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PROCESS OF OBTAINING PHOSPHATIDES
FROM SOAP STOCKBenjamin H. Thurman, Bronxville, N. Y., assign-
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tion of NevadaNo Drawing. Application January 21, 1939,
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12 Claims. (Cl. 260-403)

This invention relates to the recovery of phosphatides from soap stock that is obtained in the purification of vegetable oils. This soap stock is customarily obtained by treating an oil with caustic alkalis or alkaline carbonates or phosphates or other reagents that will saponify the free fatty acids in the oil and then separating the soap stock from the oil. While the phosphatides of the higher quality more highly saturated oils, such as cottonseed or corn, sesame or rape seed oil, have more desirable qualities and greater usefulness, the process of the present invention is applicable to the recovery of the phosphatides contained in the soap stock from the alkali refining of more highly unsaturated oils such as soya bean oil or linseed oil.

It has heretofore been known that soya beans contained vegetable lecithin or phosphatides which could be obtained by direct extraction of the beans with a lecithin solvent. This constituted the sole source of commercial vegetable lecithin as it was not known that substantial amounts of phosphatides were present in recoverable form in vegetable oils separated from the beans or seeds by the usual processes of producing oil, for example, by hot or cold pressing operations. The presence of phosphatides in vegetable oils and methods of recovery of the phosphatides from the oil are disclosed in my copending application Serial No. 6,446, filed February 14, 1935. When such vegetable oils are refined with alkaline reagents the free fatty acids of the oil are neutralized with an aqueous solution of caustic soda or other strong alkali usually under high temperature conditions. The alkali not only neutralizes the free fatty acids to form soap but attacks neutral glycerides to form soap and glycerine. Gums and coloring matter in the oil are precipitated and the resulting soap and other precipitated materials are separated from the oil by settling or centrifugal separation along with water, excess alkali, and entrained neutral oil as "soap stock".

This soap stock is a malodorous and darkly colored product, in which the gums were formerly regarded as undesirable impurities, and which was formerly believed to be entirely worthless except for employment in low grade soaps after extensive purification treatment.

The phosphatides constitute part of the gums and are also subject to attack by the alkali to form decomposition products. The chemistry of the reaction between an alkali and phosphatides under refining conditions is complex and not fully established. As lecithin can be completely

hydrolyzed to produce glycerol-phosphoric acid, fatty acids, and choline, it was reasonable to assume that the phosphatides were substantially completely destroyed under the drastic treating conditions during refining. I have, however, found that the soap stock obtained from vegetable oils in the usual way contains up to as high as 10% of recoverable phosphatides. A part of the phosphatides of the original oil may be destroyed or the chemical composition of all or a portion of the phosphatides may be altered during the refining process but the phosphatides recovered from the soap stock, in accordance with the present invention, appear to retain their desirable qualities.

By the present invention the phosphatides may be removed in large measure or substantially entirely from the soap stock in such a way that they do not contain an appreciable or seriously objectionable amount of injurious impurities or discoloring materials.

In carrying out the invention the soap stock may be treated with any of the well known fat solvents, such as petroleum ether, ethyl ether, benzene, ethylene dichloride, trichloroethylene, carbon tetrachloride, etc. The solution may then be separated from the soap stock residue by decantation, centrifuging or filtering and the solvent is evaporated or distilled off, leaving the phosphatides as a residue.

Or, the soap stock may be treated with a solvent for the soap stock. Acetone, for example, may be used for this purpose as it will dissolve and remove the soap, free oil and water leaving the phosphatides as a residue when the solution is filtered or centrifuged. Other soap solvents, such as methyl acetate, for example, in which the phosphatides are insoluble or difficulty soluble, may be used instead of acetone for this purpose.

The following are given as specific examples of carrying out the invention, but it is to be understood that these examples are not exhaustive and that the invention is not restricted to the treatment of soap stock from any particular oil or to any particular solvent or proportion mentioned or to the temperature or time specified.

Example 1.—Approximately five parts by volume of petroleum ether were added to one part of cottonseed oil soap stock obtained by saponifying the fatty acids in cottonseed oil with soda ash. The mixture was agitated or stirred for about 20 minutes at room temperature (approximately 70° F.) and then filtered. The ether was evaporated off at a temperature of about 100–

200° F. leaving a residue which was about 10% of the weight of the soap stock that was extracted.

Example 2.—About one part by volume of cottonseed oil soap stock was agitated with five parts of acetone for a few minutes at room temperature and the mixture was filtered. The solids left on the filter were for the most part phosphatides and amounted to about 10% of the weight of the soap stock.

Example 3.—The same amount of methyl acetate was used as the amount of acetone in Example 2 and substantially the same result was obtained.

The soap stock from the alkali refining of other vegetable oils, such as those above referred to, may be treated in a manner similar to the steps in the above examples to recover phosphatides or phosphatidic material.

After the phosphatides have been separated from the soap stock, as described above, they can be purified to remove extraneous or deleterious matter, leaving a purified residue that is very valuable in the arts for many useful purposes. The solid content of the mass containing phosphatides that is obtained from the soap stock contains about 60 or 70% of the valuable phosphatides from which a large portion or substantially all of the remaining solids or deleterious matter can be removed. The remaining purified phosphatides from the more highly saturated oils are of such a character that they do not have an objectionable taste or odor and do not become rancid for a long time even when exposed to air. Certain ingredients which appear to aid in preserving the phosphatides may have been removed from the soap stock with the phosphatides and are not removed from the phosphatides during the purification step. The deleterious impurities may be removed from the phosphatide mass or residue by washing the phosphatides or solids with water, or an aqueous sodium chloride solution may be used instead of water for washing the phosphatides. About 10% of sodium chloride in the water has been found to be satisfactory. An aqueous salt solution apparently has a solvent action on some of the globulin and albuminoid substances in the phosphatide mass so that they are removed during the washing step. Also, the remaining insoluble phosphatides are left in small particles. The phosphatides may be washed repeatedly with water containing salt. The phosphatides or remaining product may be dried. The drying is preferably done in a vacuum with a temperature not exceeding 70° C. When the phosphatides have been obtained by means of solvents for the phosphatides and evaporating the solvents, the dried product may be washed with acetone to remove acetone soluble materials, such as fatty acids, coloring materials and small amounts of other undesirable substances. The acetone may be distilled off while the air is excluded from the product. By way of example, the purified dried material from cottonseed oil soap stock is yellow and in the form of a powder while that from corn oil soap stock is a gray waxy material.

It has also been found that water can be used for washing the phosphatides without having salt dissolved in it, provided the pH of the water is kept sufficiently low, say about pH 3 to pH 4.5, and preferably the lower value, to prevent emulsification. Chloride ions appear to be particularly advantageous in preventing emulsification, although other acids and acid salts, such as tartaric, citric, sulphuric acids and sodium

salts and sodium acid salts, for example, which will lower the pH of the solution can be used. However, hydrochloric acid has thus far been found to be the most satisfactory for this purpose.

The purified dry product may be dissolved in a non-solidifying oil, such as sunflower oil, sesame oil, or soya bean oil and the substances that are insoluble in these oils may be centrifuged or filtered out. The percentage of oils used for dissolving the product may be 40% or more of the weight of the product that is dissolved in the oil.

Phosphatides from the soap stock of the less unsaturated oils, such as cottonseed oil or corn oil, have the most useful properties as they contain no linolenic acid radicals and are more stable. By way of example, some of the characteristics which distinguish the phosphatides or product obtained, as described above, from cottonseed oil, from similar products are as follows:

(a) This product contains approximately the same percentage of phosphorus, namely about 1.8%, calculated on a dry basis, as the precipitate that precipitates out of the oil after it has been allowed to stand for a long time without the addition of a reagent.

(b) The iodine number of the purified product is approximately 60, while the iodine number of the purest vegetable lecithin products now known is about 90.

(c) Fatty acids obtained from this purified product or phosphatides have an iodine number of about 95 while the iodine number of cottonseed oil is about 108 and the iodine number of soya bean oil, as well as the fatty acids from lecithin obtained therefrom, is about 125. The low iodine number of the product of this invention and the fatty acids obtained from it probably explains, at least in part, why the product of this application will keep such a long time or has very little tendency to absorb air and become rancid.

(d) The product or phosphatides of this invention may be dissolved in high boiling oils, such as sunflower seed oil and heated to 440° F. without changing color very much and without having a very noticeable amount of objectionable odor or taste imparted thereto, while lecithin obtained from soya beans and heated in the same way has imparted to it a very dark or almost black color and a very nauseating odor and unpalatable taste, resembling the odor of fish or paint.

(e) A trace of gossypol or raffinose has been found in the phosphatides, but is not present in sufficient amounts to interfere with the edibility of the phosphatides.

Phosphatides obtained from the soap stock of other of the less unsaturated oils, such as corn oil, have properties very similar to these of the cottonseed oil phosphatides described above. The purified phosphatides obtained from such oils are useful for many purposes, some of which may be mentioned; as an agent for reducing the viscosity of sugar, chocolate and fat coatings; a small amount, say 0.3% thereof, added to chocolate prevents the same from blooming after several hours even in warm weather; about one-half of 1% thereof added to vegetable oils greatly decreases the tendency of these oils to become rancid even at temperatures up to 150° F. or higher over an extended period of time; about 1% or less thereof added to dressings, such as mayonnaise, materially increases the keeping

qualities of the same and prevents or greatly retards rancidity; less than 1% thereof added to margarine prevents the same from foaming or spattering when heated, thus permitting food, such as eggs, to be browned when fried therein; less than 1% added to deep frying oils or fats prevents or greatly retards rancidity and acquisition of bad flavors or odors even at temperatures somewhat above 400° F.; a small amount thereof added to fats used in making caramels improves the quality of the caramels without imparting any objectionable taste.

It has been found that mayonnaise containing soya bean oil which would become rancid and develop a characteristic odor in a few days will remain fresh when about 0.3/10ths percent of the product or phosphatides of this invention is added. This product seems to act as an anti-oxidant or at least prevents development of the objectionable odor or flavor in the soya bean oil. This may possibly be due to the prevention of the action of enzymes or bacteria in the soya bean oil used in making mayonnaise dressing. When about 0.1% of this product is added to butter it prevents formation of strong odors even when the butter is exposed to the atmosphere for a long time and it also prevents water from leaking out of the butter, probably because it is a good emulsifying agent for the butter. This product is also valuable as an apparent anti-oxidant in the manufacture of rubber, as well as an excellent anti-oxidant when put in linseed oil varnish that is to be used for painting rubber goods. The addition of even less than 1% of the product to fats or oils that are used for frying vegetable products greatly reduces the tendency of these fats or oils to split and form products that are characteristic of overheated fats, thus imparting substances to the food products that would cause them to become rancid. Food products, such as potato chips that have large surfaces are especially prone to become rancid very rapidly by oxidation. The use of the product of this invention in fats or oils for frying such vegetables protects the products and permits the same fatty oil to be used repeatedly for frying them.

This application is a continuation in part of my copending application Serial No. 688,361, filed September 6, 1933, and of my copending application Serial No. 6,446, filed February 14, 1935, now Patent No. 2,150,732, which is in turn a continuation in part of my applications Serial No. 644,137, filed November 23, 1932 and Serial No. 676,932, filed June 21, 1933.

I claim:

1. The process of recovering phosphatides which comprises treating cottonseed oil soap stock with a fat solvent which will dissolve phosphatides and in which soap is substantially insoluble, removing the solution, evaporating the solvent and washing the residue with an aqueous solution having a pH of not more than about 3.

2. The process of recovering phosphatides which comprises treating cotton seed oil soap stock with a fat solvent in which phosphatides are soluble and soap stock is substantially insoluble, removing the solution, evaporating the solvent and washing the residue with an aqueous solution containing chloride ions and having a pH of not more than about 3.

3. The process of recovering phosphatides, which comprises, treating soap stock, resulting from the alkali refining of phosphatide containing vegetable oils and containing a material consisting essentially of phosphatides and a ma-

terial consisting essentially of soap, with a solvent for only one of said materials to form a solution of said one of said materials, separating the undissolved material from said solution to separate said soap from said phosphatides, and further treating the material containing said phosphatides to purify said phosphatides.

4. The process of recovering phosphatides, which comprises, treating soap stock, resulting from the alkali refining of phosphatide containing vegetable oils and containing a material consisting essentially of phosphatides and a material containing essentially soap, with a solvent which will dissolve said material containing phosphatides to form a solution thereof without dissolving said soap, separating the undissolved material containing soap from said solution to separate said soap from said phosphatides and further treating said solution to purify said phosphatides.

5. The process of recovering phosphatides, which comprises, treating soap stock resulting from the alkali refining of cottonseed oil and containing a material including phosphatides and a material including soap, with a solvent for only one of said materials to form a solution of said one of said materials, separating the undissolved material from said solution to separate said soap from said phosphatides, and further treating material containing said phosphatides to purify said phosphatides.

6. The process of recovering phosphatides, which comprises, treating soap stock resulting from the alkali refining of cottonseed oil and containing phosphatides and soap with a solvent which will dissolve said phosphatides to form a solution thereof without dissolving said soap, separating the undissolved material from said solution to separate said soap from said phosphatides and further treating said solution to purify said phosphatides.

7. The process of recovering phosphatides, which comprises, treating soap stock, resulting from the alkali refining of phosphatide containing vegetable oils and containing a material consisting essentially of soap, with a solvent for only one of said materials to form a solution of said one of said materials, separating the undissolved material from said solution to separate said soap from said phosphatides, and washing solvent free, separated phosphatides with an aqueous solution having a pH between about 3 and 4.5 to further purify said phosphatides.

8. The process of recovering phosphatides, which comprises, treating soap stock, resulting from the alkali refining of phosphatide containing vegetable oils and containing a material consisting essentially of phosphatides and a material containing essentially soap, with a solvent which will dissolve said material containing phosphatides to form a solution thereof without dissolving said soap, evaporating said solvent and washing the residue with an aqueous solution having a pH of between about 3 and 4.5 to further purify said phosphatides.

9. The process of recovering phosphatides which comprises treating vegetable oil soap stock with a fat solvent which will dissolve phosphatides and in which soap is substantially insoluble, removing the solution, evaporating the solvent and washing the residue with an aqueous solution having a pH of not more than about 3.

10. The process of recovering phosphatides which comprises treating vegetable oil soap stock

with a fat solvent in which phosphatides are soluble and soap stock is substantially insoluble, removing the solution, evaporating the solvent and washing the residue with an aqueous solution containing chloride ions and having a pH of not more than about 3.

11. The process of recovering phosphatides from soap stock which comprises the steps of: 5
10 subjecting vegetable oils containing phosphatides, free fatty acids and other impurities to treatment with an alkaline refining reagent to react with the free fatty acids to form soap stock containing

said phosphatides without destruction to said phosphatides, thereafter subjecting said soap stock with the phosphatides contained therein to treatment with a solvent capable of separating the soap stock from the phosphatides and thereafter separating the phosphatides from said soap stock. 5

12. The process as defined in claim 11 in which the separated phosphatides are subjected to purification. 10

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