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PROCESS OF SAPONIFICATION

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This invention relates to an improved process for saponifying fatty substances, more particularly to an improved process for the saponification of vitamin-containing oils and fats to recover the unsaponifiable material therefrom.

As is well known, the standard method of saponifying fatty substances involves heating the fatty substance with an aqueous solution of a caustic alkali until the esters are converted into the free alcohol and soaps of the fatty acids. This process has been successfully applied to the preparation of vitamin concentrates from fat-soluble vitamin-containing oils and fats, since it has been found that vitamin concentrates may be recovered from the saponification mass by solvent extraction or other methods. However, this method of saponification is somewhat disadvantageous in that the soap is always obtained in the form of an aqueous solution or emulsion thereof; thus when it is attempted to recover the vitamin concentrates from the saponification mass, it is necessary to extract the vitamins from the aqueous solution or emulsion, a step which often presents great difficulties in view of the strong emulsifying properties possessed by the soap.

In order to avoid some of the above-mentioned disadvantages, it has been proposed in U. S. Patent 1,813,454 to carry out the saponification of fatty substances with anhydrous caustic soda in the presence of an inert organic diluent in which glycerine or other alcoholic components of the fatty substance are insoluble; the process described in this patent is carried out at temperatures sufficiently high so that the glycerine or other alcoholic component distills off during the course of saponification along with the solvent employed. While this process has been found to be generally satisfactory with respect to the saponification of vitamin-free fatty substances, the temperatures preferably employed in this process are such that treatment of vitamin-containing fatty substances thereby results in the destruction of an appreciable amount of the vitamins. Furthermore, the soap produced by this process is in gel form and may have a certain amount of undesirable color due to decomposition or polymerization of some of the organic materials present in the fatty substance.

It has been further proposed to obtain fat-soluble vitamin concentrates from vitamin-containing oils by adding dry sodium hydroxide to an oil such as cod liver oil, permitting the mixture to saponify, and then extracting the vitamin concentrate from the saponified mass by means of a solvent therefor. This process has not proved to be particularly practical because of the difficulties in obtaining complete saponification under these conditions and in extracting the vitamins from the complex saponification mass.

It is an object of this invention to provide a process for the saponification of oils and fats.

It is a more specific object of this invention to provide a process for the saponification of vitamin-containing oils and fats which avoids the aforementioned disadvantages.

I have made the surprising discovery that the aforementioned disadvantages, incidental to previous procedures employed for the saponification of fatty substances, may be avoided by forming a mixture containing a substantially anhydrous strong alkali and a fatty substance dissolved in an alkali-stable fat solvent incapable of dissolving substantial amounts of anhydrous soaps, and permitting this mixture to react at a temperature below about 100° C. until saponification is substantially complete. My process is particularly applicable to the preparation of fat-soluble vitamin concentrates from vitamin-containing fatty substances, since I have found that the saponification of such fatty substances in accordance with my invention produces a mixture in which the vitamin concentrates liberated by the saponification are dissolved in the fat solvent, and thus may be easily and completely separated from the soap. I prefer to employ a fat solvent which is also a solvent for the glycerine or other alcoholic component of the fatty substance, so that the alcoholic component formed by the saponification may also be readily separated from the soap. However, my invention is not intended to be limited to the use of fat solvents capable of dissolving the alcoholic component of the fatty substance, since any alkali-stable fat solvent incapable of dissolving substantial amounts of anhydrous soaps may be employed. My invention constitutes a marked improvement over other processes heretofore employed for the saponification of fatty substances, since the soap is produced in substantially anhydrous condition and thus may be easily recovered from the saponification mass because of its insolubility in the solvent employed. Moreover, when using a fat solvent capable of dissolving the glycerine or other alcoholic component of the fatty substance, as is preferred in carrying out the process of my invention, the soap and the alcoholic component may be separately recovered directly from the saponification mass. The relatively low temperatures employed in my process also permit more economical operation. The application of my process to the preparation of vitamin concentrates possesses the important additional advantage that at the low temperatures employed such concentrates may be obtained from the fatty substances without substantial loss in vitamin activity.

The alkali-stable fat solvent employed in accordance with my invention may be any fat solvent which is stable to the action of strong alkali

and which is incapable of dissolving substantial amounts of anhydrous soaps. As hereinabove pointed out, I prefer to employ fat solvents having the above characteristics which are also capable of dissolving the glycerine or other alcoholic component of the fatty substance; many such solvents are well known to the art and as examples there may be mentioned acetone, methyl ethyl ketone, methyl butyl ketone and higher liquid aliphatic ketones, benzol, isopropyl alcohol, butanol and higher liquid aliphatic alcohols, isopropyl ether, dioxane, chlorbenzol and other aromatic halogen compounds. I prefer to employ acetone in the practice of my invention, since this solvent is readily available and is capable of dissolving the alcoholic component formed by the saponification while completely precipitating the anhydrous soap formed. Mixtures containing one or more of the above solvents may advantageously be used. For example, a mixture of acetone and benzene containing about 70% acetone or a mixture of acetone and petroleum ether containing about 87% acetone are both suitable; furthermore, mixtures of isopropanol with benzene or petroleum ether containing about 30% and about 40% isopropanol, respectively, may be used with advantage. However, fat solvents having the above characteristics, but in which the alcoholic components of the fatty substance are not soluble, may be used, such as, for example, heptane, gasoline, etc.

Any saponifiable fatty substance may be treated in accordance with my invention; thus, for example, beef tallow, coconut oil, palm oil, sperm oil and other oils, fats and fatty waxes may be processed. My invention is particularly applicable, as above pointed out, to the preparation of fat-soluble vitamin concentrates by the saponification of vitamin-containing fatty substances, such as, for example, cod liver oil, sword fish liver oil, tuna liver oil, shark liver oil, etc. It is to be understood that the term "fatty substance" is used throughout the specification and claims to include oils, fats, and fatty waxes which may be saponified by treatment with strong alkalis.

The substantially anhydrous strong alkali employed in accordance with my invention may be anhydrous sodium hydroxide, anhydrous potassium hydroxide or any other anhydrous strong alkali. The anhydrous alkalis may be made in any suitable manner, but I prefer to prepare them by mixing an aqueous solution of the alkali with a relatively high boiling organic solvent such as kerosene, and then heating the mixture until all the water distills off. The alkali may be recovered from the slurry thus formed by the use of a centrifuge or the kerosene may be washed therefrom with a suitable solvent.

In carrying out the process of my invention as applied to the saponification of vitamin-containing oils, the oil may first be dissolved in an alkali-stable fat solvent incapable of dissolving anhydrous soaps. The amount of solvent employed may vary somewhat depending upon the particular solvent used, but ordinarily between about 5 and about 6 volumes of solvent for each volume of oil is suitable. The anhydrous caustic alkali may then be added to the solution, preferably in a finely powdered condition; the amount of alkali added is ordinarily determined by the amount of oil it is desired to saponify and may be calculated stoichiometrically. If desired, the mixture may then be permitted to remain at room temperature until the saponification is substantially complete. However, I greatly prefer to heat the mixture in order to accelerate the saponification, the temperature in any event not exceeding about 100° C.; when using a solvent such as acetone boiling below 100° C., the mixture is most advantageously refluxed until saponification is complete. The time necessary for the saponification ordinarily varies somewhat depending upon the temperature employed; the employment of slightly elevated temperatures, as is preferred, usually effects completion of the saponification from about 3 to about 4 hours.

Upon completion of the saponification, it will be found that the soap formed thereby has precipitated from the solution in substantially anhydrous condition. The form in which the soap precipitates may vary with the particular solvent employed; thus if acetone is employed, as is preferred, substantially anhydrous soap particles separate from the solution and may be recovered by filtration. On the other hand, the employment of solvents such as isopropyl alcohol may cause the soap to precipitate in the form of a gel; the soap may be recovered from such gels by evaporation of the solvent, or by precipitating the soap by pouring the gel into acetone. The soap recovered in accordance with my process is substantially anhydrous and has no undesirable color attributable to the presence of decomposition or polymerization products. This soap may be treated as desired. If unsaturated fatty substances have been saponified, the resulting soap may advantageously be hydrogenated in order to yield hard soaps suitable for a wide variety of purposes.

The vitamin concentrates formed during the saponification remain dissolved in the alkali-stable fat solvent and may be recovered therefrom in any suitable manner, such as, for example, by vacuum distillation in an inert gas atmosphere. Thus the vitamins are readily recovered in a form such that they are completely uncontaminated with the soap; furthermore, the yields of the vitamin concentrates are excellent because of the relatively low temperatures employed.

The glycerine formed during the saponification may remain dissolved in the alkali-stable fat solvent providing a glycerine solvent is employed. When operating in accordance with the preferred embodiment of my invention, i. e. when using acetone as the alkali-stable fat solvent, the glycerine remains dissolved in the acetone and may be recovered therefrom by evaporation of the acetone. I have found that this method of operation is particularly advantageous, since the glycerine appears to carry with it a large part of the coloring matter contained in the vitamin oils, thus yielding vitamin concentrates possessing extremely light colors. However, if a solvent such as heptane is employed in which glycerine is not soluble, the glycerine separates from the saponification mass along with the soap and may be removed from the soap by extraction with a suitable solvent.

While the above detailed description is confined to the saponification of vitamin-containing fatty substances, it is to be understood that my invention is equally applicable to the saponification of vitamin-free fatty substances and to the recovery of soap and glycerine or other alcoholic component from the reaction mass.

The following examples are illustrative of my invention; amounts are given in parts by weight.

Example I

100 parts of cod liver oil containing 1870 A units per gram were dissolved in 400 parts of acetone. Anhydrous caustic soda was prepared by adding kerosene to an aqueous caustic soda solution and evaporating the water; the resulting product contained 59.1% sodium hydroxide, the remainder being kerosene. 24 parts of this anhydrous caustic soda-kerosene mixture were washed with acetone to remove the kerosene and a slurry of the caustic soda in acetone was then added to the oil solution. The mixture was refluxed with agitation for about 2½ hours, the soap removed by centrifuging, the separated soap washed with acetone and re-centrifuged; the acetone solutions recovered were combined. The acetone was then evaporated from the combined solutions; when most of the acetone had been driven off, two layers formed. The upper layer contained the unsaponifiable material and the lower layer contained glycerine. The upper layer was removed and the remaining acetone distilled off; the resulting product was an oil containing about 10,200 A units per gram.

Example II

1,000 parts of cod liver oil containing 1780 A units per gram were dissolved in about 6,000 parts of acetone. 205 parts of anhydrous caustic soda containing 76% sodium hydroxide, the remainder being kerosene, were washed with heptane to remove the kerosene, and the anhydrous caustic soda containing a little heptane was then added to the cod liver oil solution. The mixture was refluxed with agitation for 2 hours, cooled and the precipitated soap filtered therefrom by means of a filter press in a nitrogen atmosphere and under about 5 lbs. pressure. The soap was washed with acetone and this acetone solution combined with the filtrate from the filter press. The acetone was then evaporated from the combined solutions; when most of the acetone had been driven off, two layers formed. The upper layer contained the unsaponifiable material and the lower layer contained glycerine. The upper layer was withdrawn and the remaining acetone was distilled off. The resulting product contained about 12,150 A units per gram.

Example III

100 parts of beef tallow having a saponification value of 197 were dissolved in 480 parts of acetone. 23.9 parts of anhydrous caustic soda containing 59.1% sodium hydroxide and prepared as described in Example I were washed with acetone to remove the kerosene, and the anhydrous caustic soda containing a little acetone was then added to the tallow solution. The mixture was refluxed with agitation for 2¼ hours. At the end of this time, the reaction mixture was permitted to cool and the soap was centrifuged from the mixture. The soap was washed with acetone and dried, whereby a light-gray, anhydrous soap containing only about 0.2% free alkali was obtained. Glycerine was recovered by evaporating the acetone from the solution thereof.

Example IV

100 parts of a soap stock containing 90 parts of beef tallow and 10 parts of coconut oil were dissolved in 500 parts of acetone and 14.1 parts of anhydrous crystalline caustic soda were added to the solution. The mixture was then refluxed for 2 hours, at the end of which time the soap was removed in a centrifuge, washed with acetone and dried; the soap thus obtained was substantially anhydrous and contained only 0.09% free alkali. Glycerine was recovered by evaporating the acetone solution.

Example V

100 parts of a soap stock containing 90 parts of beef tallow and 10 parts of coconut oil were dissolved in 500 parts of isopropyl alcohol and 14.1 parts of anhydrous crystalline caustic soda were added to the solution. The mixture was then refluxed for 2 hours, at the end of which time the mass was permitted to cool and the gel-like layer containing the soap was removed from the glycerine solution by filtration. The isopropyl alcohol was then evaporated from the gel, whereby an anhydrous soap containing only 0.07% free alkali was obtained. Glycerine was recovered from the solution thereof by evaporation of the isopropyl alcohol.

Example VI

100 parts of cod liver oil were dissolved in 500 parts of a mixture of acetone and petroleum ether containing about 87% acetone. 24 parts of anhydrous caustic soda containing 59.1% sodium hydroxide and prepared as described in Example I were washed with acetone to remove the kerosene, and the anhydrous caustic soda containing a little acetone was then added to the solution of cod liver oil. The mixture was refluxed for about 3½ hours, the soap formed was removed by centrifuging, the separated soap washed with additional quantities of the above mixture and re-centrifuged; the acetone-petroleum ether solutions recovered were combined and about 50 additional parts of petroleum ether were added thereto. The glycerine formed by the saponification was precipitated by the addition of the petroleum ether and was separated from the solution. The vitamin concentrate was then recovered by evaporating the solvent therefrom in a vacuum.

It will be evident from the above description that the process of my invention provides a novel and highly economical process for the saponification of oils and fats. From the above description, it will also be evident that my invention is particularly applicable to the preparation of vitamin concentrates by the saponification of vitamin-containing oils and fats. Therefore, my invention will be of great interest to those engaged in the manufacture of vitamin products, as well as to those employed in the soap making industry.

The specific Examples I–VI recite separation of the undissolved soap from the liquid remaining after saponification by filtration or centrifuging. These are examples of mechanical separation without change of state of any component of the mixture remaining after the saponification.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. In the saponification of a fat containing a fat soluble vitamin, with preservation of the vitamin, the method which comprises forming a mixture containing the fat, a substantially anhydrous alkali metal hydroxide, and a liquid that is a solvent for the fat and vitamin of the fat but a non-solvent for the said hydroxide and for anhydrous alkali metal soaps, so that the alkali metal hydroxide originally used and the soaps as formed remain in undissolved condition, warming the

mixture to a temperature not substantially above 100° C. until the fat is saponified, and separating the thus formed undissolved soap from the remaining solution, the separating of the undissolved soap from the remaining solution being effected mechanically without change of state of any component of the mixture of soap and solution.

2. The method of preparing a vitamin concentrate, which comprises forming a solution of a fat containing a fat-soluble vitamin in a liquid that is a solvent for the fat, vitamin of the fat, and glycerine but a non-solvent for alkali metal hydroxides and for anhydrous alkali metal soaps so that the alkali metal hydroxide originally used and the soaps as formed remain in undissolved condition, suspending a substantially anhydrous alkali metal hydroxide in the said solution, warming the solution and suspended hydroxide to a temperature not substantially above 100° C. until the fat is saponified and alkali metal soap is precipitated, separating the precipitated soap from the remaining solution, and then separating the said liquid from the vitamin concentrate and glycerine in the remaining solution, the separation of the precipitated soap from the remaining solution being effected mechanically without change of state of any component of the mixture of soap and solution.

3. The method described in claim 2, the alkali metal hydroxide used being sodium hydroxide and the said liquid being acetone.

4. The method described in claim 2, the said liquid being isopropyl alcohol.

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