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PROCESS FOR PREPARING ALPHA SULFO FATTY ACIDS AND SALTS THEREOF

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The present invention is concerned with alpha sulfo fatty acids and their alkali salts and, more particularly, to an improved process for preparing the same.

Detergents have gained wide acceptance in recent years due to their desirable and highly effective detergent or surface active properties. Various types of detergents are currently in use, such as the alkyl aryl sulfonates and their alkali salts, exemplified by sodium dodecylbenzene sulfonate. While such detergents have found wide application as cleansing agents, emulsifying agents and the like, they have created problems with respect to disposal after use. In particular, it has been found that most of the presently available detergents introduce foaming properties to the water in sewers, lakes and streams. This situation has become of considerable concern to municipalities due to the large amount of detergents currently in use. Further, in many areas, it has been found that the level of detergent in the available water is constantly increasing to the extent that marine lift is adversely affected and health hazards created.

It has been recognized that other types of detergents would be desirable which could be subsequently destroyed after use and upon discharge into sewers, lakes or streams. It has also been recognized that certain compositions having detergent properties are capable of being destroyed by bacteria and that if detergents of this type were economically feasible their use would tend to eliminate problems of the foregoing type. One such class of detergents, which are known to be susceptible to destruction by bacteria after use, are the alpha sulfo saturated fatty acids, for example, alpha sulfostearic acid. Detergent compositions based upon such compounds may readily be treated with certain bacteria to the extent that their detergent or surface active properties can be destroyed.

Additionally, sulfonated fatty acids exemplified by alpha sulfostearic acid offer a further advantage in that they are adaptable for use in making bar soap as compared to other more common sulfonic acids. Thus, such acids have the desired cleansing action, are only slightly soluble in water, and have no irritating qualities, all characteristics normally found in and desired for ordinary soap.

Alpha sulfostearic acid and similar fatty acid sulfonated compositions have not gained wide acceptance as of the present time primarily due to the fact that production costs are relatively high as compared to the less expensive alkyl aryl sulfonates.

Accordingly, one of the principal objects of the present invention is to provide a relatively inexpensive process for preparing alpha sulfo fatty acids and their alkali salts.

Another object is to provide a process of the foregoing which is readily adaptable to commercial operations and which results in reasonably high yields.

In those limited instances wherein alpha sulfo fatty acids have been suggested as detergent replacements for the more popular alkyl aryl sulfonates, the specific fatty acid base normally contemplated is substantially pure stearic acid. This acid is believed to be preferred in order to eliminate coloring and sludge problems involved from sulfonating unsaturated components frequently

present in less than pure grades of stearic acid and, correspondingly, eliminate the use of larger amounts of sulfur trioxide normally required. Substantially pure stearic acid is relatively expensive.

Further, at the present time, the principal method for making alpha sulfostearic acid comprises sulfonating the acid with sulfur trioxide, wherein the acid is either reacted in a fused state or in a solvent suspended state. Certain disadvantages are present in such prior art process. One disadvantage is based upon the fact that in the solvent process relatively expensive solvents are considered to be necessary to eliminate as much as possible sulfonation of the solvent. One preferred solvent is carbon tetrachloride. However, even in using carbon tetrachloride as the solvent, some disadvantage is nevertheless present, in that the SO_3 being highly reactive offers the possibility of producing the toxic compound, phosgene, with the carbon tetrachloride.

It has now been found that less expensive commercially acceptable alpha sulfo fatty acids can be made from compositions not containing substantially 100 parts of stearic acid and, particularly, from stearic acid compositions known as rubber grade stearic acids. The latter type of stearic acid compositions, in addition to containing between about 45–65% stearic acid, also contains lower saturated fatty acids having usually between 12–18 carbon atoms, such as palmitic and myristic acid, as well as about 5–10% unsaturated acids, particularly oleic acid. However, it has been found with the present process that such compositions can be used to obtain relatively high quality alpha sulfo fatty acids in reasonably good yields and having excellent detergent or surface active properties.

In particular, the present process consists of dissolving a fatty acid composition, such as a substantially pure or a rubber grade stearic acid, in a special class of solvent, introducing SO_3, preferably in combination with a diluent, for example, nitrogen or air, at a maximum temperature of 35° C. or less, preferably less than 30° C., and subsequently heating the resultant reaction product at a temperature above 35° C., preferably above 40° C. with a practical upper limit of about 100° C.

The initial product of reaction between sulfur trioxide and the fatty acids is believed to be an acid sulfate or an acyl sulfuric acid of the fatty acid and sulfur trioxide. When this intermediate reaction product is subsequently heated at a temperature above 35° C., the alpha sulfo fatty acid is formed. The rate of formation of the sulfonated fatty acid depends upon the temperature of the second heating step, the higher the temperature the faster the formation. The initial heat treatment of 35° C. or below is required to reduce the tendency for even the particular class of hydrocarbon solvents, referred to hereinafter, to undergo sulfonation.

After formation, the sulfonated fatty acids may be separated from the solvent, either by filtration or as a residue from distillation. The sulfonated acid is then dissolved in water and neutralized to a desired pH by the addition of an alkali, such as a sodium hydroxide solution. This results in the production of a mono-alkali salt, for example, the mono sodium salt of alpha sulfostearic acid. Thus, normally only the SO_3H group is neutralized. The alkali salt suspension may then be heated to redissolve the salt and subsequently cooled to recrystallize and obtain a substantially pure mono-alkali salt of alpha sulfo fatty acid.

Frequently, it will be found that the resulting product is slightly colored, usually having a tan appearance. A clearer product may be obtained by using activated charcoal and adding a bleaching agent, such as sodium hypochlorite or hydrogen peroxide, to the hot solution of the acid salt in the above process before recrystalliza-

tion. Alternately, several recrystallizations may be used to clarify the product.

The special class of reaction solvents which have been found to be effective are those which are straight chain or unbranched saturated hydrocarbons exemplified by heptane, hexane, octane and even propane or butane under pressure. Cyclohexane, which is especially suitable as solvent, is also considered within the foregoing class. Hydrocarbon solvents of this class are to be distinguished from branched hydrocarbons which have been found to be highly susceptible to sulfonation and, accordingly, not contemplated in the present process. All the solvents normally used, including those proposed herein, are susceptible in varying degrees to attack by sulfur trioxide. However, it has been found that the tendency toward reaction of sulfur trioxide with the solvent is considerably reduced when the more reactive fatty acid is present. Accordingly, it is an important aspect of the present invention that the fatty acid be suspended or dissolved in the solvent prior to reaction with the sulfur trioxide.

As indicated, it is preferable to employ the sulfur trioxide in admixture with a diluent, such as nitrogen or air. In particular, it has been found that effective reaction may be obtained when sulfur trioxide is present in the amount of between about 5–80% of such a mixture.

As further illustrating the present invention without intending to thereby limit the same, the following example is presented of the process:

A 22 liter, 4-necked Morton flask was charged with 12,000 ml. of dry cyclohexane and 2,000 g. (7.29 moles) of Neo-Fat 18–59 (Armour Company rubber grade stearic acid). The flask was equipped with a stirrer, thermometer, condenser and gas inlet tube, the latter arranged so as to discharge below the surface of the reaction medium. A nitrogen stream was arranged so that it passed through a flow-meter, a trap, a flask containing the SO_3 (but not passing below its surface), the gas inlet tube, and the condenser, leaving the system through a mineral oil bubbler and a Drierite tube. Sulfur trioxide, 850 g. (10.63 moles), was heated to a gentle boil and was carried into the stearic acid suspension by the nitrogen stream. The nitrogen was metered at 400 cc. per minute, and the addition took four hours. This indicated a SO_3 concentration of 70% in the vapor stream. The reaction was mildly exothermic but was maintained at about 30° C. by means of a cooling bath. When the addition was completed, the reaction mixture was refluxed for two hours at about 80° C. Solvent was removed by distillation until the pot temperature was 110°; the residue weighed 294 g. (111% of theory). Potentiometric titration indicated the material to be 70.1% alpha-sulfostearic acid, for an overall yield of 77.7%.

The crude material was dissolved in water and neutralized with sodium hydroxide to a pH of 4.5. The resulting thick suspension was heated to 80° C., cooled, centrifuged, the liquid removed, and the solid recrystallized from water. To the hot solution was added sufficient dilute (about 5–10%) hydrogen peroxide such that its concentration in the solution was 0.1–0.5%. On cooling, white crystals were obtained, yielding, after drying, neutralization equivalents from 372–390. The average yield was 75%.

Having described the invention and a specific embodiment thereof, we claim as our invention:

1. A process for sulfonating a saturated fatty acid which comprises dissolving said fatty acid in a saturated hydrocarbon solvent wherein the hydrocarbon is characterized by the absence of branching, introducing sulfur trioxide into said solution at a maximum temperature of 35° C. and subsequently heating the reaction mass to a temperature above 35° C. but not exceeding about 100° C.

2. A process as described in claim 1 wherein the fatty acid is stearic acid.

3. A process as described in claim 2 wherein the hydrocarbon solvent is cyclohexane.

4. A process for making the mono alkali salt of an alpha sulfo fatty acid which comprises dissolving said fatty acid in a saturated hydrocarbon solvent wherein the hydrocarbon is characterized by the absence of branching, introducing sulfur trioxide into said solution at a maximum temperature of 35° C., subsequently heating the reaction mass to a temperature above 35° C. but not exceeding about 100° C., removing the solvent, dissolving the mass in water and neutralizing the solution with sufficient alkali to obtain the mono alkali salt.

5. A process as described in claim 4 wherein the neutralized alpha sulfo acid is dissolved in warm water, treated with a bleaching agent and recrystallized by cooling.

6. A process as described in claim 5 wherein the fatty acid is stearic acid.

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