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PREPARATION OF FATTY ACID ESTERS OF POLYHYDROXY ALCOHOLS

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This invention relates to the production of fatty acid esters of polyhydric alcohols and more particularly to the separation of impurities, such as fatty acid soaps, in the production of mono- and diglycerides of the higher fatty acids.

As pointed out in our copending application Serial No. 116,128, filed December 16, 1936, the alkali- or alkaline earth-metal compounds added as catalysts in the partial esterification of glycerol, or in the treatment of glycerides to form glycerides containing one or two fatty acid radicals, results in the formation of salts or soaps which are present in the product as impurities. Previous attempts to remove these impurities and the excess glycerol suspended in the mixture with them, have presented various objectionable features from a commercial standpoint.

It is an object of the present invention to provide a new procedure for separating the excess of soap and other impurities from mixtures of them with fatty acid esters of polyhydroxy alcohols, or from other mixtures containing soaps, whereby various improvements may be obtained. It is also an object to provide an improved process whereby the removal of the excess of polyhydric alcohol in the mixtures may be facilitated. It is another object to provide a process in which such a separation may be brought about expeditiously and at reduced cost and without causing a charring or decomposition in the mixture such as would seriously interfere with its use in food products. A further object is to accomplish such a separation and obtain a product of low ash content. Other objects will become apparent.

In the past the use of concentrated sulfuric acid for the removal of soaps, by direct addition to the melted, substantially anhydrous, higher fatty acid esters of polyhydric alcohols has been avoided because of the danger of reaction with and decomposition of the fatty acid esters at temperatures resulting from the addition of the acid to the esters at temperatures above their melting points.

We have discovered that when sulfuric acid is added to a polyhydric alcohol, such for example, as a glycerol or glycol or a polyglycerol or polyglycol or some other polyhydric alcohol that is not charred or decomposed by the surfuric acid, or to ethers of such compounds, the resulting liquid may be added to melted, substantially anhydrous, higher fatty acid esters of polyhydric alcohols, containing soaps and excess polyhydric alcohol as impurities, to remove such impurities and obtain a marked improvement in the desired fatty acid esters. This liquid may be added after the completion of the partial esterification or other reaction by which the suspension of soap and free polyhydric alcohol is formed. Soap in the mixture is presumably thereby converted into the fatty acid esters of the polyhydric alcohol with which the acid is mixed (which polyhydric alcohol is preferably the same as that which is partially esterified), with the attendant formation of the sulfate or bisulfate of the alkali or alkaline earth portion of the soap. In the specific example referred to hereinafter the polyhydric alcohol is glycerol. The excess glycerol will separate into a layer and the sulfate, which is anhydrous and is practically insoluble in the anhydrous glycerol, will settle out. If the bisulfate is formed, it will dissolve in the glycerol and will be separated with that fraction. These procedures permit of the removal of the greater part of the excess glycerol and result in a product substantially free of ash and which is of excellent color and taste. Where the process is so carried out, the recovered glycerol will contain no suspended solids and is suitable for reuse in the process.

The following is a specific example of our improved procedure, although it is not intended to limit the invention to the particular embodiment given as illustrative, it being obvious that many variations may be made in utilizing it.

The liquid resulting from the addition of sulfuric acid to glycerol may be prepared by slowly adding concentrated sulfuric acid to glycerol while stirring and cooling to maintain the temperature below about 40° C.

About 275 parts by weight of a completely hydrogenated peanut oil and about 60 parts of glycerol may be heated, with stirring, to about 170–205° C. until the contents of the reaction vessel are substantially anhydrous. About three and a quarter parts of sodium bicarbonate ($NaHCO_3$) may then be added and the heating and stirring of the mixture continued for about one hour, allowing any water vapor to escape through a discharge tube from the otherwise closed vessel.

The temperature of this reaction mixture may then be allowed to fall to about 150–160° C. and the product resulting from the addition of about three and a half parts of concentrated sulfuric acid (94% H_2SO_4) to about six and a half parts of glycerol, as described above, may be added to the reaction mixture with sufficient agitation to distribute it uniformly.

Upon standing, the excess glycerol of the reaction mixture will quickly separate, carrying

with it sodium sulfate freed from the soap. Upon separation of the two clear layers resulting from a procedure carried out as described above, the upper ester layer was found to contain a total of free and combined glycerol of about 21.5%. It contained about 1.4 higher acyl groups per mol of combined glycerol and an ash content of only about 0.04%.

Reactions which we believe take place are as follows, R representing the hydrocarbon portion of the fatty acid radical.

$$RCOONa+HOSO_2OCH_2CHOHCH_2OH\rightarrow RCOOH+NaOSO_2OCH_2CHOHCH_2OH$$

$$RCOONa+NaOSO_2OCH_2CHOHCH_2OH\rightarrow RCOOCH_2CHOHCH_2OH+Na_2SO_4$$

Another example of a reaction mixture to which our invention may be applied is in the esterification of the fatty acids of cocoanut oil with an excess of ethylene glycol by the aid of an alkaline reacting catalyst. In this instance the sulfuric acid is preferably first mixed with anhydrous ethylene glycol.

Obviously many variations may be made in the procedures described above. For example, the temperatures, times and proportions given may be varied to meet various requirements as will be apparent to one skilled in the art. Also, many variations may be made in the use to which the invention is put. For instance, it may be applied to the separation of soaps from other reaction products wherein they are suspended. For example, it may be used in the removal of soaps in the preparation of other partially esterified polyhydroxy alcohols, or in the preparation of partial esterification products of the glycerides of other oils and fats (cottonseed oil, corn oil, palm oil, lard, oleo oils, etc.) or their fatty acids.

Furthermore, other polyhydric alcohols or ethers thereof may be used in place of the glycerol to which the sulfuric acid is added, as described above. Such polyhydric alcohols are preferably those containing 4 or less carbon atoms and it is preferred to use the same polyhydric alcohol as that of the reaction mixture to which it is to be added. Examples of other suitable hydrolyzable sulfuric esters are ethylene glycol sulfate, diethylene glycol sulfate, polyglycerol sulfate or polyglycol sulfate, or sulfates of polyglycol ethers, such as of ethylene glycol monomethyl ether or diethylene glycol monoethyl ether or the acid sulfate esters of any of these.

Also, instead of adding acid to the polyhydric alcohol an acid sulfate, such as sodium bisulfate, may be added. In this way the sodium salt of the acid sulfate of the polyhydric alcohol (for example, the sodium salt of glyceryl acid sulfate) may be produced in the mixture which is to be added to the reaction mixture containing the soap. Other acid sulfates may also be used whereby other salts of the acid sulfate of the polyhydric alcohol, containing edible cations, may be produced; for instance, potassium acid sulfate may be added.

The acid sulfate of the polyhydric alcohol, or the salts thereof, may be formed in other ways than that described in the preferred illustrative example. For instance, instead of producing the sulfuric esters by the elimination of water between concentrated sulfuric acid and a hydroxylic organic compound, it may be obtained by the action of sulfuric anhydride, or other sulfuric acid derivatives, upon the corresponding hydroxylic organic compound.

By following the above described procedure, the alkali or alkaline earth portion of the soap present in the mixture is converted to an inorganic salt. Such salts may be separated from the mixture so that a substantially ash-free product is obtained. When excess glycerol is present the conversion of the soap to the salt of the acid ester will liberate the glycerol held in suspension. The absence of water in the mixture avoids the formation of emulsions, whereby the separation of the salt and of the excess glycerol is facilitated.

In using the term "soaps" in the specification and claims it is intended to include the reaction products of the alkaline reacting catalysts with other organic materials present in the mixture, as well as the reaction products with fatty acids.

It is apparent that many modifications may be made in the utilization of the invention and in giving illustrative examples it is not intended to restrict the invention to such examples. The terms used in describing the invention have been used in a descriptive sense and not as terms of limitation and it is intended that all equivalents of the terms used be included within the scope of the appended claims.

We claim:

1. A process for removing a soap from mixtures of the soap with fatty acid esters of polyhydroxy alcohols comprising adding to the mixture a mixture of a polyhydric alcohol and an acid stronger than the fatty acid of the soap and maintaining the mixture at a temperature of about 100–175° C.

2. In a process of preparing partially esterified polyhydroxy alcohols in the presence of an alkaline reacting material, the step which comprises destroying the fatty acid salt present in the product by the addition of a mixture of glycerol and sulfuric acid.

3. In the process of preparing fatty acid esters in the presence of an alkaline-reacting material, whereby esters containing unesterified hydroxyl groups are obtained, the step which comprises adding, after the production of the fatty acid esters, a liquid resulting from the addition of sulfuric acid to glycerol, said sulfuric acid being slightly in excess (stoichiometrically) of the quantity of catalyst employed.

4. In the process of preparing mono- and diglycerides in the presence of an alkaline reacting material, the step which comprises adding, after the production of the mono- and diglycerides, a liquid resulting from the addition of sulfuric acid to glycerol, said sulfuric acid being slightly in excess of the quantity of catalyst employed.

5. The process as in claim 1 wherein the polyhydric alcohol is glycerol.

6. The process as in claim 1 wherein the polyhydric alcohol is ethylene glycol.

7. A process for removing a soap from mixtures containing the same comprising, adding a substance selected from the class consisting of acids and acid salts to a polyhydric alcohol and adding the mixture thus formed to the said mixture containing the soap.

8. A process for removing a soap from mixtures containing the same comprising, adding sulfuric acid to a polyhydric alcohol and adding the mixture thus formed to the said mixture containing the soap.

9. A process for removing soaps from mixtures of the same with polyhydric alcohol esters comprising adding concentrated sulfuric acid to a polyhydric alcohol which is not charred or decomposed by the addition of concentrated sulfuric acid and adding the mixture thus formed to the said soap mixture.

10. A process for removing a soap from mixtures containing the same comprising, adding concentrated sulfuric acid to a polyhydric alcohol containing 4 or less carbon atoms and adding the mixture thus formed to the said mixture containing the soap.

11. A process for removing a soap from mixtures containing the same comprising, adding concentrated sulfuric acid to a polyhydric alcohol of the group consisting of glycerol, glycol, polyglycerols and polyglycols, and adding the mixture thus formed to the said mixture containing the soap.

12. A process for removing a soap from mixtures containing the same comprising, adding a bisulfate containing an edible cation to a polyhydric alcohol and adding the mixture thus formed to the said mixture containing the soap.

13. A process for removing a soap from mixtures containing the same comprising, adding concentrated sulfuric acid to glycerol and adding the mixture thus formed to the said mixture containing the soap.

14. A process for removing a soap from mixtures containing the same comprising, adding to the said mixture a polyhydric alcohol ester of an acid salt containing an edible cation said acid salt being of an acid stronger than the fatty acid of the soap.

15. A process for removing a soap from mixtures containing the same comprising, adding to the said mixture a polyhydric alcohol ester of sulfuric acid.

16. A process for removing a soap from mixtures containing the same comprising, adding to the said mixture a salt of a polyhydric alcohol ester of sulfuric acid said salt containing an edible cation.

17. A process for removing a soap from mixtures containing the same comprising, adding to the said mixture an acid sulfate ester of a polyhydric alcohol containing 4 or less carbon atoms, said acid sulfate containing an edible cation.

18. A process for removing a soap from mixtures containing the same comprising, adding to the said mixture an acid sulfate ester of a polyhydric alcohol of the group consisting of glycol, glycerol, polyglycols and polyglycerols.

19. A process for removing a soap from mixtures containing the same comprising, adding to the said mixture an acid sulfate ester of glycerol.

20. A process for removing soap from mixtures containing the same, comprising treating the said mixture in the absence of substantial quantities of water with a mixture of a polyhydric alcohol and a substance selected from the class consisting of acids and acid salts of an acid stronger than the fatty acid of the soap.

21. A process for removing soap from mixtures containing the same, comprising treating the said mixture in the absence of substantial quantities of water with an acid sulfate ester of a polyhydric alcohol of the group consisting of glycol, glycerol, polyglycols and polyglycerols.

22. A process for removing soap from mixtures containing the same, comprising treating the said mixture in the absence of substantial quantities of water with a mixture of glycerol and concentrated sulfuric acid.

23. A process for removing a soap from mixtures containing the same, comprising adding a substance selected from the classes consisting of mineral acids and mineral acid salts to a polyhydric alcohol and adding the mixture thus formed to the said mixture containing the soap.

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