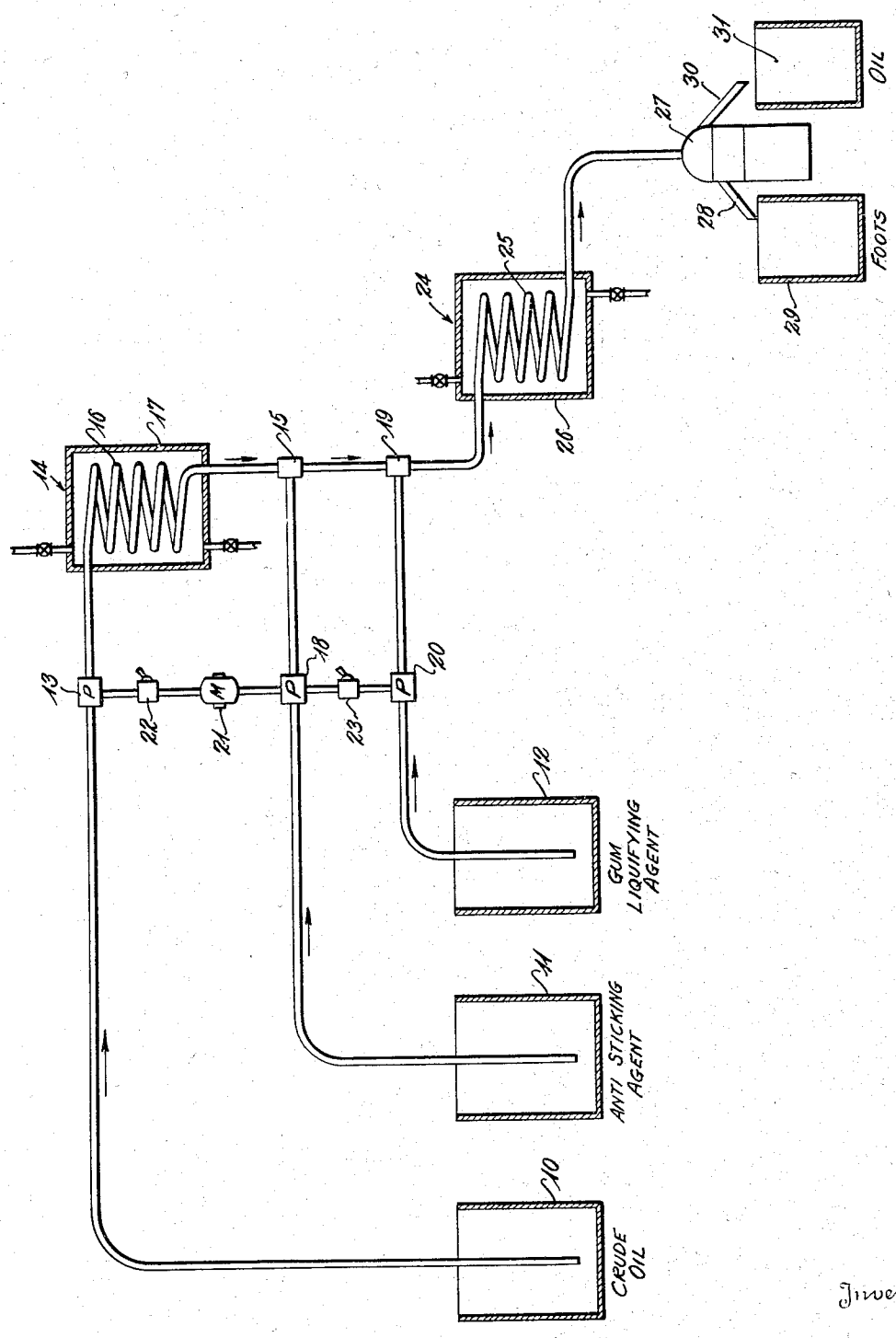
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REFINING OF VEGETABLE OILS

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REFINING OF VEGETABLE OILS

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15 Claims. (Cl. 260—425)

Ths invention relates to the refining of vegetable oils, and more particularly to a process of partial refining in which gummy material carried by the oils is removed prior to complete refining, although the gum liquefying agents disclosed herewith may also be employed in complete refining processes to decrease the entrainment of oil in foots separated therefrom so as to decrease refining losses.

The invention is particularly applicable to so-called degumming processes in which gummy materials such as phosphatides, proteins, resins and carbohydrates are removed from the oil prior to an alkali refining step.

In such separations the gummy material referred to is precipitated from the oil and then separated therefrom by a difference in specific gravity. This material is a valuable by-product either as a phosphatidic material as separated or as a source of valuable phosphatides and other materials. A considerable amount of oil is ordinarily entrained with the separated gums, and represents a major refining loss. It is difficult to recover the oil entrained with the gums, and the present invention is directed to minimizing the amount of this oil.

It is, therefore, an object of the present invention to provide an improved process of removing gums from vegetable oils.

Another object of the invention is to provide a process of removing gums from vegetable oil in which a gum liquefying agent is employed to enable more complete separation of oil from the gums.

A further object of the invention is to provide a degumming operation involving continuous centrifugal separation of gums from the oil, in which a gum liquefying agent is employed to improve separation of oil from the gums and an anti-sticking agent is employed to prevent separated gums from sticking to the walls of the centrifugal bowl.

The gum liquefying agent is also advantageously employed in complete alkali refining operations, in which sufficient alkali is added to the crude oil in amounts and concentrations known to the art to completely neutralize the free fatty acids therein as well as to reduce colors in highly colored oils. In such operations the gums are present in the soap stock separated from the oil, and the gum liquefying agent improves the separation so as to reduce entrainment of neutral oil with the soap stock.

It is therefore a still further object of the invention to provide an improved alkali refining process in which entrainment of neutral oil in the soap stock is reduced.

The process of the present invention is preferably carried out as a continuous operation in a closed system, although marked improvement over conventional batch operations is accomplished in accordance with the present invention even in batch operations. The invention will be specifically described with reference to the accompanying drawing, which is a schematic diagram of an apparatus suitable for carrying out a continuous degumming operation in accordance with the present invention.

Referring to the drawing, 10 indicates a tank or other source of supply of crude vegetable oil; 11 indicates a source of supply for an anti-sticking agent, and 12 indicates a source of supply of a gum liquefying agent. In the preferred operation, a stream of crude oil is withdrawn from the tank 10 by a proportioning pump 13 and forced through a heat exchange device 14 to a mixing device 15. The heating device 14 preferably includes a heating coil 16 positioned in a casing 17 through which any desired heating or cooling medium may be circulated. Anti-sticking agent is withdrawn from the tank 11 by means of a proportioning pump 18 and delivered to the mixing device 15. The crude oil and anti-sticking agent are thoroughly admixed in the mixer 15 which is preferably of the type disclosed in my copending application Serial No. 190,673, filed February 15, 1938, now Patent No. 2,142,062, granted Sept. 29, 1938, but which may be any type of closed flow mixer such as a closed mechanical agitator. The mixture from the mixing device 15 is preferably delivered to a second mixing device 19, which may be of the same type as the mixing device 15. Gum liquefying agent is withdrawn from the tank 12 by a proportioning pump 20 and delivered to the mixer 19. The proportioning pumps 13, 18 and 20 may be driven by a variable speed electric motor 21 with variable speed devices 22 and 23 between the motor and the pumps 13 and 20. This proportioning mechanism is given merely as an example, as any suitable proportioning mechanism capable of accurately proportioning streams under pump pressure can be employed. The resulting mixture from the mixer 19 is then preferably passed through a second heat exchange device 24 including a heating coil 25 positioned in a casing 26 through which any desired heating or cooling medium may be passed. Both the liquefying agent and anti-sticking agent are preferably aqueous solutions and either or both act as

gum precipitating agents to render the gums insoluble in the oil and capable of being separated therefrom as foots.

The resulting mixture of oil and foots is then delivered to a continuous centrifugal separator 27 which is preferably of the heated type disclosed in Patent No. 2,100,277, granted November 23, 1937. The precipitated gums or foots are separated from the oil in the centrifugal 27 and delivered as the heavy effluent through a spout 28 into a receiver 29. The degummed oil is delivered as the light effluent through a spout 30 into a receiver 31.

Substantially all vegetable oils contain gummy materials such as above described which must be removed in order to produce a commercial refined oil. The gums are preferably removed prior to the removal of free fatty acids, also contained in the oil, although both the gums and fatty acids may be removed in the same operation. Examples of vegetable oils which may be treated by the present invention are cottonseed oil, soya bean oil, sesame oil, corn oil, rapeseed oil, etc. The gums are to a large extent soluble in the oil, but may be rendered to a large extent insoluble therein by the addition of water to the oil. The addition of water alone, however, does not precipitate all of the gums, and the resulting mixture of precipitated gums and oil is difficult to separate without leaving large amounts of oil admixed with the gums. It has been found that solutions of weak acid, for example, boric acid, tartaric acid, citric acid, etc., as well as extremely dilute solutions of strong acids such as sulfuric or hydrochloric acid, accomplish a more complete precipitation of the gums and the same is true of relatively dilute solutions of neutral salts such as sodium chloride or sodium sulfate and also relatively dilute solutions of weak alkalies or very dilute solutions of strong alkalies. Although the gums are more completely precipitated by such degumming reagents, the separated gums are quite viscous and are excellent emulsifying agents, so that they entrain considerable valuable oil.

In accordance with the present invention, I have found that certain agents appear to render the gums more liquid in nature, thereby enabling a more complete separation to be made. These agents also decrease the emulsifying action of the gums. In general water soluble salts such as salts of alkali metals or alkaline earth metals, ammonium salts, etc., other than alkali metal halides or strongly alkaline salts are suitable as gum liquifying agents in the present invention. The term "strongly alkaline salts" is employed herein to mean salts which are sufficiently alkaline in reaction to react readily with free fatty acids. Certain salts of alkalies for example sodium carbonate and tri-sodium phosphate come within this term and function as alkaline refining reagents, as is known by those skilled in the art of vegetable oil refining. The halides of alkali metals, for example, sodium chloride, have a hardening effect upon the gums instead of a gum softening or liquefying action.

The preferred liquefying agent is sodium thiosulfate, which, when added in relatively small amounts and concentration, causes a much more complete separation of the gums from the oil. Other thiosalts are also very effective, for example, sodium thiocyanate and other alkali thiosulfates and thiocyanates such as ammonium and potassium thiosulfates and thiocyanates. These materials, particularly the sodium thiosulfate, also produce a greater precipitation of the gums, so that the other reagents, namely, the acid alkaline or neutral salt solutions, are not essential for good precipitation, but may be employed in admixture therewith, if desired. However, other water soluble salts, such as calcium chloride, ammonium chloride, ammonium acetate, calcium thiocyanate, magnesium sulfate, potassium tartrate, potassium sulfate, sodium sulfate, barium chloride, etc. may also be employed. It will be apparent that the extent of gum liquefying will depend upon the water soluble salt selected and also that care must be exercised in employing such gum liquefying agents in admixture with acid or alkaline refining reagents or alkaline anti-sticking agents to avoid precipitating insoluble compounds from reactions between the refining or anti-sticking reagent and the gum liquefying agent. For example, insoluble alkaline earth metal hydroxides or carbonates will precipitate if water soluble alkaline earth metal salts are employed with refining agents comprising alkali metal hydroxides or carbonates and insoluble sulfates will precipitate if water soluble barium of calcium salts are employed with sulfuric acid as a refining agent. Also, mixtures of water soluble salts may be employed as gum liquefying agents if such insoluble precipitates are not formed. The amount and concentration of the gum liquefying agent will vary with the nature of the oil and the amount of gums contained therein. Thus, a concentration of from 1 to 20% in amounts of from 1 to 15% based on the weight of the oil may be employed. In ordinary operations, 10% solutions of the gum liquefying agent can ordinarily be employed in amounts ranging from 1 to 5%.

Although the gum liquefying reagents referred to produce a much cleaner separation of the oil from the foots, it is found in some cases that portions of the gummy materials adhere to the walls of a centrifugal bowl so as to build up a layer of gummy material interfering with proper separation in continued operations. The most effective means of preventing this is to add to the oil a small percentage of a relatively dilute solution of a strong alkali prior to adding the gum liquefying agent. Such alkalies neutralize a small portion of the free fatty acids of the oils to form a small amount of soap. This soap apparently acts as a lubricant or slipping agent for the gums in the centrifugal bowl and prevents adherence thereof. Thus, from .1 to 5% of 12° Bé. caustic soda has been found particularly effective, although other alkalies may be employed. It has been consistently noted that the addition of small amounts of alkali such as above described not only cause the foots to flow continuously from the centrifuge without building up a layer of gummy material but also reduce the fatty acid content of the oil to a greater extent than would be expected from the amount of alkali employed. The soap formed from the alkali appears to be the primary factor in preventing the building up of a layer in the centrifugal separator. Such soap is preferably formed in situ, as above described, but can be added in solution as a separate material. Also, it has been found that other materials, such as small amounts of starch or dextrin solutions, will accomplish a somewhat similar result.

The centrifugal separating operation is most effective at somewhat elevated temperatures, for example, temperatures between 110° and 160° F. depending upon the nature of the oils and the amount of gums contained therein. The elevated temperatures further reduce the viscosities of the oil and gums and help to break any

emulsion which may tend to form. According to the present invention, separation temperatures may be obtained either by preheating the oil, for example in the heat exchange device 14 prior to mixing, or may be obtained by heating the mixture after it has been formed in the heat exchange device 24. Alternatively, all or a portion of the heat desired for separation may be imparted to the mixture within the centrifugal 27 if a heated centrifugal such as described in Patent No. 2,100,277, referred to above, is employed. The most effective place for imparting the desired temperature for separation will vary with different oils, and no general statement with respect thereto can be made. It is sometimes found desirable to mix cold and then heat the mixture. The best mixing temperature with a given oil may be even below room temperature, in which case the heat exchange device 14 may be employed to cool the oil. In other cases, it is desirable to mix at a higher temperature than the preferred separating temperature, in which case the heat exchange device 14 may be employed to elevate the temperature above the desired separation temperature and the heat exchange device 24 employed to cool the mixture to the desired separating temperature. In some cases both the heat exchange devices 14 and 24 may be eliminated, although it is usually desirable to provide a short treating time between mixing and separation, in which case the coil 25 of the heat exchange device 24 may be employed to give such additional treating time, even though no heating or cooling of the mixture takes place therein.

While it is preferred to add the anti-sticking agent to the oil prior to the gum liquefying agent, it will be appreciated that it is possible to reverse the order of adding of these two agents and also to simultaneously add them to the oil. In many cases the anti-sticking agent can be omitted when the nature of the gums contained in the particular oil being treated do not tend to form a layer in the centrifugal separator bowl. It is even possible to add the gum liquefying agent, if employed alone, directly to the crude oil in a container provided with an agitator, keep the resulting mixture under sufficient agitation to prevent stratification of the foots, and then pump the mixture of oil and foots to the centrifugal separator. If an anti-sticking agent is also necessary, this may likewise be added directly to the crude oil container. In such an operation, the gum liquefying agent is preferably added thereafter in a flow mixer but may be added to the container along with the anti-sticking agent. Although batch separation is not as effective as continuous centrifugal separation, improved results over batch degumming operations can be secured by the batch mixing step above referred to, followed by a settling step after agitation of the mixture has been discontinued. The gums, being more liquid in nature, settle more cleanly from the oil than is possible in ordinary batch operations to produce less entrainment of oil in the gums.

As indicated above, a gum liquefying agent can also be advantageously employed in complete alkali refining operations in which sufficient alkali is added to the crude oil to completely neutralize the free fatty acids, and, if necessary with highly colored oils such as most cottonseed oil, to provide an excess for reaction with color impurities. In this case the liquefying agent is preferably added prior to adding the alkali, as this agent is apparently not quite as effective when added after complete neutralization. The liquefying agent may be employed in processes involving either preheating of the oil or heating of the resulting mixture to a correct separating temperature for the oil being refined. Thus the liquefying agent may be added to the oil at room temperature, the oil then heated and the alkali refining reagent added; both the liquefying agents can be added to the oil before heating; or both can be added after the oil is heated. The precise process employed in a given case will depend upon the oil being treated, as different oils respond to different treating conditions. Ordinarily the separation temperature falls between 110° and 160° F. but in some cases it has been found possible to separate at lower temperatures such that no heat need be applied to the oil or cooling of the mixture performed after it has once been heated to break or prevent the formation of any emulsion which might tend to form. Continuous mixing, heating, and centrifugal separation is preferred, but improved results over conventional batch operations are secured even in batch operations. The gum liquefying agent renders the resulting soap stock containing the gums more liquid and decreases emulsification difficulties so as to provide for a more complete separation of the oil from the soap stock either in batch or continuous operations. The gum liquefying agents may also be employed for similar purposes in so-called "acid" refining, wherein relatively concentrated solutions of strong mineral acids such as sulfuric or hydrochloric acids are employed to precipitate foots which can be separated from the oil. Thus the present invention provides an improved process in which the foots separated from vegetable oils are rendered more liquid and the amount of oil entrained with the foots is markedly reduced.

By the employment of the term "aqueous solution" or "gum liquefying agents" in the claims, I intend to define an aqueous medium of such dilution as to permit substantially complete hydration of the gums, as distinguished from saturated solutions, and also functioning to decrease the emulsifying action of the gums, thus improving centrifugal separation.

This application constitutes a continuation-in-part of my copending application Serial No. 248,355, filed December 29, 1938.

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

I claim:

1. The process of partially refining vegetable oils containing gums, which comprises, mixing an aqueous solution of water soluble salt other than alkali metal halides and strongly alkaline salts with said oil to precipitate gums and reducing the viscosity thereof, and thereafter centrifugally separating the precipitated gums from said oil, whereby the oil entrained with said gums is reduced.

2. In the process of refining vegetable oils containing gums, which includes the steps of adding a refining reagent to a vegetable oil and centrifugally separating the resulting foots by difference in specific gravity, the improvement which comprises, incorporating an aqueous solution of a water soluble salt other than alkali metal halides and strongly alkaline salts with the mixture of oil and foots resulting from adding said refining reagent to said oil, so as to

liquefy gums contained in said foots in order to reduce the oil entrained with the foots after separation.

3. The process of refining vegetable oils containing gums, which comprises, mixing a refining reagent with said oil which reacts with impurities in said oil to precipitate foots, adding an aqueous solution of a water soluble salt other than an alkali metal halide or a strongly alkaline salt to said oil prior to mixing said refining reagent therewith in order to liquefy gums contained in said foots, and centrifugally separating said foots from said oil by difference in specific gravity, whereby the amount of oil entrained in said foots is minimized.

4. The process of refining vegetable oils containing gums, which comprises, mixing a stream of a refining reagent which reacts with impurities in said oil to precipitate foots with a flowing stream of said oil, incorporating a gum liquefying agent comprising a water soluble salt other than alkali metal halides or strongly alkaline salts with said mixture in order to liquefy gums contained in said foots and continuously centrifugally separating said foots from said oil by difference in specific gravity in order to minimize the amount of oil entrained in said foots.

5. The process of refining vegetable oils containing gums, which comprises, mixing a stream of a refining reagent which reacts with impurities in said oil to precipitate foots with a flowing stream of said oil, incorporating an aqueous solution of a water soluble salt other than alkali metal halides and strongly alkaline salts with said mixture in order to liquefy gums contained in said foots, and continuously centrifugally separating said foots from said oil, whereby the amount of oil entrained in said foots is minimized.

6. The process of partially refining crude vegetable oils containing gums and free fatty acids, which comprises, mixing an alkali refining reagent with said oil to precipitate said gums but in an amount insufficient to neutralize all of the free fatty acids of said oil, also adding an aqueous solution of a water soluble salt other than the alkali metal halides and strongly alkaline salts with said oil to assist in precipitating said gums and to reduce the viscosity thereof, thereafter separating said gums from said oil by continuous centrifugal separation, whereby said gums flow continuously from the centrifugal separator employed and contain a reduced amount of entrained oil.

7. The process of partially refining vegetable oils containing gums, which comprises, mixing a gum precipitating and liquefying reagent comprising a water soluble salt other than an alkali metal halide and a strongly alkaline salt with said oil to precipitate gums having a reduced viscosity, and thereafter centrifugally separating the precipitated gums from said oil, whereby the oil entrained in said gums is reduced.

8. The process of partially refining vegetable oils containing gums, which comprises, mixing an aqueous solution of soluble alkali thiosulfate with said oil to precipitate gums having a reduced viscosity, and thereafter separating the precipitated gums from said oil, whereby the oil entrained with said gums is reduced.

9. In the process of refining vegetable oils containing gums, which includes the steps of adding a refining reagent to a vegetable oil and separating the resulting foots by difference in specific gravity, the improvement which comprises, incorporating sodium thiosulfate with the mixture of oil and foots resulting from adding said refining reagent to said oil, so as to liquefy gums contained in said foots in order to reduce the oil entrained with the foots after separation.

10. In the process of refining vegetable oils containing gums, which includes the steps of mixing a refining reagent with an oil in order to form a mixture of oil and foots including gums and separating said foots from said oil, the improvement which comprises incorporating sodium thiosulfate with said mixture in order to reduce the amount of oil entrained with the separated foots.

11. The process of refining vegetable oils containing gums, which comprises, mixing a refining reagent with said oil which reacts with impurities in said oil to precipitate foots, adding an aqueous solution of sodium thiosulfate to said oil prior to mixing said refining reagent therewith in order to liquefy gums contained in said foots, and separating said foots from said oil by difference in specific gravity, whereby the amount of oil entrained in said foots is minimized.

12. The process of refining vegetable oils containing gums, which comprises, mixing a stream of a refining reagent which reacts with impurities in said oil to precipitate foots with a flowing stream of said oil, incorporating sodium thiosulfate with said mixture in order to liquefy gums contained in said foots, and continuously centrifugally separating said foots from said oil, whereby the amount of oil entrained in said foots is minimized.

13. The process of partially refining crude vegetable oils containing gums and free fatty acids, which comprises, mixing an alkali refining reagent with said oil to precipitate said gums but in an amount insufficient to neutralize all of the free fatty acids of said oil, also adding an aqueous solution of sodium thiosulfate with said oil to assist in precipitating said gums and to reduce the viscosity thereof, thereafter separating said gums from said oil by continuous centrifugal separation, whereby said gums flow continuously from the centrifugal separator employed and contain a reduced amount of entrained oil.

14. The process of partially refining vegetable oils containing gums, which comprises, mixing an aqueous solution of sodium thiosulfate with said oils to precipitate gums having a reduced viscosity, and thereafter separating the precipitated gums from said oil, whereby the oil contained in said gums is reduced.

15. The process of partially refining vegetable oils containing gums, which comprises, mixing an aqueous solution of a gum precipitating and liquefying reagent selected from the group consisting of soluble alkali thiosulfates and thiocyanates, and thereafter separating the precipitated gums from said oil.

BENJAMIN H. THURMAN.

CERTIFICATE OF CORRECTION.

Patent No. 2,242,188. May 13, 1941.

BENJAMIN H. THURMAN.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 51, for "5%" read --.5%--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of June, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)