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MANUFACTURE OF SALTS OF ALKYL ACID SULFATES IN ONE STEP

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5 Claims. (Cl. 260—247.1)

This invention relates to the preparation of substituted ammonium salts of sulfated alcohols. More particularly it relates to the manufacture in one step of such sulfated alcohol salts.

Sulfation or sulfonation or the like treatment of various organic compounds including long chain alcohols is well known procedure in the industry as described in various texts such as "Unit Processes in Organic Synthesis," Groggins, 1938. Also other publications such as "Industrial & Engineering Chemistry" for September 1954, describe a number of sulfating processes.

Sulfation in general is accomplished with a large number of sulfating agents, predominant among which are sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, sulfamic acid and pyridine-sulfur trioxide complexes. In prior art methods of sulfating alcohols with these materials, problems such as the formation of color and the attack on double bonds in the fatty alcohol molecule have been encountered. While some of the prior art processes and sulfating agents will accomplish one aim, they may fail drastically at some other point. In general in the prior art procedures after sulfation with sulfating agents of the aforementioned type, the sulfated fatty alcohol must be neutralized with ammonia, sodium or potassium hydroxide or the like, which may present further problems.

In further detail, in most prior art sulfation methods it is difficult to sulfate materials containing an olefinic double bond, such as oleyl alcohol, without sulfating across this double bond. When such reaction takes place, a compound is formed having much lower surface active characteristics than when only the alcohol group is sulfated. Furthermore, in general sulfation reactions in accordance with the prior art, a certain amount of degradation may take place and the reaction mixture may develop an undesirable dark color. Also, the problem of neutralizing sulfated alcohols as mentioned above must be resolved, and while this can be done in accordance with prior art procedures with a reasonable amount of equipment, it does represent a second step and adds to expense. However, there is an especially troublesome problem if high temperatures are created during neutralization, since alkyl sulfates tend to decompose when heated in the acidic state.

It is therefore apparent that the development of an improved process whereby the aforementioned type of difficulties may be eliminated or minimized represents a highly desirable result. Not only are certain process advantages obtained by my one-step type of method which will be described in detail hereinafter, but added advantages may be obtained in the production, in many instances, of a better colored product. That is, it is apparent in some instances, in the use of such salts, as for example in the treatment of yarns with textile treating agents containing salts of the aforementioned type by old methods of manufacture and which may not be of good color characteristics, that possibly damage to the yarn to some extent can occur. Hence, the present invention which provides a simpler and improved process of making such products, as well as the production of a better type product, is believed to possess particular merit.

This invention has for one object to provide an improved procedure for producing substituted amine or ammonium salts of sulfated alcohols. Still another object is to provide a substantially one-step method of producing compounds of the class aforesaid. An additional object is to provide a new process of sulfation which may be applied to unsaturated alcohols without material danger of sulfation of the olefinic double bond. A still further object of this invention is to produce substituted ammonium salts of sulfated alcohols characterized by being light in color. Another object is to provide a simplified, improved process for producing salts of sulfated alcohols of the class indicated which are suitable for use as surface active agents, detergents, wetting agents, components of yarn treating compositions and the like. Other objects will appear hereinafter.

In the broader aspects of my invention I have found that organic compounds to be converted to substituted ammonium salts of alkyl acid sulfates, such as long chain alcohols exemplified by oleyl alcohol, lauryl alcohol and the like, may have added thereto an amine before sulfating, or, as will be described in connection with certain variations of my invention, the amine or certain other agents may be added to the sulfating material prior to the one-step reaction with the alcohol to be sulfated. In either instance this invention gives a method of sulfating along with salt formation at the same time. In other words, I have found an efficient one-step process from the fatty alcohol to the formation of the salt of the sulfated alcohol. By thus producing the salt in one step, the color produced during the typical prior art sulfation reaction is usually bypassed and in most instances lighter colored products are thus obtained. The one-step method in accordance with the present invention makes possible the sulfation of olefinic alcohols without the deleterious attack at the double bond.

The equipment required for this invention is relatively simple, consisting only of an open heated kettle equipment with a stirrer. The controls are also very simple, and furthermore there is no problem of the prior art type concerning solvent removal or final neutralization. That is, in my invention at the end of the one reaction the final product ready for use is obtained.

The broader aspects of my process may be considered under two headings, depending on whether the compound is precombined with the alcohol or whether the compound is precombined with the sulfating medium.

(A) In accordance with the reaction under this heading, the alcohol to be processed in accordance with the present invention, is premixed with, for example, an alkylol amine. Considering lauryl alcohol as the long chain alcohol desired treated, the lauryl alcohol is mixed with a chemical such as an amino alkyl propanol, with stirring. Thereafter the mixture of the alcohol and amine is subjected to treatment with a sulfating agent under certain conditions which will be described in detail hereinafter. In general I prefer in several respects to employ the procedure just described. However, certain alternative procedures may be carried out as will be briefly mentioned in the next paragraph.

(B) In accordance with the procedure under this heading the amine may be added to the sulfating medium, such as to the sulfuric acid in a certain manner, and the resultant combination then reacted with the long chain alcohol. Further details concerning this aspect of my invention will be set forth in detail toward the end of the instant specification.

I have found by proceeding as just briefly indicated, that a substantially one-step process can be accomplished and that in addition to improved operation there may also be obtained an improved product. That is, products produced by my one-step process in many instances are lighter colored than conventionally produced products. Accordingly, my lighter colored products in many instances possess particular merit and utility in formulating compositions for use in treating textiles.

A more complete understanding of my invention will be had by reference to the several examples which follow. These examples are set forth primarily for illustrating certain preferred embodiments of my invention. In Examples I through VIII the reference to oleyl means a hydrocarbon chain of the following formula:

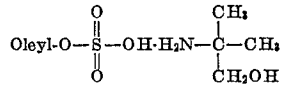
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2—$$

In Examples IX through XV the reference to lauryl means a hydrocarbon chain having the following formula:

$$C_{12}H_{25}\ (\text{sat.})$$

Example I

This example describes the preparation of N-(1,1-dimethyl-2-hydroxy ethyl) ammonium oleyl sulfate having the formula:



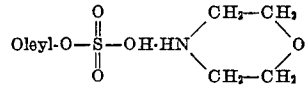
One mole (89 grams) of 2-amino-2-methyl-1-propanol is mixed with one mole (268 grams) of oleyl alcohol. This mixture is agitated and to it is added one mole (98 grams) of concentrated sulfuric acid at such a rate that the temperature of the reaction mass reaches 110° C. When the temperature begins to drop it is maintained at about 100° C. for 4 hours. A reasonably light colored material having high emulsification powers and having a degree of sulfation of 68% was obtained by this procedure.

Example II

This example also describes the preparation of N-(1,1-dimethyl-2-hydroxy ethyl) ammonium oleyl sulfate but using lower temperatures. One mole (89 grams) of 2-amino-2-methyl-1-propanol is mixed with one mole (268 grams) of oleyl alcohol (commercial Ocenol). One mole (98 grams) of concentrated sulfuric acid is added to the mixture with strong agitation. The temperature is allowed to reach 100° C. during this addition and is maintained at 100° C. for 1½ hours. The temperature is then lowered to 90° C. for 6 hours at which time the product is recovered as a brown viscous liquid which by analysis is shown to be about 55% sulfated.

Example III

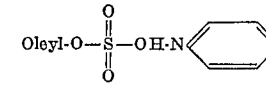
This example describes the preparation of the morpholine salt of oleyl sulfate, having the formula:



One mole (87 grams) of morpholine is mixed with one mole (268 grams) of oleyl alcohol. To this is added one mole (98 grams) of concentrated sulfuric acid while the whole reaction mass is vigorously agitated. The temperature is allowed to go to 110° C. during this step and is maintained thereafter at 100° C. for 7½ hours. The product obtained from this reaction solidifies to a light solid showing a degree of sulfation of 68%. This N-morpholine oleyl sulfate has very good emulsifying powers.

Example IV

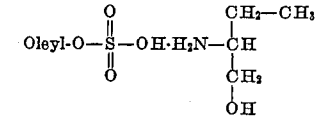
This example describes the preparation of pyridine oleyl sulfate having the formula:



One mole (79 grams) of pyridine is mixed with one mole (268 grams) of oleyl alcohol. This mixture is vigorously stirred and to it is added one mole (98 grams) concentrated sulfuric acid. The temperature reaches about 92° C. during the addition and is thereafter maintained at 100° C. for 7 hours. At the end of this time the reaction product solidifies to a light solid which shows good emulsifying powers and is 73% sulfated.

Example V

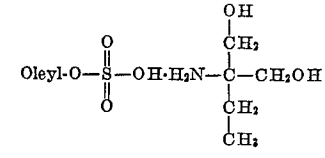
This example describes the preparation of N-(1-ethyl-2-hydroxy ethyl)ammonium oleyl sulfate, having the formula:



One mole (268 grams) of oleyl alcohol is mixed with one mole (89 grams) of 2-amino-1-butanol. The mixture is well stirred and to it is added one mole (98 grams) of concentrated sulfuric acid at such a rate that the temperature reaches 110° C. At the end of this addition the temperature is maintained at 100° C. for 7½ hours. The reaction product is a liquid and shows good emulsifying properties.

Example VI

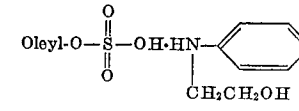
This example describes the preparation of N-(1,1-bis hydroxy methyl propyl)ammonium oleyl sulfate having the formula:



One mole (268 grams) of oleyl alcohol is mixed with one mole (119 grams) of 2-amino-2-ethyl-1,3-propanediol. This mixture is stirred and to it is added one mole (98 grams) of concentrated sulfuric acid. The rate of addition of the sulfuric acid is adjusted so that the temperature reaches a maximum of 110° C. during the reaction. After the addition is complete the temperature is maintained at 100° C. for 7½ hours. The product obtained from this reaction is a viscous slightly dark material having good emulsifying properties and showing 70% sulfation.

Example VII

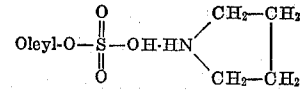
This example describes the preparation of N-phenyl-N-hydroxy ethyl ammonium oleyl sulfate having the formula:



One mole (268 grams) of oleyl alcohol is mixed with one mole (133 grams) of phenyl ethanolamine. One mole (98 grams) of concentrated sulfuric acid is added with agitation to this mixture and the temperature allowed to reach 90° C. At the end of this time the temperature is adjusted to 100° C. for 7 hours. The product collected from this reaction is a gray solid showing good emulsifying characteristics.

Example VIII

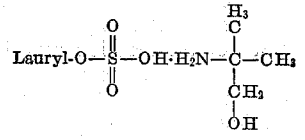
This example describes the preparation of pyrrolidinium oleyl sulfate having the formula:



One mole (268 grams) of oleyl alcohol is mixed with one mole (71 grams) of pyrrolidine. This mixture is well agitated and one mole (98 grams) of concentrated sulfuric acid added at such a rate that the temperature reaches 110° C. After the addition of the sulfuric acid is complete the temperature is adjusted to 100° C. and kept there for 7 hours. The product obtained from this reaction is a liquid showing good emulsifying properties.

Example IX

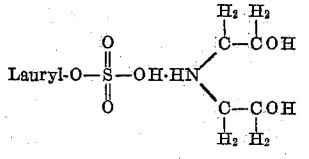
This example describes the preparation of N-(1,1-dimethyl-2-hydroxy ethyl)ammonium lauryl sulfate having the formula:



One mole (186 grams) of lauryl alcohol is mixed with one mole (89 grams) of 2-amino-2-methyl-1-propanol. To this well stirred mixture is added one mole (98 grams) of concentrated sulfuric acid. The addition of the sulfuric acid is adjusted to give a temperature rise up to 120° C. At the end of this time the temperature is adjusted to 100° C. and kept there for 7½ hours. The product resulting from this reaction is a white solid having good emulsifying properties and showing a degree of sulfation of 58%.

Example X

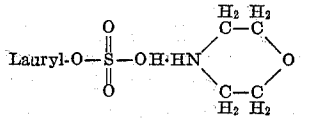
This example describes the preparation of N-(bis hydroxy ethyl)ammonium lauryl sulfate, having the formula:



One mole (186 grams) of lauryl alcohol is mixed with one mole (105 grams) of diethanolamine. This mixture is well agitated while one mole (98 grams) of concentrated sulfuric acid is added at such a rate that the temperature reaches 120° C. After the addition is complete the temperature is adjusted to 100° C. and kept there for 7½ hours. The product thus obtained shows fair emulsifying properties.

Example XI

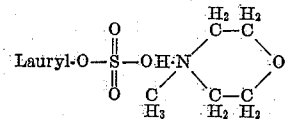
This example describes the preparation of N-morpholyl lauryl sulfate, having the formula:



One mole (186 grams) of lauryl alcohol is mixed with one mole (87 grams) of morpholine. This mixture is well stirred and to it is added one mole (98 grams) of concentrated sulfuric acid. The temperature is allowed to go to 130° C. during the addition of acid and is later adjusted at 100° C. for 7½ hours. A very clear, light colored material is obtained which has very good emulsifying powers and shows a degree of sulfation of 78%.

Example XII

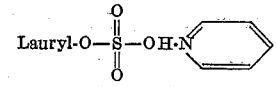
This example describes the preparation of N-methyl morpholine salt of lauryl sulfate having the formula:



One mole (186 grams) of lauryl alcohol is mixed with one mole (101 grams) of N-methyl morpholine. This mixture is stirred vigorously and to it is added one mole (98 grams) of concentrated sulfuric acid at such a rate that the temperature rises to 120° C. When all of the acid is added the temperature is maintained at 120° C. for 7½ hours. The resulting product is a light tan solid showing good emulsifying characteristics and showing a degree of sulfation of 73%.

Example XIII

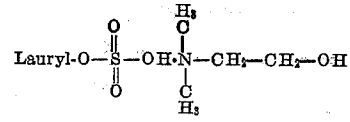
This example describes the preparation of the pyridine salt of lauryl sulfate, having the formula:



One mole (79 grams) of pyridine is added with vigorous stirring to one mole (186 grams) of lauryl alcohol. Then one mole (98 grams) of concentrated sulfuric acid is added gradually so that the temperature rises to 120° C. The temperature is then settled at 100° C. for 6 hours. At the end of this time a product is obtained which is a white solid and has a degree of sulfation of 68%. This material also shows high emulsifying characteristics.

Example XIV

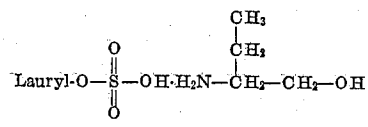
This example describes the preparation of the N,N-dimethyl amino ethanol salt of lauryl sulfate having the formula:



One mole (89 grams) of N,N-dimethyl amino ethanol is added to one mole (186 grams) of lauryl alcohol. This mixture is rapidly stirred and to it is added one mole (98 grams) of concentrated sulfuric acid at such a rate that the temperature rises to 115° C. The mixture is maintained at 100° C. for 7½ hours at which time the reaction is considered complete. a white solid is obtained from this reaction showing fair emulsifying characteristics.

Example XV

This example describes the preparation of N-(1-ethyl-2-hydroxyethyl)ammonium lauryl sulfate having the formula:



One mole (89 grams) of 2-amino-1-butanol is added to one mole (186 grams) of lauryl alcohol. This mixture is vigorously agitated while one mole (98 grams) of concentrated sulfuric acid is added at such a rate that the temperature reaches 122° C. The temperature is then adjusted to 100° C. and kept there for 7½ hours. At the end of this time a very light colored viscous liquid was obtained as the product and it showed good emulsifying characteristics along with a degree of sulfation of 65%.

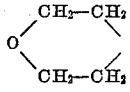
Description will now be set forth relative to carrying out my invention in accordance with modification B. referred to earlier in the specification. It will be recalled that in accordance with this modification the alkylol amine or the like compound is premixed in a certain manner with the sulfating medium. The product obtained is then used to react with the alcohol thereby producing a substituted ammonium salt of a sulfated alcohol in good yield and having a good color. It is already indicated above that this feature of premixing of the present invention permits the treatment of unsaturated fatty alcohols without obtaining a reaction at the double bond.

The sulfating agents obtained by the premixing in accordance with part B. of the present invention are described by the following formula:

$$(R)(R')(R'')\ NHSO_3OH$$

R is (*a*) $HOCH_2CH_2$— (*b*) $HOCH_2C(CH_3)_2$—

(*c*)



In (*a*) and (*b*), R′ can be (*d*) CH_3—; (*e*) CH_3CH_2—, or (*f*) H.

In (*d*) and (*e*), R″ is H

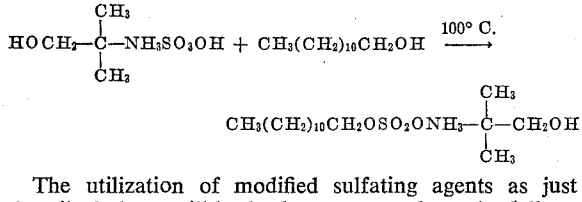
In (*c*), R′ is H, and there is no R″.

These sulfating agents are easily prepared by dissolving one mole of the alkylolamine, for instance, in an inert solvent such as ether or carbon tetrachloride (many different chlorinated hydrocarbons and ethers will do as well). To this rapidly stirred mixture, one mole of concentrated sulfuric acid is added and the resulting precipitate collected. This precipitate, the alkylolamine sulfate, is freed from inert solvent, and mixed in molar proportions with the fatty alcohol. This mixture is well agitated and heated over a period of 2 to 7 hours. At the end of this time, the alkylol substituted ammonium fatty alcohol sulfate is collected and is ready for use as a detergent or emulsifying agent, for example. This reaction is described by the following equation:

$$(R)(R')(R'')NHSO_3OH + R'''OH \xrightarrow{100^\circ\ C.} R'''OSO_2ONH(R)(R')(R'')$$

R‴ is C_{10} to C_{20}.

A more specific example follows:



The utilization of modified sulfating agents as just described above will be further apparent from the following specific examples:

Example XVI

Preparation of N-(1,1-dimethyl-2-hydroxyethyl) ammonium lauryl sulfate. One mole of N-(1,1-dimethyl-2-hydroxyethyl) ammonium sulfate was prepared by adding one mole of concentrated sulfuric acid to a solution of 1 mole of 2-amino-2-methyl-1-propanol in ether. The resulting white, crystalline solid was collected and added to 1 mole (186 grams) of lauryl alcohol. This mixture was well stirred and heated to 135° C. for 2 hours. A light colored material of high surface activity was obtained from this reaction.

Example XVII

Preparation of N-(1,1-dimethyl-2-hydroxyethyl) ammonium oleyl sulfate. One mole of N-(1,1-dimethyl-2-hydroxyethyl) ammonium sulfate was prepared in the manner described in Example XVI, and added to 1 mole

(268 grams) of oleyl alcohol. The mixture was stirred and heated at 100° C. for 8 hours. At the end of this time, a light amber colored material having good surface active properties was collected.

Example XVIII

Preparation of morpholinium lauryl sulfate. One mole of morpholine sulfate was prepared by adding 1 mole (98 grams) of concentrated sulfuric acid to 1 mole (87 grams) of morpholine dissolved in 1 liter of diethyl ether. The morpholine sulfate was collected and added to 1 mole (186 grams) of lauryl alcohol. This mixture was heated to 110° C. for 5 hours along with vigorous stirring to give a light-colored, solid morpholine salt of sulfated lauryl alcohol. This material had good emulsifying and surface active qualities.

It can be seen from the above description that we have provided a relatively simple, economical method of manufacturing substituted ammonium salts of alkyl acid sulfates. Our method is particularly beneficial in enabling the production of such salt products, particularly sulfated alcohol salts, of excellent light color.

The temperature of the reaction may be from about 50° C. to 150° C. While in many instances it is preferred to incorporate the additive, such as the alkylol amine, with the long chain alcohol to be treated, in some instances as shown by certain of the examples, such type compound may be incorporated with the sulfating medium in a particular manner.

While my invention is particularly directed to the treatment of the illustrative alcohols oleyl and lauryl, certain aspects thereof may be applied to other alcohols containing from 5 to 20 carbon atoms in the straight or branched chain, examples of which are amyl, isoamyl, octyl, lauryl, octadecyl and the like. Likewise, alcohols containing more than one primary hydroxyl group or a secondary hydroxyl group, exemplified by decanediol-1,10, may be similarly treated.

For further showing the utility of products produced in accordance with my invention as above described, cellulose acetate yarn of 150 denier, 38 filament, bright type was used in a test. This yarn was treated with 1.0% of an alcohol sulfate salt produced generally in accordance with Example III. The yarn was subjected to the following treatment which indicated that products produced in accordance with this invention possessed good yarn treating properties. A sample of this treated yarn was placed in a test tube and heated at 125° C. for a period of two hours.

The color of the treated yarn was examined contemporaneously with the treatment and no noticeable change of color (darkening) was observed when examined under natural light. A sample of the same yarn treated with conventionally prepared alcohol sulfate of the same chemical type, was examined under the same conditions. A darkening of the yarn was noticeable, substantially immediately.

Observation of the yarn treated with the material of the present invention after a period of 90 days under normal storage conditions showed no material darkening, thereby indicating that the improved color obtainable was relatively stable.

While the products of the present invention which have improved color are particularly useful in the textile trade, they may also be used for other purposes such as shampoo, household detergents and other washing and cleaning compounds.

I claim:

1. A process of manufacturing substituted ammonium salts of sulfated long chain alcohols wherein the alcohol chain is of 5–20 carbon atoms, the salts having good color and being produced in substantially one step which comprises premixing said 5–20 carbon atom alcohol with a nitrogen containing compound from the group consisting of alkylol amines and morpholine, then bringing the

aforementioned premixture into reactive contact with a sulfating agent from the group consisting of sulfuric acid and chlorosulfonic acid while agitating the aforesaid materials.

2. A process of manufacturing substituted ammonium salts of oleyl alcohol in substantially one step which comprises premixing oleyl alcohol with morpholine, then bringing the aforementioned premixture into reactive contact with a sulfating agent from the group consisting of sulfuric acid and chlorosulfonic acid while agitating the aforesaid materials.

3. A process of manufacturing substituted ammonium salts of oleyl alcohol in substantially one step which comprises premixing oleyl alcohol with an amino alkyl propanol, then bringing the aforementioned premixture into reactive contact with a sulfating agent from the group consisting of sulfuric acid and chlorosulfonic acid while agitating the aforesaid materials.

4. The process in accordance with claim 1 wherein the alcohol is from the group consisting of oleyl and lauryl alcohols.

5. A process of manufacturing substituted ammonium

salts of sulfated long chain alcohols wherein the alcohol chain is of 5–20 carbon atoms, the salts having good color and being produced in substantially one step which comprises premixing said 5–20 carbon atom alcohol with a nitrogen containing compound from the group consisting of alkylol amines and morpholine, then bringing the aforementioned premixture into reactive contact with a sulfating agent from the group consisting of sulfuric acid and chlorosulfonic acid while agitating the aforesaid materials, and maintaining the temperature of the reaction between 50°–150° C. for not more than eight hours and thereafter isolating the salt prepared by the aforesaid process.

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