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PROCESS FOR PRODUCING LECITHIN PRODUCTS FROM SOAPSTOCKS

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FIG. 1

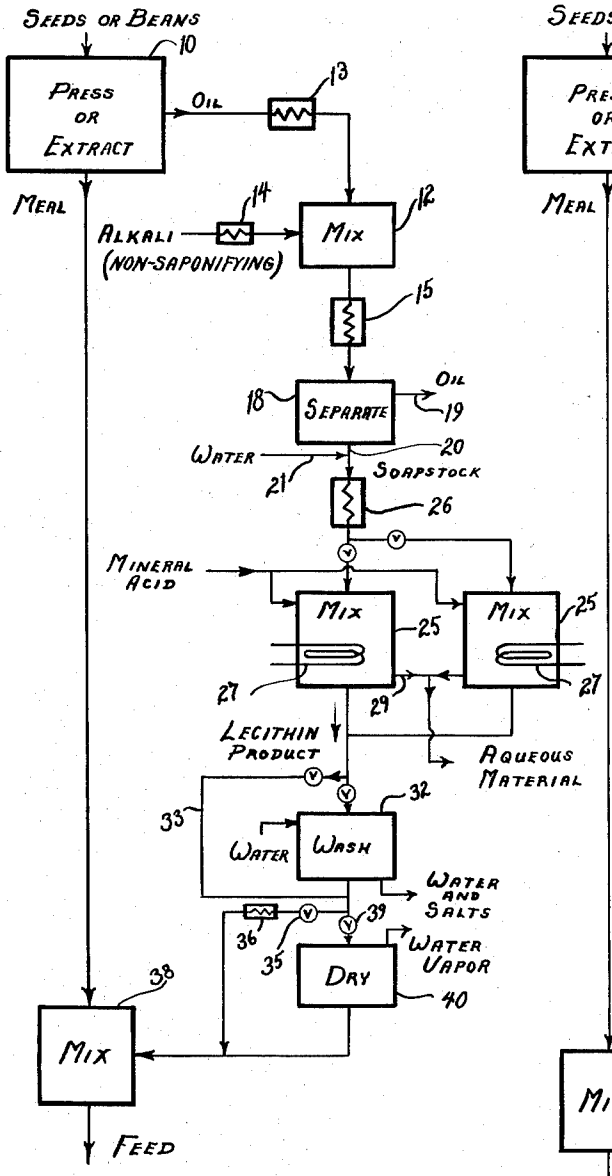
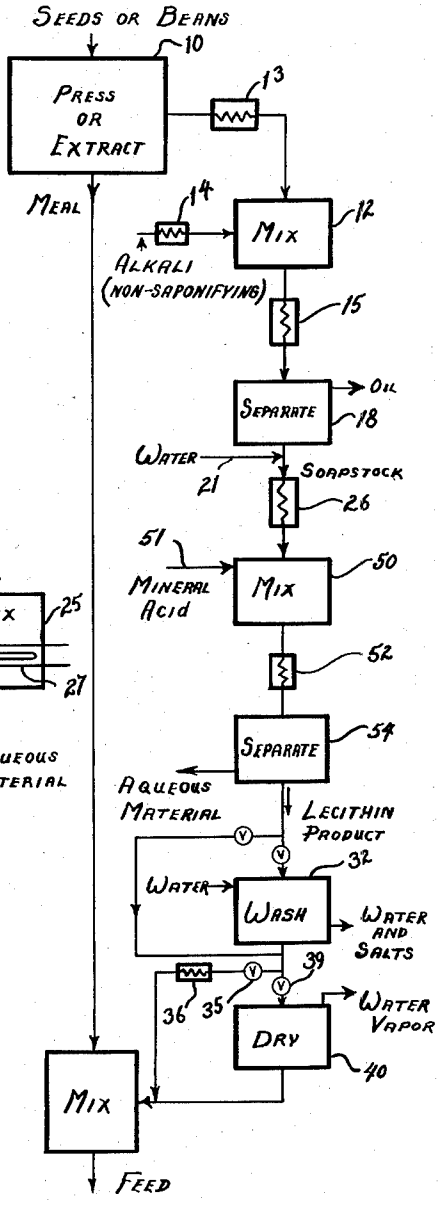


FIG. 2



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PROCESS FOR PRODUCING LECITHIN PRODUCTS FROM SOAPSTOCKS

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13 Claims. (Cl. 99—2)

This invention relates to the production of lecithin products obtainable by acidulation of certain soapstocks. It will be particularly exemplified as concerns a process of refining a crude vegetable oil by use of a non-saponifying alkali to produce a soapstock which, when acidulated in accordance with the invention, yields a nutritive lecithin product or phosphatidic product excellently suited as a feed additive.

Crude glyceride oils contain gum-like materials known as phosphatides which are of value if they can be recovered and if they are not degraded when the oil is refined. For example, crude vegetable oils contain high nutritive phosphatides which heretofore have been largely degraded or destroyed by use of refining techniques which convert the phosphatides to soaps, choline, trimethylamine and other intermediate products. For example, crude oils refined with caustic soda yield soapstocks in which the phosphatides have been attacked and largely decomposed. All such soapstocks containing degraded or decomposed phosphatides have little value, being merely a source of low-grade fatty acids when treated with large excesses of sulfuric acid to split the soaps and char the phosphatides and other gum-like substances. Such a process involves boiling for many hours and consumption of acid far in excess of that required to neutralize the excess caustic soda and convert the soaps to fatty acids.

It is an object of the present invention to refine crude glyceride oils in such way as to produce a valuable lecithin product. In this connection, the invention includes mixing the crude oil with a non-saponifying alkali, such as soda ash, and uniquely processing the resulting soapstock to produce a lecithin product. By a non-saponifying alkali, as the term is herein used, I have reference to a non-volatile alkali, such as soda ash, sodium bicarbonate, sodium sesquicarbonate, or disodium phosphate, which is a mild alkali as concerns any attack on triglycerides and phosphatides and which does not saponify substantial amounts of the oil during the refining operation.

It is a further object of the invention to acidulate soapstocks resulting from the refining of crude glyceride oils with a non-saponifying alkali, the acidulation involving adding only enough mineral acid to lower the pH to below 8 and usually enough to neutralize any excess alkali and convert the soaps into fatty acids and corresponding salts. A small amount of aqueous material is separated from the acidified soapstock, leaving a highly nutritive lecithin or phosphatide product.

It is another object of the invention to produce a lecithin product containing the phosphatides of the crude oil. It is a further object to produce a feed product by mixing such a lecithin product with meal produced in the process of extracting or pressing the crude oil from the seeds, beans, or other source material. A further object of the invention is to dry such a lecithin product before adding it to the meal or before use for other purposes, the dried product being fluid at normal temperatures.

Further objects and advantages of the invention will be evident to those skilled in the art from the following description of exemplary embodiments, two of which are schematically illustrated in the accompanying drawing, in which:

Fig. 1 is a schematic flow diagram of a process of the inventon in which the acidulated soapstock can be separated by gravity; and

Fig. 2 is a schematic flow diagram illustrating a process in which the acidulated soapstock is continuously separated.

The soapstocks with which this invention is concerned are those resulting from the refining of crude glyceride oils by non-saponifying, non-volatile alkalis so that the soapstocks still contain the indigenous phosphatides substantially unmodified. Hereinafter, soda ash soapstocks will be exemplified. Those resulting from the usual soda-ash processes or so-called low-excess soda ash refining process are good sources of valuable lecithin products. Such low-excess soda ash processes employ soda ash in amount not more than about three times that required to neutralize the free fatty acids of the crude oil.

In accordance with the invention, such soapstock is acidulated with only sufficient mineral acid largely to convert any excess soda ash to sodium sulfate, the soaps to fatty acids and sodium sulfate, and the soda ash phosphatide complex to free phosphatides. Upon settling or centrifuging, a minor portion or layer of aqueous material will separate, leaving a major portion or layer of a lecithin product comprising free oil, fatty acids and hydrated phosphatide. Most of the sodium sulfate and other inorganic salts will appear largely in the separated aqueous material. Any salts in the remaining lecithin product can be washed therefrom or can be permitted to remain therein as the small amount thereof is unobjectionable as a component of feeds.

Any relatively concentrated mineral acid can be used to acidulate the soapstock, typically sulfuric, phosphoric or hydrochloric acid. Sulfuric acid is preferred, usually of a concentration between 98% and 10%, usually about 25%. The amount of acid will desirably be such as to reduce the pH of the soapstock to about pH 5–7. Sometimes a pH slightly above 7 but below 8 is practical and produces a separated fatty layer containing somewhat more water than if the pH is within the range of 5–7. Addition of acids to reduce the pH to a value in the neighborhood of pH 5 is particularly desirable but use of larger amounts of acid as would char the phosphatides is to be avoided. The consumption of acid depends upon the free fatty acid content of the crude oil but is comparatively small, particularly when acidulating soapstock from a low-excess soda ash refining.

The fatty material or lecithin product which separates from the aqueous material contains the phosphatides in substantially the same state and amount as in the crude oil. It can be shipped economically because of its comparatively low water and high T.F.A. contents. The product can be readily pumped into and from a tank car or from one portion of a refinery to another.

This lecithin product may be added directly to products used in animal feeding or may be dried before being added to such products. Particularly desirable results arise from mixing the lecithin or concentrated-phosphatide product with meals produced when the source oil or other glyceride oil is separated from the seeds or beans by solvent extraction or by pre-pressing and solvent extraction. The phosphatide concentrate added to the meal, especially meal from solvent extraction, adds to the nutritive value because of the increased fat and phosphatide

content of the concentrate. Additionally, the color of the meal is improved. Furthermore, the phosphatide concentrate or lecithin product has adhesive tendencies which facilitate pelletizing and eliminate dusting when mixed with meal.

The dried lecithin product often has a fruit-like odor and at room temperature is usually still a liquid product. It will typically contain not more than a small amount of residual water, usually under 1%. Its phosphorous content (P) will usually be in the neighborhood of 0.8 to 3.0%. Acetone insolubles (phosphatides) will be in the neighborhood of 30–60%. The T.F.A. content would usually be about 45–80%, all of the aforesaid percentages being by weight.

Any ratio of phosphatide product to meal will improve the nutritive values. Excellent results have been obtained by adding 0.5–5.0% of the phosphatide product to the meal. Feeding tests show much faster growth of steers on a diet of this type as compared with the meal without the product.

Fig. 1 diagrammatically illustrates a practice of the invention on a commercial scale. The seeds or beans are delivered to a conventional pressing or extracting apparatus **10** producing a crude glyceride oil and a residual meal, as shown. A non-saponifying, non-volatile alkali is mixed with the crude oil either continuously or batchwise in a mixer **12**. The oil and alkali may be preheated in heaters **13** and **14**, if desired, or may be heated during mixing in the mixer **12**. Alternatively, or in addition, the mixture may be heated before being separated, as suggested by a heater **15**. The numeral **18** indicates any conventional separator operating in a batch or continuous manner and which produces a refined oil, indicated by arrow **19**, and a soapstock, indicated by arrow **20**. The refined oil may be re-refined by use of caustic soda to improve its color, as is well known in the art. No novelty is claimed in the instant process as concerns the steps per se thus far described with reference to Fig. 1 as these steps are well known in the art of refining crude glyceride oils. It is essential to the invention, however, that a non-saponifying alkali be employed so that the separated soapstock will contain the indigenous phosphatides of the oil in substantially their original form, as distinct from being substantially degraded, reacted or destroyed by the alkali refining agent.

A typical low excess soda ash soapstock will have the following composition: 20–45% water (most commonly 25–33%); 10–20% free oil, dry basis; and 30–45% T.F.A. Such soapstocks can be acidified as produced. However, it is usually better if the soapstock contains about 50–75% water when acidulated. As the soapstocks often contain less than this amount of water, it is sometimes desirable to add additional water to the soapstock, up to its own weight in some cases, as suggested by the arrow **21**.

In Fig. 1, the soapstock is delivered alternately to large vessels **25**, either with or without heating in a heater **26**. The aforesaid proportions of mineral acid are mixed alternately with the soapstock batches in the containers **25**, the mixture being heated or cooled by a heat-exchange coil **27** in each vessel. After mixing, the mass is permitted to settle for a time varying from a few minutes to several hours. An aqueous layer will settle, leaving a supernatant fatty layer comprising the lecithin products of the invention. The layer of aqueous material can first be withdrawn from the containers **25** as suggested by the numeral **29**, leaving the lecithin product therein.

Separating temperatures are desirably in the range of from about 70° F. up to 300° F. The usual temperature for gravitational or centrifugal separation is about 160–210° F. and it is never desired to employ temperatures and times of treatment that would split the gums or phosphatides of the lecithin product. Temperatures above 210° F. would be normally used only for supplemental purposes, such as the detoxification of gossypol to be described, and if used would be accompanied by sufficient pressure to prevent vaporization of water.

The lecithin product can be withdrawn alternately from the containers **25** to produce a continuous stream, which may be washed in a washer **32** or by-passed therearound, as indicated at **33**, if washing is not desired. Such a water wash will remove residual salts, typically sodium sulfate, albeit such washing is usually not essential if the lecithin product is to be incorporated in feeds.

The washed or unwashed lecithin product can be delivered through a valve **35** and a heater **36** to a mixer **38** for mixing with the meal from the pressing or extracting apparatus **10**, producing a high nutritive feed product. In many instances, however, it is desirable to close the valve **35** and open a valve **39** to deliver the washed or unwashed lecithin product to a dryer **40** where it is dried under vacuum before being delivered to the mixer **38**. Drying at temperatures of about 180–220° F. under a vacuum of about 26–29½ inches of mercury will be found quite satisfactory. The lecithin product may be dried by the same equipment and in substantially the same manner as employed for the drying of hydrated lecithins or phosphatides for the production of commercial lecithin, e.g., heating in vacuo to a temperature of 150–210° F.

It will be apparent that all of the steps suggested in Fig. 1 can be performed batchwise in a single vessel, if desired. Alternatively, many of the steps can be performed in separate vessels in a continuous or semi-continuous process.

In Fig. 2 is suggested a continuous acidulation in which the soapstock is continuously supplied to a mixer **50** by any suitable pumping system, not shown. Similarly, a continuous stream of mineral acid is supplied by a proportioning pump, not shown, the mineral acid being delivered to the mixer **50** as suggested by the numeral **51**. The mixture then flows, with or without temperature adjustment in a heat exchanger **52**, to a separator **54** which may be a conventional centrifuge discharging streams of the aqueous material and lecithin product. The remaining equipment in Fig. 2 is similar to that shown in Fig. 1.

The process greatly reduces the water content of the soapstock. As compared with the original soapstock, which normally may have a water content of about 35–45% or more, the water content of the separated lecithin product will usually be less than 30% and often less than 20%. Even lower water contents may be obtained by heating under pressures of approximately 5–50 p.s.i. to corresponding temperatures of about 225–300° F. This treatment causes further amounts of emulsified water to be released and can produce a product containing no more than about 10–15% water.

Such higher temperatures, preferably applied during or after the initial separation of the aqueous material from the acidified soapstock, are of particular value when acidifying cottonseed soapstock high in free gossypol. West Texas and many pre-pressed or solvent-extracted cottonseed oils contain substantial amounts of free gossypol, as do the soapstocks obtained therefrom when refining with non-saponifying alkali such as soda ash. Such free gossypol is toxic to certain animals and it may be necessary to reduce the gossypol content of many of these soapstocks before they can be used as feeds. Heating the soapstocks to temperatures of about 285° F. (140° C.) for about 1 hour will substantially detoxify the soapstock, albeit higher temperatures applied for shorter times will also be effective. The initial free gossypol, dry basis, before acidification and heating of the soapstock, will usually vary from 2–8% or even 2–10%, while the free gossypol after acidification and heating will be below 0.25% and thus entirely unobjectionable in the feed product. Specifically, if the present process is used in treating soda ash soapstock from

cottonseed oil high in free gossypol, the soapstock may be heated to a temperature of about 285–350° F. for respective times of 1 hour to 10 minutes in the presence of or after separation of the aqueous material that separates when the pH is adjusted to about 5. Commonly, such temperature may be applied in the heaters 36. If such temperatures are applied in the containers 25 of Fig. 1, pressure vessels will be required unless the aqueous material is separated before application of the high temperatures.

In no instance, however, does the present invention contemplate the use of such high temperatures and such large amounts of water as to split the gums or phosphatidic materials present in or from the original crude oil. Due to the relatively low water content of the soapstock and to the fact that temperatures in the present process are always below 350° F., the present process does not involve any substantial splitting of the gums under the action of heat and pressure in the presence of large amounts of water.

While the process can be practiced in numerous ways, the following examples illustrate typical results.

Example 1

A soda ash soapstock containing 40% moisture and produced from the refining of a crude soya oil with soda ash was mixed with a 25% sulfuric acid solution in sufficient quantity to reduce the pH of the soapstock to approximately 5. Eight parts of the acid was required for 100 parts by weight (dry basis) of the soda ash soapstock. A fatty layer separated and was liquid at temperatures of 180–200° F. The fatty layer of lecithin product had a water content of 24%. After being dried in vacuo at 70° C., the dried product was a phosphatide concentrate, fluid at room temperature, containing 0.44% water, 2.11% phosphorous, 53.4% acetone in solubles and 66.8% T.F.A.

Example 2

To 125 parts of a low excess soda ash cottonseed soapstock was initially mixed 65 parts by weight of warm water. The hydrated soapstock was acidified with 8 parts of a 25% aqueous sulfuric acid solution, which brought the mixture to a pH of 5. The fatty layer or lecithin product was settled at a temperature of 180–200° F., withdrawn and dried in vacuo at 160° F. The dried product, fluid at room temperature, contained 0.44% water, 1.21% phosphorous, 49.6% acetone in solubles (phosphatides), 73.6% T.F.A. (of which about 33% was free fatty acids), and 0.75% free gossypol, dry basis. The gossypol content of the soapstock before treatment was 2.0%, dry basis.

Example 3

In this instance, 150 parts of corn oil soapstock, resulting from a soda ash refining of crude corn oil was mixed with 150 parts by weight of hot water. To bring the pH of the soapstock to a value of pH 5 required 83 parts by weight of a 25% sulfuric acid solution. Separation was in a steam bath for 4–6 hours after which the fatty layer was withdrawn and dried in vacuo. The dried product was liquid at room temperature and contained 0.3% water, 1.3% phosphorous, 45.2% acetone insolubles (phosphatides) and 53.6% T.F.A.

Various changes and modifications will be apparent to those skilled in the art and fall within the scope of the appended claims.

I claim as my invention:

1. A process for refining crude glyceride oils containing nutritive phosphatides, which process includes the steps of: mixing such glyceride oil with a non-saponifying alkali and separating the mixture into a refined oil and a soapstock containing said phosphatides; treating said soapstock with a mineral acid at temperatures and pressure insufficient substantially to split or char said phosphatides,

the amount of mineral acid being only sufficient to bring the pH of the soapstock to a value of about pH 5–8; and separating the acid treated soapstock into a volume of aqueous material and a volume of a lecithin product comprising free oil, fatty acids and hydrated phosphatides from the glyceride oil still in nutritive state.

2. A process as defined in claim 1 in which said non-saponifying alkali is a non-volatile alkali in aqueous solution.

3. A process as defined in claim 1 in which said alkali is soda ash and in which the amount of mineral acid is adjusted to reduce the pH of the soapstock to about pH 5.

4. A process for refining crude glyceride oils containing nutritive phosphatides, which process includes the steps of: mixing such glyceride oil with a non-saponifying alkali and separating the mixture into a refined oil and a soapstock containing said phosphatides; treating said soapstock with a mineral acid at a temperature and pressure insufficient substantially to split said phosphatides, the amount of mineral acid being only sufficient to bring the pH of the soapstock to a value of about pH 5–8; separating the acidified soapstock into an aqueous material and a lecithin product comprising free oil, fatty acids and hydrated phosphatides from the glyceride oil; and drying the lecithin product to produce a dried lecithin product containing said phosphatides in nutritive state.

5. In the process of refining glyceride oils produced from seeds or beans by processes involving the production of a residual meal and a crude oil containing free fatty acids and nutritive phosphatides, the steps of: mixing said crude oil with a non-saponifying alkali; separating the mixture into an oil containing substantially none of said free fatty acids and a soapstock containing said nutritive phosphatides largely in their original state; treating said soapstock with a mineral acid at a temperature insufficient substantially to split said phosphatides, the amount of said mineral acid being only sufficient to bring the pH of the soapstock to a value of about pH 5–8; separating the acidified soapstock into an aqueous material and a lecithin product comprising free oil, fatty acids and hydrated phosphatides from the glyceride oil; and mixing about 0.5–5% by weight of said lecithin product with such meal to form a feed product.

6. A process as defined in claim 5 including the step of drying said lecithin product under vacuum before adding to said meal.

7. A process for refining crude glyceride oils containing free fatty acids and nutritive phosphatides, which process includes the steps of: mixing the glyceride oil with soda ash in amount not substantially more than required to convert said free fatty acids into soaps; separating the mixture into a refined oil and a soapstock containing said phosphatides in substantially their original state; mixing with the soapstock a mineral acid in amount sufficient only to reduce the pH of the soapstock to about pH 5–8 and insufficient to char the phosphatides of the soapstock; separating the acidified soapstock into an aqueous material and a lecithin product; and drying such lecithin product.

8. A process as defined in claim 7 in which said dried lecithin product is added to a glyceride oil meal to form a feed product.

9. In the process of refining glyceride oils produced from seeds or beans as the source material by processes involving the production of a residual meal and a crude oil containing free fatty acids and nutritive phosphatides, the steps of: Mixing said crude glyceride oil with soda ash in amount not substantially more than three times that required to neutralize said free fatty acids; separating from the mixture a soapstock containing said nutritive phosphatides; treating said soapstock with a mineral acid at a temperature insufficient substantially to split said phosphatides, the amount of said mineral acid being only sufficient to bring the pH of the soapstock to a value of

about pH 5–8; separating the acidified soapstock into an aqueous material and a lecithin product comprising free oil, fatty acids and hydrated phosphatides from the glyceride oil; and mixing said lecithin product with said meal to form an animal feed product.

10. In the process of refining glyceride oils produced from seeds or beans as the source material by processes involving the production of a residual meal and a crude oil containing free fatty acids and nutritive phosphatides, the steps of: mixing said crude glyceride oil with soda ash in amount not substantially more than required to convert said free fatty acids into soaps; separating from the mixture a soapstock containing said nutritive phosphatides; adding to the separated soapstock an amount of water to bring the water content of such soapstock to about 50–75%; treating the resulting soapstock with a mineral acid at a temperature insufficient substantially to split said phosphatides, the amount of said mineral acid being only sufficient to bring the pH of the soapstock to a value of about pH 5–8; separating the acidified soapstock into an aqueous material and a lecithin product comprising free oil, fatty acids and hydrated phosphatides from the glyceride oil; and mixing said lecithin product with said meal to form an animal feed product.

11. A process for producing a nutritive phosphatidic product from crude glyceride oils containing nutritive phosphatides, which process includes the steps of: mixing such glyceride oil with a non-saponifying alkali and separating the mixture into a refined oil and a soapstock containing said phosphatides; mixing a mineral acid with said soapstock under conditions of temperature and pressure insufficient substantially to split or char said phosphatides, the amount of mineral acid being only sufficient to bring the pH of the soapstock to a value of about pH 5–8; and separating the acid treated soapstock into a volume of aqueous material and a volume of a phosphatidic product comprising about 30–60% by weight of acetone insoluble phosphatides in substantially the same state and amount as in said crude oil before such oil was mixed with said alkali.

12. A process for producing a nutritive phosphatidic product from a crude glyceride oil containing nutritive phosphatides and free fatty acids, which process includes the steps of: mixing such glyceride oil with an amount of soda ash no more than three times that required to neutralize said free fatty acids of such oil; separating

from the resulting mixture a soapstock containing said phosphatides as a soda ash phosphatide complex, a small amount of soda ash, and sodium soaps of said fatty acids; mixing only enough mineral acid with said soapstock to reduce its pH to a value between about pH 5 and pH 8 under conditions of temperature and pressure insufficient to substantially split or char said phosphatides, the amount of said mineral acid being only sufficient to largely convert said small amount of soda ash to sodium sulfate, the sodium soaps to fatty acids and sodium sulfate, and the soda ash phosphatide complex to free phosphatides; and separating the acid treated soapstock into a volume of aqueous material and a volume of a phosphatidic product containing said nutritive phosphatides in substantially the same state and amount as in said crude glyceride oil.

13. A process for refining crude glyceride oils containing nutritive phosphatides, which process includes the steps of: mixing such glyceride oil with a non-saponifying alkali and separating the mixture into a refined oil and a soapstock containing said phosphatides; adding water to the separated soapstock to bring the water content thereof to about 50–75%; treating the resulting soapstock with a mineral acid at a temperature and pressure insufficient substantially to split or char said phosphatides, the amount of mineral acid being only sufficient to bring the pH of the soapstock to a value of about pH 5–8; and separating the acid treated soapstock into a volume of aqueous material and a volume of a lecithin product comprising free oil, fatty acids and hydrated phosphatides from the glyceride oil still in nutritive state.

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