieth batch, obtained after the column had been used and regenerated 19 times, was 3.8.

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