SURFACE ACTIVE AGENT COMPOSITIONS

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10 Claims

ABSTRACT OF THE DISCLOSURE

A biodegradable surface active composition that does not irritate the eyes comprising an aqueous solution of a compound having the formula

\[ R-CO-NH-(CH_2CH_2O)_n-SO_3M \]

in which R is an alkyl or alkenyl group and M is a cation.

This application is a continuation-in-part of application 525,345 filed Feb. 7, 1966, which has been abandoned.

SUMMARY OF THE INVENTION

A number of known surface-active agents are used as ingredients in shampoos for the hair.

A first category of such known surface-active agents comprises the sulfates of fatty alcohols, in the form of the alkali salts, such as sodium, ammonium, etc., which the fatty alkyl remainder, hereinafter designated by R, comprises 12-18 carbon atoms. These sulfates may respond to one of the two formulas RO—SO_3H or RO(CH_2CH_2O)_n—OSO_3M

according to whether the product is or is not oxyethylated. (In the formulas n is a number from 1 to 4 and M is a cation, such as sodium, potassium, ammonium, etc.) The products falling in this category have excellent detergent qualities, but they irritate the skin and mucous membranes, and their use makes the hair feel rough after shampooing.

A second category of known surface-active agents comprises the sulfated amides, which have the advantages that their use imparts an agreeable feel to the hair after shampooing and they are less irritating to the skin and mucous membranes. However, the sulfated amides heretofore known tend to hydrolyze after a few days in solution, so that it is necessary to prepare the solution containing them just before use. These sulfated amides are therefore suitable only for use in powders, and not for use in shampoos sold in solution form.

The objects of the present invention is to avoid the disadvantages of the sulfate of fatty alcohols, i.e., the tendency to irritate the skin and the undesirable “feel” with which the hair is left after shampooing, without accepting the lack of stability in solution which is characteristic of the known sulfated amides.

The present invention is therefore directed to the new article of manufacture which is an anionic surface-active agent in the form of an amide sulfate having the following formula:

\[ R-CO-NH-(CH_2CH_2O)_n-SO_3M \] (I)

in which R is a linear or branched chain alkyl or alkenyl, having from 11 to 26 and preferably 11-17 carbon atoms, and M is an alkali metal, alkaline earth metal, ammonium, or a short-chain mono, di or tri alkyl-ammonium or alkylol ammonium.

A further object of the present invention is to provide new cosmetic compositions containing, preferably in aqueous solution, at least one composition responding to Formula I, these compositions being especially useful for shampooing the hair. It is clear that these compositions may contain other products and additives conventionally used in cosmetics such as thickening agents, other ionic or nonionic surface active agents, etc.

Surprisingly, it has been found that compositions containing the compounds of Formula I are particularly resistant to hydrolysis so that they may be used in the manufacture of shampoos to be sold as aqueous solutions. It should be noted that the hydrolysis stability of the amide sulfates of this invention cannot be predicted from the stability of the corresponding amide because an amide may be stable to hydrolysis even though its sulfates are unstable.

The cosmetic compositions of this invention generally contain from 5 to 20%, and preferably about 10% by weight of the compounds of Formula I. The pH of these compositions may be between 6 and 9 and preferably about 7. These compositions at this concentration and pH range will not hydrolyze and will not irritate the skin and mucous membranes of the eyes.

The perfect stability of these compounds against hydrolysis is particularly well demonstrated by the following tests:

The quantities of an amide sulfate representative of the present state of the art (specifically, the sodium salt of the sulfuric ester of the mono-ethanolamide of copra), and of an amide sulfate of this invention, which hydrolyzed as a function of time have been studied. The two amide sulfates were studied in a 1% aqueous solution at a pH of 9 and a temperature of 75°C. The method of measurement was that described by Desmuelle and Micaelli in the periodical “Oleagineux,” No. 6, 1949, on pages 353-357 and 720-725. The results are summarized in the following table:

<table>
<thead>
<tr>
<th>Time in hours</th>
<th>Test on R-CO-NH-(CH₂CH₂O)₂-SO₃Na with R an alkyl radical derived from copra and n=1</th>
<th>Test on R-CO-NH-(CH₂CH₂O)₂-SO₃Na with R an alkyl radical derived from copra and n=2</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 hours</td>
<td>28</td>
<td>76</td>
</tr>
<tr>
<td>60 days</td>
<td>35.9</td>
<td>06.3</td>
</tr>
<tr>
<td>6 months</td>
<td>45</td>
<td>55</td>
</tr>
</tbody>
</table>

Note: A=Percentage of fatty chains associated with non-sulfated molecules; B=Percentage of fatty chains associated with sulfated molecules.

It should be noted that the results of the analysis made using the Desmuelle and Micaelli method were verified by passing the products through an ion exchange column. The results were the same.

The foregoing comparative table shows that the prior art amide sulfate undergoes substantial hydrolysis within 6 hours, whereas the amide sulfate of this invention remains substantially unchanged.

The compositions of this invention, when used in shampoos, impart an agreeable feel to the hair, and they do not irritate the mucous membranes, especially those of the eye, a fact which has been verified by tests on the eyes of live rabbits. These compositions are also readily bio-degradable.

Another object of the present invention is to provide a method of preparing compositions containing the compounds of Formula I essentially characterized by the fact that a fatty acid, such as one derived from copra, having the formula R—COOH, in which formula R designates an alkyl or alkenyl group having 11-26 carbon atoms is reacted with di-glycolamine and the alcohol function of the amide thus obtained is sulfated. The sulfation step
may be followed by salification or the salification may occur concurrently.

This process may be carried out in several different ways.

The first step of the process, which consists in obtaining the amide itself may be carried out in any of the following illustrative ways:

(a) By condensation of a single fatty acid or a fatty acid mixture derived from copra having the formula R—COOH with diglycolamine at a temperature of the order of 160° C. to 200° C., eliminating any water.

(b) By amination of an ester of a fatty acid, for example, a methyl or ethyl ester of a fatty acid, eliminating the corresponding alcohol, the amination reaction being preferably carried out in the presence of a known catalyst. The glycerides may also be used to make the compounds of Formula I by this method.

(c) Beginning with a fatty acid chloride.

The second step of the process, which consists of sulfinating the amide obtained in the first step, may also be carried out in several different illustrative ways, particularly:

(a) By using sulfamic acid. This method has the advantage of yielding the ammonium salts immediately, so that it is not necessary to salify a sulfonic acid function after the sulfation, at the risk of forming a mineral salt in the resulting product. The resulting ammonium salt may be used directly in aqueous solution. If the amonia is eliminated by heating, amine salts may be obtained, particularly alkylamine salts, and if desired, salts of alkali metals.

(b) By using sulfuric acid. In this case sulfuric acid is added slowly to the melted amide in a mixing device which is vigorously actuated. An approximately 100% excess quantity of the sulfiting agent is used. The fluidity of the reaction medium may be increased by adding a hydrosoluble solvent. After having determined that the reaction has been completed, using a test of solubility in an aqueous medium, the sulfitated product is neutralized by pouring it into a mixture of carbonate and bicarbonate of soda. The end product is powder.

(c) By using chlorosulfonic acid. This step is carried out in a chlorinated solvent, such as chloroform, at a temperature of 15–25° C. The hydrochloric acid formed is drawn off by a current of inert gas or by use of a slight vacuum. After elimination of the solvent, the sulfitated product may be neutralized with soda, ammonia, or with alkylamines such as ethanamine or isopropanolamine to form the desired salt.

In order to further illustrate the invention a method of preparing the ammonium salt of the sulfuric ester of the diglycolamide of the acids of copra will now be described, and several examples will be given showing the use of the compositions responding to Formula I as ingredients for shampoos. Similar results are obtained by forming the sodium, potassium, and alkylamine salts and by using unmixed fatty acids as the starting materials to form unmixed salts.

**EXAMPLE 1**

Preparation of the ammonium salt of the sulfuric ester of the diglycolamide of the acids of copra.

(a) Preparation of N-acyl(copra)-diglycolamine

A mixture of 207 grams of the fatty acids of copra and 112 grams of diglycolamine are heated and agitated under a nitrogen atmosphere to a temperature of 170°–180° C., distilling off the water formed in the course of the reaction.

After three hours of heating 97% of the fatty acids introduced are condensed with the diglycolamine. After 7 hours of heating the percentage of condensation is 98.3%. The product obtained is in the form of a white waxy mass melting at 50° C.

(b) Sulfation of N-acyl(copra) - diglycolamine with sulfamic acid

20 grams of sulfamic acid and 5 grams of urea are added to 39 grams of melted N-acyl(copra)-diglycolamine. The mixture is vigorously agitated while being heated to 120° C. The reaction mixture thickens rapidly as sulfation progresses, and the process is completed in a few minutes.

After cooling a yellowish waxy product is obtained, which dissolves readily in water and is the ammonium salt of sulfuric ester of the diglycolamide of the acids of copra.

**EXAMPLE 2**

The following mixture is prepared: Solution containing 26.8% of—

Sulfuric ester of the diglycol amide of copra acids, ammonium salt—40 g.

Lauric diethanolamide—4 g.

Water, q.s.p.—100 cm³.

**EXAMPLE 3**

The following mixture is prepared: Solution containing 26.8% of—

Sulfuric ester of the diglycolamide of copra acids, ammonium salt—20 g.

Ammonium lauryl sulfate—15 g.

Lauric diethanolamide—5.5 g.

Water, q.s.p.—100 cm³.

**EXAMPLE 4**

The following mixture is prepared: Solution containing 26.8%—

Sulfuric ester of the diglycolamide of copra acids, ammonium salt—25 g.

Polyoxyethylene lauric alcohol having 12 molecules of ethylene acid—5 g.

Lauric diethanolamide—4 g.

Water, q.s.p.—100 cm³.

The composition described in each of Examples 2–4, when used as a shampoo, have good detergent properties, and produce plenty of foam having an agreeable consistency. After shampooing with the product the hair is glossy, bright, and feels soft to the touch.

The RCO group in Formula I may be derived from the following illustrative fatty acids caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, pelargonic acid, undecylic acid (10-undecenoic acid).

From a commercial standpoint the RCO group in Formula I may also be obtained from mixtures of fatty acids obtained from oils and fats of animal or plant origin such as palm, cabbage palm, tallow, etc.

The RCO group may also be obtained from isoacids having the general formula:

\[
\text{RCO}_2\text{H} + \text{CH}_2-\text{COOH} \rightarrow \text{RCO}_2\text{H} \quad \text{CH}_2-\text{COOH}
\]

and the isoacids having the general formula:

\[
\text{RCO}_2\text{H} + \text{CH}_2-\text{CH}_2-\text{COOH} \rightarrow \text{RCO}_2\text{H} \quad \text{CH}_2-\text{CH}_2-\text{COOH}
\]

in which **n** is between 14 and 22 and 12 and 22 respectively. These acids can be prepared in the form of a mixture for saponification from lanolin.

The mixture of fatty acids prepared under the designation “isostearic acid” according to U.S. Pat. 2,812,342.
Fatty ramified acids sold under the name of "neoacids" as for example the neo-tridecanoic acid having the formula:

\[
R-CO\text{CH}_3
\]

in which R is hydrocarbon radical containing 9 carbon atoms. These neoacids can be transformed according to the known methods with diglycolamine to sulfatable hydroxyl amides. Illustrative salts include those in which M in Formula I is:

1. alkaline ions: such as Na, K, etc.
2. NH₄
3. an alkylol ammonium such as:

(a) \[ \text{CH}_3\text{CH}_2\text{OH} \]
(b) \[ \text{CH}_3\text{CHOHCHOH}_2 \]
(c) \[ \text{CH}_3\text{CHOHCHOH}_3 \]
(d) \[ \text{CH}_3\text{CHOHCHOH}_4 \]
(e) \[ \text{CH}_3\text{CHOHCHOH}_5 \]
(f) \[ \text{CH}_3\text{CHOHCHOH}_6 \]

4. alkyl ammonium, such as:

(a) \[ \text{CH}_3\text{CH}_2\text{NH} \]
(b) \[ \text{CH}_3\text{NH} \]
(c) \[ \text{CH}_3\text{CH}_2\text{NH} \]

(5) Alkaline earth metal ions, such as calcium and magnesium.

Illustrative compounds of the invention include:

1. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{Na} \]
2. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{Cl} \]
3. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{NH}_4 \]
4. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{Na} \]
5. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{NH}_3 \]
6. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{NH}_2 \]
7. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{NH}_2 \]
8. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{NH}_2 \]
9. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{NH}_2 \]
10. \[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_2\text{SO}_3\text{NH}_2 \]

We have found that the compositions which contain laurie and myristic acid derivatives and mixtures containing at least 50% of these acids have the best foaming characteristics.

EXAMPLE 5

The following comparative test was made to further show the advantages of using the following method to obtain the compounds of this invention in which \( n=2 \):

We prepared, using the method of this invention, laurie diglycolamide having the following formula:

\[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3\text{CH}_2\text{OH} \] (A)

and the compound:

\[ \text{C}_1\text{H}_2\text{CONHCH}_2\text{CH}_2\text{O(CH}_2\text{CH}_2\text{O})_n\text{H} \] (B)

in which \( n \) has a statistical average value of 1.

Compound A was prepared by the aminolysis of methyl laurate using diglycolamine (\( H_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \)) in excess of 100% required, the reactive mixture being progressively heated up to 160°C to eliminate the methanol. The excess of diglycolamine was then evaporated under vacuum. The product thus obtained was recrystallized in the ethyl acetate.

Compound B was prepared by condensing ethylene oxide on lauric monoenothanolamine

\[ (\text{C}_1\text{H}_2\text{CONHCH}_2\text{CH}_2\text{OH}) \]

which was obtained by aminolysis of methyl laurate with monoenothanolamine. Its melting point after recrystallization was 85°C.

The condensation of ethylene oxide is effected in the following fashion:

To 75 g. of lauryl monoenothanolamine, add 3.5 g. of a methanol solution containing 24.8% \( \text{CH}_2\text{ONa} \). The \( \text{CH}_2\text{ONa} \) is eliminated under vacuum. In 73.5 g. of the mixture thus obtained, heated to 153°C, pass the ethylene oxide after having purged the equipment with nitrogen. In 45 minutes of reaction at 153°C to 145°C, condensed 12.8 g. of ethylene oxide being 0.96 mole per mole of ethanolamine. The product of condensation is a yellow-white wax having a hydroxyl index of 207.

We made a gas phase chromatography, after siliylation, using the method of Sulfis et al. (J. Soc. Cosm. Chemists, 76, 783–794, 1965). The condensation product contains the compounds \( \text{C}_1\text{H}_2\text{CONHCH}_2\text{CH}_2\text{OH} \) and \( \text{C}_1\text{H}_2\text{CONHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \) in approximately equal proportions.

Results—This comparative test shows that the prior art composition (B) is a mixture containing a high proportion of monoenoanolamides which form sulfate derivatives that are unstable and hydrolyze. One could lessen the proportion of monoenoanolamides by augmenting the rate of condensation of ethylene oxide, but in this case, the products obtained would be less active because of their excessive hydrophile character.

The reaction of diglycolamine and diglycolamide avoids these disadvantages because the degree of condensation \( n=2 \) is already present. In contrast to this in the methods already known, the condensation of ethylene acid on the monoenothanolamide the degree of condensation of the group (\( \text{CH}_2\text{CH}_2\text{O} \)) is only a mean statistical value and the product (B) is in reality a mixture in which a great proportion of the ethanolamides are not oxyethylated and they hydrolyze.

The compounds in which \( n=2 \) all produce desirable foams. The compounds in which \( n=5 \) or more are not foaming agents. Compositions in which \( n \) is a variety of values but statistically equal to 2 tend to hydrolyze, irritate the eyes and do not produce desirable foams.

EXAMPLE 6

Preparation of ammonium and magnesium sulfate salts of dodecanoyl amido ethoxy ethanol having the formula:

\[ \text{C}_1\text{H}_2\text{CONH}-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3\text{CH}_2\text{OH} \]

The hydroxylated amide is prepared by aminolysis of methyl laurate with diglycolamine in excess of 100% required for a complete reaction, the mixture is progressively heated up to 160°C to eliminate the methanol. The excess diglycolamine is then evaporated under vacuum. The product is then recrystallized in ethyl acetate.

This compound is then sulfated with sulfamic acid according to the conditions which were given in Example 1.
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50 g. of this sulfated product was dissolved in 150 ml. of water; to this solution is added 2.25 g. of pulverized and sifted magnesium oxide, a little at a time, until it is heated to the boiling point to remove the ammonia.

After 24 hours in a heated water bath the mixture is filtered to remove the unreacted magnesium oxide, 59% of the ammonium salt was transformed to the magnesium salt.

One obtains a solution which has good foaming properties.

EXAMPLE 7

Preparation of the magnesium salt of dodecanoyl sulfate amido ethoxy ethanol in the form of a powder.

Dissolve 57.4 g. of dodecanoyl amido ethoxy ethanol in 100 ml. of chloroform. Cool this solution to 150° C., add drop by drop 25.6 g. of sulfuric chlorohydrin maintaining the temperature below 25° C., under strong agitation over a 20 minute period. The reaction mixture stood at ambient temperature for 1 hour under agitation then, in order to eliminate the hydrochloric acid, we passed nitrogen through the product under reduced pressure.

The sulfonation product was neutralized in the following manner:

Milk of magnesia was prepared by dispersing 8 g. of magnesia in 20 ml. of water. This dispersion of magnesia was added under agitation to the chloroform solution of the sulfonation product. After one and one-half hours, the mixture having then a very acid reaction, we added 2 g. of pulverized magnesium. The mixture was left for one night, then we filtered the excess magnesia. The chloroform and water were evaporated. The yield was 80%. The residue was put in acetone and the magnesium salt precipitated. It was separated easily by filtration. This compound, after drying, is a white solid that can be pulverized. It dissolves very easily in water to form a foaming solution.

It will be appreciated that the foregoing examples have been given purely by way of illustration, and may be modified as to detail without departing from the basic principles of the invention as defined by the following claims.

Particularly the composition of the present invention contains conventional shampoo ingredients chosen among the following:

carboxymethyl cellulose, oxyethylated lauric alcohol (12 mol. ethylene oxide), glycerol mono stearate, etc.

What is claimed is:

1. A surface active composition consisting essentially of an aqueous solution consisting essentially of an amide surfactant surface active agent having the formula

\[ R-CO-NH-(CH_2CH_2O)_n-SO_3M \]

in which R is selected from the group consisting of alkyl and alkenyl groups having 11 to 17 carbon atoms, and M is an ion selected from the group consisting of alkali metals, alkaline earth metals, ammonium, alkylammonium, and alkylolammonium, having a pH of about 6 to 9.

2. A method for shampooing hair comprising shampooing the hair with an effective amount of the composition of claim 1.

3. A shampoo composition comprising the composition of claim 1 which also contains a compound selected from the group consisting of cetyl trimethyl ammonium bromide, lactic acid, diethanolamide of copra, polyethylene glycol, stearic acid, paraffin oil, glycerin, ammonium laurel sulphate, lauric diethanolamide, triethanolamide laurel sulphate, carboxymethyl cellulose, oxyethylated lauric alcohol (12 mol. ethylene oxide) and glycerol mono stearate.

4. The composition of claim 1, wherein the amide sulfite surface active agent is the only surface active agent present.

5. The composition of claim 4, wherein R is \( \text{C}_{16}- \).

6. The composition of claim 4, wherein R is \( \text{C}_{18}- \).

7. The composition of claim 4, wherein R is derived from copra.

8. The composition of claim 4, which contains 5 to 20% by weight of said surface active agent.

9. The composition of claim 4, wherein M is \( \text{H}_4- \).

10. A method of shampooing hair comprising shampooing the hair with a shampooing amount of the composition of claim 4.

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