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PRODUCTION OF SULPHONATION DERIVATIVES

Eugene D. Crittenden, Syracuse, N. Y., assignor to The Solvay Process Company, New York, N. Y., a corporation of New York

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The present invention relates to a process for the production of sulphonation derivatives of saturated higher fatty acids, which derivatives are valuable as detergent, wetting, and the like agents.

An object of the invention is to provide a process for the production of alpha-sulphonic acid derivatives of saturated higher fatty acids from relatively inexpensive and readily available raw materials. A further object of the invention is to provide a process for the production of such sulphonation derivatives of saturated higher fatty acids characterized by a particularly good color. Another object of the invention is to provide a process for the production of such derivatives which may be practiced efficiently on a commercial scale.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has been found in accordance with the present invention that alpha-sulphonic acid derivatives of saturated higher fatty acids can be efficiently prepared by sulphonating salts of saturated higher fatty acids (i. e., soaps) with sulphur trioxide in the presence of liquid sulphur dioxide.

The presence of the cation in the molecules of the salts not only does not interfere with this essentially acidic reaction but, on the contrary, has been found to involve several advantages. Thus, by sulphonating an alkali metal salt of a saturated higher fatty acid containing a certain percentage of alkali metal salts of unsaturated higher fatty acids with sulphur trioxide in liquid sulphur dioxide, a product of better color (which is indicative of the purity of the product) can be obtained than when sulphonating in this way a saturated higher fatty acid containing the same percentage of unsaturated higher fatty acids. This is a distinct advantage since the amount of hydrogenation required of a material containing both saturated and unsaturated bodies to be used in the production of sulphonation derivatives of comparable quality, is reduced. For example, satisfactory products can be obtained in the present process when using as starting materials alkali metal salts of saturated higher fatty acids containing from five to ten per cent by weight of alkali metal salts of unsaturated higher fatty acids, and products of excellent quality can be obained by using alkali metal salts of saturated higher fatty acids containing less than five per cent, or better, less than two per cent, by weight of alkali metal salts of unsaturated higher fatty acids. It appears probable that the above result is due to the fact that unsaturated higher fatty acids in the form of alkali metal salts are less susceptible to the charring that ordinarily takes place when unsaturated compounds are reacted with sulphur trioxide in the presence of liquid sulphur dioxide under conditions adapted to introduce sulphonic acid groups into saturated fatty acid bodies. The present process has the further advantage that it can be made a part of the usual soap-making process merely by the addition of hydrogenation, drying and sulphonation steps.

It has been found to be important to control the water content of the sulphonation reaction mixture. As the amount of water present during the sulphonation is increased, there is a corresponding decrease in the yields of the desired sulphonation derivatives. Further, while in certain cases it is possible to secure fair yields of sulphonation derivatives in the presence of a relatively large amount of water by increasing the vigor of the sulphonating conditions, such as the temperature, this is unsatisfactory because the products obtainable by such procedure are highly colored. For these reasons, it has been found to be preferable to carry out the sulphonation in a reaction mixture containing not more than three per cent of water based on the weight of sulphur trioxide used. In fact, for best results, the water content of the reaction mixture should be reduced as low as is technically feasible. Because alkali metal soaps, which would be the ordinary starting materials in the present process, are difficult to prepare free from water, it has been found to be impractical to reduce the water content of the reaction mixture much below two per cent based on the weight of sulphur trioxide used. In accordance with optimum procedure, however, the water content of the reaction mixture is kept at or below this figure.

That this process is productive of the results noted is surprising from another aspect. The usual sulphonating procedures, if applied to the sulphonation of salts of saturated higher fatty acids, are unsatisfactory because they result in the production of dark-colored products, or in a small degree of sulphonation. Thus, if oleum, concentrated sulphuric acid, or chlorsulphonic acid is used in the sulphonation, significant yields of alpha-sulphonic acids are not obtained at low temperatures, while at high temperatures serious carbonization of the organic material occurs. The results obtained with the first two of these sulphonating agents appear to be due to the fact that they contain combined water which is deleterious. In the case of chlorsulphonic acid, hydrochloric acid is formed which must be removed.

The alpha-sulphonic acid derivatives of saturated higher fatty acids prepared by the present process constitute valuable detergent, wetting, and the like agents which are active in hard water and in acid and alkaline solutions. Thus, as compared with ordinary soaps, they are not hydrolyzed to the free fatty acids in acid solutions. Also, they do not have the disadvantage of soaps of being precipitated in the form of sticky curds from solutions containing calcium or magnesium salts which have no detergent value, but which constitute impurities. As compared with ordinary sulphonated fatty acids obtained by the sulphonation of unsaturated and/or hydroxy fatty acids, of which the Turkey red oils are outstanding examples, the derivatives possess considerably superior wetting and detergent properties and are more stable against hydrolysis. The properties of the derivatives, as compared with the properties of ordinary sulphonated fatty acids, appear to be due to the facts that the sulphonic acid group in the derivatives is at the end of a long carbon chain, and they contain a sulphonic acid group rather than the more easily hydrolyzed sulphuric acid ester group.

The saturated fatty acid salts used as starting materials in the process are preferably alkali metal salts of the saturated fatty acids obtainable from naturally occurring fats and oils, of which tallow, cocoanut oil, babassu oil, palm oil, and fish oils, e. g., menhaden fish oil, are examples. When starting with a naturally occurring fat or oil, it is ordinarily advisable at some stage of the process to employ hydrogenation, since the fats and oils contain glycerides of unsaturated, as well as saturated, higher fatty acids. Tallow, for example, contains glycerides of the saturated fatty acids, stearic acid, palmitic acid, and myristic acid, and the glycerides of the unsaturated fatty acids, oleic acid and linoleic acid. These fats or oils can be subjected to hydrogenation before or after conversion to the fatty acid salts by saponification with an appropriate alkaline material. The hydrogenation is preferably carried out by contacting the material to be treated with hydrogen at an elevated temperature and at a superatmospheric pressure in the presence of a hydrogenation catalyst, such as nickel. When the fat or oil is subjected to this treatment, the resulting product is composed substantially entirely of glycerides of saturated fatty acids, the unsaturated glycerides in the material having been saturated. In proceeding in this way, the saturated glycerides are then converted to the alkali metal salts of the saturated fatty acids present therein by saponification with an appropriate alkali metal compound; e. g., sodium hydroxide.

In accordance with preferred procedure, however, the saturated fatty acid salts used in the process are prepared by saponification of the fat or oil whereby, after removal of glycerine, an ordinary soap is obtained comprising a mixture of saturated and unsaturated fatty acid alkali metal salts. This mixture is then subjected to hydrogenation in the presence of a hydrogenation catalyst to convert the unsaturated fatty acid salts to the corresponding saturated compounds. This procedure is of advantage since it has been found that the hydrogenation of a mixture of fatty acid salts proceeds with particular efficiency due to the fact that the mixture is substantially free from free fatty acids, which appear to have a deleterious effect on the hydrogenation catalyst.

It will be understood of course that the starting material in the process may be a salt or a mixture of salts of saturated higher fatty acids from any source provided that these materials do not contain substantially more than ten per cent by weight of unsaturated fatty acid bodies. In this connection, the term "saturated higher fatty acids" is used herein to denote saturated fatty acids which contain at least 8 carbon atoms and which are free from hydroxyl groups. The preferred starting materials are those derived from saturated fatty acids containing 8 to 24, and especially 14 to 18, carbon atoms. These fatty acids may be any of those present in the above fats or oils after hydrogenation. Examples of suitable saturated higher fatty acids are the following: myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, and lignoceric acid.

As already stated, it is important to carry out the present process in the absence of a material amount of water. Salts of saturated higher fatty acids prepared by either of the above described methods ordinarily contain a proportion of water which should be substantially removed prior to sulphonation if commercially satisfactory products are to be obtained. For this reason the salts of the saturated fatty acids are ordinarily subjected to a drying treatment, which may be accomplished in any convenient or satisfactory manner, prior to sulphonation. The dried salts are then subjected to sulphonation by reacting them with sulphur trioxide in the presence of liquid sulphur dioxide. This is preferably accomplished by dissolving and/or suspending the salts in liquid sulphur dioxide, and then introducing sulphur trioxide, preferably in solution in liquid sulphur dioxide, into the solution or suspension. At the completion of the sulphonation, the sulphonation derivatives are recovered from the remainder of the reaction mixture as such or in admixture with sulphates. For example, the liquid sulphur dioxide may be distilled off and condensed for use in a succeeding run of the process.

The sulphonation derivatives prepared in this way are alpha-sulphonic acid derivatives of the saturated higher fatty acids whose salts were employed as the starting materials. The sulphonation derivatives appear to be predominantly in the forms of the free acids; i. e., they contain a free sulphonic acid group and a free carboxylic acid group. When the sulphur dioxide is largely removed by distillation, the mixture remaining also contains a proportion of the sulphate of the cation of the fatty acid salt used as the starting material. Since the sulphonation derivatives are preferably employed in the form of their partially or wholly neutralized salts, this mixture is treated so as to neutralize the free fatty acids contained therein. To this end it is preferably dissolved in a minimum of water, residual sulphur dioxide is removed as by heating or by passing air or steam through the solution, and the desired neutralizing material is introduced into the solution. In this connection it has been found that relatively little charring or other discoloration occurs in the neutralization reaction and consequently the wholly neutralized salts may be prepared having good color at this stage of the process; it not being necessary in order to obtain products of especially good color to precipitate the partially neutralized salts from the solution, as is best procedure when the free fatty acids are sulphonated. At the completion of the neutralization, if the partially neutralized

salts have been prepared, they may be precipitated from the solution and recovered by filtration; or if the partially or wholly neutralized salts have been prepared, the solution (or slurry) may be dried, as by means of a spray or rotary drum drier, to form a dry product containing salts of alpha-sulphonic acid derivatives of saturated higher fatty acids admixed with a proportion of a sulphate of the neutralizing agent. A solution of this product has valuable detergent, wetting, and the like properties. The sulphate present appears to improve the valuable properties of the product. If desired, salts (in addition to the sulphate formed in the reaction) such as, for example, sodium sulphate, ammonium sulphate, monosodium phosphate, disodium phosphate, sodium tetraborate, sodium silicate, and sodium sesquicarbonate, can be added to the product. Also, in certain cases it may be found of advantage to combine the dry product with other detergents and/or wetting agents, such as ordinary soaps and other sulphonated products.

In order that the invention may be more fully understood, reference should be had to the following specific examples in which are disclosed processes coming within the scope of the present invention. It will be understood that these examples are given for illustrative purposes merely and are not intended as limitations of the invention. The parts are by weight and the temperatures are in degrees centigrade.

Example 1.—318 parts of sodium stearate (1 mol) containing less than 10 per cent by weight of salts of unsaturated higher fatty acids, and 240 parts (3 mols) of sulphur trioxide are added to 7170 parts of liquid sulphur dioxide in a vessel provided with a gas-tight sealing means. After the formation of the mixture, the vessel is sealed and the mixture is allowed to stand in the vessel which is at room temperature. After about 15 hours, the seal is broken and the sulphur dioxide is removed by evaporation and recovered for use in a succeeding run of the process. The mixture remaining in the vessel is introduced into water, heated to remove residual sulphur dioxide, and is neutralized to a pH of about 7 with an aqueous solution of sodium hydroxide. The resulting neutralized mixture is then evaporated to dryness whereby there is obtained a dry product comprising essentially the sodium salt of the alpha-sulphonic acid derivative of stearic acid which product has valuable detergent, wetting, and the like properties.

Example 2.—Soap is prepared in the usual manner by saponification of mutton tallow by treatment with caustic soda. The glycerol is separated and recovered as a by-product. The soap obtained in this way contains about 48 per cent by weight of unsaturated fatty acid bodies and is then hydrogenated at a temperature of 200° and under superatmospheric pressure employing nickel deposited on calcined magnesite as a catalyst and gaseous hydrogen from a suitable source. The hydrogenation is continued until the unsaturated bodies are reduced in amount so as to comprise less than two per cent by weight of the soap. One part of the hydrogenated soap is then suspended and/or dissolved in 40 parts of liquid sulphur dioxide contained in a reaction vessel provided with a sealing means, and 20 parts of a solution of sulphur trioxide in liquid sulphur dioxide containing one part of sulphur trioxide is introduced into the resulting solution or suspension. The vessel is sealed and the reaction mixture is maintained at a temperature of about 35° for a period of 8 hours or until sulphonation is completed as determined by separating a small aliquot portion of the reaction mixture, neutralizing an aqueous solution of this portion with caustic soda, and extracting the unreacted material, if any, with ether. At the completion of the sulphonation the vessel is opened and the sulphur dioxide is distilled off and recovered for use in a succeeding run of the process. The remaining mixture is then finished as described in Example 1 using as the neutralizing agent sufficient caustic soda to bring the pH of the solution to 7.

Example 3.—Beef tallow is hydrogenated at an elevated temperature and under superatmospheric pressure using a nickel catalyst and hydrogen gas from a convenient source (e. g., from a synthetic ammonia plant) and the substantially completely saturated glycerides obtained are separated from the catalyst by filtration and treated with caustic alkali to form a soap and liberate glycerine which is recovered. The soap obtained in this way, which contains less than two per cent of salts of unsaturated higher fatty acids, is sulphonated and further treated as described in Example 2. A product is obtained possessing valuable detergent, wetting, and the like properties.

When proceeding in accordance with the general procedure of the above examples it will be understood that additional salts may be added during the neutralization and drying procedures (e. g., up to 20 to 50 per cent by weight of the sulphonated compound), or, if desired, an excess of sulphur trioxide over that required in the sulphonation may be used and neutralized with an alkaline material (e. g., a caustic alkali or ammonia) to form in situ an inorganic salt constituting a filler.

It will be understood of course that the starting materials employed in the examples may be replaced by other salts of saturated higher fatty acids and fats or oils; for example, any of those referred to above. For example, in place of the sodium stearate employed in Example 1, there may be used other alkali metal salts of stearic acid, or instead of these salts of stearic acid similar salts of any other saturated higher fatty acid, for example, any of those previously mentioned, may be used. Further, in place of the fats employed in Examples 2 and 3 there may be used an equivalent amount of any other suitable fat or oil; e. g., any of those mentioned above. In this connection, however, it should be noted that a fat or oil containing hydroxylated fatty acids should not be employed in the present process since the products resulting from the treatment of such fatty acids are of considerably less value than the sulphonation derivatives of saturated fatty acids. Furthermore, the treatment of hydroxylated fatty acid with sulphur trioxide in liquid sulphur dioxide under conditions necessary to replace an alpha-hydrogen atom by a sulphonic acid group produces products containing dark-colored impurities which are difficult, if not impossible, to remove. As previously stated, it is important that the saturated fatty acid salt should not contain more than ten per cent of unsaturated fatty acids. If products having particularly good color are desired, a saturated fatty acid salt should be used containing less than five per cent, or better, less than two per cent, of salts of unsaturated higher fatty acids.

In place of the neutralizing agents used in the

examples, there may be used any other alkaline material capable of reacting with a sulphonic acid group. Thus, sodium carbonate, potassium carbonate, caustic potash, ammonia, and methyl amine can be used for this purpose.

The amount of sulphur trioxide employed in the process can be varied within relatively wide limits, but in order to produce satisfactory yields of the desired products it should not be reduced below 2.5 mols for each mol of the saturated fatty acid salt or salts subjected to treatment. For most cases, it is unnecessary to use more than 4 mols of this reagent. For most efficient operation it is generally preferable to employ from 3 to 3.5 mols of sulphur trioxide for each mol of the saturated fatty acid salt. As indicated above, however, an excess of the sulphur trioxide ordinarily does not have a critical effect on the operativeness of the process and, in some cases where it is desired to form a sulphate in situ, it is of advantage. With respect to the amount of liquid sulphur dioxide required as the solvent medium it will be understood that this amount is dependent in large measure upon the solubility in this medium of the particular saturated fatty acid salt or mixture of salts used as the starting material in the process. As compared with the free saturated fatty acids, for example, these salts have lesser solubility in liquid sulphur dioxide, and, consequently, a relatively large quantity of this solvent medium is usually required. This does not add materially to the cost of the process because the sulphur dioxide may be efficiently recovered for reuse in a succeeding run of the process by distillation and condensation.

As appears from the examples, the sulphonation reaction can be carried out at ordinary temperatures, and, because of simplicity of operation, such temperatures are usually employed. If desired, however, a higher or lower temperature can be used; for example, temperatures varying from 20° to 50° C. are suitable. The time required for the sulphonation reaction is also a variable factor, being dependent upon the specific saturated fatty acid salt or salts subjected to treatment, the apparatus employed, the temperature, and other conditions. Under ordinary conditions of operation, a reaction period of from 3 to 20 hours is sufficient to complete the sulphonation.

In the appended claims where "a salt of a saturated higher fatty acid" is referred to it will be understood that this term is intended to include mixtures of such salts as well as single salts.

Since certain changes may be made in the above process without departing from the scope of the invention, the above description should be interpreted as illustrative and not in a limiting sense.

I claim:

1. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises sulphonating a salt of a saturated higher fatty acid with sulphur trioxide in the presence of liquid sulphur dioxide.

2. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises sulphonating a salt of a saturated higher fatty acid containing from 8 to 24 carbon atoms and containing not substantially more than ten per cent of salts of unsaturated higher fatty acids with sulphur trioxide in a reaction mixture in which liquid sulphur dioxide is the solvent medium.

3. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises sulphonating an alkali metal salt of a saturated higher fatty acid with sulphur trioxide in the presence of liquid sulphur dioxide.

4. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises sulphonating an alkali metal salt of a saturated higher fatty acid containing 8 to 24 carbon atoms and containing not substantially more than five per cent of alkali metal salts of unsaturated higher fatty acids with sulphur trioxide in a reaction mixture in which liquid sulphur dioxide is the solvent medium, said reaction mixture being free from more than three per cent of water based on the weight of sulphur trioxide used.

5. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises sulphonating an alkali metal salt of a saturated higher fatty acid containing not substantially more than five per cent of alkali metal salts of unsaturated higher fatty acids with 2.5 to 4 mols of sulphur trioxide for each mol of said alkali metal salt of a saturated higher fatty acid in a reaction mixture in which liquid sulphur dioxide is the solvent medium, said reaction mixture being free from more than three per cent of water based on the weight of sulphur trioxide used.

6. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises sulphonating an alkali metal salt of a saturated higher fatty acid containing from 8 to 24 carbon atoms and containing not substantially more than ten per cent of salts of unsaturated higher fatty acids with sulphur trioxide in a reaction mixture in which liquid sulphur dioxide is the solvent medium, said reaction mixture being free from more than three per cent of water based on the weight of sulphur trioxide used, mixing the resulting sulphonation mass with water to form a mixture comprising the alpha-sulphonic acid derivative of the saturated higher fatty acid and sulphuric acid, and neutralizing said alpha-sulphonic acid derivative.

7. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises hydrogenating a soap consisting essentially of alkali metal salts of saturated higher fatty acids and unsaturated higher fatty acids but being substantially free from salts of hydroxyl-containing higher fatty acids to produce a hydrogenated soap free from more than five per cent of alkali metal salts of unsaturated higher fatty acids, sulphonating said hydrogenated soap with sulphur trioxide in the presence of liquid sulphur dioxide, and neutralizing the resulting sulphonation products.

8. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises hydrogenating a soap consisting essentially of sodium salts of saturated higher fatty acids and unsaturated higher fatty acids but being substantially free from salts of hydroxyl-containing higher fatty acids to produce a hydrogenated soap free from more than five per cent of salts of unsaturated higher fatty acids, sulphonating said hydrogenated soap with sulphur trioxide in a reaction mixture in which liquid sulphur dioxide is the solvent medium, said reaction mixture being free from more than three per cent of water based on the weight of sulphur trioxide used, to convert said hydrogen-

ated soap to alpha-sulphonic acid derivatives of saturated higher fatty acids, and converting said alpha-sulphonic acid derivatives to the corresponding sodium salts.

9. The process for the preparation of alpha-sulphonic acid derivatives of stearic acid which comprises sulphonating an alkali metal stearate containing not substantially more than five per cent of salts of unsaturated higher fatty acids with sulphur trioxide in a reaction mixture in which liquid sulphur dioxide is the solvent medium, said reaction mixture being free from more than three per cent of water based on the weight of sulphur trioxide used.

10. The process for the preparation of alpha-sulphonic acid derivatives of saturated higher fatty acids which comprises sulphonating the sodium salt of a saturated higher fatty acid containing not substantially more than five per cent of salts of unsaturated higher fatty acids with 2.5 to 4 mols of sulphur trioxide for each mol of said sodium salt of a saturated higher fatty acid at a temperature of 20° to 50° C. in a reaction mixture in which liquid sulphur dioxide is the solvent medium, said reaction mixture being free from more than three per cent of water based on the weight of sulphur trioxide used.

EUGENE D. CRITTENDEN.