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SOAP PRODUCT

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This invention relates to soap products and more particularly to products including soap and at least a portion of the minor constituents which occur in the residual products resulting from the refining or partial refining of vegetable oils.

In the alkali refining of vegetable oils, an excess of an alkali refining reagent over that necessary to combine with the free fatty acids contained in the oil is added to and mixed with the oil. The refining reagent, which is usually an aqueous solution of caustic alkali, such as caustic soda, reacts with the free fatty acids in the oil to produce soap. The alkali also attacks a portion of the neutral oil to produce soap and glycerine. Also the refining reagent reacts with or otherwise causes minor constituents present in the oil, commonly called gums and coloring matter, to precipitate or become adsorbed by the soap. The soap along with the minor constituents are separated from the oil either by a gravity settling operation or by centrifugal separation. Elevated temperatures are usually employed to facilitate separation. The heavier material separated from the oil is called soapstock and includes soap, glycerine, neutral oil, water, uncombined alkali and the minor constituents referred to. The minor constituents contain extremely complex chemical compounds, the exact compositions of many of which are unknown. It is known that they include phosphatides, proteins, resins and carbohydrates. More specifically stated they include phospholipids, phytin phosphorus compounds, glycerol phosphates, mucins, glycerine, carotinoid pigments and in the case of cottonseed oil other coloring material such as gossypol. Such minor constituents frequently amount to as much as 10% or more of the soapstock and have heretofore been considered undesirable impurities therein. A typical analysis of cottonseed oil foots or soapstock from "Modern Soap Making," Thomssen & Kemp, McNair-Dorland Co., 1937, in which the gums are listed as "Foreign organic matter," is as follows:

Composition of cottonseed oil foots

	Per cent
Fatty anhydrides	48.50
Glycerine	3.98
Caustic soda (Na ₂ O)	3.20
Foreign organic matter	5.90
Water	36.00
Coloring matter	2.42
	100.00

Soapstock has been utilized to some extent as a raw material for soap making processes. When so used, the soapstock has been subjected to extensive purification treatments to remove the minor constituents prior to incorporating the remaining soap into soap products. Thus, the soapstock has been boiled in kettles with additional alkali for saponifying the entrained neutral oil and the impurities including glycerine repeatedly washed and salted out in order to produce as pure soap as practicable. Because of its poor detergent and foaming properties, resultant soap has been employed only in low grade soaps or washing powders in relatively small percentages and even this use is decreasing.

Also the fatty acids forming part of the soap in soapstock have been recovered and employed in soap making processes by acidulating the soapstock and distilling off the fatty acids leaving a decomposed insoluble residue known as "pitch" having substantially no value and no detergent properties. The fatty acids recovered and employed as soap making materials are substantially free from the minor constituents. Also when employing vegetable oils as soap making bases, they have been carefully refined to remove and discard the gums and other minor constituents prior to use in soap making processes. Thus the minor constituents have been systematically avoided in soap products.

The soapstock recovered from a refining process containing such minor constituents as well as large amounts of water is susceptible to rapid fermentation and decomposition. It has, therefore, been impossible to store or ship soapstock without putrefaction unless it had been purified. Any attempt to employ even a partly fermented soapstock in a soap product results in an evil smelling and highly discolored product.

In accordance with the present invention, I have discovered that the minor constituents of soapstock perform extremely valuable functions in soap products both for detergent and other uses. I have found that these minor constituents have extremely valuable detergent enhancing properties and not only give to the soap product improved foaming and emulsifying properties but also provide excellent wetting or surface tension reducing and water softening properties. By "water softening properties" I mean the capability of preventing the deposition of insoluble alkaline earth compounds and not the precipitation and separation from the water of such compounds. I have further discovered that ferment-

tation and putrification of the soapstock or products including the same can be prevented.

It is, therefore, an object of the invention to provide a new product containing the detergent enhancing constituents present in the original oil or contained in the material separated from vegetable oils during refining or semi-refining thereof.

Another object of the invention is to provide an improved soap product containing substantial quantities of the minor constituents of vegetable oil which have detergent enhancing properties.

Another object of the invention is to provide an improved process of incorporating soapstock from the alkali refining of vegetable oils into soap products so as to prevent decomposition of the minor constituents of said soapstock.

Another object of the invention is to provide a new water softening and cleaning product containing the detergent enhancing constituents present in the residue from the refining or semi-refining of vegetable oils.

A further object of the invention is to provide a new soap product capable of being used as a wetting agent or as a foaming or flotation agent.

The products of the present invention have been found to have particular utility in cleaning compositions suitable for spray cleaning devices. Such devices usually include a heating device, such as a heating coil, through which a solution of the cleaning composition is pumped, heated to a high temperature in the coil and thereafter sprayed upon a surface for removing greasy or tarry deposits thereupon. These devices are employed, for example, in cleaning automobile frames and motors, and provide a severe test of the stability and detergent properties of a cleaning composition.

Solutions of cleaning compositions employed in such devices must have good wetting, rinsing and emulsifying properties in order to remove the deposits referred to and leave a clean surface. Also any precipitate of insoluble soaps or other insoluble compounds due to the employment of hard water in the cleaning solution not only sticks to the surfaces to be cleaned but forms deposits upon the walls of the heating coil. These deposits form large amounts of scale interfering with heat transference and eventually plug the heating coil. Cleaning compounds employed with such devices have, heretofore, included expensive alkali metal soaps to secure sufficient cleaning action, for example, linseed oil sodium and potassium soaps and also have included substantial amounts of expensive water softening chemicals, for example, sodium hexameta phosphate or sodium pyro phosphate. The water softening chemicals were employed to prevent the formation of insoluble soaps or other insoluble compounds in the heating coil by the reactions between the soaps or the alkalies also employed in such compounds and the magnesium or calcium salts present in hard waters.

In accordance with the present invention, I have found that soapstock produced by the alkali refining of crude vegetable oils originally containing the detergent enhancing constituents above referred to, for example, cottonseed oil, corn oil, soya bean oil, linseed oil, etc., can be employed in such cleaning compositions instead of expensive soaps, such as, linseed oil soap, and that expensive water softening chemicals are rendered unnecessary. The minor constituents in the soapstock apparently render even such in-

ferior soaps as cottonseed oil soap capable of producing large amounts of stable foam as well as giving the soap excellent surface tension reducing and water softening properties.

The exact explanation of why the detergent enhancing constituents prevent the precipitation of insoluble alkaline earth metal compounds when hard water is used in cleaning devices, is not known to applicant. Alkali metal soaps are present for reaction with the alkaline earth metal salts, such as calcium or magnesium salts and in this respect the present product is different from such surface tension reducing agents as sulphated fatty acid alcohols, which form no insoluble products with hard water. Such sulphated alcohols have very little cleaning power and also do not prevent the deposition of insoluble soap if alkali metal soaps are present. It is believed that the phosphatides, phytin phosphorus compounds or other of the minor constituents either have the property of retaining the insoluble soaps or other insoluble compounds in suspension or that they prevent the formation of such insoluble compounds. As the soap, including the minor constituents, has effective emulsifying or suspending properties, as well as being a good foaming agent forming large quantities of stable foam, it is probable that the former explanation is correct. Linseed oil soap has been employed because of its high solubility resulting in good rinsing properties, but such linseed oil soap does not form the stable foam necessary for effective suspension of the substances to be removed. The minor constituents of the present products not only increase the solubility or suspensibility of normally difficultly soluble soaps but also cause such soaps to produce large quantities of stable foam. It is believed that the phosphatides, at least a part of which are amphoteric and dispersible in both oil and water, are responsible for the wetting or surface tension reducing properties of the product but applicant does not wish to be bound by any precise theories of operation.

The excellent detergent properties of the composition of the present invention, particularly when employed in spray cleaning devices, are apparently due, in part, to the formation of substantial quantities of ammonia or amines or both, which compounds are known to have good detergent properties. The composition is subjected to elevated temperatures and pressures in such spray cleaning devices and it is believed that proteinaceous material is decomposed so as to liberate ammonia and amines in active form. The minor constituents of the soapstock, therefore, constitute an inexpensive source of such detergent agents.

The various properties of the detergent enhancing constituents of the present invention persist even in combination with large quantities of various alkali materials commonly used in cleaning compositions. Thus the soapstock containing such constituents may be mixed with such alkalies as trisodium phosphate, sodium carbonate, caustic soda or sodium meta silicate. When mixed with one or more of these substances, for example, sodium carbonate or caustic soda having no water of crystallization or only small amounts thereof, the alkali will combine with the water in the soapstock to produce a dry mixture which is stable against fermentation or putrification. As stated before, no water softening materials, such as sodium pyrophosphate or sodium hexa meta phosphate are nec-

essary. As typical of several formulas which have been successfully employed in spray cleaning devices in admixture with water containing substantial amounts of calcium and magnesium salts, the following is given:

Example I

	Per cent
Corn oil soapstock (H ₂ O 40%) (8.4% dry basis) -----	14.50
Trisodium phosphate -----	11.50
Soda ash (Na ₂ CO ₃) -----	41.9
Caustic soda (NaOH) -----	9.27
Meta-silicate of soda -----	22.93
	100.00

Calculated water 21%.

Example II

	Per cent
Soya bean oil soapstock -----	25.00
Trisodium phosphate -----	8.3
Soda ash -----	49.8
Caustic soda -----	8.3
Sodium metasilicate -----	8.6
	100.00

Example III

	Per cent
Corn oil soapstock -----	7.77
Trisodium phosphate -----	12.08
Soda ash -----	45.15
Caustic soda -----	10.00
Sodium metasilicate -----	25.00
	100.00

Example IV

	Per cent
Cottonseed oil soapstock -----	80
Soda ash -----	20

It will be noted that the proportions of the alkalies admixed with the soapstock can be varied widely. It will further be noted that less expensive alkalies, such as soda ash and caustic soda, sodium metasilicate, etc., can be employed or that more expensive alkalies, as trisodium phosphate, can be omitted. By mixing wholly or partly dehydrated alkalies in powdered form with the soapstock in the condition it is separated from the oil in refining processes, a stable powdered material is produced even though the product may contain substantial amounts of water. In preparing the composition, it is possible to mix one alkali, for example, soda ash or caustic soda with the soapstock as it comes from the refinery in which event a product stable against decomposition is produced, which product can be shipped and stored. One or more other alkalies can be admixed therewith at a later time if desired. For example, dry soda ash containing not more than 2 molecules of water per molecule of Na₂CO₃ is commercially available and will combine with the water of the soapstock to form Na₂CO₃·10H₂O. If such procedure is not practicable the soapstock may be rendered stable by drying the same, for example, in accordance with the processes disclosed in my copending application, Serial No. 180,621, filed December 18, 1937, or the soapstock may be filmed upon a heated roll to dry the same and then scraped from the roll in dried condition. As long as the dried soapstock is maintained in relatively dry condition it is stable against fermentation or decomposition and can be stored or shipped prior to admixing the alkalies therewith.

Also fermentation and decomposition of the soapstock can be prevented by mixing therewith a fermentation retarding agent, for example, essential oils such as oil of cassia, which will effectively prevent the growth of fermentation bacteria when added in as small amounts as 1½%. Other fermentation retarding agents which can be employed are phenol, cresol, pine oil, alcohol, benzol, toluene or gasoline in amounts ranging from 0.5 to 5% depending upon the particular soapstock or agent employed. Phenol or cresol are particularly desirable as they react with alkalies to form products having good detergent and solubilizing properties.

In alternative oil refining procedures, at least a portion of the gums are removed from the oil prior to complete refining by so-called degumming or semi-refining processes. The gums recovered, to a large extent, contain the detergent enhancing constituents. The recovery of these constituents can be effected by semi-refining, for example, with an alkali such as trisodium phosphate so as to neutralize only a portion of the free fatty acids or by employment of water or acid reagents, for example, boric acid, phosphoric acid or hydrogen peroxide. Certain of the preserving reagents, such as alcohol, can be added with the degumming or refining reagents to obtain an even distribution in the soapstock or minor constituents. The boric acid, when employed as a degumming agent, is also an effective preserving agent. The gums or minor constituents can also be stabilized against fermentation or putrefaction by drying the same or admixing them with dry alkali or with the fermentation retarding agents referred to with respect to soapstock. These gums or minor constituents may be mixed with ordinary sodium or potassium soaps made from animal or vegetable oils or fats to form the equivalent of the soapstock resulting from the alkali refining of crude oils containing the minor constituents and employed in the composition of the present invention. Alternatively, the minor constituents from a partial refining or degumming operation may be mixed with alkalies without the addition of soap. Certain of these constituents contain fatty acids which will result in the formation of soaps when heated with sufficient alkalies. The sodium soap in such composition may be the soapstock recovered from the alkali refining of the degummed or semi-refined oil. Such soapstock contains soap, glycerine, neutral oil, uncombined alkali, water, and any of the detergent enhancing minor constituents which were not removed during the degumming process. It has at least in part the properties of the ordinary soapstock containing all of the minor constituents. It may, therefore, be employed alone or with additional minor constituents from degumming or semi-refining processes in the product of the present invention.

The neutral oil in the soapstock from refining processes is not detrimental for certain uses. For example, in the spray cleaning devices referred to, the excess alkali of the cleaning compositions employed, combines with the neutral oil to form soap during the passage of the solution through the heating device so that no substantial amount of oil is present in the spray.

Since the soapstock from continuous refining processes, for example, those disclosed in Patents Nos. 2,100,274 and 2,100,275, granted November 23, 1937, contains less neutral oil, because of more efficient separation from the oil, they are

preferably used in the present invention. Also, the long interval of time necessary to effect gravity separation in batch refining processes many times produces soapstock which is already in the incipient stages of fermentation or decomposition so that such batch soapstock is not as desirable as the soapstock from continuous refining processes although such batch soapstock may be employed for certain uses in accordance with the present invention.

In employing the soap product of the present invention containing large amounts of alkalis in spray cleaning devices, the preferred operation is to make up a relatively concentrated solution of the soap product and then mix a small metered stream of the resulting solution with a flowing stream of water, which stream is then heated to form the cleaning spray. For example, a 10% solution of the soap product may be pumped into a stream of water to produce a final solution containing about $\frac{1}{4}\%$ of the soap product. In many cases, the soap incorporated into solutions of 10% or higher concentrations, grain out or produce an emulsion so that a uniform proportioned mixture cannot be pumped. I have found that a small proportion of a liquid volatile soap solvent such as isopropyl alcohol, which is miscible with water, avoids this difficulty. For example, about 2% of isopropyl alcohol admixed with the 10% solution above referred to will make the entire soap product soluble so as to produce a clear and thin solution which is easily pumpable. Larger proportions of solvent will be employed with more concentrated solutions and smaller proportions with less concentrated solutions. The solvent is preferably admixed with the soap product and sold as an article of commerce so that the relatively concentrated solution referred to can be made up by merely adding the requisite amount of water, but may be added at the time the relatively concentrated solution is prepared. The solvent also performs a valuable detergent action in softening or dissolving deposits to be removed and enabling them to be removed by the spray. While isopropyl alcohol has been given as the preferred material, other soap solvents which are miscible with water such as ethyl alcohol, butyl alcohol, cresol-cresylic acids, etc. can be employed. The cresol or cresylic acids are particularly valuable as they react with the alkali to form detergent compounds and also prevent decomposition of organic compounds in the composition and the formation of ammonia or amines until the composition is subjected to elevated temperatures in a spray cleaning device.

While the invention has been described above particularly with relation to compositions suitable for use in spray cleaning devices, the stabilized product can also be employed alone or in combination with other ingredients for various other purposes. The powdered material resulting from mixing alkalis, such as tri-sodium phosphate, soda ash or caustic soda, with the soapstock makes an extremely efficient washing powder for uses other than spray cleaning. A product containing the minor ingredients referred to is also particularly effective for employment in insecticide sprays along with suitable chemicals. The wetting and emulsifying properties of the composition give the spray excellent covering properties and retain the chemicals, even in powdered form, in even suspension in the spray solution. The composition is particularly useful with such compounds as chromium

salts which tend to precipitate insoluble chromium compounds. Also, the surface tension reducing and foaming properties thereof render the product especially suitable for flotation operations, such as ore separation processes particularly where hard water must be employed. The product may be employed alone or with other flotation agents and in certain of such processes the presence of unsaponified oil is desirable. It has also been found that the minor constituents of the product are effective agents in solvent spraying processes for retarding evaporation of the solvent. Thus, organic solvents are frequently sprayed upon surfaces to remove accumulations of grease or tars, or as paint removers. Large amounts of the solvents are lost by evaporation in the spray before contact with the surface and also considerable evaporation from the surface takes place before the solvents effectively dissolve the accumulations to be removed. Substantially all of the minor constituents are soluble in many of such organic solvents and at least portions thereof are soluble in most organic solvents. The portion which dissolves in the solvents has been found to decrease the rate of evaporation of the solvents so as to effect substantial savings in the amount of solvent necessary to cover or dissolve accumulations upon a surface from which they are to be removed. Thus, the compositions of the present invention find general utility in soap and other products.

This application is a continuation-in-part of my copending application Serial No. 225,063, filed August 15, 1938.

While I have disclosed the preferred embodiments of my invention, it is understood that the invention is not limited to the details disclosed but may be varied within the scope of the following claims.

I claim:

1. As a product of manufacture, a composition of matter which comprises, alkali metal soap, a substantial amount of gums recovered from crude vegetable oils, a substantial amount of at least one alkali metal compound having an alkaline reaction in addition to any alkali present in said gums when recovered from said crude oil, and an organic soap solvent miscible with water, said composition being stable against fermentation.

2. As a product of manufacture, a composition of matter which comprises, alkali metal soap, a substantial amount of gums recovered from crude vegetable oils, and a substantial amount of at least one alkali metal compound having an alkaline reaction in addition to any alkali present in said gums when recovered from said crude oil, said composition being sufficiently free from water to be stable against fermentation, and an organic soap solvent miscible with water admixed with said composition.

3. As a product of manufacture, a composition of matter which comprises, alkali metal soap, a substantial amount of gums recovered from crude vegetable oils, a substantial amount of at least one alkali metal compound having an alkaline reaction in addition to any alkali present in said gums when recovered from said crude oil, and an organic soap solvent miscible with water, said composition containing a fermentation inhibiting agent for said gums in sufficient amount to render said composition stable against fermentation.

4. As a product of manufacture, a composition of matter which comprises, soap stock from the alkali refining of crude vegetable oils including

soap, gums, an alkali, said composition also containing a substantial amount of at least one alkali metal compound having an alkaline reaction in addition to any alkali present in said soap stock, and sufficient organic soap solvent miscible with water to prevent graining out of soap when said product is in an aqueous solution of the order of 10% concentration, said composition containing substantially all of said gums in said soap stock and being stable against fermentation.

5. As a product of manufacture, a composition of matter which comprises, soap stock from the alkali refining of crude vegetable oils including soap, gums, and an alkali, said composition also containing a substantial amount of at least one alkali metal compound having an alkaline reaction in addition to any alkali present in said soap stock, said composition containing substantially all of said gums in said soap stock and being sufficiently free of water to be stable against fermentation, and sufficient organic soap solvent miscible with water admixed with said composition to prevent graining out of soap when said product is incorporated in an aqueous solution of the order of 10% concentration.

6. As a product of manufacture, a composition of matter which comprises, soap stock from the alkali refining of crude vegetable oils including soap, gums, an alkali, said composition also containing a substantial amount of at least one al-

kali metal compound having an alkaline reaction in addition to any alkali present in said soap stock and sufficient organic soap solvent miscible with water to prevent graining out of soap when said product is in an aqueous solution of the order of 10% concentration, said composition containing substantially all of said gums in said soap stock and containing a fermentation inhibiting agent for said gums in sufficient amount to render the same stable against fermentation.

7. As a product of manufacture, a cleaning composition for use in spray cleaning devices, which comprises, soap stock from the alkali refining of crude vegetable oils including water, soap, gums and an alkali, said composition also containing a substantial amount of soda ash in addition to any alkali present in said soap stock and being sufficiently free of water to be stable against fermentation, said composition containing substantially all of said gums in said soap stock and said gums being present in sufficient amount to prevent the deposition of insoluble compounds when said composition is mixed with hard water and heated and to substantially increase the foaming, rinsing and emulsifying properties of the soap, and sufficient organic soap solvent miscible with water admixed with said composition to prevent graining out of soap when said product is incorporated in an aqueous solution of the order of 10% concentration.

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