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3,303,213

N-TERTIARY AMINOALKYL-N'-HYDROCARBON ASPARAGINE AMIDES

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888,177

6 Claims. (Cl. 260—534)

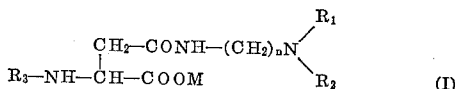
This invention relates to a new product comprising new amphoteric chemical compositions and a process for preparing these compositions.

This application is a continuation-in-part of applicants' copending application Serial No. 256,142, filed February 4, 1963, now abandoned.

It has been found that the new compositions according to the invention comprise very valuable surface-active agents which may be used either alone or mixed with other cationic, anionic or non-ionic surface active agents, in many different fields, and particularly for shampooing the hair and in the preparation of hair dyeing solutions.

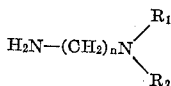
Their use in shampooing is the more attractive because they offer the valuable advantage of being very well tolerated by the mucous membrane of the eye.

The new surface active compositions according to the invention may be considered as derivatives of asparagine and are characterized by the following general formula:

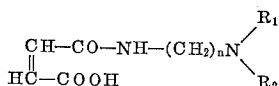


in which R₁ and R₂ are identical or different lower alkyls which may comprise up to 4 carbon atoms, R₁ and R₂ may also form part of a heterocycle, n is an integer having a value of 2 to 5 and preferably 2 or 3, R₃ designates an aliphatic hydrocarbon residue comprising 10-18 carbon atoms, and M designates hydrogen, sodium, potassium or ammonium.

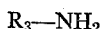
The process of preparing the new surface-active compositions according to the invention consists in condensing maleic anhydride with an alkylene-diamine having the following general formula:



in which n, R₁ and R₂ have the significances indicated in the above Formula I; then, after salification, treating the maleamic acid derivative thus obtained, which has the formula:



in which n, R₁ and R₂ also have the significances previously assigned, with a primary fatty amine having the following formula:



in which R₃ has the above-mentioned significance, thus obtaining the composition of Formula I.

As an example of particularly suitable alkylene diamines the following may be mentioned:

- N,N-dimethyl- or N,N-diethylethylenediamines,
- N,N-dimethyl- or N,N-diethyl- or N,N-dipropylpropylene-diamines,
- N-(β-amino-ethyl)-morpholine,
- N-(β-aminopropyl)piperidine).

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The following may, of course, also be used:

- N,N-dimethyl- or N,N-diethylbutylenediamines,
- N,N-dimethyl- or N,N-diethylpentamethylenediamines.

As examples of particularly suitable fatty amines the following may be cited: decylamine, dodecylamine, the amines derived from the fatty acids of copra or tallow, etc.

The new amphoteric chemical compositions according to the invention may be used in aqueous solutions at acid, neutral or alkaline pH values. In the first case they act as cationic surface active agents; in the last case, as anionic surface active agents.

The invention thus also envisages, as a new article of manufacture, a surface active composition characterized by the fact that it contains a composition having the general Formula I as given above.

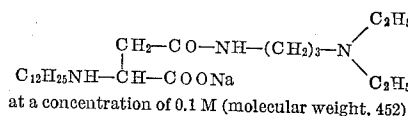
The new composition according to the invention may naturally comprise other known cationic, anionic, or non-ionic surface active agents. It is particularly valuable for use in shampooing the hair.

I have moreover found, and this was entirely unforeseeable, that aqueous solutions of the compositions of Formula I are remarkably innocuous to the mucous membrane of the eye.

This harmlessness has been established by many tests made by applicants and these tests are summarized in the following tables:

TABLE I

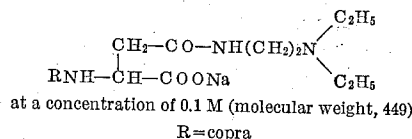
Application of a solution of



pH	Rabbits	Observation 24 h. after application	Observation 7 days after application
40 pH 3	No. 1	3+	Recovered. Do. Do. Do.
	No. 2	3	
	No. 3	3++	
	No. 4	2+	
pH 7	No. 1	3 weak	Do. Do. Do. Do.
	No. 2	2	
	No. 3	2+	
	No. 4	2	
45 pH 8	No. 1	2+	Do. Do. Do. Do.
	No. 2	2	
	No. 3	2	
	No. 4	2 weak	

TABLE II

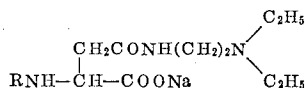
Application of a solution of



pH	Rabbits	Observation 24 h. after application	Observation 7 days after application
60 pH 3	No. 1	2+	Recovered. Do. Do. Do.
	No. 2	2+	
	No. 3	2+	
	No. 4	2+	
65 pH 7	No. 1	2	Do. Do. Do. Do.
	No. 2	2	
	No. 3	2	
	No. 4	2	
70 pH 8	No. 1	2	Do. Do. Do. Do.
	No. 2	2	
	No. 3	2	
	No. 4	2 weak	

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TABLE III
Application of a solution of



at a concentration of 0.1 M (molecular weight, 505)
R = tallow

pH	Rabbits	Observation 24 h. after application	Observation 7 days after application
pH 3	No. 1	2+	Recovered.
	No. 2	2	
	No. 3	2+	
	No. 4	2++	
pH 7	No. 1	3++	Do.
	No. 2	2++	
	No. 3	2++	
	No. 4	Nothing	
pH 8	No. 1	3++	Do.
	No. 2	2 weak	
	No. 3	2++	
	No. 4	2	

By way of contrast, the following table shows the effect of the introduction of a conventional surface-active agent into the eyes of rabbits:

TABLE IV

Application of a solution of cetyltrimethylammonium bromide in a concentration of 0.1 M

pH=3.5

Rabbits	Observation 24 h. after application	Observation 7 days after application
No. 1	5++ a	Healed.
No. 2	5+++ b	Healed—cornea less shiny.
No. 3	5++ b	Eyelid deformed—opaque cornea.
No. 4	2+++ b	Partially opaque cornea.

$\begin{array}{c} \text{R}_1 \\ \\ \text{CH}-\text{CONH}(\text{CH}_2)_n-\text{N} \\ \quad \\ \text{CH}-\text{COOH} \quad \text{R}_2 \end{array}$	Solvent	Temp. in ° C.	Concentration of Reactants (in grams/100 g.)	Percent Yield	Amine nitrogen in meqs. per gram		Acid index in meqs. per gram	
					Calc.	Found	Calc.	Found
R ₁ =R ₂ =C ₂ H ₅	Ethyl acetate	0-5	38.8	100	4.38	4.39	4.38	4.41
R ₁ =R ₂ =CH ₃	t-Butyl alcohol	50	33.4	98	5.00	4.87	5.00	5.13
R ₁ =R ₂ =C ₂ H ₅	do.	50	35	89	4.67	4.59	4.67	4.49

The symbols employed in these tables have the following significances:

- 1=irritation of the bulbar or palpebral conjunctiva
- 2=irritation of the bulbar and palpebral conjunctiva
- 3=2 plus watering of the eye (curable)
- 4=3 plus non-purulent secretion (curable)
- 5=4 plus purulent secretion—closing of the eyelids, cornea roughened with possible loss of sensitivity. (Recovery slow, but possible.)
- 6=5 plus damage to the palpebral edges and even the skin.

The numerals 1-6 may be followed by from 1 to 5 crosses according to the acuteness of the effect.

The corneal lesions being of two types, the numbers corresponding to the most serious damage may also be followed by:

- (a) Which corresponds to a loss of brilliance (cornea roughened),
- (b) Which corresponds to the more or less complete destruction of the corneal epithelium with more or less extensive ulceration and loss of corneal sensitivity.

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The cornea may be attacked in cases 5 and 6 either by the product itself or by the pathological conjunctival secretion caused by the product.

The loss of corneal sensitivity facilitates ulceration.

- 5 The tests summarized in the foregoing tables clearly show that products according to the invention do not attack the cornea, as is frequently the case with cationic, anionic, or non-ionic products.

- 10 The new compositions according to the invention which have valuable surface active properties may be used in various fields and especially in the cosmetic field.

- 15 They are particularly valuable for the preparation of shampoos having excellent foaming and detergent properties. Their application to hair renders it supple and easy to comb. Moreover hair which has been shampooed with them does not have an accumulated electrostatic charge after drying.

- 20 The preparation of the maleamic acids by condensation of alkylene diamine with maleic anhydride is taught by U.S. Patent No. 2,821,521, wherein the preparation of N-(N',N'-diethylaminopropyl) maleamic was first described. The present invention describes an improvement over the process described in said patent, which improvements may be classed into two categories:

- 25 A. Those which permit the very easy isolation of the pure maleamic acid; and

- 30 B. Those which permit the recovery of the maleamic acid in a solution, which can be directly employed for the ultimate condensation reaction with a fatty amine, described later in the present application.

- The following examples illustrate methods of preparing the maleamic acids in each of the above categories:

A. PROCESS OF PREPARING MALEAMIC ACID WHICH PERMITS THE RECOVERY AND ISOLATION OF THAT ACID

- 35 Ethyl acetate or tertiary butyl alcohol is used as a solvent. The reaction conditions are specified in the table below:

- 55 The reaction is carried out in a homogeneous medium and the products begin to precipitate only at the end of the maleic anhydride addition.

A solid white product is obtained directly, easy to dry and usable without further purification.

By way of example, two particular preparations corresponding to this general process can be described:

- 60 *Example A-1.—Preparation of N,N-diethylaminopropyl maleamic acid*

- 65 To 390 g. (3 moles) of N,N-diethylaminopropylamine dissolved in 600 ml. of ethyl acetate, 297 g. of maleic anhydride dissolved in 600 ml. of ethyl acetate is added with agitation, through a dropping funnel. The temperature is maintained between 0° and 5° C. during the addition of the anhydride. The length of this operation is 2 hours 30 minutes, and the N,N-diethylaminopropyl maleamic acid begins to precipitate several minutes before the end of this addition.

- 75 The reaction mixture is allowed to stand, at ambient temperature, for a few hours. The maleamic acid which has formed is then separated by filtration. After washing with ethyl acetate, the product is dried and recovered in the form of a white powder.

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The yield is 100%.

Example A-2

204 g. (2 moles) of N,N-dimethylaminopropylamine is dissolved in 800 g. of t-butyl alcohol, and the temperature of the solution thus obtained is brought to 50° C. 198 g. of powdered maleic anhydride is added with agitation. This operation is completed over one hour at a temperature of 50° C.

The reaction mixture is allowed to stand for several hours. The dimethylaminopropyl maleamic acid forms a precipitate. It is separated by filtration. After washing with acetone, draining, and drying, the product is recovered in the form of a white powder.

The yield is 98%.

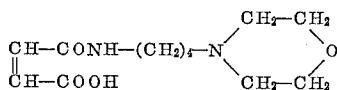
B. PROCESS OF SYNTHESIS OF MALEAMIC ACID PERMITTING THE RECOVERY OF THE ACID IN A SOLUTION WHICH IS DIRECTLY USABLE FOR A FINAL CONDENSATION WITH A FATTY AMINE

The solvents which are usable are lower alcohols, such as methanol and ethanol, as well as water.

The choice of temperature is important; it should be less than 30° C. in order to avoid esterification, when an alcohol is the solvent, and hydrolysis, when water is the solvent.

The yield of the amide is always greater than 90%.

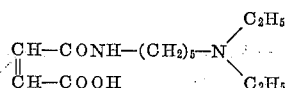
Example B-1.—Preparation of N-(morpholinobutyl)-maleamic acid



To 31.6 g. (0.2 mole) of morpholinobutylamine dissolved in 160 g. of methanol, 19.8 g. of powdered maleic anhydride is added, with agitation. The temperature is maintained between 5° and 10° C. After the end of the maleic anhydride addition, the reaction mixture is maintained at 10° C. for one hour, then at 25° C. for 2 hours.

N-(morpholinobutyl)-maleamic acid in methanol is obtained.

Example B-2.—Preparation of N-(N',N'-diethylaminopentyl)-maleamic acid



The same procedure employed in Example B-1 is used, and N-(N',N'-diethylaminopentyl)-maleamic acid is obtained in a methanol solution starting with diethylamino-5-pentylamine and maleic anhydride.

Example B-3

In the same manner as Example B-1, N-(piperidinopropyl)-maleamic acid in an ethanol solution is prepared, starting from piperidinopropylamine and maleic anhydride.

Example B-4.—Preparation of N,N-(diethylaminopropyl)-maleamic acid in water solution

To 1955 g. of N,N-diethylaminopropylamine dissolved in 3475 g. of distilled water, 1495 g. of powdered maleic anhydride are added while agitating, the temperature being maintained at between 0° and 5° C. The length of this addition is about 1½ hours. The mixture is allowed to return to ambient temperature under agitation.

The maleic anhydride being entirely dissolved, the amino nitrogen and the acidity were quantitatively determined. The results corresponding to the dry product are the following:

	Milliequivalents/gram
Acidity	4.54
Amino nitrogen	4.36

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Example B-5.—Preparation of N,N-(dimethylaminopropyl)-maleamic acid in water solution

To 52 g. of dimethylaminopropylamine of 98% purity, dissolved in 110 g. of water, 52.5 g. of powdered maleic anhydride are added with agitation. The temperature is maintained at 0° C., and the addition of the anhydride is made over a period of 40 minutes. The mixture is agitate for 2 hours at 5° C., then the temperature is allowed to rise to 25° C.

The maleic anhydride being entirely dissolved, the amine nitrogen and the acidity can be determined. The results corresponding to the dry products are the following:

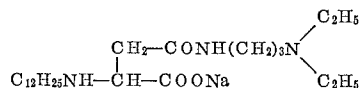
	Milliequivalents/gram
Acidity	5.39
Amine nitrogen	5

The following examples illustrate ways of preparing the new chemical compositions according to the invention.

EXAMPLES OF THE PREPARATION OF NEW COMPOSITIONS

Example 1

Preparation of the sodium salt of N-(N',N'-diethylaminopropyl)-N²-dodecyl-asparagine having the following formula:



N-(N',N'-diethylaminopropyl)-maleamic acid is first prepared in the manner described in U.S. Patent No. 2,821,521, issued January 28, 1958.

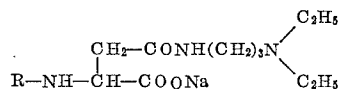
To a solution of 0.2 mol plus a 5% excess of this substituted maleamic acid in 100 cc. of ethanol there is added a stoichiometric quantity of soda dissolved in a minimum of water.

The solution of the sodium salt of N-(N',N'-diethylaminopropyl) maleamic acid thus obtained is added drop by drop, while stirring, to 0.2 mol of dodecylamine.

The mixture is then caused to reflux for six hours. After evaporation of the alcohol a pasty product is obtained which is soluble in water at any pH, and the purity of which, after dosing with amine functions, rises to 93%. A 10% aqueous solution has a pH of 11.2.

Example 2

Preparation of the sodium salt of N-(N',N'-diethylaminopropyl)-N²-alkyl (fatty) asparagine having the following formula:

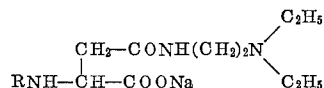


R=alkyl residue derived from the fatty acids of copra.

The procedure is the same as in Example 1, but the primary amines deriving from the fatty acids of copra are used instead of dodecylamine. A product having the following formula and a purity of 95% is thus obtained, in the form of a viscous clear yellow mass, soluble in water at any pH. A 10% aqueous solution has a pH of 11.9.

Example 3

Preparation of the sodium salt of N-(N',N'-diethylaminoethyl)-N²-alkyl (fatty) asparagine having the following formula:



R=alkyl residue derived from the fatty acids of copra.

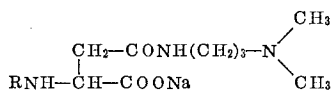
N-(N',N'-diethylaminoethyl)-maleamic acid is first prepared in the same way as in Example 1 by reacting N,N-diethylaminoethylamine with maleic anhydride. Then the

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primary amine of the fatty acids of copra is reacted with the sodium salt of this acid. This yields a viscous mass which is soluble in water at any pH, with a purity of 94%. A 10% aqueous solution has a pH of 11.5.

Example 4

Preparation of the sodium salt of N-(N',N'-dimethylaminopropyl)-N²-alkyl (fatty) asparagine having the following formula:

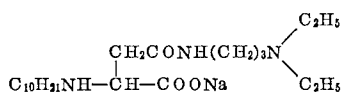


R=alkyl residue derived from the fatty acids of tallow.

Proceeding in the same manner as in the case of Example 1, N-(N',N'-dimethylaminopropyl)-maleamic acid is first prepared in the form of a white solid, having its melting point at 158-159° C. The primary amine derived from the fatty acids of tallow is reacted with the sodium salt of that acid, yielding in the manner already described a thick viscous mass soluble in water at any pH, and having a purity of 92%. A 10% aqueous solution has a pH of 10.6.

Example 5

Preparation of the sodium salt of N-(N',N'-diethylaminopropyl)-N²-decyl asparagine having the formula:

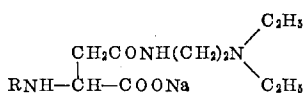


This product is obtained in the same manner as in Example 1, except for using decyl-amine in place of dodecyl-amine.

This asparagine derivative is obtained in a purity of 96%, in the form of a viscous clear yellow mass, soluble in water at all pH values. A 10% aqueous solution has a pH of 11.1.

Example 6

Preparation of the sodium salt of N-(N',N'-diethylaminoethyl)-N²-alkyl (fatty) asparagine having the formula:

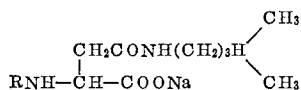


in which R is an alkyl residue derived from the fatty acids of tallow.

This product is obtained by following the procedure hereinbefore described, using N,N-diethyl-ethylene diamine and the fatty amines derived from the fatty acids of tallow. Its purity is 94%. A 10% aqueous solution has a pH of 11.7.

Example 7

Preparation of the sodium salt of N-(N',N'-dimethylaminopropyl)-N²-alkyl (fatty) asparagine, having the formula:



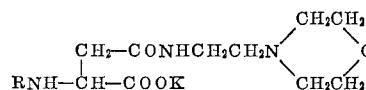
R being an alkyl residue derived from the fatty acids of copra.

Proceeding as in Example 1, but replacing dodecyl-amine with the primary amine derived from the fatty acids of copra, the above-mentioned asparagine derivative is obtained in a purity of 98%. A 10% aqueous solution has a pH of 11.5.

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Example 8

Preparation of the potassium salt of N-(morpholinoethyl)-N²-alkyl (fatty) asparagine, having the formula:



R being an alkyl residue derived from the fatty acids of copra.

N-(morpholinoethyl)maleamic acid is first prepared in the same way as in Example 1, by reacting N-(β-aminoethyl) morpholine with maleic anhydride.

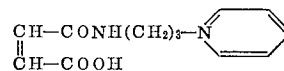
The product is in the form of a white solid having its melting point at 161-162° C.

The primary amines derived from the fatty acids of copra are then reacted with the potassium salt of that acid. The desired product is obtained in a purity of 90%, in the form of a yellow-orange viscous mass, soluble in water at all pH values.

A 10% aqueous solution has a pH of 11.6.

Example 9

(a) Preparation of N-(piperidinopropyl)-maleamic acid, having the formula:



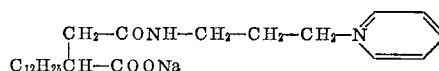
To 14.2 g. (0.1 mole) of N-(β-aminopropyl)-piperidine dissolved in 100 g. of ethyl alcohol, 10 g. of pulverized maleic anhydride is added over a period of 30 minutes with agitation, maintaining the temperature between 6 and 8° C.

After agitation of the mixture for 2 hours at 25° C., the amino nitrogen and the acid are quantitatively determined.

The corresponding results were obtained from the dry products:

	Milliequivalents/gram
Acidity -----	3.87
Amino nitrogen -----	4.2

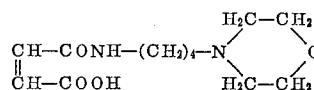
(b) Preparation of the sodium salt of N-piperidinopropyl-N²-dodecyl asparagine, having the formula:



The N-(piperidinopropyl)-maleamic acid obtained in alcoholic solution is neutralized with 11.1 g. of 33.8% sodium hydroxide solution after which 17.5 g. of dodecylamine are added. The mixture is then heated at 65° C. for 5 hours, and concentrated by the evaporation from the solution of 60 g. of alcohol, the temperature being maintained at 65° C. for another 3 hours. The alcohol and the water are removed under vacuum; a pasty product is obtained, which is soluble in water.

Example 10.—Preparation of the sodium salt of N-(morpholinobutyl)-N²-alkyl (fatty) asparagine

(a) Preparation of N-(morpholinobutyl)-maleamic acid, having the formula:

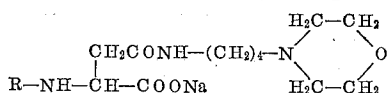


To 31.6 g. (0.2 mole) of morpholinobutylamine dissolved in 160 g. of methanol, 19.8 g. of powdered maleic anhydride is added, with agitation. The temperature is maintained between 5 and 10° C. After the end of the maleic anhydride addition, the reaction mixture is maintained for 1 hour at 10° C., and then for 2 hours at 25° C.

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N-(morpholinobutyl)-maleamic acid in methanol is obtained.

(b) Preparation of the sodium salt of N-(morpholinobutyl)-N²-alkyl (fatty) asparagine, having the formula:

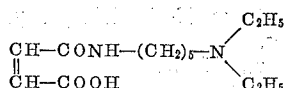


wherein R is an alkyl residue derived from the fatty acids of copra.

The N-(morpholinobutyl)-maleamic acid (0.2 mole) obtained in methanol solution above, is neutralized by a stoichiometric amount of a 33% aqueous solution of sodium hydroxide. 0.2 mole of primary amines derived from the fatty acids of copra is added, and the mixture is heated to 65° C. for 12 hours. On evaporation to dryness, a white paste containing 90% of the product of the above formula is obtained.

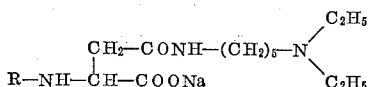
Example 11.—Preparation of the sodium salt of N-(N', N'-diethylaminopentyl)-N²-alkyl (fatty) asparagine

(a) Preparation of N-(N',N'-diethylaminopentyl)-maleamic acid, of the formula:



The same procedure employed in Example 10(a) is used, and N-(N',N'-diethylaminopentyl)-maleamic acid is obtained in a methanol solution starting from diethylamino-5-pentylamine and maleic anhydride.

(b) Preparation of the sodium salt of N-(N',N'-diethylaminopentyl)-N²-alkyl (fatty) asparagine, of the formula:

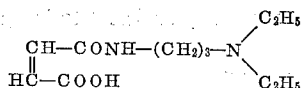


wherein R is an alkyl residue derived from the fatty acids of copra.

The N-(N',N'-diethylaminopentyl)-maleamic acid obtained in part (a) above in methanol solution is neutralized by a stoichiometric amount of sodium hydroxide. The mixture is heated at 65° C. for 8 hours, with the primary amine derivatives of the fatty acids of copra. On evaporation to dryness, a pasty product is obtained, which is water-soluble.

Example 12.—Preparation of the sodium salt of N-(N', N'-diethylaminopropyl)-N²-alkyl (fatty) asparagine

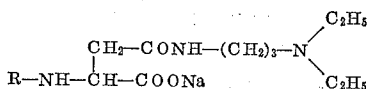
(a) Preparation of N,N-(diethylaminopropyl)-maleamic acid, of the formula:



To 1955 g. of N,N-diethylaminopropyl amine dissolved in 3475 g. of distilled water, 1495 g. of powdered maleic anhydride are added while agitating, the temperature being maintained between 0° and 5° C. The time of addition is about 1½ hours. The mixture is then allowed to return to ambient temperature under agitation.

The maleamic acid derivative is thereby obtained.

(b) Preparation of the sodium salt of N-(N',N'-diethylaminopropyl)-N²-alkyl (fatty) asparagine, of the formula:



wherein R is an alkyl radical derived from the fatty acids of copra.

The maleamic acid derived according to the above procedure is neutralized with 1362 g. of 46.3% aqueous sodium hydroxide solution, the temperature being main-

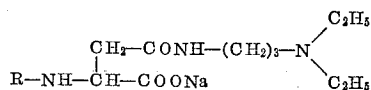
10

tained between 12° and 15° C. The aqueous solution of the sodium salt of N,N-diethylaminopropylmaleamate (3300 g. or 15 moles), is added to a mixture of primary amines derived from the fatty acids of copra. The mixture is heated with agitation at 65° C. for 10 hours. A transparent paste is obtained, which, when diluted in water, gives a clear, foaming solution.

Example 13

Preparation of a sodium salt of a derivative of asparagine in which the fatty radical is derived from the fatty acids of copra and tallow:

By using the same method of operation as used in Example 12, diluting the reaction medium by introduction during the course of the reaction of 1575 g. of water at 70° C. into the mixture, and by using a mixture of 11.55 moles of fatty amines derived from the fatty acids of copra and 3.45 moles of the fatty amines derived from the fatty acids of tallow, a product represented by the following formula is obtained:



wherein R is a radical derived from the fatty acids of copra and tallow. The content of the primary fatty amines corresponding to the dry material is 5.6%.

While the following examples disclose a pH range of 4 to 8.6 in the shampooing compositions, and while this is the preferred range for the pH of these compositions when utilized as shampoos, any pH between 4 and 11.9 may be used.

EXAMPLES OF THE APPLICATION OF THE NEW COMPOSITIONS IN SHAMPOOING HAIR

Example 1A

A solution is prepared which contains:

Sodium salt of N-(N',N'-diethylaminopropyl)-N²-dodecyl asparagine, 10 g.
Lactic acid in a quantity sufficient to bring the pH value to 4.
Water, q.s.p., 100 cc.

This solution gives a foamy shampoo and permits the hair to be easily combed.

Example 2A

The following solution is prepared:

	G.
Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	7.5
Sodium salt of N-(N',N'-diethylaminoethyl)-N ² -alkyl (tallow) asparagine	2.5
Sufficient lactic acid to bring the solution to pH 6.	
Water, q.s.p. 100 cc.	

This yields an excellent foaming shampoo which renders the hair soft and easy to comb. Moreover, hair which has been shampooed with it does not have an accumulated electrostatic charge after drying.

Example 3A

A solution is prepared which contains:

Sodium salt of N-(N',N'-diethylaminopropyl)-N²-dodecyl asparagine, 10 g.
Sufficient lactic acid to bring to a pH of 7.5.
Sufficient water to bring to a total of 100 cc.

This yields an excellent foaming shampoo which renders the hair soft and easy to comb.

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Example 4A

An aqueous solution is prepared which contains the following:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	4
Lauryl alcohol condensed with 10 mols of ethylene oxide per mol of alcohol	8
Sufficient lactic acid to bring to pH 4.	
Sufficient water to bring to 100 cc.	

The shampoo thus obtained foams well and imparts great softness to the washed hair.

Example 5A

An aqueous solution is prepared which contains the following:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	4
Sodium salt of N-(N',N'-dimethylaminopropyl)-N ² -alkyl (tallow) asparagine	2
Nonyl phenol at 12 mols of ethylene oxide per mol of nonyl phenol	8
Sufficient lactic acid to bring to pH 6.	
Sufficient water to bring to 100 cc.	

This shampoo foams well and imparts great softness to the washed hair.

Example 6A

An aqueous solution is prepared which contains the following:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	1.1
100% technical ammonium lauryl sulfate	9
Lauryl hydroxy ethylamide	0.8
Sufficient lactic acid to bring to pH 7.	
Sufficient water to bring to 100 cc.	

This solution constitutes shampoo which is an effective detergent, foams well, and imparts great softness to the washed hair.

Example 7A

An aqueous solution is prepared which contains:

Sodium salt of N-(N',N'-dimethylaminopropyl)-N ² -alkyl (tallow) asparagine	0.5
100% technical ammonium lauryl sulfate	12
Oleic acid	0.2
Lauryl dihydroxy ethyl amide	2
Sufficient lactic acid to bring to a pH of 6.5.	
Sufficient water to bring to 100 cc.	

This viscous shampoo is a good detergent and foams well. It imparts great softness to the hair which is washed with it.

Example 8A

An aqueous solution is prepared which contains:

Potassium salt of N-(morpholino-ethyl)-N ² -alkyl (fatty) asparagine, 7 g.	60
Sufficient lactic acid to bring to a pH of 7.5.	
Sufficient water to make 100 cc.	

This solution constitutes an excellent shampoo which is an effective detergent, foams well and imparts great softness to the washed hair.

Example 9A

An aqueous solution is prepared which contains:

Ammonium salt of N-(N',N'-diethylaminopropyl)-N ² -alkyl (fatty) asparagine wherein the fatty residues are constituted by $\frac{2}{3}$ of the fatty chain deriving from the fatty acids of copra and by $\frac{1}{3}$ of the fatty chain deriving from the fatty acids of tallow, 10 g.	70
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Sufficient water to make 100 cc.
Sufficient lactic acid to bring to a pH of 8.6.

This solution constitutes a shampoo having good foaming and detergent properties. It makes the hair supple and easy to comb.

Example 10A

An aqueous solution is prepared which contains:

Sodium salt of N - (N',N' - diethylaminopropyl) - N ² -alkyl (fatty) asparagine wherein the fatty residues are constituted by $\frac{2}{3}$ of the fatty chain deriving from the fatty acids of copra and by $\frac{1}{3}$ of the fatty chain deriving from fatty acids of tallow, 10 g.	10
Sufficient lactic acid to bring to a pH of 8.5.	15
Sufficient water to make 100 cc.	

This yields an excellent foaming shampoo which renders the hair soft and easy to comb.

Example 11A

An aqueous solution is prepared which contains:

The sodium salt of N-piperidinopropyl-N-dodecyl asparagine, 7 g.	25
Lactic acid, q.s.p., pH 7.5.	
Water, q.s.p. 100 cc.	

This solution constitutes an excellent shampoo, which has good detergent and foaming properties, and gives the hair a brilliant sheen.

While in the above examples the shampooing compositions have been adjusted to have a pH of 4 to approximately 8.6 by the addition of lactic acid, other acids may be used, and a higher pH may also be used.

Example 12A

A solution is prepared which contains:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine, 10 g.	40
Hydrochloric acid in a quantity sufficient to bring the pH value to 4.	
Water, q.s.p. 100 cc.	

This solution gives a foamy shampoo and permits the hair to be easily combed.

Example 13A

A solution is prepared which contains:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine, 9 g.	50
Acetic acid in a quantity sufficient to bring the pH value to 5.	
Water, q.s.p., 100 cc.	55

This solution gives a foamy shampoo and permits the hair to be easily combed.

Example 14A

The following solution is prepared:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine,	7.5
Sodium salt of N-(N',N'-diethylaminoethyl)-N ² -alkyl (tallow) asparagine	2.5
Sufficient phosphoric acid to bring the solution to pH 6.	
Water, q.s.p., 100 cc.	

This solution constitutes a shampoo having foaming and detergent properties and making the hair supple and easy to comb.

Moreover, hair which has been shampooed with it does not have an accumulated electrostatic charge after drying.

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Example 15A

The following solution is prepared:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	8	G.
Sodium salt of N-(N',N'-diethylaminoethyl)-N ² -alkyl (tallow) asparagine	2	
Sufficient formic acid to bring the solution to pH 6.		
Water, q.s.p., 100 cc.		

This solution constitutes a shampoo having foaming and detergent properties and making the hair supple and easy to comb.

Moreover, hair which has been shampooed with it does not have an accumulated electrostatic charge after drying.

Example 16A

A solution is prepared which contains:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine, 10 g.	20
Sufficient tartic acid to bring the solution to a pH 7.5.	
Water, q.s.p., 100 cc.	

This yields an excellent foaming shampoo which renders the hair soft and easy to comb.

Example 17A

A solution is prepared which contains:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine, 10 g.	30
Sufficient citric acid to bring the solution to a pH 7.5.	
Sufficient water to bring to 100 cc.	

This yields an excellent foaming shampoo which renders the hair soft and easy to comb.

Example 18A

An aqueous solution is prepared which contains the following:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	4	G.
Lauric alcohol condensed with 10 mols of ethylene oxide per mol of alcohol	8	
Sufficient acetic acid to bring the solution to a pH 5.		
Sufficient water to bring to 100 cc.		

The shampoo thus obtained foams well and imparts great softness to the washed hair.

Example 19A

An aqueous solution is prepared which contains the following:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	4	G.
Sodium salt of N-(N',N'-dimethylaminopropyl)-N ² -alkyl (tallow) asparagine	2	
Nonyl phenol at 12 mols of ethylene oxide per mol of nonyl phenol	8	
Sufficient citric acid to bring the solution to a pH 6.		
Sufficient water to bring to 100 cc.		

This shampoo foams well and imparts great softness to the washed hair.

Example 20A

An aqueous solution is prepared which contains the following:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	1.1	G.
100% technical ammonium lauryl sulfate	9	
Lauryl hydroxy ethylamide	0.8	
Sufficient hydrochloric acid to bring the solution to a pH 7.		
Water, q.s.p., 100 cc.		

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This solution constitutes shampoo which is an effective detergent, foams well and imparts great softness to the washed hair.

Example 21A

An aqueous solution is prepared which contains:

Potassium salt of N-(morpholino-ethyl)-N ² -alkyl (fatty) asparagine, 7 g.	
Sufficient citric acid to bring to a pH of 7.5.	
Sufficient water to make 100 cc.	10

This solution constitutes an excellent shampoo which is an effective detergent, foams well and imparts great softness to the washed hair.

EXAMPLES OF THE APPLICATION OF THE NEW COMPOSITIONS IN DYEING HAIR

Example 1B

A hair dyeing composition is prepared, which contains the following:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	g--	4
Nonyl phenol+4 mols ethylene oxide	g--	20
Nonyl phenol+8.75 mols ethylene oxide	g--	20
Diethylene glycol	g--	17
Ethyl alcohol	g--	3
Ammonia at 22° Bé.	ml--	12
Paratolulene diamine	g--	0.6
Metadiaminoanisol sulfate	g--	0.5
Resorcine	g--	0.5
Paraaminophenol	g--	0.4
Metaaminophenol	g--	0.1
Water, q.s.p., 100 cc.		

This solution is diluted weight by weight with hydrogen peroxide to 20 volumes. The final pH is 9.9. The shade of dyeing which is obtained is chestnut.

Example 2B

A hair dyeing solution is prepared which contains:

Sodium salt of N-(N',N'-diethylaminopropyl)-N ² -dodecyl asparagine	g--	3
Sodium salt of N-(N',N'-diethylaminoethyl)-N ² -alkyl (tallow) asparagine	g--	1
Nonyl phenol+4 mols ethylene oxide	g--	20
Nonyl phenol+8.75 mols ethylene oxide	g--	20
Diethylene glycol	g--	17
Ethyl alcohol	g--	3
Ammonia at 22° Bé.	ml--	12
Paratolulene diamine	g--	0.2
Metadiaminoanisol sulfate	g--	0.01
Resorcine	g--	0.1
p-Aminophenol	g--	0.3
m-Aminophenol	g--	0.05
Water, q.s.p., 100 cc.		

This solution is diluted weight for weight with hydrogen peroxide to 20 volumes. The final pH is 9.7. The shade of dyeing obtained is blonde.

Example 3B

A hair dyeing solution is prepared which contains the following:

Potassium salt of N-(morpholino-ethyl)-N ² -alkyl (fatty) asparagine	g--	4
Nonyl phenol+4 mols ethylene oxide	g--	20
Nonyl phenol+8.75 mols ethylene oxide	g--	20
Diethylene glycol	g--	17
Ethyl alcohol	g--	3
Ammonia at 22° Bé.	ml--	12
Paratolulene diamine	g--	0.6
Metadiaminoanisol sulfate	g--	0.025
Resorcine	g--	0.2
p-Aminophenol	g--	1
m-Aminophenol	g--	0.1
Water, q.s.p., 100 cc.		

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This solution is diluted weight for weight with hydrogen peroxide to 20 volumes. The final pH is 10. The shade of dyeing obtained is golden chestnut.

Example 4B

A hair dyeing solution is prepared which contains:

Ammonium salt of N-(N',N'-diethylaminopropyl)-N²-alkyl (fatty) asparagine, in which the fatty residues are composed of 2/3 of the fatty chain portion of the fatty acids of copra and 1/3 of the fatty chain portion of the fatty acids of tallow

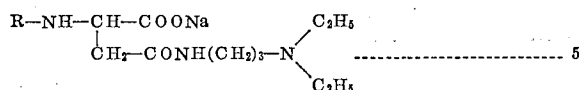
low	g	4
Nonyl phenol+4 mols ethylene oxide	g	20
Nonyl phenol+8.75 mols ethylene oxide	g	20
Diethylene glycol	g	17
Ethyl alcohol	g	3
Ammonia at 22° Bé.	ml	12
Paratoluylene diamine	g	0.6
Metadiaminoanisol sulfate	g	0.15
Resorcine	g	0.5
p-Aminophenol	g	0.4
m-Aminophenol	g	0.1
Water, q.s.p., 100 cc.		

This solution is diluted weight for weight with hydrogen peroxide to 20 volumes. The final pH is 9.5.

The shade of dyeing obtained is chestnut brown.

Example 5B

The following composition is prepared:



wherein R is a copra group (100%).

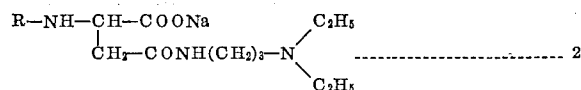
Nonyl phenol+4 mols ethylene oxide	g	250
Nonyl phenol+9 mols ethylene oxide	g	250
Ethyl alcohol at 96° Bé.	g	150
Ammonia (20% solution) to bring pH to 9.		
Paratoluylenediamine	g	5.5
Metadiaminoanisol sulfate	g	0.15
Resorcine	g	3
p-Aminophenol	g	0.5
m-Aminophenol	g	0.75
Water, q.s.p., 1000 g.		

This solution is mixed with an equal volume of hydrogen peroxide and applied in the usual manner to the hair.

The shade imparted to the hair is chestnut brown.

Example 6B

The following solution is prepared:



wherein R is 80% copra residue and 20% tallow residue.

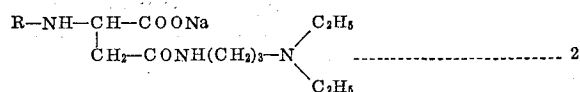
Oxyethylene lauryl alcohol, with 15 to 20 mols of ethylene oxide	g	3
Diethanolamide of coca	g	2
p-Nitrophenylenediamine	g	0.5
Citric acid (40%) solution to bring to a pH of 8.		
Water, q.s.p., 100 g.		

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This solution is applied in the usual manner to the hair, and gives a mahogany shade on the hair.

Example 7B

The following composition is prepared:



wherein R is 80% copra residue and 20% tallow residue.

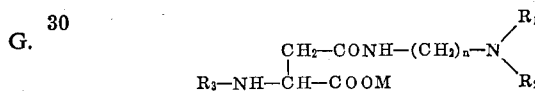
Oxyethylene lauryl alcohol, with 15 to 20 mols of ethylene oxide	g	3
Diethanolamide of coca	g	2
p-Nitrophenylenediamine	g	0.5
Methyl violet	g	0.1
Citric acid (40% solution) to bring pH to 5.		
Water, q.s.p., 100 g.		

This solution is applied to the hair in the usual manner, and gives the hair a violine color.

While the foregoing examples disclose a pH range of 5 to 10 in the dyeing compositions, and while the preferred range for the pH of these solutions when utilized as hair dyes is between 9 and 10, any pH between about 4 and about 11.9 may be used.

What is claimed is:

1. A compound of the formula:



wherein R₁ and R₂ are alkyl of up to four carbon atoms or together with the nitrogen atom to which they are attached form morpholino or piperidino, n is an integer having a value between 2 and 5 inclusive, R₃ is a saturated aliphatic hydrocarbon having from 10 to 18 carbon atoms inclusive, and M is selected from the group consisting of sodium, hydrogen, potassium and ammonium.

2. A compound as claimed in claim 1 in which M is sodium.

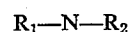
3. A compound as claimed in claim 1 in which M is potassium.

4. A compound as claimed in claim 1 in which



is dimethylamino.

5. A compound as claimed in claim 1 in which



is diethylamino.

6. The compound of claim 1, wherein said R₃ is selected from the group consisting of copra or tallow.

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