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2,415,301

REFINING OF GLYCERIDE OILS AND RECOVERY OF BY-PRODUCTS

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15 Claims. (Cl. 260—210)

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This invention relates to the refining of glyceride oils and recovery of byproducts, and more particularly to a process in which valuable byproducts of the class usually grouped under the heading "unsaponifiables" are recovered as part of a refining operation.

Glyceride oils, particularly vegetable oils, contain a large number of materials other than the glycerides of fatty acids the latter being the main constituent constituting substantially all of the refined oil. The other materials include free fatty acids which are removed as soap in alkali refining operations, phosphatides which may be either removed in an initial degumming step or as part of the soap stock in the alkali refining operation, and a class of materials above referred to as unsaponifiables, some of which remain in the refined oil and some of which are removed in the various refining steps such as degumming or alkali treating steps. The present invention is chiefly concerned with the recovery of unsaponifiables, particularly sterols and glycosides including sterol glucosides.

While glyceride oils usually contain between 1 and 2% unsaponifiables, many of which can be isolated and identified by laboratory analytical procedures, it is extremely difficult to recover these materials in commercial quantities and concentration either from the crude or refined oils or from the gums or soap stock removed from the oil during refining. Because of the large amounts of materials which must be handled and the difficulty with which the unsaponifiables are separated from these materials, such operations as solvent extractions, etc., are expensive and time consuming.

An initial degumming operation results in the separation from the oil of a material consisting predominantly of phosphatides and usually containing in the neighborhood of 3% unsaponifiables. These unsaponifiables are, however, largely intimately bound up with the gummy materials, including phosphatides, and it is difficult to recover the same. Such recovery steps also usually destroy the valuable phosphatides. The degumming operation, however, does not remove all of the unsaponifiables from the oil, and in general this is true of all of the usual refining operations conventionally practiced upon glyceride oils. For example, a conventional caustic alkali refining step, either a batch or a continuous operation, usually leaves in the neighborhood of 1% unsaponifiables in the oil although a considerable amount of unsaponifiables is separated with the soap stock. This is true irrespective of whether

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the oil has been subjected to a prior degumming step. A greater amount of unsaponifiables is present in the soap stock when no prior degumming operation has been carried out since the phosphatides with their associated unsaponifiables are also present in the soap stock. In any case the unsaponifiables separated in the soap stock are also difficult to recover because of the large amount of other materials such as soap or gums present. The unsaponifiables left in the oil after a caustic alkali refining step appear to be intimately bound up with the oil and are also extremely difficult to remove therefrom.

While alkali refining steps employing soda ash or other non-saponifying alkalies also cause removal of a considerable amount of unsaponifiables in the soap stock in difficultly recoverable form, it is an unexpected fact that such non-saponifying alkali refining treatments remove a substantially less amount of unsaponifiables from the oil than caustic alkali treatments and that a substantial portion of the unsaponifiables left in the oil is rather easily removable therefrom and can be recovered in concentrated form. Thus, aqueous agents, including pure water, can be employed to remove a portion of the unsaponifiables left in the oil after a soda ash or similar refining step with non-saponifying alkalies, and these unsaponifiables may be recovered in extremely concentrated form with a minimum of contamination with other materials. Separate recoveries of different types of unsaponifiables can also be obtained by employing different types of agents in succession on the oil. It should be apparent from the above that it is not the actual concentration of the unsaponifiables in the oil at any given time during a refining operation which is of primary importance, but that it is the condition of the oil and unsaponifiables in the oil at the time of the recovery treatment which enables the recovery of unsaponifiables in concentrated form and in a form in which they may be readily purified.

It is, therefore, an object of the present invention to provide an improved process of refining glyceride oils and recovering unsaponifiables therefrom.

Another object of the invention is to provide a process of recovering unsaponifiables from glyceride oils in which the oil and unsaponifiables are conditioned for separation of said unsaponifiables and the unsaponifiables are recovered in concentrated relatively pure form during a refining operation.

Another object of the invention is to provide

a method of recovering unsaponifiables from glyceride oils in which an oil, after treatment with a non-saponifying alkali and removal of the soap stock therefrom, is treated with an aqueous agent to recover unsaponifiables.

A further object of the invention is to provide a process in which a separation between various types of unsaponifiables may be produced during the recovery operation so that at least two different types of unsaponifiables are separately recovered.

The unsaponifiables of common crude vegetable oils, such as corn oil, cottonseed oil, soya bean oil, etc., vary from approximately 1 to 2%. These unsaponifiables are defined in terms of analytical procedure as all substances in the oil which are insoluble in water or incapable of forming soluble soaps with alkalies but which are soluble in petroleum ether and ethyl ether. The unsaponifiables have also been defined as all unsaponifiable substances which are insoluble in water but soluble in light petroleum ether. The unsaponifiables comprise a mixture of extremely complex substances. They contain carotinoid pigments, vitamins A, D, K and E, sterols, hydrocarbons, inhibitols, tocopherols and combinations of certain of these substances with carbohydrates, as well as other materials some of which are unidentified. Vitamin E or alpha tocopherol is present in crude vegetable oils to the extent of from 0.1 to 0.2% and is a particularly valuable byproduct recovered in accordance with the present invention. The tocopherol content of the unsaponifiable material recovered by the present invention may range from approximately 5 to 33%. Sterols also represent valuable byproducts and are usually present in the recovered material as free sterols, as sterol esters, and as sterol glucosides. Free sterols can be obtained from the esters and glucosides by acid hydrolysis thereof, although the sterol glucosides themselves have important uses. They are excellent emulsifiers, particularly when employed in conjunction with other emulsifying or wetting agents. The present invention furnishes an important source of such glucosides.

In carrying out the present invention, substantially all of the gummy materials, including phosphatides, and substantially all of the free fatty acids are first removed from the glyceride oil by an alkali refining operation employing soda ash or other non-saponifying alkali as a neutralizing agent. A degumming operation may or may not be employed prior to the alkali refining operation. In general, the recovery of unsaponifiables will be somewhat greater when no prior degumming operation is employed, but this is at the expense of separating the valuable phosphatides in admixture with the soap stock from the alkali refining operation. Since the gums are removed from the oil in either a degumming step or the alkali refining step, the unsaponifiables recovered in the present invention are not substantially contaminated by gummy materials. The soda ash or similar refining step appears to condition the unsaponifiables for easy removal. It is apparent that this is the case, as an oil which has merely been degummed is not susceptible to treatment for the removal of unsaponifiables by the aqueous treatment step of the present invention until after it has been subjected to a refining operation with a non-saponifying alkali.

The preferred non-saponifying alkali for conditioning of the oil in accordance with the present invention is soda ash, although other non-saponifying alkalies, such as those mentioned in the patent to Clayton 2,249,701, granted July 15, 1941, can be employed. Examples of such other non-saponifying neutralizing agents are disodium phosphate, trisodium phosphate and equivalent potassium salts, including potassium carbonate. The refining operation of said patent, including dehydrating and rehydrating steps as disclosed therein, is also the preferred type of alkali refining operation, although simpler procedures using non-saponifying neutralizing agents may be employed, such as that disclosed in Clayton Patent 2,190,594, granted February 13, 1940. Thus, substantially any primary refining operation or operations employing non-saponifying alkalies so as to reduce the fatty acid and gum contents to low values, while leaving a substantial amount of recoverable unsaponifiables in the oil may be practiced in accordance with the present invention. In general, continuous processes, particularly that shown in Clayton 2,249,701, produce oils having the highest recoverable unsaponifiables content, but the present invention is not limited to such continuous process for primary refining.

In accordance with the present invention, it has been found that a portion of the unsaponifiable content left in the oil after an alkali refining step with a nonsaponifying alkali can be removed by mixing water with the oil and subjecting the resulting mixture to continuous centrifugal separation. The heavier effluent is predominantly water, but carries out of the oil a substantial quantity of unsaponifiables, which action is unexpected as the unsaponifiables are substantially insoluble in water. In fact, the unsaponifiables tend to separate from the water during centrifugal separation to form an intermediate layer between the water and the oil. That is to say, the mixture stratifies into three layers in the centrifugal. It is difficult to adjust a continuous centrifugal separator so that the layer of unsaponifiables is discharged with the water as the heavy effluent, since a portion of the unsaponifiables of this layer tend to come out with the oil layer and a portion with the water. Such stratification can be largely prevented by employing relatively large amounts of water, for example, amounts of water between 10 and 50% of the oil. However, when water is mixed with oil with sufficient intensity to cause the unsaponifiables to separate with the water, inevitably a small amount of oil is emulsified in the water so that such large amounts of water tend to cause losses of valuable neutral oil. This loss can, to a large extent, be overcome by employing a small amount of water in the initial admixture of water with the oil, for example 1 to 5%, and then adding a larger amount of water to the oil in a loose mixture just prior to the centrifugal separation operation. In such cases, 5 to 35% additional water will ordinarily cause substantially complete separation of the unsaponifiables with the water without material loss of oil.

In fact, it has been found unnecessary to add the additional water to the oil and water mixture entering the centrifugal so long as the additional water is present in the centrifugal separator during separation. Thus, the additional water may be added to the heavier effluent in the centrifugal just after separation of the water from the oil, for example, in an apparatus such as shown in Clayton application Serial No. 483,953, filed April 21, 1943. Introducing the additional water just

before or during the actual separation in the centrifugal produces a somewhat improved operation. A particularly effective apparatus for this purpose is that disclosed in Clayton Patent No. 2,301,110, granted November 3, 1942, in which the water is added at or just inside the neutral zone of separation in the centrifugal so that any unsaponifiables which tend to come out with the oil are washed from the oil into the aqueous phase and are carried out as part of the heavy effluent.

No difficulty is encountered in separating the unsaponifiables from the heavier effluent from the centrifugal separation just discussed. These unsaponifiables collect as an upper layer when the separated heavy effluent is allowed to stand, and can be removed therefrom by decantation, skimming, etc. It is also possible to immediately run the heavy effluent through a second continuous centrifugal separator correctly adjusted so that a lighter effluent is discharged which is predominantly unsaponifiables, and a heavier effluent discharged which is substantially free of unsaponifiables.

It has been found that an increased recovery of unsaponifiables is attained if the water used to remove the unsaponifiables is made acidic, for example by adding acids which ionize to a substantial extent such as mineral acids, salts of strong acids and weak bases, or even strongly ionizing organic acids such as acetic acid. In general, a small amount of acidity, i. e., even a slight lowering of the pH of the water, causes a considerable increase in the amount of unsaponifiables. Relatively strong acid solutions may also be employed, but have the disadvantage that they impart acidity to the neutral oil which is difficult to remove without a subsequent alkali treatment. As discussed below, such subsequent alkali refining operations are in some cases desirable to remove additional unsaponifiables, in which case relatively strong acids may be employed in the first unsaponifiables-removal step.

When aqueous acid solutions are employed to remove the unsaponifiables, even slightly acid solutions tend to raise the acidity of the oil. This can be overcome by employing a slightly alkaline solution as a flush in the centrifugal to prevent stratification of the unsaponifiables and carry the same out of the centrifugal with the heavier effluent. Addition of the alkaline solution to the heavier effluent in the centrifugal after it has been separated from the oil has some effect in reducing this acidity, but it is preferred to add the alkaline solution in the zone of separation, preferably slightly inside of the neutral zone; for example, by the apparatus disclosed in Clayton Patent No. 2,301,110 referred to above. When using acid aqueous agents the amount of precipitating or extracting agent and the amount of additional liquid added to the centrifugal will in general fall within the ranges above given when employing neutral or pure water.

It is also possible to increase the amount of unsaponifiables recovered over that recovered when a neutral water is employed by employing a caustic alkali solution such as a solution of sodium hydroxide. Such alkaline solutions are particularly desirable when the oil being treated is a highly colored oil such as cottonseed oil or palm oil. Strong caustic alkali solutions can be employed to remove coloring materials which themselves fall under the broad classification of unsaponifiables. The best removal of color is

ordinarily obtained with highly concentrated caustic alkali solutions, for example, solutions between 16 and 50° Bé. caustic alkali, although in some instances weaker solutions ranging between 5 and 16° Bé. may be employed. Even weak or slightly alkaline solutions will remove a substantial amount of unsaponifiables, but ordinarily are not effective color-removing agents. The stratification problems referred to above when employing neutral water or slightly acidic solutions also occur when alkali solutions are employed, and this is particularly true both with an extremely strong alkali solution and very weak alkali solutions. In such cases, additional water can be added to the mixture of oil and alkaline solution just prior to centrifugal separation or during centrifugal separation, as described above, addition during centrifugal separation being preferred. That is to say, amounts of alkaline solution between 1 and 5% are ordinarily added in the initial mixing step and then additional amounts of aqueous agent, for example, between 5 and 35% are added as a flushing agent, the usual amounts being between 10 and 20%. In general, adding the diluting or flushing agent just inside and close to the neutral zone in the centrifugal (for example, in the apparatus disclosed in Clayton Serial No. 483,953, filed April 21, 1943) requires the least amount of flushing solution. In some cases neutral water is adequate for such flushing solution, but weakly alkaline solutions are desirable where acid solutions have been employed as the precipitating agent and sometimes it is desirable to add weak acid solutions where acidity in the final oil is not deleterious since such acid solutions facilitate the separation of the unsaponifiables from the heavier effluent.

It should be apparent from the above that neutral water or acid precipitating solutions, in general, do not remove much of the coloring matter and that there is a difference between the unsaponifiables removed by water, by acid solutions and by caustic alkali solutions. For light colored oils, for example, corn oil, water alone removes most of the unsaponifiables which are present in the oil in removable form. Acid solutions remove more of the unsaponifiables and the same is true of alkali solutions although the additional unsaponifiables removed by alkali solutions will usually differ from those removed by acid solutions. It is possible to first employ a removal operation using water or weak acid or alkaline solutions, and then subsequently treat the oil with a caustic alkali solution to obtain additional unsaponifiables. In the case of highly colored oils such as cottonseed oil, a first treatment with water or weak acid or weak alkaline solutions does not remove a substantial amount of the coloring material, and a subsequent treatment with a strong alkali does remove a substantial amount of unsaponifiables including carotinoid pigments, etc. It will be apparent that two successive treatments as discussed above can be employed to remove light colored unsaponifiables, including the greater portion of the sterols and sterol glucosides, and then a caustic alkali treatment can be employed to remove carotinoids, tocopherols, etc. It is further apparent that the strong caustic can be employed initially to remove substantially all of the unsaponifiables, in which case the various types of unsaponifiables are recovered in admixture and require extensive subsequent separation steps, which are many times difficult to perform.

It is further apparent from the above that a large number of electrolytes may be employed in conjunction with water, or water alone may be employed as an unsaponifiable-removing agent after the oil has been conditioned by a proper refining operation to condition the unsaponifiables for separation. Thus, acids, including mineral acids such as hydrochloric and sulfuric, may be employed, various salts either neutral, basic or acidic may be employed, as well as strong alkalies. Among the alkaline agents possible to be employed are sodium phosphate, sodium pyrophosphate, lithium hydroxide, potassium hydroxide, sodium borate, borax, sodium peroxide, etc. Even substantially neutral salts such as sodium sulfate or sodium chloride in some cases increase the amount of unsaponifiables recovered over pure water. Thus substantially any aqueous solution of an electrolyte or pure water is contemplated as an unsaponifiables-removing agent. Various agents can be used in succession to obtain different types of unsaponifiables although a large number of treatments of all of the oil is in general uneconomic.

When neutral or acidic or even slightly alkaline solutions are employed as the unsaponifiables-removing agent, no difficulty is encountered in separating the unsaponifiables from the solution after separation from the oil. However, when strongly alkaline solutions are employed, particularly when these strong alkaline solutions are diluted during separation from the oil, the unsaponifiables tend to remain in suspension in the aqueous material. This tendency can be overcome by slightly acidulating the heavy effluent either in the centrifuge as above mentioned or thereafter. This acidulation need not be and preferably is not sufficient to decompose the small amounts of soap formed due to treating the oil with strong alkalies, since decomposing the soap formed due to treating the oil with strong alkalies, since decomposing the soap liberates free fatty acids which would be separated with the unsaponifiables. It has been found that sufficient acid, such as a mineral acid or relatively strong organic acid, can be added to the aqueous effluent of the centrifugal to render te unsaponifiables separable and at the same time leave the soap substantially undecomposed, so that the soap remains in solution in the aqueous phase. Alternatively acidulation of the heavier effluent can be preformed later as part of the step of separating the unsaponifiables from the aqueous heavier effluent.

As indicated above, the oil, after separation of unsaponifiables in relatively pure form as discussed above, still contains a substantial amount of unsaponifiables which are apparently extremely intimately bound up with the oil itself. It is possible to recover certain of these unsaponifiables by treatment of the oil with an adsorbent such as activated alumina, silica gel, synthetic resins, etc., and filtering the oil from the filter cake. The filter cake can then be extracted with acetone, alcohol or ether to remove the unsaponifiables. Instead of filtering it is also possible to centrifugally separate the adsorbent carrying the unsaponifiables from the oil in a batch type of centrifugal, or this material may be separated in a continuous centrifugal separator with the aid of a stream of flush material directed into the bottom of the centrifugal bowl and outwardly to the walls thereof so as to wash the solid adsorbent out of the centrifugal. The solid adsorbent can then be decanted or filtered from the aqueous phase and treated with solvents as above described. Such an operation can even be employed for separating all of the unsaponifiables after the non-saponifying alkali refining step, but in general is not as effective or as easily performed as the operations described above. Nevertheless, such adsorbent treatment can sometimes be carried out as a practical operation after treatment with aqueous solutions as above described to recover still another type of unsaponifiables.

As the soda ash or similar non-saponifying refining step contemplated in the present invention does remove a substantial amount of unsaponifiables, it is advantageous to use the minimum possible amount of refining agent which can be employed to produce a neutral oil and provide effective separation of soap-stock. In other words, minimizing the reagent in the alkali refining step results in an increased recovery of unsaponifiables in the subsequent recovery steps. Also, as indicated above, maximum recovery of unsaponifiables is accomplished when no degumming step is employed prior to the alkali refining step, so that the phosphatides with their associated unsaponifiables are present during the treatment of the oil with the non-saponifying alkali in the refining step.

It will thus be seen that the present invention provides for the recovery of a concentrate high in unsaponifiables from glyceride oils as a result of the conditioning of these oils for separation of the unsaponifiables by a refining operation employing a non-saponifying alkali, which refining operation is of the type in which the losses of neutral oil are reduced to almost a theoretical minimum. The unsaponifiables recovered are valuable products commanding a high price on the market. They constitute an excellent source of vitamins, sterols and sterol glucosides. These various materials can be relatively easily individually separated from the concentrate by solvent extraction or distillation operations, and this is particularly true where the more highly colored unsaponifiables such as carotin, xanthophylls and chlorophylls are separated from other unsaponifiables predominantly sterols and sterol compounds during the recovery process. The carrying out of the present process enables a high quality of edible refined oil to be produced and adds substantially no expense to the refining process. The material recovered from the heavier effluent when water or slightly acidic or alaline solutions are employed runs extremely high in unsaponifiables which are predominantly sterols and sterol glucosides. Thus the unsaponifiables concentration after separation from the aqueous phase may be 80% or greater, and it is usually greater than 50%, the remaining materials being soap washed from the oil and a small amount of gums not removed in degumming or the prior alkali refining operation. When strong caustic alkali is employed in the unsaponifiables-removal step, substantially greater amounts of soap are present, but even so this material may run as high as 75% unsaponifiables. Substantially 100% concentrations of unsaponifiables may be produced from any of these materials by one or more successive solvent treatments, for example, with petroleum ether, acetone or other solvent.

The process of the present invention is preferably carried out in a continuous manner. That is to say the refining steps or steps for conditioning the oil may be operative in which the

oil and agents are mixed in continuous stream flow and separations of soap stock or foots from the oil are carried out in continuous centrifugal separators. The mixing of the agent for rendering the unsaponifiables separable is also preferably carried out in stream flow by bringing proportioned streams of oil and agent together in a mixer and the resulting mixture delivered as a stream to a continuous centrifugal separator. When employed, a stream of diluting or flushing agent may be delivered into the stream of mixture entering the centrifugal or delivered directly into the centrifugal as above described. The stream of the resulting heavier effluent may be directly delivered to a second centrifugal for further concentrating the unsaponifiables or concentration may be effected by settling and decantation.

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 refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with an aqueous agent which will render unsaponifiables separable from said neutral oil, separating said aqueous agent along with unsaponifiables from the resulting oil and separating unsaponifiables from the separated aqueous agent.

2. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing soda ash and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with an aqueous agent which will cause unsaponifiables to be separable from said neutral oil, separating said aqueous agent along with unsaponifiables from the resulting oil and separating unsaponifiables from the separated aqueous agent.

3. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a nonsaponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with an aqueous agent which will render unsaponifiables separable from said neutral oil continuously centrifugally separating said aqueous agent along with unsaponifiables from the resulting oil and separating unsaponifiables from the separated aqueous agent.

4. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with a small amount of aqueous agent which will render unsaponifiables separable from the neutral oil, continuously centrifugally separating said aqueous agent along with unsaponifiables from the resulting oil, adding an additional amount of aqueous agent to the centrifugal separator so as to mix with the heavier effluent therein to facilitate separation of said unsaponifiables with said heavier effluent, and separating unsaponifiables from the heavier effluent discharged from said centrifugal.

5. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with a small amount of aqueous agent which will cause unsaponifiables to be separable from the neutral oil, continuously centrifugally separating said aqueous agent as a heavier effluent along with unsaponifiables from the resulting oil, introducing an additional amount of aqueous agent into the centrifugal separator adjacent the neutral zone of separation therein to assist in separating said unsaponifiables with said heavier effluent, and separating unsaponifiables from the separated heavier effluent.

6. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with sufficient water to cause said unsaponifiables to be separable with said water, continuously centrifugally separating said water along with unsaponifiables from the resulting oil, and separating unsaponifiables from the separated water.

7. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with an aqueous alkaline agent which will render unsaponifiables separable from the neutral oil, continuously centrifugally separating said aqueous alkaline agent along with unsaponifiables from the resulting oil, and separating unsaponifiables from the separated agent.

8. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with a concentrated solution of caustic alkali to cause unsaponifiables to be separable from the neutral oil, continuously centrifugally separating said agent along with unsaponifiables from the resulting oil, diluting said agent during centrifugal separation with an aqueous medium to assist in separation of said unsaponifiables with said agent, and separating unsaponifiables from the separated agent.

9. The process of refining glyceride oils and re-

covering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables therefrom, thereafter mixing the separated neutral oil with an aqueous acid solution to cause unsaponifiables to be separable from the neutral oil, continuously centrifugally separating said acid solution along with unsaponifiables from the resulting oil, thereafter mixing the resulting oil with an alkali solution to cause unsaponifiables to be separable from the resulting oil and continuously centrifugally separating said alkali solution along with unsaponifiables from the resulting oil, and separating unsaponifiables from both the separated acid solution and the separated alkali solution.

10. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a soda ash as a neutralizing agent and including the separation of soap stock from neutral oil in order to condition the resulting oil for separation of unsaponifiables, thereafter mixing the conditioned oil with a small amount of aqueous acid agent which will render unsaponifiables separable from the neutral oil, continuously centrifugally separating said aqueous agent as a heavier effluent along with unsaponifiables from the resulting oil, introducing an amount of aqueous alkaline agent into the centrifugal separator adjacent the neutral zone of separation therein to assist in separating said unsaponifiables with said heavier effluent and neutralize acidity in the resulting oil, and separating unsaponifiables from the separated heavier effluent.

11. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing soda ash as a neutralizing agent and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables, thereafter mixing the separated neutral oil with sufficient water to cause said unsaponifiables to be separable with said water, continuously centrifugally separating said water along with unsaponifiables from the resulting oil, and separating unsaponifiables from the separated water.

12. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing soda ash as the neutralizing agent and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables, thereafter mixing the separated neutral oil with an aqueous agent

which will cause unsaponifiables to be separable from the neutral oil, continuously centrifugally separating said aqueous agent as a heavier effluent along with unsaponifiables from the resulting oil and separating unsaponifiables from the separated heavier effluent by subjecting said heavier effluent to a second continuous centrifugal separation.

13. The process of refining glyceride oils and recovering unsaponifiables therefrom, which comprises subjecting a glyceride oil containing unsaponifiables to a neutralizing step employing a non-saponifying alkali including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of unsaponifiables, thereafter mixing the separated neutral oil with an aqueous alkaline agent which will render unsaponifiables separable from the neutral oil, continuously centrifugally separating said aqueous alkaline agent as a heavier effluent along with unsaponifiables from the resulting oil, acidulating said heavier effluent and separating unsaponifiables from the acidulated heavier effluent.

14. In the art of recovering unsaponifiables from vegetable oils wherein said oils are refined by subjecting the same to treatment with a non-saponifying reagent for the removal of substantial quantities of the free fatty acids originally present therein and wherein the resulting soapstock is separated from the oil, the improvement which comprises the steps of adding an agent to said refined oil which will render unsaponifiable material remaining in the oil separable without destruction of the oil, separating a material containing unsaponifiable material from the oil and separating unsaponifiable material from the separated material.

15. The process of refining glyceride oils and recovering glucosides therefrom, which comprises subjecting a glyceride oil containing glucoside to a neutralizing step employing a non-saponifiable alkali and including the separation of soap stock from neutral oil in order to condition the glyceride oil for separation of said glucoside, thereafter mixing the separated neutral oil with an aqueous agent which will render glucosides separable from said oil, separating said aqueous agent along with glucosides from the resulting oil and separating glucosides from the separated aqueous agent.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,249,701	Clayton	July 15, 1941
2,306,547	Langlois	Dec. 29, 1942

Dedication

2,415,301.—*Morris Mattikow*, New York, N.Y. REFINING OF GLYCERIDE OILS AND RECOVERY OF BY PRODUCTS. Patent dated Feb. 4, 1947. Dedication filed June 30, 1964, by the assignee, *Benjamin Clayton, doing business as Refining, Unincorporated.*

Hereby dedicates to the public the terminal part of the term of said patent effective December 31, 1963.

[*Official Gazette September 29, 1964.*]