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PROCESS FOR ALKALI-REFINING CRUDE NATURAL OILS

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The invention herein described may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to us of any royalty thereon.

This invention relates to processes for removing color bodies from crude natural oils by refining them with an aqueous alkali.

More particularly, this invention provides an improvement in the step of bringing the aqueous alkali into contact with the color bodies. This improved contact results in a more complete conversion of the color bodies into removable substances and in a reduction of the undesirable side reactions inherent in alkali refining processes as heretofore practiced.

The seemingly simple process of alkali-refining a natural oil, i. e., contacting the oil with an aqueous alkaline solution and separating the oil from the solution and oil-insoluble substances, involves a complicated interaction of chemical and physical phenomena. When contacted with the alkali, the fatty acids present form oil-insoluble soaps and pass into the aqueous phase where most of them remain suspended, rather than dissolved, due to the "salting out" effect of the high ion concentration of the aqueous phase. The aqueous phase tends to become an enormous number of minute particles of a soft gelatinous nature. At the same time the phosphatides, proteins or protein fragments, and gums are hydrated and forced out of solution or at least into coarse suspension in the oil. At the same time a portion of the oil is saponified by the alkali into soaps and glycerol.

Since the particles of the aqueous phase coalesce, and since during their growth or coalescence the color bodies along with other impurities in the oil phase are isolated from the oil phase and adsorbed into the water phase, refining procedures have heretofore been directed toward quickly mixing the aqueous alkali with the oil to form an emulsion, and, from that point on, avoiding undue agitation while increasing the rate of growth of the particles of the aqueous phase. For example in a typical commercial refining operation in which crude cottonseed oil is refined with aqueous sodium hydroxide in large open kettles, the kettles have a capacity of 60,000 pounds of oil each, are cylindrical in shape, and have a conical bottom. Each kettle is provided with a steam coil for heating the charge and an agitator for mixing. The oil is charged to the kettle at a temperature of about 70° F. After all trapped air bubbles have escaped from the oil,

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the agitator is set for "rapid mixing," which means that the agitator is made to revolve at a rate of 30 to 35 revolutions per minute. The correct amount of lye is added, and a milky emulsion forms immediately. As mixing continues small particles of soapstock appear and commence to grow in size. After a mixing period which may range anywhere between 10 and 45 minutes, the agitator is slowed to 8 to 10 revolutions per minute, steam is passed into the heating coil, and the temperature is raised to the point where relatively large flakes of soft soap form (about 140° F.). At this point heating and agitation is discontinued, and the mixture is allowed to separate into an upper layer of clear, refined oil and a lower layer of semi-solid soapstock or foots.

While numerous improvements in the mixing of aqueous alkali with the oil have been proposed, and while better results in re-refining processes (where the oil treated contains practically no free fatty acids and emulsifies more slowly) are known to be obtained when high rates of agitation are used; the improvements in crude oil refining have all been directed toward rapidly mixing the aqueous alkali with the oil so that the naturally resulting milky-appearing emulsion is quickly formed and avoiding, as far as is practically possible, mixing further, so as to allow the rapid breaking of the emulsion due to the growth of the particles of the aqueous phase. Since crude natural oil-aqueous alkali mixtures rapidly form a relatively stable emulsion of a milk-like consistency, and since the removal of nonglyceride components (fatty acids, etc.) with the least possible loss of glyceride components (oil) is a principal object of the refining; it was heretofore believed that since the soap and other surface active agents are good emulsifying agents, as soon as the milky emulsion was formed, any further vigorous agitation defeated an objective of the refining process by mechanically forcing more and more oil to remain as fine droplets in the aqueous phase. Such additional agitation is avoided even in continuous processes where for example, proportioned oil and alkali streams at from about 75 to 85° F. are combined in a mixing chamber where the milky emulsion forms, quickly raised to about 140° F. until the emulsion breaks and quickly separated by high speed centrifuges, with only about 3 minutes being allowed to elapse between the time the oil leaves the proportionometer until it emerges as a refined oil. It being strongly believed that longer periods of mixing merely increased refining losses due to the reten-

tion of more oil droplets in the aqueous phase and to an increased period in which saponification was occurring, the improvements proposed for such continuous process either increase the rate of mixing prior to the formation of the emulsion, or shorten the time that the phases are allowed to remain in contact with each other after the formation of the emulsion.

We have surprisingly found that, contrary to the previous teachings and beliefs regarding alkali-refining; if the aqueous alkali has an alkali concentration equivalent to a sodium hydroxide solution of greater than 10%, and if the agitation of the crude oil and aqueous alkali mixture is far greater than that heretofore employed, an actual "shearing-together" of the oil and aqueous alkali; if this agitation is continued for from 0.5 to 40 minutes, the refining process can be conducted, employing the usual apparatus and conditions for all but the mixing step, without an increase in the refining loss, but with a color reduction far above any heretofore obtained; particularly in the refining of dark crude oils containing a high percentage of color bodies which are reactive only with strong alkali.

As employed throughout the specification and claims, the term "shearing-together" refers mixing at a rate equal to or greater than the minimum rate at which we have found that a crude oil-lye mixture must be mixed in the practice of the present invention.

Recognizing that rate of agitation is very difficult to define we have devised a simple test whereby one skilled in the art can tell whether a given increase in rate of agitation of an oil-aqueous alkali mixture amounts to a mere change in degree or crosses the threshold into the realm of shearing-together the oil and aqueous alkali wherein entirely unobvious and advantageously different effects are produced. We have found that the approximately minimum rate of agitation which amounts to shearing-together is one which emulsifiies the oil-aqueous alkali mixture in a fraction of a second and which, continued at the same rate under substantially isothermal conditions after the heat due to the reaction of the aqueous alkali with the oil has been dissipated, increases the temperature of the mixture at the rate of at least 0.5° F. per minute. In general, rates so increasing the temperature of the mixture of from 0.5 to 3° F. have been found to be sufficient in the practice of the present invention.

The shearing-together of the oil-aqueous alkali mixture can be accomplished in any mixing apparatus capable of providing the above rate of agitation. The agitation need not be continuous in the sense of a paddle continuously turning in a liquid but can be intermittent (for example as in the forcing and reforcing of the mixture through very small or sharply curving passages) so long as the overall agitation causes the temperature to rise at the above rate. The stirring of an oil-aqueous alkali mixture in a vessel having sufficient baffles to insure a thorough mixing, with an agitator having 18 inches of cutting edges per pound of mixture at a rate at which the cutting edges of the agitator pass through the mixture at about 800 feet or more per minute has been found to accomplish the shearing-together of the oil and aqueous alkali.

While increasing the rate of agitation of the oil-aqueous alkali mixture to the point of shearing-together the components makes a marked improvement in the amount of color removal in the refining process, further increases in the rate of agitation have been found to produce but little effect upon the color removal.

The mere application of a substantially instantaneous shearing-together agitating action upon the oil-aqueous alkali mixture followed by an immediate separation of the aqueous and oil phases does not accomplish the advantages of the present process. Particularly in the early stages, the length of time for which the oil-aqueous alkali mixture is sheared-together effects the color of the refined oil. We have found that in refining crude cottonseed oil in accordance with the process of our invention, at least one-half minute is required. However, the improvement in color with increased shearing-together time becomes decreasingly small as the time becomes longer, and in general, the improvements obtained by shearing-together for more than about 40 minutes are relatively small. We have found the preferred shearing-together times to be from about 1 to 15 minutes with the exact time to be used for a particular oil varying with the character of the oil and the economics of the application of longer times.

The temperature at which the oil-aqueous alkali mixture is sheared-together should be as low as is economically feasible (the power requirements increase rapidly with the increase in viscosity). We have found that the color of the refined oil from crude cottonseed oil increases rapidly as the temperature at which the shearing-together operation is increased beyond 160° F. In general this operation is preferably conducted at a temperature of from about 60 to 120° F. with the exact temperature best suited for a particular oil varying with the characteristics of the oil and the economics of using the lowest temperature.

The process of this invention has been found to vastly improve the alkali refining of glyceridic mixtures, such as those of the natural oils, containing color bodies which react with strong alkali to form oil-insoluble substances. Crude cottonseed oil is a particularly preferred natural oil to be refined by the process of this invention. In this connection, the step of shearing-together the oil and aqueous alkali in accordance with this invention provides the entirely unobvious and highly advantageous result of forming an aqueous phase-oil phase mixture from which the fatty acids in the form of soaps can be readily separated from the oil without necessary additional treatments or careful control to insure the breaking of the emulsion into two separable phases. This result is particularly surprising since while mixing a comparable aqueous alkali with a refined cottonseed oil at a comparable rate under comparable conditions provides an improvement in the amount of color so removed as compared to that removed by a refining process employing a conventional mixing step; in order to remove as much soapstock as would be removed in the conventional process, it is necessary to add water and slowly and carefully stir the mixture produced by the rapid mixing of the refined oil and aqueous alkali. In contrast, when the cottonseed oil in the crude state is sheared-together with the aqueous alkali in accordance with the process of this invention, the color removal is not only much greater than that obtainable by a conventional refining of the same oil, but the soapstock removal is as easy and as complete, and the application of special steps or

precautions is not required in removing the soapstock.

The process of this invention can suitably be conducted employing any of the readily available alkali metal hydroxides in an aqueous solution containing an amount of alkali metal equivalent to that of a 10% sodium hydroxide solution. We have found that solutions containing less than about 10% sodium hydroxide or the equivalent of lithium or potassium hydroxide remove substantially less color than those containing from about 10 to 36%. Aqueous solutions containing between about 14 and 26% sodium hydroxide are particularly preferred for employment in the present process.

As in the conventional alkali refining processes, the amount of aqueous alkali used should be sufficient to provide the stoichiometric equivalent of alkali based upon the fatty acid content of the oil and about a 0.1 to 1.0% excess. As in the conventional processes, increasing the amount of excess alkali increases the amount of color removal but also increases the amount of refining loss, and the amount of excess to be used depends upon the balance desired between most completely attainable color removal and the refining loss.

The process of the present invention can be employed in a continuous or batch-wise manner. In general, with the exception of the conditions specified above for the mixing step, it can be suitably accomplished under conventional conditions employing the various types of apparatus now commonly used.

The following examples are submitted to illustrate certain phases of the present invention in detail. However since numerous other materials and processing conditions can suitably be used, the scope of the invention is defined by the claims and is not to be construed as being limited to the particular substances, steps, or conditions recited in the examples.

EXAMPLE I

The effect of shearing-together the oil and aqueous alkali

Four samples of crude cottonseed oils obtained by conventional extraction processes from cottonseed produced in areas scattered throughout the cotton belt were refined by the official method of the American Oil Chemists' Society, Method Ca9a—41, modified only in that 20° Bé. lye was used in an amount providing a 0.5% excess of sodium hydroxide.

The following refined oil colors and refining losses were obtained in the above refining processes.

Sample	Refined oil color, Lovibond units	Refining loss, percent
1	35 yellow, 5.5 red	5.7
2	35 yellow, 5.6 red	4.4
3	35 yellow, >32 red	12.6
4	35 yellow, 24.5 red	6.2

When the same oils were refined in the same way except that the 15 minutes of "rapid agitation" specified in the official A. O. C. S. refining test was replaced by the shearing-together of the oil-aqueous alkali mixture in a baffled vessel with a dissolver type impeller operating at 1720 R. P. M. (16.8 inches of cutting edges per pound of oil with the cutting edges traveling at 1125 feet per minute), the following refined oil colors and refining losses were obtained.

Sample	Refined oil color, Lovibond units	Refining loss, percent
1	35 yellow, 5.4 red	5.7
2	35 yellow, 5.2 red	4.8
3	35 yellow, 9.5 red	14.7
4	35 yellow, 14.8 red	6.7

It is apparent that even without adapting the operating conditions to the particular oil being refined, a markedly greater (up to nearly 4 times greater) reduction in color is obtained with substantially the same refining loss by merely shearing-together, rather than simply mixing together, the oil and aqueous alkali.

EXAMPLE II

The effect of temperature

Sample 4 was refined by shearing-together (16.8 inches of cutting edges per pound of oil and the cutting edges traveling at 1125 feet per minute) for 10 minutes the crude oil and an amount of 20° Bé. sodium hydroxide providing a 0.5% excess of sodium hydroxide over that required to react with the free fatty acids. The following relationship between the temperature at which the shearing-together was performed and the Lovibond color of the refined oil was observed.

Temperature, ° C.	Color of refined oil, Lovibond red units
20	35 yellow, 10.7 red.
40	35 yellow, 12.8 red.
50	35 yellow, 15.1 red.
65	35 yellow, 17.7 red.

EXAMPLE III

The effect of alkali concentration

Sample 4 was refined by shearing-together (16.8 inches of cutting edges per pound of oil and the cutting edges traveling at 1125 feet per minute) for ten minutes the crude oil with various strengths of sodium hydroxide added in an amount providing a 0.5% excess of sodium hydroxide over that required to react with the free fatty acids. The following relationship between the strength of the sodium hydroxide solution used in the refining and the Lovibond color of the refined oil was observed.

Strength of sodium hydroxide, ° Bé.	Color of refined oil, Lovibond units
8	>32.0 red.
14	>32.0 red.
20	35 yellow, 15.1 red.
26	35 yellow, 11.6 red.
30	35 yellow, 11.3 red.

EXAMPLE IV

The effect of excess alkali

Sample 4 was refined by shearing-together (16.8 inches of cutting edges per pound of oil and the cutting edges traveling at 1125 feet per minute) for ten minutes the crude oil with amounts of 20° Bé. sodium hydroxide providing various excesses of alkali. The following relationship between excess alkali over that needed to react with

the free fatty acids and the Lovibond color of the refined oil was observed.

Excess sodium hydroxide, percent	Color of refined oil, Lovibond units
0.1	>32.0 red.
0.3	35 yellow, 22.0 red.
0.5	35 yellow, 15.1 red.
0.9	35 yellow, 12.5 red.

EXAMPLE V

The effect of time

Sample 4 was refined by shearing-together (16.8 inches of cutting edges per pound of oil and the cutting edges traveling at 1125 feet per minute) for various lengths of time the crude oil with an amount of 20° Bé. sodium hydroxide proving a 0.5% excess of sodium hydroxide. The following relationship between times of shearing-together and Lovibond color of the refined oil was observed.

Time of shearing-together, min.	Color of refined oil, Lovibond units
2.5	35 yellow, 15.1 red.
10.0	35 yellow, 15.1 red.
30.0	35 yellow, 14.7 red.
50.0	35 yellow, 13.7 red.

Having thus described our invention, we claim:

1. A process for refining a crude natural oil containing color bodies which react with a strong alkali to form oil-insoluble substances, comprising mixing the said oil with an aqueous alkali containing an amount of alkali equivalent to the amount contained in a sodium hydroxide solution containing about from 10 to 36% of sodium hydroxide, agitating the resulting mixture for about from .5 to 40 minutes at a temperature below about 160° F. in a vessel containing baffles and fitted with an agitator having 18 inches of cutting edges per pound of mixture and moving at a rate causing the cutting edges to pass through the mixture at a rate of at least 800 feet per minute so that the agitation emulsifies the mixture in a fraction of a second, and, when continued under substantially isothermal conditions after the heat due to the reaction of the oil and the aqueous alkali has been dissipated, increases the temperature of the mixture at the rate of at least 0.5° F. per minute, and separating the resulting aqueous and oil phases.

2. The process of claim 1 wherein the crude natural oil is a crude vegetable oil.

3. The process of claim 1 wherein the crude natural is crude cottonseed oil.

4. The process of claim 1 wherein the aqueous alkali is an aqueous solution containing about from 14 to 26% of sodium hydroxide.

5. A process for refining crude cottonseed oil containing color bodies which react with sodium hydroxide to form oil-insoluble substances, comprising mixing the said crude cottonseed oil with an aqueous solution containing about from 14 to 26% of sodium hydroxide, agitating the resulting mixture for about from 1 to 15 minutes at a temperature of about from 60° to 120° F. in a vessel containing baffles and fitted with an agitator having 18 inches of cutting edges per pound of mixture and moving at a rate causing the cutting edges to pass through the mixture at a rate of at least 800 feet per minute so that the agitation emulsifies the mixture in a fraction of a second, and, when continued under substantially isothermal conditions after the heat due to the reaction of the oil and the aqueous sodium hydroxide has been dissipated, increases the temperature of the mixture at the rate of at least 0.5° F. per minute, and separating the resulting aqueous and oil phases.

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