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PROCESS OF REFINING OIL

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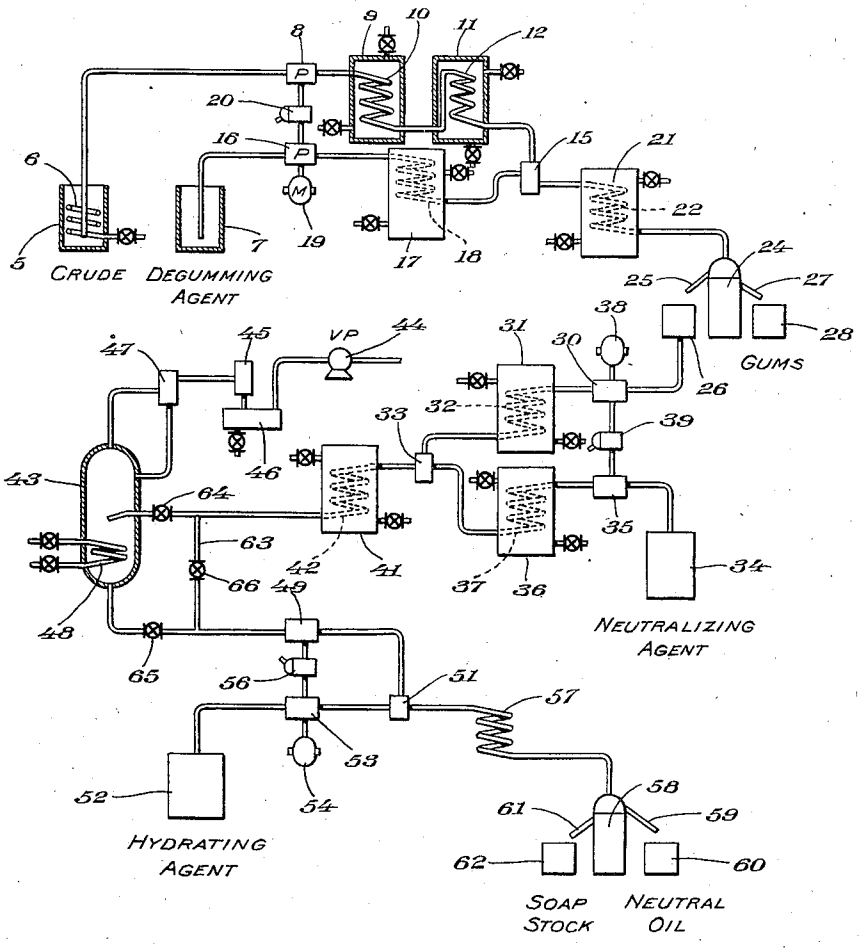

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PROCESS OF REFINING OIL

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13 Claims. (Cl. 260—398)

This invention relates to a process of refining fatty oils and more particularly to a process of refining animal and vegetable oils in which the oil is neutralized but in which certain of the constituents which are removed in conventional refining processes are left in the oil to produce a new oil product having certain desirable uses.

In the refining of vegetable and animal oils caustic alkalies have been conventionally employed to remove not only the free fatty acids but gums including phosphatidic material and as far as possible the coloring matter of the oil. The oils resulting from such refining processes are substantially pure glycerides.

In accordance with the present invention the free fatty acids within the animal and vegetable oils are neutralized and removed in the form of soap and a portion of the gums are removed along with some of the coloring matter. The finished oil however contains a small amount, for example, $\frac{1}{10}$ to $\frac{5}{10}$% of phosphatidic material intimately associated with the oil and this phosphatidic material imparts extremely valuable properties to the oil for many purposes for which the oil may be employed. Since the color of the oil is ordinarily not drastically reduced the present process is particularly applicable to light colored oils such as corn oil, but if a dark colored oil is not undesirable, the process may be employed for darker colored oils such as cottonseed oil.

I have found that if the oil is subjected to a relatively high temperature while it contains all or a substantial portion of its original gums, some of the phosphatidic material remains intimately associated with the oil and is not removed by the refining steps. The heating of the oil may be performed before any refining agents such as degumming or neutralizing agents are added to the oil or while such agents are present, so long as the heating is accomplished before separating substantially all of the gums from the oil. Thus the present process may have several modifications.

One modification of the process of the present invention includes a degumming step followed by a refining step in which a non-saponifying refining agent is employed. It has been found that the oil may be pretreated so that the degumming and neutralizing steps of the present invention will not remove all of the phosphatidic material from the oil although a substantially neutral oil is produced. Also the neutralizing step may be followed, if desired, by a washing or filtering step to remove suspended or dissolved soap or alkali from the oil without materially diminishing the amount of phosphatidic material left in the neutral oil.

It has been found that preheating the oil including a phosphatidic material, to a relatively high temperature but below that at which a major portion of the gums are thrown out of solution to produce a "break," will "set" the phosphatidic material in the oil so that degumming or alkali refining steps or both may be carried out to leave a substantial portion of the phosphatidic material in the oil intimately associated therewith. Thus a neutral oil may be produced which contains a substantial amount of phosphatidic material which is much more stably held by the oil than phosphatidic material added to the neutral oil after refining. After the heating step referred to the oil may be cooled to any desired refining or degumming temperature. Employment of non-saponifying neutralizing agents such as soda ash in the alkali refining step is preferred as a larger portion of the more desirable phosphatidic materials is retained in the oil after refining.

The preferred process of the invention may be carried out in the apparatus shown in the drawing in which 5 indicates a source such as a tank for the crude oil to be refined which tank may include a heating coil 6, 7 indicates a source such as a tank for the degumming agent. The crude oil may be withdrawn from the tank 5 by a proportioning pump 8 and delivered through a heat exchanger 9 including a coil 10, and a second heat exchanger 11 including a coil 12, to a mixer 15. The degumming agent may be withdrawn from a tank 7 by means of a proportioning pump 16 and delivered through a heat exchanger 17 including a coil 18 to the mixer 15. The proportioning pumps 8 and 16 are shown as being driven by a motor 19 with a change speed device 20 positioned between the pumps. However, any other suitable type of proportioning equipment may be employed instead of the proportioning equipment shown. The mixer 15 may be of any suitable type such as a mechanical mixer but is preferably of the flow type disclosed in the patent to Benjamin H. Thurman, No. 2,142,062, granted December 27, 1938. This mixer rapidly produces an intimate mixture between the oil and degumming agent.

The resulting mixture may be passed through another heat exchanger 21 provided wtih a coil 22, and then delivered to a continuous centrifugal separator 24 from which the partially degummed oil is delivered as the light effluent through a

spout 25 into a container 26 and the gums are delivered as the heavy effluent through a spout 27 into a container 28.

The gums may be discharged from the process but the oil in the container 26 may be withdrawn therefrom by means of a proportioning pump 30, passed through a heat exchanger 31 provided with a coil 32 and delivered to a mixer 33. The neutralizing agent may be withdrawn from a source of supply shown as a tank 34 by a proportioning pump 35 and delivered through a heat exchanger 36 provided with a coil 37 to the mixer 33. The proportioning pumps 30 and 35 are shown as being driven by a motor 38 with a change speed device 39 between the pumps but any suitable type of proportioning apparatus may be employed instead of the proportioning apparatus shown. The mixer 33 may be of any suitable type such as a mechanical mixer, but is preferably of the flow mixer type referred to relative to the mixer 15.

The resulting mixture of oil and refining reagent produced in the mixer 33 may be passed through another heat exchanger 41 provided with a coil 42 and delivered into a dehydrating chamber 43 so as to flow down the walls of the dehydrating chamber. A relatively high vacuum is preferably maintained in the dehydrating chamber 43 by means of a vacuum pump 44 operating through a condenser 45 provided with a receiver 46 and an entrainment separator 47. Heat may be supplied to the vapor separating chamber 43 in any suitable manner, for example, by means of a heating coil 48 positioned in the evaporating chamber below the liquid level therein. A substantial amount of water and other volatile materials may be removed from the mixture in the vapor separating chamber 43 and preferably the mixture is substantially completely dehydrated therein. The dehydrated mixture may be withdrawn from the vapor separating chamber 43 by means of a pump 49 and delivered to a mixer 51. A hydrating agent may be withdrawn from a source of supply 52 by a proportioning pump 53 and also delivered to the mixer 51. The pumps 49 and 53 may be driven by a motor 54 and have a variable speed device 56 positioned between the pumps. The mixture from the mixer 51 may be delivered through a heat exchanger 57 to a continuous centrifugal separator 58 from which the neutral oil is discharged as the light effluent through a spout 59 into a suitable container 60 and the soapstock is discharged as the heavy effluent through a spout 61 into a suitable container 62.

The dehydration in the vapor separating chamber 43 followed by hydration in the mixer 51 provides for excellent separation of the soapstock from the oil even though a non-saponifying neutralizing agent is contemplated in the present invention, which type agent ordinarily produces a soapstock which is extremely difficult to separate from the neutral oil. In certain cases, however, such soapstock can be adequately separated from the oil without dehydration, particularly if relatively large excesses of the non-saponifying neutralizing agent are employed and the resulting mixture is diluted with a substantial quantity of a hydrating agent. In such cases the vapor separating chamber may be by-passed. This can be accomplished by passing the mixture from the heat exchanger 42 through the pipe 63 by closing the valves 64 and 65 and opening the valve 66 in the pipe 63.

The temperature to which the crude oil containing phosphatidic material may be heated to "set" the gum therein will vary with different oils but will usually fall between 200° and 450° F. In some cases this temperature may be even higher but should not be high enough to throw the gums or phosphatidic materials out of solution to produce a "break" which usually takes place at about 500° to 600° F. By heating the oil as above described the phosphatidic materials become set or changed in character so that they become more resistant to removal or destruction by the reagents employed to degum or neutralize the oil.

The heating referred to may be accomplished in a continuous manner in the heat exchanger 9, the heat exchanger 11 being employed to again cool the oil to a desired temperature for a subsequent step in the process. Usually a very short time of treatment at the high temperature is sufficient, but if desired, the coil 10 of the heat exchanger 9 can be of sufficient length to provide a longer time of treatment or a plurality of heat exchangers in series can be employed. Alternatively the crude oil can be heated in batch in the tank 6 to the required temperature and the heat exchanger 9 eliminated or by-passed.

Any suitable type of degumming agent which has no deleterious effect upon the oil may be mixed with the crude oil in the mixer 15. Thus, water alone or water containing a small amount of an electrolyte may be employed. Nearly any electrolyte such as very small amounts of strong acids or bases or relatively larger amounts of weak acids or bases or salts either neutral or having acidic or basic reactions may be employed. For example, boric acid is an effective degumming agent even when used in extremely dilute solution and has the added advantage of being an extremely effective preserving agent for the gums separated from the oil. Thus the preferred degumming agent is a weak solution of boric acid but dilute solutions of neutral or slightly acidic salts are also extremely effective. Since in the present invention it is not desired to remove all of the gums, water alone is many times sufficient and has been satisfactorily employed and if other degumming agents are employed, weak solutions of the less drastic agents are ordinarily employed.

Separation of gums from the oil is most effective at temperatures somewhat above atmospheric, for example, between 100° and 130° F. although temperatures somewhat below this range and also above this range up to approximately 160° F. have been employed. The best temperature of mixing will vary with different oils certain of which respond better to relatively high temperatures of mixing and others to lower temperatures, but the mixing temperature will usually fall between 80° and 160° F. By employing the heat exchangers 16, 11 and 17 to subtract or add heat to the oil, degumming agent or mixture, any desired temperature of mixing and separation can be secured. With most oils it is sufficient to cool the oil in the heat exchanger 11 so that mixing a degumming agent at room temperature with the oil will produce the desired separating temperature.

The neutralizing agent of the present invention is preferably a non-saponifying neutralizing agent, soda ash being preferred because of its excellent action as well as its cheapness and availability. Non-saponifying neutralizing agents neutralize the free fatty acids without attacking the neutral oil and in this respect are distin-

guished from caustic alkalies which will saponify neutral oil. Thus the neutralizing agents may in general be any salt of a strong base and a weak acid, for example, trisodium phosphate, sodium acetate, etc. Also other materials having an alkaline reaction and not attacking neutral oils, such as ammonia or amines, for example, triethanolamine may be employed as a non-saponifying neutralizing agent. Even caustic alkalies may be employed if used in amounts not substantially greater than that necessary to neutralize the free fatty acids.

The most effective temperature of mixing with the neutralizing agent will vary with different oils and different neutralizing agents and such temperature may be secured by either heating or cooling the degummed oil from container 26 or the neutralizing agent or both in the heat exchangers 31 and 36. Thus the temperature of mixing will vary within a wide range but will usually fall within 80° to 160° F.

Substantially any of the neutralizing agents almost immediately neutralize the free fatty acids when intimately mixed with the oil in the mixer 33. However additional time for the neutralizing reaction may be provided in the coil 42 of the heat exchanger 41 which may also be employed to adjust the temperature to a desired separating temperature, and if dehydration of the mixture followed by rehydration is found necessary to provide for effective separation of the resulting soapstock from the oil, the heat exchanger 41 may be employed to raise the temperature of the mixture in order to enable water and other vaporizable impurities to be separated in vapor form from the soap in the vapor separating chamber 43. Such temperatures may be varied between 160° and 212° F. for ordinary operations, but in some cases it has been found desirable to employ much higher temperatures in the vapor separating chamber 43, for example, temperatures up to 450° F. in order to remove volatile materials having an undesirable odor found in some oils. Additional heat may be supplied to the materials in the vapor separating chamber 43 by the heating coil 48 is desired.

The hydrating agent mixed with the dehydrated oil-soapstock mixture withdrawn from the vapor separating chamber 43 may be any aqueous medium which will hydrate and weight the soapstock of the rehydrated mixture. Thus water alone may constitute the hydrating agent although this agent preferably comprises an aqueous solution of a substantial neutral salt or salts, particularly those having separating promotion properties such as sulphates, or thiocyanate of alkali metals, although solutions of salts having a basic reaction may be employed. The temperature found most suitable for separating a particular mixture may be obtained by heating or cooling the mixture in the heat exchanger 57, and this temperature will ordinarily range between 100° and 160° F. although in some instances higher temperatures may be employed. The various heat exchangers illustrated can thus be employed to heat or cool the materials passed therethrough depending upon the oil being treated and the agents employed; they can be used to provide additional reaction time for mixtures passed therethrough in which case no heat may be added or subtracted; or they can be eliminated from the apparatus if not necessary for a particular operation.

The process is preferably carried on so that a substantial amount of phosphatidic material remains in the oil discharged into the receiver 62 from the centrifugal separator 58. The high temperature pretreatment of the oil containing gums makes a portion of the phosphatidic material extremely difficult to remove by degumming and refining steps and, in general, a substantial amount phosphatidic material remains in the oil even after relatively drastic alkali refining steps. However, by correlating the temperature and time of the pretreatment with the amounts and concentrations of the agents and conditions employed in the subsequent steps, the amount of bound phosphatidic material in the final oil may be varied. Thus for a particular pretreated oil, a degumming agent is selected and its amount and concentration adjusted so that a substantial amount of the gums is discharged with the oil through the spout 25 of the separator 24. The gummy materials retained in the oils are to a large extent phosphatidic and depending upon the amount of this material removed by the degumming agent and conditions employed in the degumming step the amount of gums remaining in the oil discharged into the receiver 26 may vary, for example, from ¼ to 1%. With this oil fed to the neutralizing step and mixed with a neutralizing agent of sufficiently low concentration or amount a final oil delivered to the receiver 60 may be obtained containing, for example, 1/10 to 5/10% of phosphatidic material. In general the only subsequent treatment needed to remove traces of other impurities in the oil is a filtering step with a small amount of filter aid such as fuller's earth, acitivated clay, etc. Such a filtering step does not remove an appreciable amount of the phosphatidic material as any of such material remaining in the oil is extremely bound up with the oil. Even a washing and drying step may sometimes be employed without appreciably diminishing the amount of phosphatidic material remaining in the oil.

The separate degumming and neutralizing steps above described are advantageous in certain cases since a more selective action upon phosphatidic material retained in the oil is secured thereby, the gums from the degumming step constitute a valuable by-product, and the soapstock from the neutralizing step is of higher quality. It is possible, however, to carry out both degumming and neutralizing in a single step, as the non-saponifying neutralizing agents will also function as partial degumming agents to still produce an oil containing associated phosphatidic material. Also it is not necessary to cool the oil after it has been heated to the phosphatide or gum setting temperatures before adding a degumming agent or non-saponifying neutralizing agent. That is to say the high temperatures in such cases set the phosphatidic material in the oil even in the presence of a degumming or non-saponifying neutralizing agent. Thus it is also possible to first add such an agent at a relatively low temperature and then bring the mixture to the gum setting temperature. The heated mixtures resulting from such operations may then be cooled to a desired separating temperature or in some instances may be separated at the elevated temperature or in case a non-saponifying neutralizing agent is employed the mixture may be delivered directly to a vapor-separating zone without cooling.

In any event the phosphatidic material remaining in the neutral oil is more intimately associated or bound with the neutral oil than is the case where phosphatidic materials are

later added to an oil from which substantially all of the phosphatidic materials have been removed. The neutral oil containing phosphatidic material resulting from the process of the present invention is extremely stable against oxidation or the acquiring of disagreeable odors when compared with oils from which all of the phosphatidic material has been removed or even the latter oil to which phosphatidic material has been added. Since phosphatidic materials are valuable ingredients in margarine and shortening the oils of the present invention may be employed therein either as compounding oils with harder fats or after hydrogenation. Since the present process does not reduce the color of the oil to the extent secured in processes employing large excesses of caustic alkalies, the process is particularly valuable with light colored oils such as corn oil but may be employed in the production of neutral oils containing phosphatidic materials in which a dark color is not objectionable. The invention is also particularly applicable to vegetable oils, but the other glyceride oils such as animal oils also usually contain phosphatidic materials analogous to those found in vegetable oils, and may also be treated by the present invention. The continuous process disclosed enables a high quality oil to be produced with low losses but it is apparent that at least certain of the steps may be batch operations.

By the employment of the term "set" in the product claims, I intend to embrace and be restricted to a product in which the phosphatidic material, as originally contained in the oil, has been treated in such a way that it is incapable of removal by an aqueous separation during the separation of the soap stock from the refined product, irrespective of whether separation of the phosphatidic material is attempted by centrifuging, filtering or settling, whereby such material becomes intimately a part of the oil and performs the functions and advantages herein described.

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. In the process of recovering a neutral oil from crude fatty oils containing gums including phosphatidic material, which process includes mixing said oil with a non-saponifying neutralizing agent and separating the resulting soap stock from said oils in the presence of substantial amounts of water, the improvement which comprises, supplying sufficient heat to said oil prior to separating said soap stock therefrom to set a substantial portion of said phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, to thereby produce a substantially neutralized oil containing a substantial amount of said phosphatidic material after separation of said soap stock.

2. In the process of recovering a neutral oil from crude fatty oils containing gums including phosphatidic material, which process includes mixing said oil with a non-saponifying neutralizing agent and separating the resulting soap stock from said oils in the presence of substantial amounts of water, the improvement which comprises supplying sufficient heat to said oil prior to separating said soap stock therefrom to raise the temperature thereof to between 200 and 450° F. and sufficiently high to set a substantial portion of said phosphatidic material therein and produce a substantially neutralized oil containing a substantial amount of said phosphatidic material after separation of said soap stock.

3. In the process of recovering a neutral oil from crude fatty oils containing gums including phosphatidic material, which process includes mixing said oils with an aqueous degumming agent, separating the resulting foots containing water from the oil, mixing the resulting oil with a non-saponifying neutralizing agent and separating the resulting soap stock from the neutral oil, the improvement which comprises, supplying sufficient heat to said oil prior to separating said foots to raise the temperature thereof to a degree which will set a substantial portion of said phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, to thereby produce a substantially neutralized oil containing a substantial amount of said phosphatidic material after separation of said soap stock.

4. The process of refining crude animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, mixing said oil with a non-saponifying neutralizing agent, heating said mixture to a temperature sufficiently high to set a substantial portion of the phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil and separating the resulting soap stock from the neutral oil in the presence of substantial amounts of water to produce a substantially neutralized oil containing a substantial amount of phosphatidic material.

5. The process of refining crude animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, mixing an aqueous degumming agent with said oil, heating said mixture to a temperature sufficiently high to set a substantial portion of the phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, separating gums from said oil, thereafter neutralizing the resulting oil with a non-saponifying neutralizing agent and separating the resulting soap stock therefrom to produce a substantially neutralized oil containing a substantial amount of phosphatidic material.

6. The process of refining crude animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, preheating said oils containing gums to a temperature sufficiently high to set phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, thereafter mixing the resulting oils with a non-saponifying neutralizing agent and separating the resulting soapstock from the neutral oil in the presence of substantial amounts of water to produce a substantially completely neutralized oil containing a substantial amount of phosphatidic material.

7. The process of refining crude animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, preheating said oils containing said gums to a temperature sufficiently high to set phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, thereafter partially degumming the re-

sultant oils with an aqueous degumming agent under conditions which leave a portion of the gums in the oil, thereafter neutralizing the partially degummed oils with a non-saponifying neutralizing agent, and separating the resulting soap stock therefrom under conditions leaving a substantial amount of phosphatidic materials in the neutral oil.

8. The process of refining crude animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, heating the oil containing gums to a temperature sufficiently high to set phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, thereafter partially degumming the crude oil with an aqueous degumming agent in sufficiently small amount to leave a substantial portion of the gums therein, thereafter neutralizing the resultant oils with a neutralizing agent in sufficient amount to substantially completely neutralize the resulting oil, but insufficient to precipitate all of the phosphatidic material, and separating the resulting soap stock from the neutral oil to produce a neutral oil containing a substantial amount of phosphatidic material.

9. The process of refining crude animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, heating the crude oils to a temperature sufficiently high to set phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, thereafter mixing the stream of the oil containing gums with a stream of aqueous degumming agent in an amount insufficient to precipitate all of said gums, delivering the combined stream to a continuous centrifugal separator and continuously centrifugally separating a portion of said gums from said oil to produce a partially degummed oil, continuously mixing a stream of said partially degummed oil with a stream of a neutralizing agent in sufficient amount to substantially completely neutralize said partially degummed oil but insufficient to precipitate all of the remaining gums therein, delivering the resulting stream to a continuous centrifugal separator and separating the resulting soap stock resulting from the neutral oil to produce a substantially neutral oil containing a substantial amount of phosphatidic material.

10. The process of refining crude animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, heating said crude oil to a temperature sufficiently high to set phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, cooling the heated oil, and mixing therewith a non-saponifying neutralizing agent and separating the resulting soap stock in the presence of substantial amounts of water from neutral oil containing a substantial amount of phosphatidic material.

11. The process of refining animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing phosphatidic material, which comprises, heating said oil to a temperature sufficient to set phosphatidic material therein but insufficient to cause gums to be rendered insoluble in dry oil, cooling the heated oil and mixing therewith an aqueous degumming agent to precipitate a portion of said gums, separating the precipitated gums from the resulting oil and thereafter neutralizing said resulting oil and separating the resulting soap stock therefrom to produce a neutral oil containing substantial amounts of phosphatidic material.

12. The process of refining animal and vegetable oils containing gums including phosphatidic material to produce a neutral oil containing substantial amounts of phosphatidic material, which comprises, heating the oil containing gums to a temperature between 200° and 450° F. and sufficiently high to set phosphatidic material therein, cooling the heated oil to a temperature between 80° and 160° F. and mixing a non-saponifying neutralizing agent therewith and separating the resulting soap stock from neutral oil in the presence of substantial amounts of water and at a temperature between 100° and 160° F. to produce a neutral oil containing substantial amounts of phosphatidic material.

13. As a product of manufacture a glyceride oil derived from crude glyceride oils containing free fatty acids and gums including phosphatidic material, said product being substantially neutral and being substantially free of gums other than phosphatidic material but containing a substantial amount of "set" phosphatidic material which is not removed from the oil by precipitation with water and centrifugation, settling or filtration and which is thus contradistinguished from identical oils having such phosphatidic material added thereto, said product being further characterized by heat treatment of the oils following refining prior to separation of the resultant soap stock, to an extent sufficient to "set" the said phosphatidic material and to render the same inseparable by water precipitation and centrifugation.

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