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METHOD OF REFINING OILS WITH POLYCARBOXYLIC ACIDS

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This invention relates to the refining of glyceride oils and fats containing free fatty acids by treatment thereof with aqueous alkali solutions, and more particularly to a continuous process of alkali-refining such glyceride oils and fats in the presence of a small amount of an aliphatic polycarboxylic acid, such as citric acid, to reduce refining losses.

Alkali-refining is a well-known method of removing free fatty acids from glyceride oils and fats by converting them into soaps. As practiced commercially, alkali-refining is carried out either by a batch process or a continuous process. In the batch process, measured quantities of oil are individually mixed with the amounts of aqueous alkali necessary to neutralize the free fatty acids, after which the oil and soap are permitted to stratify by gravity and then separated. In the continuous process, streams of oil and aqueous alkali are continuously mixed in proper proportions, and the soapstock is then separated from the refined oil centrifugally. These are conventional processes, and further details thereof are found in "Industrial Oils and Fatty Products" by Alton E. Bailey, Interscience Publishers, Inc., New York, New York (1945), at pages 502 to 512.

A serious problem in alkali-refining has been the loss of neutral oil, a large proportion of which results from the emulsification or occlusion of neutral oil in the soapstock, together with some saponification. These losses are relatively high in batch processes, but have been reduced substantially in the continuous process. Nevertheless, because of the tremendous quantities of oil refined by the process these losses represent a considerable item. Moreover, they are subject to considerable variation, depending upon the oil and upon the amount of naturally occurring surface-active substances therein.

Heretofore it has been proposed to add various materials to the refining mixture in order to reduce the refining losses. Tetrasodium pyrophosphate, for example, has been proposed as an additive for use in the batch process and in that process has been successful in reducing refining losses. Since, however, refining losses in the continuous process already are very low, such additives have not been suggested for use in such a process, for it would not be expected that by

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their use a further reduction in refining losses could be accomplished in the continuous type process.

Accordingly, it is an object of this invention to provide an improved process of continuously alkali-refining glyceride oils and fats containing free fatty acids in which losses of oil during refining are held at a minimum.

It is a further object to provide a continuous process wherein alkali-refining losses are reduced to a more uniformly low level, despite the variations in the oils referred to above.

These objects are achieved by carrying out the continuous alkali-refining process in the presence of a polycarboxylic acid, such as citric acid. The acid may be incorporated with either the oil or the aqueous alkali solution prior to mixing, or it may be blended with the refining mixture during or after its formation. The amount of polycarboxylic acid required is very small.

The continuous process of alkali-refining glyceride oils and fats is well known in the art and the conventional steps thereof form per se no part of the present invention.

A continuous alkali-refining process, employing saponifying alkali, and to which the invention is particularly applicable, is the Sharples centrifugal process, details of which are set forth at pp. 510 and 511 of Bailey. In this process, streams of glyceride oils and fats containing free fatty acids and of aqueous alkali solution are fed continuously through proportioning pumps and blended in a series of one or more mixers wherein the oil and alkali are thoroughly mixed. The soapstock and refined oil are separated in high speed centrifuges. In order to facilitate breaking the emulsion of soapstock and oil, it is preferred that the mixture be hot when centrifuged. This heating may be accomplished at least in part by the injection of steam at any point in the process, such as, for example, in the unrefined oil. After centrifuging, the refined oil may be washed once or twice with about 10% of its own weight of hot water to separate entrained soapstock therefrom.

This process has been subjected to considerable modification since it was first introduced, and there are numerous patents describing variations of the process. The present invention is equally applicable to these processes, as well as other

continuous alkali-refining processes, whether saponifying or nonsaponifying alkalis are employed.

The polycarboxylic acid for use in the process of the invention may be regarded as branched or straight chain aliphatic hydrocarbons, preferably having two to five carbon atoms, and substituted at several or all of the carbon atoms thereof with the carboxylic acid group or the equivalent thereof, i. e., —COOH, and anhydrides thereof, and preferably in addition substituted at one or more of said carbon atoms with hydroxyl groups. Satisfactory carboxylic acids, for example, are citric, tartaric, maleic, malic, and oxalic acids. These acids give exceptionally low refining losses when applied in the continuous refining method as described.

Use of mixtures of polycarboxylic acids and of anhydrides thereof, are included in the invention. The term "polycarboxylic acid" as used herein will be understood to refer to the acid in its normal and anhydride forms, but is not inclusive of the salts thereof.

The required amount of alkali as NaOH is calculated by the formula:

$$\frac{\text{f. f. a.}}{5.2}+0.54 \text{ mol}$$

This may be varied somewhat depending on the particular oil as is well known in the art. For example, extracted soybean oils require slightly less than expeller soybean oils.

Any alkali metal hydroxide or carbonate may be employed in forming the aqueous alkali-refining solution, but sodium hydroxide is generally used commercially.

Whether the additive is incorporated in the crude oil or in the aqueous alkali or blended therewith during or after formation of the refining mixture is largely a matter of choice. However, it is preferred to add the additive in the form of an aqueous solution, generally from a 5% to saturated solution.

Alkali-refining processes in which the components of the refining mixture may be blended at room temperature, i. e., at about 65–75° F., yield a satisfactory product. Nevertheless, in the commercial process it is often preferred to introduce from 1 to 2% of steam into the mixture of unrefined oil and additive, before mixing with the alkali.

The following examples illustrate the application of the polycarboxylic acids of the invention in the Sharples centrifugal continuous alkali-refining process.

Example 1

A nondegummed expeller soybean oil containing 0.55% free fatty acid was refined with caustic lye by a continuous refining method using a Sharples centrifugal machine, and injecting 1½% steam as described above, with the following results:

	Percent Refining Loss	Percent Reduction in Loss	Percent Refining [1] Efficiency
Control	4.53		97.99
With 0.06% Citric Acid (10% solution)	4.22	0.31	98.31
With 0.06% Tartaric Acid (10% solution)	4.12	0.41	98.41

[1] The neutral oil recovered divided by the neutral oil in the unrefined stock expressed in percentage.

Example 2

Crude cottonseed oil containing 1% free fatty acids was refined by the same method, using tartaric acid as an additive. In runs 1*a* and 2*a* the additive was added to the crude oil in a 10% water solution, and in runs 1*b* and 2*b* it was dissolved in a minimum amount of water and that solution mixed with the aqueous alkali. The results were as follows:

Run No.	Percent Refining Loss	Percent Reduction in Loss	Percent Refining Efficiency
1. Control (mixing oil and lye at 75° F.)	4.89		97.02
1*a*. 0.04% Tartaric Acid in Oil	3.89	1.0	98.04
1*b*. 0.04% Tartaric Acid in Lye	4.03	0.86	97.92
2. Control (1½% Steam Injected)	4.62		97.31
2*a*. 0.04% Tartaric Acid in Oil	3.91	0.71	98.02
2*b*. 0.04% Tartaric Acid in Lye	3.83	0.79	98.12

It will be noted that there was little difference whether the additive was added to the oil or to the alkali solution.

Example 3

Crude cottonseed oil containing 0.7% free fatty acids was treated by the same process, using aqueous alkali solution and 0.4% citric acid (10% solution) injecting 1½% steam, with the following results:

	Percent Refining Loss	Percent Reduction in Loss	Percent Refining Efficiency
Control	3.00		98.05
With 0.4% Citric Acid	2.64	0.36	98.41
Do	2.65	0.35	98.40

Example 4

Nondegummed expeller soybean oil containing 0.55% free fatty acids was refined with sodium hydroxide solution using the Sharples continuous method with 1½% steam injected. The refining loss was 4.2%, and the refining efficiency was 97.55%. When this process was repeated with a second portion of the same oil, adding 0.04% citric acid to the oil before blending, the refining loss was 3.98%, a reduction of 0.22%, and the refining efficiency was increased to 97.77%.

In the above examples, in some instances, the improvement may not be regarded as marked, viewed merely as an improvement in percentage but it is significant industrially. This is especially so when the process is applied to many thousands of tank cars of oil, and where a small improvement in percentage gives marked results in the total saving of oil. This is also especially true because the process has been highly developed and perfected and the room for further improvement is small.

Example 5

2000 gram batches of extracted soybean oils and 20° Bé. (14.36%) sodium hydroxide solution with and without 0.1% tartaric acid were agitated at room temperature for 20 minutes and then continuously introduced into a laboratory Sharples continuous centrifuge. Each batch took about 30 minutes to pass through the machine. The losses were then calculated from the weight of foots separated and the per cent re-

fining efficiency was determined as explained heretofore. The following results were obtained:

Run No.	Percent Refining Loss	Reduction in Loss in Percent	Percent Refining Efficiency
1 Control (no Tartaric Acid)	1.50		98.99
1 With 0.1% Tartaric Acid	0.70	0.80	99.80
2 Control (no Tartaric Acid)	1.40		99.09
2 With 0.1% Tartaric Acid	0.90	0.50	99.60
3 Control (no Tartaric Acid)	1.0		99.59
3 With 0.1% Tartaric Acid	0.55	0.45	100.04
4 Control (no Tartaric Acid)	1.80		98.78
4 With 0.1% Tartaric Acid	0.55	1.25	100.04

It will be noted that the reduction in loss by addition of tartaric acid to the aqueous alkali solution was significant in all runs, amounting to as much as 1.25% in run No. 4.

During this work, it was observed that a faster and better break was obtained in the runs with tartaric acid containing alkali and the foots were firmer than usual.

Example 6

The process of Example 5 was repeated using extracted soybean oil. The same refining technique and amount of lye were used with each refining except that in other than the control, 0.1% of the acid listed below was added to the lye. The following results were obtained:

Acid added to Lye	Refining Loss in Percent	Difference in Loss, Percent	Percent Refining Efficiency
None	3.54		97.90
Tartaric acid	2.76	0.78	98.70
Citric acid	2.54	1.00	98.92
Oxalic acid	3.14	0.40	98.32
Malic acid	2.04	1.50	99.43

The oil refined by the process of the invention is substantially completely neutral and free of residual impurities, is of excellent quality and meets the color requirements of the art. The process of the invention is especially useful in the alkali-refining of vegetable oils used in making edible products. The oils most commonly used for this purpose are soybean oil and cottonseed oil. It may be used on other oils such as linseed oil, corn oil, sesame oil, etc., including both the degummed and the nondegummed oils. Animal oils, and fish oils such as sardine, menhaden and herring oils, may also be alkali-refined in accordance with the process of the invention.

In general, the amount of the polycarboxylic acid should be sufficient to reduce the refining loss. It is economically important that small amounts can be used. Large amounts may have an adverse effect, but in any case they would not be used because of the expense. A fraction of 1%, preferably an amount in the range of 0.02 to about 0.2% by weight calculated as anhydrous based on the weight of the oil, generally is suitable, and 0.04 to 0.1% is about optimum.

The polycarboxylic acids have no deleterious effects on the normal operation of continuous alkali-refining processes, and there is no change in primary machine operation at any stage of the refining. Refined oils produced by the process wash easily, with reduced or even no foaming.

Other variations and modifications of the invention will be apparent to those skilled in the art, and the invention contemplates all such variations and modifications which come within the scope of the appended claims.

I claim:

1. In the continuous processes of alkali-refining degummed glyceride fats and oils containing free fatty acids and alkali-refining nondegummed glyceride fats and oils containing free fatty acids in which at the same time the gums are decomposed by the alkali and dissolved therein, including the steps of mixing the same with an aqueous alkali solution in an amount to neutralize the free fatty acids and decompose and dissolve the gums, if any and centrifugally separating an aqueous phase containing soapstock, gum residues, if any, and undesirable impurities from a refined oil phase, the improvement which comprises introducing at any stage in the alkali refining step a small amount up to a fraction of 1% of an aliphatic polycarboxylic acid on an anhydrous weight basis relative to the amount of oil treated to reduce the refining losses.

2. The process of claim 1 wherein the glyceride oil is an edible vegetable oil.

3. The process of claim 2 in which the oil is undegummed crude oil.

4. The process of claim 1 wherein the polycarboxylic acid is citric acid.

5. The process of claim 4 wherein the amount of citric acid is about 0.04 to 0.1%.

6. The process of claim 5 in which the acid is mixed with the oil before adding the alkali.

7. The process of claim 6 in which steam is injected before adding the alkali.

References Cited in the file of this patent

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