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REFINING FATS AND OILS

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This invention relates to the refining of fatty material and more particularly to the refining of crude glyceride oils to remove therefrom gums, free fatty acids and coloring matter.

The present invention is concerned with the removal of free fatty acids and gum and coloring matter from such oil by a process involving a solvent extraction step so as to produce a high quality oil while minimizing refining losses. In the most widely employed process of refining vegetable oils with strong caustic alkali solutions, a great deal of the valuable neutral oil is lost both as the result of saponification of neutral oil by the caustic solution employed and by entrainment of the oil in the foots or soapstock separated from the oil after the caustic treatment. Prior attempts to treat crude glyceride oils with a selective solvent for the fatty acids in an attempt to produce neutral or substantially neutral oils has resulted in oils having relatively high free fatty acids, poor color and also the removal of considerable amounts of the neutral oil with the fatty acids so as to result in relatively high refining losses. Any attempt to remove additional fatty acids and improve the color of the oil by alkali treatment has resulted in additional refining losses, and furthermore attempts to reduce the color of the oil by treatment with adsorbent material such as adsorbent earths after solvent treatment has been largely ineffective and resulted in the loss of considerable oil in the residual adsorbent material because of the large quantity of such material required.

An object of the present invention is to provide an improved process involving solvent treatment for refining glyceride oils and fats so as to produce a high quality oil with minimized refining losses.

Another object of the invention is to provide an improved process of refining glyceride oils and fats to remove impurities therefrom by a series of cooperating steps involving degumming and solvent treatment to produce a refined oil having low color and fatty acid content with reduced refining losses.

A further object of the invention is to provide an improved process of refining glyceride oils in which gums and substantial amounts of fatty acids are simultaneously removed from the oil by a combined degumming and solvent treatment operation.

A still further object of the invention is to provide an improved process of refining oil in which a solvent treated oil is treated to remove

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residual color and fatty acids without substantial refining losses.

In accordance with the present invention, it has been found that removal of the gums from the crude oil prior to solvent treatment results in much more effective extraction of the free fatty acids and produces an oil of relatively low color which can be easily reduced in color and fatty acid content by a mild caustic wash. The degumming operation involves precipitation of the gums with an aqueous medium which may be water or an aqueous solution of various salts which may be neutral or slightly acidic or slightly basic. Depending upon the amount of gums contained in the oil the amount of water or aqueous medium employed may range from approximately 1% to 10% but will usually range between 2% and 5%. Precipitated gums which include phosphatides, proteinaceous material, carbohydrates, resins, etc., may be separated from the body of oil by decantation, filtration or centrifugal separation, continuous centrifugal separation at temperatures ranging from approximately 90° to 140° F. depending upon the nature of the oil being preferred. This degumming operation referred to, materially reduces the color of the oil and in most cases somewhat decreases the acidity of the oil as certain of the gummy materials are acidic. If properly carried on losses of neutral oil by entrainment of the oil in the separated gums can be made very small and the resulting oil is conditioned for solvent treatment.

The solvent treatment of the present invention involves treating the oil with a solvent or solvent mixture which selectively dissolves fatty acids in preference to glycerides and the solvent employed may be any one of a large number of solvents. The solvent selected should not react with the fatty material, and examples of such solvents which can be used in the present invention are furfural and isopropyl alcohol. The solvent power of the selective solvents, including those specifically mentioned, increase with temperature and at higher temperatures substantially all of the fatty material is soluble in the solvent. As the temperature is decreased the various glycerides become progressively insoluble in the solvent depending upon the number of carbon atoms in the fatty acid radicals and the degree of unsaturation of the fatty acid radicals. The free fatty acids are more soluble than glycerides and for any given oil or oils and selective solvent a temperature is found at which the glycerides are substantially all insoluble in the solvent while the

fatty acids are substantially all soluble therein. At such temperature two phases will be formed, one a solvent phase containing the free fatty acids and the other an oil phase. These phases can be separated by decantation or centrifugal separation. In most cases the separation can be carried on at temperatures at which both phases are liquid, but in some instances at least certain of the glycerides may be in solid form. The amount of solvent employed will likewise depend upon the nature of the oil being treated and the solvent selected, but will usually range between one volume to one volume of oil being treated and ten volumes of solvent to one volume of oil. The greater the amount of solvent the more selective the separation between the fatty acids and glycerides, but in most cases effective separation can be effected with an amount of solvent ranging between two volumes of solvent to one of oil up to five volumes of solvent per volume of oil, the least amount of solvent which will produce effective separation being preferred.

The solvent extraction step may be carried on in batch by mixing solvent and degummed oil and allowing the resulting mixture to stand, although a preferred operation is a continuous countercurrent extraction of the oil in an extraction tower. The resulting oil after separation of the solvent phase containing the free fatty acids is much reduced in color and acidity. In many cases this oil forms an acceptable commercial product but in any case can easily be still further reduced in acidity and color by a relatively mild caustic washing operation. A dilute alkali solution effectively neutralizes remaining free fatty acids to reduce the oil to a neutral oil commercially acceptable for edible purposes, oils containing between approximately .02% to .05% free fatty acids being easily obtained. After mixing the alkali solution with the oil, the oil and aqueous solution will separate into two phases upon standing, one an upper oil phase and the second a lower aqueous phase containing soap, coloring material and small amounts of residual gums which may be left in the oil after the degumming operation and solvent treatment. These phases may be separated by decantation or alternatively the mixture may be subjected to continuous centrifugal separation to cause the phases to separate in the centrifuge and be discharged in separate effluents.

The amount and concentration of alkali solution will vary with the nature of the oil but will usually range in concentration between that approximately equal to 1% to 5% caustic soda and be employed in amounts between approximately 1% and 20% of the oil. In most cases 10% of a 2% caustic soda solution will produce a substantially neutral oil having colors at least as low as those obtained by conventional caustic alkali refining employing large excesses of strong caustic solutions followed by a treatment with adsorbent earth. The temperature of separation between the oil phase and aqueous phase of the caustic wash will also depend upon the nature of the oil being refined and the amount of concentration of the caustic solution. In general these temperatures will range between 100° and 200° F., the usual temperature being in the neighborhood of 160° to 180° F. It has been found that very little if any neutral oil is saponified in the alkali washing operation even when caustic soda is employed and that very little if any neutral oil is entrained in the aqueous phase during separation if the oil to be washed contains no more

than about 0.2 of free fatty acids. The solvent treatment is effective to reduce the free fatty acid content of the oil to at least 0.2% and the refining losses for the entire process are therefore extremely low. While caustic soda is preferred because of its cheapness, availability and excellent color reducing properties, other caustic alkalies such as caustic potash or even non-caustic alkalies such as carbonates, etc., may be employed in the alkali washing step although they are not, in general, as effective for color reduction as caustic alkalies.

The gums removed in the degumming operation are not subjected to partial or complete destruction by strong caustic solutions as in conventional refining processes and constitute a valuable by-product as they may be employed in their crude form as emulsifying agents in certain instances, and valuable materials such as phosphatides, useful for many purposes, can be relatively easily recovered therefrom. Also, the fatty acids from the solvent treatment step are of relatively high quality as they are substantially free of gums and much of the coloring matter is removed in the degumming step.

With certain selective solvents, namely those which are substantially immiscible with water or have limited solubility in water, the solvent treatment step may be carried on simultaneously with the degumming step. In such a process the crude oil is simultaneously admixed with both the solvent and water or other aqueous medium. In general the solvent is saturated with water and employed in substantially the proportions discussed above for solvent treatment of the degummed oil and is admixed with additional water so as to provide substantially the amount of additional water discussed above relative to the degumming step. The presence of water admixed with the solvent in most cases renders the solvent even more selective in its action. The free fatty acids are selectively dissolved by the solvent and at the same time the gums are precipitated by the aqueous medium. Upon allowing the mixture to stand, in general three phases are formed, one an aqueous phase containing the gums, another a solvent phase containing the free fatty acids, and the third an oil phase. A small amount of solvent may be present in the aqueous phase and the oil phase. These phases can ordinarily be separated by decantation. The precipitated gums may also be removed from the mixture prior to separation of the oil and solvent phases by filtering the gums from the mixture in which case it is desirable to employ substantially only that amount of water or aqueous medium which will be absorbed by the gums in the precipitation thereof, thus avoiding excess water forming a substantial aqueous phase in subsequent separation of the oil and solvent phase. As a preferred operation, the mixture containing oil solvent and precipitated gums is subjected to continuous centrifugal separation to separate the oil and solvent phases. If the solvent phase is of greater specific gravity than the oil the precipitated gums separate with the solvent phase and if the solvent phase is of less specific gravity than the oil the precipitated gums separate with the oil phase. In either case the precipitated gums may then be separated from its associated solvent or oil phase by filtration or decantation or in some cases by a subsequent centrifugal separation operation.

By employing a selective solvent which is substantially immiscible with water or has slight

solubility only in water, the solvent and aqueous medium operate substantially independently and an oil of relatively low color and low acidity is produced. The aqueous medium renders the gums insoluble in the oil, fatty acids and solvents so as to effectively remove the gums from the oil and fatty acids even prior to physical separation so that the solvent does not act on the oil and fatty acids in the presence of the gums. If desired, this oil can be subjected to a caustic washing operation as above described to further reduce the color and acidity. As in the modification of the present process involving separate degumming and solvent steps, the refining losses are extremely low. In operations involving simultaneous degumming and solvent extraction, the temperature of separation of the oil phase and solvent phase will be determined by the temperature at which free fatty acids are still soluble in the solvent phase while the glycerides remain insoluble.

As a specific example of the modification of the present process involving separate degumming and solvent treatment steps, a crude cottonseed oil having a free fatty acid content of .45% and a color of 85 yellow-21.6 red, and containing substantial amounts of gum, was degummed with 2% water, the water being intimately mixed with the oil. The resulting mixture was subjected to continuous centrifugal separation at 135° F., the resulting oil having a free fatty acid content of .44. This oil was then extracted with two volumes of furfural saturated with water at 110° F. by continuous countercurrent operation. The resulting oil had a free fatty acid content of .11. This resulting oil was then washed with 10% of a 2% caustic soda solution, separation being accomplished by continuous centrifugal separation at 180° F. The resulting oil had a free fatty acid content of .04 and a color of 35 yellow-4.5 red, the refining losses in the entire process being 2.4%.

To illustrate the improved results obtained over attempting to apply solvent extraction to the crude oil without degumming, the same crude oil was directly extracted with two volumes of wet furfural at 110° F. by the said countercurrent extraction operation. The oil resulting from this operation had a fatty acid content of .15, a color of 85 yellow-20 red. This oil was then washed with 10% of 2% caustic soda solution at 180° F. in the same manner as above described to produce an oil containing .04 free fatty acids and a color of 35 yellow-16.6 red, the refining losses for the process being 3.5%. Thus the total refining loss in the example involving degumming, solvent extraction and caustic washing was 2.4% as against 3.5% when the degumming step was omitted. Also the color of the oil resulting from the example involving prior degumming was 35 yellow-4.5 red in contrast to a color of 35 yellow-16.6 red when prior degumming was omitted.

As another specific example of a process involving degumming, solvent extraction and caustic washing, the same crude above discussed was degummed with 2% water at 135° F. and extracted with two volumes of 90% isopropyl alcohol at 90° F. in a continuous countercurrent operation. The resulting oil had a free fatty acid content of .15. This oil was then washed with 10% of a 2% caustic soda solution at 180° F. and produced an oil having .03% free fatty acids and a color of 30 yellow-4.0 red, the total refining loss being 1.4%.

As a specific example of a process involving simultaneous degumming and solvent extraction, the same crude cottonseed oil having a free fatty acid content of .45% was treated with two volumes of saturated furfural to which water in an amount equal to 2% of the oil had been added and the resulting mixture was continuously centrifugally separated into an oil phase and a solvent phase containing the precipitated gums, the latter phase being the heavy effluent from the centrifugal. The precipitated gums were then removed from the solvent phase by filtration. The resulting oil contained .15 free fatty acids. This oil was then washed with 10% of 2% caustic soda solution at 180° F. and the resulting mixture continuously centrifugally separated. The refining loss was substantially the same as the example previously given in which the crude cottonseed oil was first degummed, then extracted with wet furfural, and washed with a dilute caustic soda solution and the color was only slightly higher. It is thus apparent that low refining losses and high quality oil can also be obtained by employing a simultaneous degumming and solvent extraction step and such operation has the advantage of being a less complicated process requiring less apparatus and less labor and time. In any of the modifications and processes above described, the refining losses are markedly lower than with the conventionally employed refining operations employing strong caustic solutions and bleaching with adsorbent earth and the resulting oil is as good or better in quality.

As stated above, a large number of solvents can be employed for fatty acid extraction when the extraction is carried on separately from degumming. In general, these solvents are non-reactive polar solvents, preferably organic. These solvents usually contain one or more of the following groups; alcohol, phenol, carboxylic acid, acid nitrile, acid anhydride, acid amide, carboxylic ester, aldehyde, ketone, mercaptan, primary amine or primary amine bases, nitro, sulphate, carbonate, and phosphate groups, and also may contain one or more of the following groups which assist the above listed functional groups: Namely, ether, thio ether, olefine, secondary amine and tertiary amine and the corresponding bases. In the case of organic solvents the number of carbon atoms usually should not be greater than six, and the compound may have three carbon atoms for each of the groups listed in the first series, and one carbon atom for any other groups in the compound which are listed in the second series. It is essential that the properties of these materials and the temperatures employed should be such that two phases are formed and that the solvents are not reactive under the treatment conditions. Miscible polar solvents, which do not meet the above requirements and also miscible non-polar solvents may be used in conjunction with the selective polar solvents employed in the present process in order to alter the solubility of certain of the constituents under treatment. Likewise it is possible to increase the selectivity of the process by employing non-miscible non-polar solvents which tend to hold the glycerides while the polar solvent extracts the fatty acids.

The polar solvents which may be employed for the present purposes include methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, allyl alcohol, methylallyl alcohol, phenol, resorcinol, ethylene glycol, ethylene chlorhydrin, diethylene glyco, diethylene thioglycol, ethylene glycol monomethyl ether, ethylene glycol mono-

ethyl ether, ethylene glycol monoacetate, ethylene glycol diacetate, ethylene glycol diformate, ethylene glycol monolactate, ethylene glycol monoglycolate, triethylene glycol, propylene glycol, butylene glycol, 1,4, pentandiol, pentantriol 1,2,5, propylene glycol chlorhydrin, glycerol, glycerol monoacetate, glycerol diacetate, glycerol triacetate, glycerol monobutyrate, glycerol dibutyrate, glycerol monocaproate, glycerol monoproprionate, methyl glycolate, ethyl glycolate, ethyl acetoglycolate, methyl lactate, ethyl lactate, methyl malonate, ethyl oxylate, lactonitrile, propionitrile, methyl allylnitrile, formic acid, acetic acid, acetic anhydride, lactic acid, methyl formate, ethyl formate, methyl levulinate, ethyl N-methyl carbamate, ethylidine diacetate, ethyl acetoacetate, methyl acetoacetate, methyl maleate, methyl furoate, methyl chloracetate, methyl cyanoacetate, acetaldehyde, methoxyacetaldehyde, furfural, furfuryl alcohol, nitrobenzaldehyde, nitromethane, nitroethane, 2-nitroethyl propionate acetone, diacetyl, diacetone alcohol, acetonyl acetone, formamide, acetamide, propionamide, butyramide, N-ethanolacetamide, aniline, ethyl diamine, diethyl triamine, triethylene tetramine, ethanolamine, diethanolamine, triethanolamine, mono-glycerolamine, diglycerolamine, triglycerolamine, tris-hydroxymethyl aminoethane, hydroxyethyl ethylene diamine, trimethylphosphate, triethylphosphate, diethylsulphate, acetylmethylcarbinol, acetochlorhydrin, dichlorotriethylene glycol, 2-hydroxymethyl, 1,3 dioxolone, methyl butanolone, acetone plus sulphur dioxide, liquid sulphur dioxide, liquid carbon dioxide, carbon bisulphide, and the like.

For simultaneous degumming and solvent extraction of fatty acids, in addition to being nonreactive, the selective solvents employed must be substantially immiscible with water or have limited solubility therein. Thus, such solvents as phenol, glycerol triacetate, ethyl oxylate, methyl formate, ethyl formate, ethyl acetoacetate, methyl acetoacetate, methyl furoate, furfural, nitromethane, nitroethane, aniline, etc., may be employed in conjunction with water or aqueous solutions of materials which do not react with the solvent for simultaneously degumming and solvent extraction. The above lists of solvents are not intended to be complete but are given merely by way of example to show the large number of solvents which can be employed.

Mixtures of suitable solvents may likewise be employed. In many cases it may be advantageous to use one or more immiscible non-polar solvents in conjunction with the polar solvent or solvents in order to set up opposed solubilizing action on the oil and fatty acids, particularly when using polar solvents possessing very high solvent action. It is also possible to employ miscible non-polar solvent or miscible anti-solvents along with the polar solvents in order to improve or produce or otherwise control solvent properties on the materials which are not desired to be extracted.

Various types of solvent extraction treatment may be employed. For example, continuous countercurrent extraction in an extraction tower at constant temperature as employed in the specific examples above given are particularly effective. Such countercurrent operations may also be carried on in a series of chambers through which the oil phase progresses in one direction and the solvent fatty phase in the other direction. Also, the extraction steps may be carried out in batch either by mixing the solvent with the oil at the temperature desired for separation and then centrifugally separating the mixture or allowing separate strata to form followed by decantation. Also the temperature during the mixing may be increased to an extent which causes substantially all of the fatty material to be dissolved followed by cooling to the temperature at which separate phases can be separated either by centrifugal separation or by settling and decanting. Since degumming can be effected over a considerable range of temperatures, it is usually possible to carry on such degumming simultaneously with solvent extraction with solvents which are substantially immiscible with water at the temperature of separation between the solvent phase and the oil phase.

While we have disclosed the preferred embodiments of our invention, it is understood that the details thereof may be varied within the scope of the following claims:

We claim:

1. The process of refining glyceride oils containing gums, free fatty acids and coloring matter, which comprises, degumming said oils with an aqueous medium to effectively remove gums from said oil and treating said oil with a selective solvent for fatty acids, said process including the steps of separating from the oil a solvent phase containing free fatty acids and an aqueous phase containing gums to produce a resulting oil substantially free from gums and having reduced color and fatty acid content, and the step of further treating the resulting oil with a dilute alkali solution to further reduce the color and fatty acid content of the oil.

2. The process of refining glyceride oils containing gums, free fatty acids and coloring matter, which comprises, mixing said oil with an aqueous medium in an amount between about 1% and 10% of the oil to precipitate gums therein, separating the precipitated gums from said oil, and thereafter treating said oil with a selective solvent for fatty acids in an amount between approximately one and ten volumes of solvent per volume of oil to remove a substantial amount of fatty acids from said oil and produce a resulting oil substantially free from gums and having a reduced color and fatty acid content and thereafter treating the resulting oil with a dilute alkali solution having a concentration equivalent to approximately 1% to 5% caustic soda and in an amount of between approximately 5% and 20% of the oil to further reduce the color and fatty acid content of said oil.

3. The process of refining glyceride oils and fats containing gums, free fatty acids and coloring matter, which comprises, simultaneously treating said oil with an aqueous medium for precipitating gums and a selective solvent for fatty acids for dissolving free fatty acids in preference to said oil and separating from said oil an aqueous phase containing said gums and a solvent phase containing a substantial amount of free fatty acids, to produce a resulting oil substantially free from gums and having a reduced color and fatty acid content, and thereafter treating the resulting oil with a dilute alkali solution to further reduce the color and free fatty acid content of the oil.

4. The process of refining glyceride oils and fats containing gums, free fatty acids and coloring matter, which comprises, simultaneously treating said oil with an aqueous medium for precipitating gums and a selective solvent for fatty acids for dissolving free fatty acids in preference to said oil, said solvent being sufficiently

immiscible with water to form a solvent phase separate from said aqueous medium, and separating from said oil an aqueous phase containing said gums and a solvent phase containing a substantial amount of free fatty acids, to produce a resulting oil substantially free from gums and having a reduced color and fatty acid content, and thereafter treating the resulting oil with a dilute alkali solution to further reduce the color and free fatty acid content of the oil.

5. The process of refining glyceride oils and fats containing gums, free fatty acids and coloring matter, which comprises, simultaneously treating said oil with an aqueous medium for precipitating gums and a selective solvent for fatty acids for dissolving free fatty acids in preference to said oil, said solvent being substantially immiscible with water, and separating from said oil an aqueous phase containing said gums and a solvent phase containing a substantial amount of free fatty acids to produce a resulting oil substantially free from gums and having a reduced color and fatty acid content and thereafter mixing a dilute solution of caustic soda with said resulting oil and separating from said oil an aqueous phase containing soap and coloring matter to further reduce the color and free fatty acid content of said oil.

6. The process of refining glyceride oil containing gums, free fatty acids and coloring matter, which comprises, degumming said oils with an aqueous medium sufficient in amount to effectively precipitate gums from said oil and treating said oil with a selective solvent for fatty acids in sufficient amount to selectively dissolve

fatty acids in preference to said oil, said process including the steps of separating from the oil said precipitated gums and solvent containing a substantial amount of free fatty acids to produce a resulting oil substantially free from gums and having reduced color and fatty acid content, thereafter admixing with said oil a dilute solution of caustic soda in sufficient amount to neutralize the remaining free fatty acids and further reduce the color of said oil and separating from said oil an aqueous phase containing soap and coloring matter.

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