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Kalopissis et al.

[54] SURFACE ACTIVE COMPOSITIONS CONTAINING ASPARAGINE DERIVATIVES

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Related U.S. Application Data


Foreign Application Priority Data


Int. Cl.----------------------------- A61K 7/06

Field of Search........... 424/70; 8/10.1; 260/534 R, 260/247.2, 252/546, 316

[56] References Cited

UNITED STATES PATENTS

FOREIGN PATENTS OR APPLICATIONS
1,146,332 5/1957 France...................... 424/70
1,344,212 10/1963 France...................... 260/247.2

Primary Examiner—Stanley J. Friedman
Assistant Examiner—Vera C. Clarke
Attorney, Agent, or Firm—Brisebois & Kruger

[57] ABSTRACT

Surface active compositions which contain a surface-active compound having the formula

\[
\begin{align*}
R' & \quad \text{in which } R \text{ and } R' \text{ are an alkyl or alkenyl group which has 10–18 carbon atoms, } \\
\text{CH}_2 - \text{CO} - N - (\text{CH}_2)_n - N & \quad \text{with the } N \text{ atom a morpholino group and } n \text{ is 2–5.}
\end{align*}
\]

9 Claims, No Drawings
SURFACE ACTIVE COMPOSITIONS CONTAINING ASPARAGINE DERIVATIVES

This application is a continuation-in-part of application Ser. No. 424,846, filed Jan. 11, 1965, now U.S. Pat. No. 3,534,032.

This invention relates to cosmetic compositions which contain new asparagine derivatives having surface-active properties, and to hair treating compositions containing them.

U.S. Pat. Nos. 2,303,213 and 2,331,781 describe and claim asparagine derivatives having very interesting surface-active properties, which are of particular use in hair shampoo. We have now found that certain related asparagine derivatives not only show surface activity, but possess other properties which are of considerable interest in relation to the treatment of hair.

The asparagine derivatives used in the composition of this invention are compounds having the formula:

\[
R - \text{NH} - \text{CH} - \text{COOH}
\]

where R and R' are each an alkyl or alkanyl group which has 10-18 carbon atoms which can be the same or different. R' and R2 are each lower alkyl, which can be the same or different, or together with the nitrogen atom to which they are attached constitute a morpholino residue and n is an integer of 2-5 inclusive (especially 2 or 3), and sodium, potassium, ammonium and acid addition salts, such as lactate, phosphate, citrate and acetate salts, thereof. Preferred compounds are those in which R' and R2 are alkyl groups having 1-4 carbon atoms, for instance methyl or ethyl.

These compounds possess not only remarkable detergent properties, but also good softening and conditioning properties for the hair. Thus they can be used to advantage in hair shampoo or hair dyeing compositions.

Moreover, in aqueous solutions these compounds show a very pronounced thickening and gelling effect. Since products currently employed as thickeners or gelling agents generally do not possess in themselves any detergent or hair treating property, it will be seen that compounds of the invention are particularly advantageous, and because of this combination of properties they have a very wide range of use, for example, in aqueous solutions which may contain other surface-active substances, especially those of cationic or non-ionic character, and in aqueous solutions of dyes.

The compounds of the invention can be prepared by a process which comprises condensing maleic anhydride with an alkylene diamine having the formula:

\[
R - \text{NH} - (\text{CH}_2)_n - \text{NH} - R
\]

where R', R1, and R3 and n have the meanings given above, modifying the reaction product to obtain the corresponding sodium, potassium or ammonium salt, and reacting said salt with a primary fatty amine of the formula:

\[
R - \text{NH} - \text{CH} - \text{COOH}
\]

where R has the meaning given above. Preferred alkylene diamines are, for example, N-dodecyl-N', N'-diethylenediamine, N-cetyl-N', N'-diethylenediamine, N-dodecyl-N', N'-diethyltrimethylenediamine, and \beta-(dodecylamino)ethylmorpholine.

Preferred primary fatty amines are, for example, decylamine and dodecylamine. It has been found that excellent results have been obtained using as primary amine a mixture of fatty amines derived from copra acid or tallow acid, which yield a mixture of compounds of formula (1) differing only in the value of the substituent R, the various R substituents being the various alkyl radicals present in tallow or copra acids respectively.

The invention is illustrated by the following Examples.

EXAMPLE 1

Preparation of the sodium salt of \( N^2-\text{alkyl(tallow)}-N-(\text{dodecyl})-N-(N',N'')-\text{diethylenediamino} \)ethylasparagine.

1. Preparation of N'N'-diethyl-N-dodecyl-ethylenediamine

There are mixed with stirring 2 moles of dodecyl bromide and 10 moles of N',N'-diethylenediamine (96.6 %) the temperature being maintained below 50°C. At the end of several hours, the reaction is complete. There are then added 4.3 moles of potassium hydroxide in pellet form, with vigorous stirring. The excess of potassium hydroxide and the potassium bromide formed are separated by filtration. The excess of N',N'-diethylenediamine is thereupon evaporated under reduced pressure, and the crude product thus obtained is washed with water and dried in vacuo on the water bath.

N',N'-diethyl-N-dodecyl-ethylenediamine is thus isolated in an almost quantitative yield and in a purity of 98 %.

2. Preparation of N-dodecyl-N-(N',N''-diethylaminoethyl) maleamic acid

One mole of N',N''-diethyl-N-dodecyl-ethylenediamine is dissolved in 300 ml of ethyl acetate.

To this solution is added with stirring, in an hour and a half, 1 mole of maleic anhydride in solution in 300 ml of ethyl acetate, the temperature being maintained between 35°C and 40°C. The solid which precipitates is separated, washed with ethyl acetate and dried in vacuo, and N-dodecyl-N',N''-diethylaminoethylmaleamic acid is isolated as a white, water-soluble powder in a yield of 80 %.

3. Addition of the primary amine derived from tallow fatty acids.

0.7 mole of N-dodecyl-N-(N',N''-diethylenaminoethyl) maleamic acid is dissolved in 300 ml of ethyl alcohol, and the solution is neutralized with a calculated quantity of concentrated aqueous sodium hydroxide solution.

There is then added 0.7 mole of a mixture of primary amines derived from tallow fatty acids, and the mixture is heated at 65°C. for 11 hours. After evaporation of the alcohol, the product obtained takes the form of an oil dispersible in water, which contains 4 % of unreacted primary amine.

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EXAMPLE II
Preparation of the sodium salt of N\textsuperscript{2-}[alkyl(copra)]-N-(cetyl)-N-(N',N'-diethylaminoethyl) asparagine.

By proceeding in an analogous fashion to Example I, N-cetyl-N'-(N',N'-diethylaminoethyl) maleamic acid is obtained from N',N'-diethyl-N-cetyl-ethylenediamine and maleic anhydride. The desired product is obtained by the addition to the sodium salt of the maleamic acid of a mixture of primary amines derived from copra fatty acids in an analogous way to Example I.

EXAMPLE III
Preparation of the sodium salt of N\textsuperscript{2-}[alkyl(tallow)]-N-(cetyl)-N-(N',N'-diethylaminoethyl) asparagine

By the process analogous to that described in Example I, this product is obtained by the addition of a mixture of primary amines derived from tallow fatty acids to sodium N-cetyl-N'-(N',N'-diethylaminoethyl) maleate.

EXAMPLE IV
Preparation of the sodium salt of N\textsuperscript{2-}[alkyl(copra)]-N-(dodecyl)-N-(N',N'-diethylaminoethyl) asparagine

This product is obtained by reacting the mixture of primary amines derived from copra fatty acids with sodium N-dodecyl-N'-(N',N'-diethylaminoethyl) maleate in a process analogous to that described in Example I.

EXAMPLE V
Preparation of the sodium salt of N\textsuperscript{2-}[alkyl(tallow)]-N-(dodecyl)-N-(morpholinoethyl) asparagine

By a process analogous to that described in Example I, there is obtained from dodecyl bromide and aminoethylmorpholine, β-(dodecylamino)ethylmorpholine. The condensation of this diamine with maleic anhydride gives the corresponding maleamic acid which, after neutralization with sodium hydroxide, is reacted with the mixture of primary amines derived from tallow fatty acids yielding the desired product in the form of an oil.

EXAMPLE VI
Preparation of the potassium salt of N\textsuperscript{2-}[alkyl(tallow)]-N-(dodecyl)-N(N',N'-diethylaminopropyl) asparagine

N',N'-diethyl-N-dodecyl-trimethylenediamine is first prepared by a process analogous to that described in Example I. Maleic anhydride is reacted with this diamine in solution in t-butyl alcohol. The maleamic acid thus formed is neutralized by an aqueous potassium hydroxide solution, and the potassium salt is reacted with the mixture of primary amines derived from the fatty acids of tallow. By evaporation of the solvent, the desired product is obtained in the form of a viscous oil.

EXAMPLE VII
Preparation of the sodium salt of N\textsuperscript{2-}[alkyl(copra)]-N-(cetyl)-N(N',N'-diethylaminopropyl) asparagine

This product is obtained by a process analogous to that described in Example VI. It takes the form of a viscous oil.

EXAMPLE VIII
The following mixture is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium salt of N\textsuperscript{2-} [alkyl(tallow)]-N-(dodecyl)-N(N',N'-diethylaminoethyl) asparagine</td>
<td>3 g</td>
</tr>
<tr>
<td>Lactic acid, q.s. for water, pH 5.5</td>
<td></td>
</tr>
</tbody>
</table>

A transparent jelly is obtained.

EXAMPLE IX
In the same way, by mixing:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium salt of N\textsuperscript{2-} [alkyl(tallow)]-N-(cetyl)-N(N',N'-diethylaminoethyl) asparagine</td>
<td>3 g</td>
</tr>
<tr>
<td>Lactic acid, q.s. for water, pH 4</td>
<td></td>
</tr>
</tbody>
</table>

A translucent gel is obtained.

EXAMPLE X
There is prepared an aqueous solution containing:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate obtained from 1 mole of tridecyl alcohol and 15 moles of ethylene oxide</td>
<td>7 g</td>
</tr>
<tr>
<td>Sodium salt of N\textsuperscript{2-} [alkyl(tallow)]-N-(dodecyl)-N(N',N'-diethylaminoethyl) asparagine</td>
<td>6 g</td>
</tr>
<tr>
<td>Lactic acid, q.s. for water, pH 5</td>
<td></td>
</tr>
</tbody>
</table>

This solution is of oily consistency and when used as a shampoo imparts suppleness to the hair and makes it easy to comb. The viscosity of this shampoo is substantially higher than that obtained by replacing the compound of the invention with a cationic product in current use.

EXAMPLE XI
There is prepared a solution containing:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate obtained from 1 mole of copra fatty alcohol and 12 moles of ethylene oxide</td>
<td>8 g</td>
</tr>
<tr>
<td>Sodium salt of N\textsuperscript{2-} [alkyl(copra)]-N(N',N'-diethylaminopropyl) asparagine</td>
<td>4 g</td>
</tr>
<tr>
<td>Sodium salt of N\textsuperscript{2-} [alkyl(tallow)]-N-(dodecyl)-N(N',N'-diethylaminoethyl) asparagine</td>
<td>3 g</td>
</tr>
<tr>
<td>Lactic acid, q.s. for water, pH 5</td>
<td></td>
</tr>
</tbody>
</table>

There is thus obtained a shampoo of viscous consistency which imparts suppleness to hair and makes it easy to comb. Moreover, the hair after having been washed with this shampoo does not exhibit any accumulation of electrostatic charge. The viscosity of this shampoo is clearly higher than that obtained in the absence of the compound according to the present application.
EXAMPLE XII

There is prepared a solution containing:

- the condensate of 1 mole of octylphenol and 18 moles of ethylene oxide: 7 g
- dodecanolamide of copra fatty acids: 4 g
- cetyltrimethylammonium bromide: 2 g
- sodium salt of N-[alkyl( tallow)-N-(cetyl)-N-N'-diethylaminomethyl] asparagine: 6 g
- lactic acid, q.s. for pH 5, water, q.s. for 100 cc:

A thick solution is obtained. This product constitutes a shampoo which renders the hair very soft and makes it easy to comb.

EXAMPLE XIII

There are prepared:

- a solution containing:
  - sodium bromate: 15 g
  - water: 60 g
- an emulsion containing:
  - the condensate of 1 mole of cetyl alcohol and 5 moles of ethylene oxide: 2 g
  - sodium salt of N-[alkyl( tallow)-N-(dodecyl)-N-N'-diethylaminomethyl] asparagine: 3 g
  - phosphoric acid, q.s. for pH 6.5: 15 g

a) and b) are mixed at about 40°C and make up to 100 cc with water. There is thus obtained a creamy fixative, of which 100 cc diluted with 150 cc of hot water are used to neutralize a permanent wave.

EXAMPLE XIV

There is prepared by conventional procedure a cream containing:

- sodium salt of N-[alkyl( tallow)-N-(cetyl)-N-N'-diethylaminomethyl] asparagine: 5 g
- the condensate of 1 mole of steareth alcohol and 10 moles of ethylene oxide: 3 g
- water: 70 cc

The mixture is allowed to cool to 40°C and acidified by the addition of citric acid until a pH of 4 is reached, whereafter it is made up to 100 cc with water.

From 5 to 10 g of this cream are applied to hair sensitised by a decoloration, which is massaged for several minutes and then rinsed. The hair thus acquires softness and a gloss and is easy to comb.

EXAMPLE XV

The following mixture is prepared:

- sodium salt of N-[alkyl( tallow)-N-(dodecyl)-N-N'-diethylaminomethyl] asparagine: 5 g
- picramic acid: 0.5 g
- water: 10 g

There is thus obtained a shampoo of viscous consistency which makes the hair very soft and easy to comb.

EXAMPLE XVI

The following mixture is prepared:

- nitrophenylenediaamine: 1 g
- diethanolamine of copra fatty acids: 4 g
- the condensate of 1 mole of lauryl alcohol and 10 moles of ethylene oxide: 6 g
- sodium salt of N-[alkyl( copra)-N-(cetyl)-N-N'-diethylaminomethyl] asparagine: 3 g
- acetic acid, q.s. for pH 5.5, water, q.s. for 100 cc:

There is thus obtained a viscous dyeing solution which, when applied to the hair, besides dyeing it, imparts to it a gloss and suppleness.

EXAMPLE XVII

The following mixture is prepared:

- sodium salt of N-[alkyl( copra)-N-N'-diethylaminopropl] asparagine: 3 g
- sodium salt of N-[alkyl( tallow)-N-(dodecyl)-N-(morpholino ethyl) asparagine: 3 g
- the condensate of 1 mole of lauric alcohol and 12 moles of ethylene oxide: 7 g
- diethanolamine of copra fatty acids: 3 g
- lactic acid, q.s. for pH 3, water, q.s. for 100 cc:

There is thus obtained a shampoo of viscous consistency which makes the hair very soft and easy to comb.

EXAMPLE XVIII

The following solution is prepared:

- cetyl trimethyl ammonium bromide: 3 g
- sodium salt of N-[alkyl( tallow)-N-(dodecyl)-N-(morpholino ethyl) asparagine: 3 g
- the condensate of 1 mole of lauric alcohol and 12 moles of ethylene oxide: 10 g
- diethanolamide of copra fatty acids: 3 g
- lactic acid, q.s. for pH 3, water, q.s. for 100 cc:

There is thus obtained a viscous shampoo which makes the hair supple and easy to comb.

The mixtures of primary amines used in Examples I to VII have been used commercially.

Other illustrative surface-active asparagine compounds having the formula I include:

1) \( C_{10}H_{31}NH - CH - COOH \)

2) \( CH_2 - CO - N - \left( CH_2 \right)_2 - N\)
Illustrative other detergent or shampoo detergents that may be used in the detergent or shampoo compositions include sodium lauryl sulphate, sodium decyl benzene sulphonate, N-(sodium sulphonyl) oleamide, sodium dioctyl sulphosuccinate, sodium lauryl sulphoacetate, etc.

Illustrative hair dyes that may be used in the hair dye compositions include 1,4-diethylamino-3-nitro benzene, 1-(β-ethylamino)-2-amino-4-nitrobenzene, 1-hydroxy-2-amino-5-nitrobenzene, and direct dyes such as those shown in U.S. Pat. Nos. 2,983,651, 3,040,064, 3,049,393, 3,100,739, etc.

The compositions of this invention have preferably an acid pH.

What is claimed is:
1. A surface active composition having an acid pH comprising an effective amount of a surface active compound having the formula:

\[
\text{R} - \text{NH} - \text{CH} - \text{COOH}
\]

2. The composition of claim 1, in the form of a gel.
3. The composition of claim 1, in which \( n \) is 2 or 3.
4. The composition of claim 1, in which \( R_1 \) and \( R_2 \) are alkyl having 1-4 carbon atoms.
5. The composition of claim 1, in which \( R_1 \) and \( R_2 \) and the N atom form morpholino.
6. The composition of claim 1, which also contains an effective amount of a detergent compound.
7. The composition of claim 1, which also contains an effective amount of a shampoo detergent.
8. The process of softening and conditioning live human hair comprising applying to the hair an effective amount of the composition of claim 1.
9. The process of shampooing and softening live human hair comprising applying to the hair an effective amount of the composition of claim 7.