tests showed the fatty acids to be highly concentrated in the alcohol-water phase.

Flaked cottonseed meats were extracted in continuous extraction apparatus with 91% isopropanol, 99% isopropanol, and mixtures of commercial hexane and isopropanol. Analytical data on the extractions show that 91% isopropanol is an efficient solvent for extracting active gossypol along with the oil.

Rat and swine feeding tests of the isopropanol extracted meal showed it to be highly superior to hydraulic meal as a source of protein.

A method was developed for treatment of the cottonseed-isopropanol miscella by liquid-liquid extraction to separate purified oil and fatty acid fractions from other materials in the extract.

Acknowledgments

This work was carried out with funds from the Cotton Research Committee of Texas and the Texas Engineering Experiment Station.

Appreciation is expressed to B. R. Holland for assistance in the gossypol determinations.

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Soap Content of Some Commercially Refined Oils; Effect of Soap on the Bleachability of the Oils

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IN the commercial refining of vegetable oils by means of an alkali, such as sodium hydroxide, there is always a small residue of soap left in the oil. Various procedures, as waterwashing and filtering are used to remove these traces of soap, but even after washing and filtering there is usually a detectable trace of mineral matter, presumably largely sodium, left. That the determination of these traces of residual soap is important is well attested by the numerous articles (2, 3, 4, 5) which have appeared describing and discussing analytical methods adapted to their estimation. However, there is very little in the literature regarding the results which are obtained when these analytical methods are applied to commercial oil products.

The report of the A.O.C.S. Soap in Refined Oil Committee for 1936, contained the following statement, "A freshly refined oil will contain from 0.05% to 0.15% of soap depending on the oil and method of neutralization. After bleaching this content will be reduced to below 0.005%." No actual analytical values were shown however, except for those obtained in the cooperative work on selected samples and directed at evolving a satisfactory analytical method. Boekenoogen (3) reported some values for soap in refined cottonseed oil, but his work was concerned largely with methods of analysis and the solubility of sodium soap in cottonseed oil.

Part of the reason for the lack of reported values for soap in commercially refined oils may lie in the somewhat unreliable nature of the analytical methods available (5). Regardless of the reliability of the methods, however, the refinery chemist is often called upon to make determinations of soap in refined oil, and, in the absence of any published values, he may find it difficult to form an opinion as to whether a given result is reasonable or not. It is believed, therefore, that the results reported here will be of some interest.

Samples have been analyzed and results compiled to show the amount of soap remaining in refined cottonseed and soybean oils at various steps in the continuous centrifugal refining process using sodium hydroxide as the neutralizing agent and employing a single stage of waterwashing. At the same time experiments were conducted to determine what effect an excessive amount of soap remaining in a refined oil might have on its bleachability and how effective the bleaching would be in removing the excess soap. The results reported were taken from analyses run in the laboratories of two independent refineries on oils produced in the respective refineries. Since the two sets of results are in agreement, it seems reasonable to assume that they are representative of average commercial oils refined under similar conditions.

Description of Refining Process and Definition of Terms

The process by which the oils were refined has been described in detail by James (6), and it is probable that most readers will be familiar with the terms which will be used to identify the samples analyzed. A brief description of the process, however, with particular references to the points at which sampling was done, will be given. Crude oil, upon entering the refinery, is mixed with a definite volume of sodium hydroxide solution in closed mechanical mixers. The emulsion thus formed is led into a heater where it is heated and the emulsion broken. At this point most of the sodium hydroxide has combined with the free fatty acids and other acidic impurities present to form flocs of hydrated soap which occlude other insoluble impurities. The neutralized oil containing the precipitated soap and impurities is then passed through a set of continuous centrifuges, which separate more or less completely the clear oil from the suspended soap and impurities. These centrifuges which separate the bulk of the soap from the refined oil are often termed the primary machines. Therefore, samples referred to as having come from the primary machines comprise oil which has been refined and the soap separated but which has undergone no other treatment. From the primary centrifuges the neutralized oil flows into small tanks where fresh water is sprayed over it. It is then pumped into a second set of centrifuges which separate the oil from the wash water. The centrifuges which separate the wash water from the oil are often referred to as the secondary machines hence, in speaking of samples from these machines, reference is made to oil which has been refined and washed once.

In many refineries it is the practice to have two or more stages of waterwashing and in fact the equipment on which these tests were run is now equipped with more than one stage. However, the results reported here covered only one stage of waterwashing.

From the secondary or waterwash machines the oil goes to a vacuum dryer where the moisture content is reduced from several tenths of 1% to less than 0.10%. The term, "samples from the dryer," then refers to oil which has been refined, washed with water once, and then freed of its moisture by reduced pressure and heat. Up to this point most of the soap found by analysis of the oil is very possibly dissolved or suspended in the water droplets present rather than in the oil itself, but after drying any soap found must be considered as dissolved in the oil. After drying the refining process is complete and the oil goes either to storage or the bleaching kettles.

Methods of Sampling and Analysis

In taking the samples on which the present analyses were obtained, the effort was at all times to obtain portions representative of normal routine practice. At no time during the tests was the usual refining procedure interrupted, but in all cases the oil and soapstock issuing from the various machines was checked for normal appearance before the samples were taken.

To obtain the composite samples on which the results in Table 3 were obtained, small portions of oil were taken from the various points at regular intervals, while the oil described was being refined. These small samples were then thoroughly mixed in order to give a composite. Samples for the analyses shown in Table 4 were obtained in a similar manner except that they were caught over a period of one day each, and may have included oil from more than one source.

All of the analytical results were obtained by the original method of Durst (2), based on the extraction of the sodium present with 1:1 hydrochloric acid and its determination volumetrically with silver nitrate solution. Naturally any mineral matter present in the oil and soluble in 1:1 hydrochloric acid will be reported as soap by this method. It is to be understood, therefore, that the soap content reported on the various oils refers to their apparent soap content as determined by the method above.

The limitations of the method are well known, and, in order to determine the order of accuracy obtained, analyses were made on a number of suspensions of sodium soap in cottonseed oil, in which the content of non-volatile material soluble in hydrochloric acid was very accurately known. The results obtained are shown in Table 1.

TABLE 1.

Efficiency of HCl Extraction Method for Determination of Soap in Refined Oil.

% Soap		Difference	% Recovery
Actual	Found		
0.761	0.678	0.083 Low	89.0
0.248	0.221	0.017 Low	89.2
0.109	0.091	0.018 Low	83.6
0.044	0.043	0.001 Low	97.8
0.044	0.044	0.000	100.0

It may be seen that only about 83% to 89% of the sodium added to the oil could be recovered when the concentration calculated to sodium oleate was above 0.100%. However, at a concentration of the order of 0.044% the recovery was very good. It is of interest to note that Schuette and Hine (4) found a modification of this method to be more efficient at low concentrations than at high although they worked in the range of 0.020% and below only. In view of the poor recovery at high concentrations and apparently good recovery at low ones, it was felt that the results would be more nearly correct if adjustments, based on a recovery of only 85% of the soap present, were made on all results of 0.10% or over. For example, where a value of 0.173% is reported the actual analyzed value was 0.147%. On values below 0.100% no corrections were made, not only because two determinations had indicated recovery to be good at a level of 0.044%, but also because it was not felt that corrections of values below 0.100% would change the figures significantly.

In the course of this work a number of samples of refined, washed, and dried soybean oils were also analyzed by an independent laboratory. It is of interest to see how the two sets of analytical results agree. Examples are shown in Table 2.

TABLE 2.

Soap Content of Refined, Washed, and Dried Soybean Oils; Comparison Between Results Obtained by Two Independent Laboratories Working on Duplicate Samples.

Sample	Lab. No. 1	Lab. No. 2	Difference
	%	%	%
1	0.016	0.012	0.004
2	0.028	0.018	0.010
3	0.050	0.047	0.003
4	0.050	0.051	0.001
5	0.005	0.010	0.005
Average	0.030	0.028	0.002

If comparisons are made on a percentage basis the agreement is, in some cases, very poor indeed. On Sample 5 for instance, the result reported by Laboratory No. 2 is 100% greater than that of Laboratory No. 1. However, the two results are 0.010% and 0.005%, and from a practical viewpoint it seems of doubtful importance whether a refined oil contains 0.010% of sodium soap or 0.005%. Furthermore, when it is considered that no attempt was made to standardize details of the procedures used in the two laboratories, the agreement on most of the samples does not seem unduly poor.

Percentages of Soap in Different Samples

The object of the first series of analyses was to determine what percentage of soap is normally left in the refined oil produced from different types and grades of crude oil at various points in the processing cycle. Soap determinations were made on samples taken from the primary machines, the secondary machines, and the dryer, and also on a sample of the dried oil bleached in the laboratory. As has been pointed out before, the soap found in undried oil is very probably dissolved in the water droplets rather than in the oil itself; however, its concentration is of interest in order to determine how efficient the various processing steps are in effecting its removal. The results are given in Table 3 and, for purposes of comparison, there has also been included in this table analytical results obtained independently by and in another refinery.

TABLE 3.

Soap Content of Oil Samples Taken at Various Points in the Neutralizing Process.

Sample	% Soap
Cottonseed oil No. 1, from primary machines,	0.038
Same from secondaries (waterwashed)	0.004
Same from dryer	0.004
Same bleached in laboratory	0.002
Cottonseed oil No. 2, from primaries	0.672
Same from secondaries (waterwashed)	0.015
Same from dryer	0.011
Same bleached in laboratory	0.004
Soybean oil, from primaries	0.183
Same from secondaries (waterwashed)	0.030
Same from dryer	0.015
Same bleached in laboratory	0.000
Comparative Results From Another Refinery	
Cottonseed oil from primary machines	0.173
Same from secondaries (waterwashed)	0.017
Same from dryer	0.023
Soybean oil from secondaries (ref. & Wash.)	0.130
Soybean oil refined, washed and dried	0.038

Note: Cottonseed oil No. 1 was an off-grade oil with 9.1% FFA and 22.3% refining loss. No. 2 was a prime oil, very low in settlings, with 0.8% FFA and 6.0% refining loss. The soybean oil was an average crude of 0.4% FFA.

Examination of the results will show that the soap content of refined cottonseed oil coming from the primary machines varied quite widely between the two grades of crude oil. Naturally, other factors besides the quality of the crude oil may have contributed to this variation. However, it is interesting to note that the oil which retained the higher concentration of soap was produced from crude oil remarkably low in settlings, whereas a poor grade of crude retained in the refined oil an extremely small amount of soap. The present results do not establish whether there is a connection, but the difficulties of refining degummed oils which are completely free of settlings are well known. Refined soybean oil as it came from the primary machines was intermediate between the two samples of cottonseed oil.

A single stage of waterwashing reduced the soap content of the oils to 0.030% or less in all cases even when the amount of soap in the unwashed oil from the primaries was over 0.6%. Bleaching in the laboratory with 6% of A.O.C.S. official bleaching earth further reduced the soap content to a very low value but did not, except in the case of the soybean oil sample, reduce it below the sensitivity of the method.

Comparison of the results obtained in Refinery No. 2 with those obtained in Refinery No. 1 will show that, with one exception, about the same percentages of soap were found in the oil samples taken at corresponding points, and that a single stage of waterwashing effected about the same removal. This would seem to indicate that the values found are those to be expected in normal commercial refining practice using the continuous centrifugal refining system and employing sodium hydroxide as the neutralizing agent.

Following the experiments yielding the results shown in Table 3, a daily check was kept for several days on the refined oils produced; typical results are shown in Table 4.

TABLE 4.

Day to Day Variations in Soap Content of Refined Oil.

Day	Type Crude Oil	Sample From	% Soap
1st	Prime CSO	Primaries	0.282
	Prime CSO	Secondaries	0.032
2nd	Prime CSO	Primaries	0.067
	Prime CSO	Secondaries	0.012
3rd	Off CSO	Primaries	0.065
	Off CSO	Secondaries	0.010
4th	Soybean	Primaries	0.207
	Soybean	Secondaries	0.025

In general, these data simply serve to confirm those shown in Table 3 and to give a broader view of the variations which may be expected to occur.

Removal of Soap with Bleaching Clay or a Filter Aid

In Table 3 values are given for the soap contents of oils after bleaching in the laboratory with 6% of A.O.C.S. official fuller's earth. However, a 6% bleach is a somewhat more drastic treatment than is usually applied in commercial practice, and it seemed of interest to determine what degree of soap removal could be obtained in the laboratory by a mild bleaching treatment. In order to check this point a sample of refined but unwashed soybean oil with a high soap content was bleached in the laboratory with 2% of a natural bleaching clay. The results are shown in Table 5, along with results of analyses made on samples of commercially bleached oil, taken before and after filtering.

TABLE 5.

Effect of Bleaching on Soap Content of Refined Oils.

Sample	% Soap Found		
	Refined Oil	After Bleaching	
		Laboratory 2% Earth Used	Plant 1% Earth Used
Soybean oil 1	0.183	0.003	....
Cottonseed oil 2	0.049	....	0.008
Cottonseed oil 3	0..048	....	0.004

Note: Soybean oil No. 1 was freshly refined from crude oil, while cottonseed oil samples 2 and 3 were from storage tanks in which they had stood, refined, for several months.

It may be seen that bleaching with only 2% of earth in the laboratory reduced the soap content of an unwashed soybean oil from 0.183% to 0.003% so it would seem that bleaching removes the bulk of the soap present in refined oils even when the concentration is quite high. In the case of the two results obtained on commercially bleached oil, one showed fairly good soap removal while the other was not so good. Since complete data is not available as to the procedures used in these plant bleaches, no reason for the difference can be advanced but it is possible that in the case of Sample No. 2 sampling was improperly done.

The results bring up the question of whether bleaching earth removes soap from refined oil by its adsorptive powers or whether it is simply a matter of removal of colloidal soap particles by super filtration. To check this point a lot of refined soybean oil was treated in the plant with a filter aid and filtered. The oil used had by analysis a normal soap content of

0.025% before filtering. Filtering, with a filter aid only, reduced the concentration to 0.005%, or to just about as great an extent as bleaching would have.

Effect of Soap on the Bleachability of Oil

Although bleaching seems to remove most of the soap present in refined oil, even when its concentration is high, there still remains the possibility that at bleaching temperatures some damage may be done by the soap before it is removed. It seems possible that soap, being a well known catalyst in many reactions, might catalyze, or enter into, a reaction between the coloring matter and other non-glyceride substances present in the oil to produce new color bodies, more difficult to remove than those originally present. This would account for the opinion, held by many practical men in the industry, that a soapy oil is more difficult to bleach than a soap-free oil. Since there was available, as a result of the work reported in Table 4, a number of duplicate samples in which the oil was identical except as to soap content, it was decided to check this point.

Accordingly, bleaches were run in the laboratory on four sets of duplicates representing refined oils produced from different types and grades of crude oils. In each case the only difference between the oil in the two samples was the percentage of soap it contained, one sample having at least five times as great a concentration as the other. The samples having the high concentrations of soap contained a good deal more of this impurity than would usually be encountered in commercial bleaching, but samples high in soap were purposely selected to exaggerate any difference that might occur. The results of these tests appear in Table 6.

TABLE 6.

Effect of Soap in Refined Oil on the Color of Bleached Oil Produced Therefrom.

Sample	% Soap	Bleached Oil Color
Refined CSO No. 1, Table 4	0.240	2.0 Red
Washed and Dried	0.032	2.0 Red
Refined CSO No. 2, Table 4	0.067	2.0 Red
Washed and Dried	0.012	2.0 Red
Refined CSO No. 3, Table 4	0.065	7.4 Red
Washed and Dried	0.010	7.4 Red
Refined SBO No. 4, Table 4	0.176	2.9 Red
Washed and Dried	0.025	2.9 Red

Note: Bleached by old Official Method using Official Earth.

It may be seen that, as far as the Lovibond color reading is concerned, the presence of excessive amounts of soap in refined oils seemed to have no effect whatsoever on bleaching. This was true whether the bleached oils were read separately or compared to each other in the Wesson tintometer. However, if the oils were compared under conditions which permitted the reflected as well as transmitted light to be observed, a difference was immediately apparent. By holding up color tubes of the oils in front of a window and viewing them from the side it was possible in every case to pick the samples which had contained the high concentration of soap. The difference between the two is best described by saying that the oils bleached in the presence of excessive soap had a brownish cast. In view of these results it would seem that the opinion that soapy oils are necessarily hard to bleach is not well founded. However, it must be remembered that oils are normally seen under conditions where the reflected as well as the transmitted light plays a part, so that the difference in appearance noted above seems significant.

Summary

Samples of commercially refined cottonseed and soybean oils, from various points in the centrifugal sodium hydroxide refining process, were analyzed for residual soap content. The results indicate that the soap content of refined cottonseed oil, as it comes from the first stage of centrifugal separation, may vary anywhere from 0.038% to 0.672%. Soybean oil seems to be somewhat more consistent, running 0.183% to 0.207%. A single stage of waterwashing reduced the soap content of these oils to 0.03% or less and bleaching in the laboratory further reduced this concentration to below 0.005%.

Of the two samples of commercially bleached oil examined, one contained 0.004% soap and the other 0.008%. Treatment on a plant scale with a filter aid only, followed by filtration, reduced the soap content of a normal, single waterwashed, refined soybean oil about as much as bleaching would have. The presence of sodium soap in refined oil, even up to 0.240%, did not effect the color of the bleached oil produced therefrom, insofar as the Lovibond reading in the Wesson tintometer was concerned. However, the appearance of the oil bleached in the presence of excessive soap was different when the samples were viewed in reflected as well as transmitted light.

Acknowledgments

The writer wishes to express his appreciation to Mr. E. D. Gile for suggestions and assistance in obtaining the samples on which most of this work was done, to Miss Elizabeth Gulino for arranging the tables, and to the Cudahy Packing Company for permission to use information obtained in their laboratory.

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