orange as indicator. Results are satisfactory, but end-point detection is difficult, especially for highly colored oils. Another method developed here depends upon the determination of water content of the oil-soapstock mixture before centrifugation by a toluene distillation following the Dean-Stark technique. A knowledge of the water content, *i.e.*, the concentration of the alkali in the reagent permits the calculation of the proportioning of alkali since water is introduced only as the known percentage of alkali solution. It is further assumed that the crude oil is normal in respect to moisture content, which is usually about 0.1%. Though reliable, the method is necessarily slow since the distillation requires about two to three hours. So long a delay between sampling and the results of analysis in the check of a flowing system is of course objectionable and impractical because the information, when made available, is "obsolete" and may no longer be applicable.

A method of analysis has been developed for the determination of free and combined alkali in samples of the flowing oil-alkali mixture. Depending upon a direct potentiometric titration with sulphuric acid, the procedure is rapid and accurate for oils of varying free fatty acid content.

It was found that oil-alkali samples, when diluted sufficiently with water (1:4) and well stirred, can be rapidly titrated. A pH meter and the conventional glass electrode-calomel electrode assembly are satisfactory. In these experiments a Beckman Laboratory Model and an Industrial Model pH meter and the Beckman electrodes were used.

Procedure

A sample of approximately 50 g. of the oil-alkali mixture, weighed to the nearest tenth of a gram, is collected in a previously weighed 400-ml. beaker or jar. To avoid settling problems which would arise with the additional transfer it is advisable to use the sampling container as the titration vessel. Add 200 ml. of water, introduce a motor-driven stirrer (about 1,800 r.p.m.) and the glass-calomel electrode assembly. Stir one minute and proceed to titrate with 0.5 N sulphuric acid. The rate of addition of the acid should be adjusted so that the pH drops smoothly to about 5. The acid may then be added in 0.5 ml. or smaller increments until the pH remains at 4 or below for one minute. Probably because of adsorption of soap on the precipitated gums there is a tendency for the pH to drop to about 4 and drift up again to above 5 when within a few ml. of the end-point. Any error from this source is avoided by taking the end-point after a one-minute wait. The entire titration should require no more than eight to 10 min.

TABLE I
pH Titration of Mixtures of Crude Oil and Alkali Solution.
Weight of Crude Oil—50.0 g.

No.	% F.F.A.	Ml. acid used for titration, 0.5058 N	% alkali added — 15% Na_2CO_3 sol.	% alkali found calculated as 15% Na_2CO_3 sol.
			%	%
1	1	13.0	4.6	4.6
2	1	13.4	4.6	4.8
3	1	13.5	4.6	4.8
4	2	13.4	4.6	4.8
5	3	13.4	4.6	4.8
6	4	13.4	4.6	4.8
7	1	19.0	6.9	6.8
8	2	19.6	6.9	7.0
9	3	19.6	6.9	7.0
10	4	19.4	6.9	6.9
			11% NaOH sol.	11% NaOH sol.
11	1	18.2	6.7	6.7
12	1	18.2	6.7	6.7

The method was tested, using a crude cottonseed oil containing 1% free fatty acid to which up to 6% stearic acid had been added. Oil-alkali mixtures of various proportions were analyzed, utilizing 15% soda ash, 11% sodium hydroxide, and 14% ammonia solutions. Results as shown in Table I were excellent for both soda ash and sodium hydroxide. The method is accurate and reproducible. The figures in the last two columns of the table represent the percentage of 15% soda ash or 11% sodium hydroxide in the oil-alkali mixture. Blanks on representative 50-g. samples of crude fatty oils were between 0.1 to 0.2 ml. of the standard acid. For purposes of checking the proportioner no blank correction will normally be required.

Ammonia analyses yielded erratic results. However the strong odor of ammonia from hot oil-alkali mixtures would point to serious losses of ammonia in the sampling process. Before the method could be applied satisfactorily to ammonia-oil mixtures, closed container sampling and treatment with excess acid and back titration with sodium hydroxide would be indicated.

Summary

A method has been developed for the determination of soda ash and sodium hydroxide in vegetable oil-alkali mixtures as a check on proportioning equipment feeding oil and alkali. The method depends upon the potentiometric titration in one step of free alkali and soap, using a pH meter and the glass electrode-calomel electrode assembly. The analysis is sufficiently rapid to serve as a convenient control in a continuous refining process.

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[Received May 21, 1956]

Novel Method for Refining Soybean Oil

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THE USUAL PROCESSING of crude soybean oil to edible grade oil consists of degumming, alkali-refining, bleaching, winterizing, and deodorizing. Degumming by addition of a small amount of water to the crude oil has assumed greater prominence in the last decade because of increased demand for lecithin, which is obtained from the gums. Before this was the case, the bulk of crude soybean oil was alkali-refined without prior degumming. It is the object of this paper to describe the results of studies on refining crude soybean oil by a degumming procedure which allows further processing without alkali-refining.

The standard degumming procedure consists in adding from 1 to 3% of water to the oil at a temperature from 60 to 80°C. with good agitation, and separating the oil from the water phase by centrifuging. Degummed oil produced by this method contains usually a small amount of "break" (9), which makes it unacceptable for many industrial uses. Oil containing traces of break darkens on heating and is therefore not suitable for deodorization. This last trace of break material and the bulk of the free fatty acids are therefore removed by refining with alkali. Various modifications for degumming oils have been proposed. The addition of strong mineral acids to the crude oil or to the water used for degumming (2) has been suggested, but this method has the disadvantage that lecithin darkens on drying and the oils may also be damaged. Organic acids such as formic, acetic, and oxalic have been proposed as degumming agents (4, 5), and halogenated organic acids (7) as well as pH control (3) have also been mentioned. Only acids volatile enough to allow their removal on drying the wet gums can be considered if the lecithin is to be freed from these acids without additional processing steps. Steam-refining to remove residual break and color has also been described (6).

It has now been found that by treating crude soybean oil with small amounts of an organic acid anhydride before or during the degumming process, a break-free oil can be obtained. That this result is not entirely due to lowering of the pH was shown by comparing the effect of various acids, *i.e.*, acetic, propionic, succinic, and maleic with the anhydrides of these acids. The minimum amounts of anhydride required to obtain break-free oils are considerably smaller than the stoichiometric equivalents of the corresponding acids needed to achieve them. For complete removal of break, using organic acids, a temperature of 40°C. or below is required for the degumming, but the use of anhydrides allows operating temperatures close to 100°C. It was also found that anhydride treatment gives oils which can be bleached more easily than oils obtained by acid degumming. The use of acetic anhydride offers the greatest practical advantages because of low price, availability, and ease of removal.

The anhydride degummed soybean oils, after washing and drying, can be used for industrial applications where break-free soybean oils, having a free fatty acid content in the range of 0.2–0.7%, can be used. The break-free oil can be bleached by conventional bleaching procedures, winterized, and deodorized to give edible soybean oil of good flavor and stability. A deodorizer designed for collection of the distillate allows recovery of fatty acids, sterols, and tocopherols. The fatty acids in anhydride degummed break-free oils are removed by deodorization to the same level as by deodorizing alkali-refined oils.

The wet gums contain small amounts of acetic acid formed by hydrolysis of the anhydride used for degumming. The acetic acid is removed on drying at reduced pressure, and the resulting lecithin is substantially equal to lecithin obtained on water-degumming.

The anhydride degumming process, by allowing elimination of alkali-refining, gives no soap stock by-products. Thus acidulation of soap stock and disposal of crude fatty acids and acid liquor become unnecessary. The deodorizer distillate offers a by-product of more value than soap stock.

Over-all processing losses and costs of the anhydride process compare favorably with the two-step procedure of degumming and alkali-refining. More extensive studies on plant scale are required to obtain reliable quantitative data applicable to large-scale operations.

Degumming by adding small amounts of anhydride before treating with water is particularly applicable to crude oils possessing no or only small amounts of color bodies requiring alkali-refining for their removal. Thus soybean and peanut oil can be processed by this method to give oils of a color similar to that obtained by alkali-refining. Cottonseed and corn oil however require some treatment for color removal before they are comparable in color to oils processed by alkali-refining.

Experimental Procedure

Description of a Typical Degumming Procedure, Using Acetic Anhydride. To crude soybean oil (1,000 g.) containing 0.605% of free fatty acids, heated to 60°C., is added, with stirring, 1 g. of acetic anhydride. After 15 min. 15 ml. of water are added, and stirring is continued for 30 min. The aqueous layer is separated from the oil by centrifuging. The oil is washed with 100 g. of water. Phosporous analysis on 100-mg. samples was carried out by the colorimetric procedure of Allen (1) after wet-ashing the oil with nitric-perchloric acid. The crude oil contained 750 mcg. P/g.; a sample of oil obtained after degumming with 1.5% water, followed by a water-wash, contained 100 mcg. P/g. Oils treated with acetic anhydride prior to degumming contained, after washing with water, only 2 to 5 mcg. P/g. when anhydride in amount of 0.1 to 1.0% of the weight of oil was used.

Comparing Various Organic Acids with Their Anhydrides. The minimum amount of anhydride required to give a break-free oil was shown to be considerably smaller than the amount of the corresponding acid needed to produce a break-free oil. Table I gives minima of acids; in some cases less than 0.1% anhydride was sufficient to give break-free oils. The heat-bleach properties (heating quickly to 600°F. and reading on the Gardner scale after cooling) are considerably better when anhydrides are used instead of acids. The temperature range for carrying out phase separation is narrower in case acids are used. Break-free oils were obtained by centrifuging at temperatures up to 90°C. when anhydride was used, but in the case of acid addition it was difficult, if at all possible, to obtain break-free oils when centrifuged above 40°C.

TABLE I

Break-free Oils Obtained by Treating Crude With Various Anhydrides and Acids and Separating at 40°C.; 1.5% Water Used

	%	Heat bleach color Gardner scale
Maleic Anhydride	0.1	4
Maleic Acid	0.3	7 (off)[a]
Propionic Anhydride	0.1	4
Propionic Acid	0.3	7 (off)
Succinic Anhydride	0.1	3
Succinic Acid	0.3	6 (off)
Acetic Anhydride	0.1	4
Acetic Acid	0.3	7 (off)

[a] "Off": a "brownish" cast develops, and the oils do not match the Gardner color standards.

Further Processing of the Oil. The degummed oil from the anhydride process contains some acetic anhydride and acetic acid, which are removed by washing with 10% of water at 60–70°C. The washed and dried oil can be used as industrial oil or can be bleached by the conventional procedure to give a light-colored, break-free oil. The fatty acid content of this oil varies according to the free fatty acid content of the crude oil, usually within the range of 0.2–0.7%. Color and heat-bleach color are comparable to those of alkali-refined oils. Deodorization was carried out in a laboratory deodorizer similar to the one described by Schwab and Dutton (10) at a temperature of 245°C. at 1–2 mm./Hg, using about 8% of steam (based on the oil) over a two-hour deodorization time. The free fatty acids distill rapidly when the temperature reaches 215°C. The finished oil has a free fatty acid content of 0.005 to 0.01%.

Comparison of Flavors of Alkali Refined with Anhydride Degummed Oils. The flavor characteristics of anhydride-water degummed and deodorized oils were compared to those of alkali-refined and deodorized oils prepared from the same crude. To prepare the alkali-refined oils the crude was degummed, with 1.5% water, dried, alkali-refined using 14 Be′ caustic, washed and bleached with 1% active clay and 0.25% carbon. The anhydride-water degummed oils were prepared as described above. The degummed break-free oil was washed, dried, and bleached with 1.0% active clay and 0.25% carbon. All samples were deodorized for 2 hrs. at 245°C. at a pressure of 1–2 mm/Hg.

Shelf-life tests were made by storing the oils in 8-oz. clear glass bottles at room temperature in diffused light. After exposure for the desired time the samples were frozen until evaluation. The samples were submitted in pairs and rated by a panel, using rating values similar to the one described (8). The ratings and 95% confidence limits are given in Table II.

TABLE II

	Taste panel ratings Exposure			
	0 days	7 days	14 days	21 days
1. Alkali-refined	8 ± .33	8 ± 1.02	7 ± .12	5 ± .80
Anhydride degummed	9 ± .87	7 ± .87	7 ± 1.32	6 ± .60
2. Alkali-refined	8 ± .33	7 ± 1.02	6 ± 1.02	3 ± 1.2
Anhydride degummed	9 ± .58	7 ± .58	6 ± .40	5 ± 2.0
3. Alkali-refined	9 ± .66	6 ± .51	4 ± .51	5 ± 1.2
Anhydride degummed	7.5 ± .72	6.5 ± .87	6 ± 1.56	6 ± 1.3

Refining Loss Comparisons. Crude extracted soybean oil containing 0.50% free fatty acids gave on degumming with 1.5% water at 60°C. a loss of 2.9% by weight. Alkali-refining, using an excess of 0.15% of 14 Be′ sodium hydroxide (calculated on the weight of oil), gave 1.8% refining loss, and deodorization gave an additional 0.4% loss; thus the total loss amounted to 5.1%. On degumming the same stock crude, using 0.1% acetic anhydride and 1.5% water, a loss of 3.0% was encountered. Deodorization gave a loss of 0.6%; thus the total loss of 3.6% is only 70% of the loss encountered by alkali-refining. Washing and bleaching losses are the same for either process. Loss differences by the two processes are somewhat influenced by the free fatty acids content of the original oil.

Properties of the Deodorizer Distillate. Deodorizer distillate was collected in a dry ice trap. It was dissolved in hot neutral ethanol and analyzed for free fatty acids by titrating aliquots of the alcohol solutions. The residue obtained on evaporation of the alcohol was analyzed; Table III gives the analytical results. In run 4 and 8 the amount of sparge steam used was 6% of the oil, in all others 3%.

TABLE III

Composition of Deodorizer Distillate

	% F.F.A. before deod.	% Total deod. loss	% Unsap.	% F.F.A.	% Neutral oil	% Tocopherols
1. Anhydride Deg.	0.22	0.66	36.0	47.0	17.0	4.2
2. Anhydride Deg.	0.22	0.64	36.0	50.0	14.0	4.2
3. Anhydride Deg.	0.17	0.60	41.0	45.0	14.0	4.6
4. Anhydride Deg.	0.17	0.86	40.0	39.5	19.5	5.1
5. Alkali-Refined	0.05	0.42	40.0	43.0	17.0	3.1
6. Alkali-Refined	0.05	0.41	40.0	46.0	14.0	3.1
7. Alkali-Refined	0.04	0.39	48.0	38.5	13.5	5.8
8. Alkali-Refined	0.04	0.71	46.0	31.5	22.5	5.1

Properties of the Lecithin. The wet gums from the anhydride-water degumming contains some acetic acid and possibly traces of anhydride, which are removed on drying under vacuum. The resulting lecithin has properties similar to soybean lecithin prepared by the usual procedure.

Degumming Other Vegetable Oils by Anhydride Addition. Peanut oil could be processed in the same way as soybean oil. When cottonseed or corn oil were subjected to the process, a dark-colored, break-free oil resulted, which could not be bleached satisfactorily by clays and carbons.

Summary

A process for making break-free soybean oil is described in which crude oil is treated with a small amount of an organic acid anhydride and then degummed by water addition and phase separation. The break-free oil can be used for industrial applications or processed to an edible grade of oil without alkali-refining. Laboratory data are presented, comparing quality of edible oils, processing losses, and composition of deodorizer distillates of alkali-refined soybean oils with oils prepared by the degumming process described in this paper.

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[Received April 23, 1956]