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2,999,069

## DETERGENT COMPOSITION

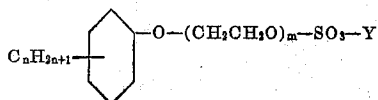
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24 Claims. (Cl. 252-152)

This invention relates to synergistic compositions comprising an amphoteric nitrogen-containing organic detergent material and a so-called nonionic detergent.

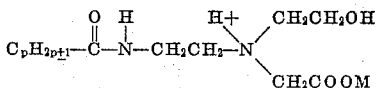
Various organic detergents have achieved considerable commercial success. However, the art is still confronted by the problem of providing detergent compositions which foam efficiently and yet are free from undesirable disadvantages, such as irritation and the like.

The discoveries associated with the invention relate to solution of the above problems, and the objects achieved in accordance with the invention as set forth herein include the provision of compositions useful as detergents, such as shampoos, comprising:

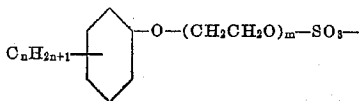
(I) A reaction of an alkylaryloxypolyoxyethylene sulfate with a product of condensation of sodium chloroacetate with a reaction product of a fatty acid having 12 to 18 carbon atoms in the molecule and an alkylene-diamine, or a product which is represented by the formula:



where Y is:



or a mixture of that compound with the corresponding aminoamide in which the  $CH_2COOM$  is replaced by H, the molar amount of aminoamide in all cases being less than the molar amount of ampholyte, and the molar excess of Y or



being no more than 20% or 5%, respectively, M is a member of the group consisting of alkali metals, triethanol ammonium, mixtures of an alkali metal with hydrogen, and mixtures of triethanol ammonium with hydrogen, n is a whole number from 0 to 9, inclusive, m is a number from 1 to 23, inclusive, and p is a whole number from 11 to 17, inclusive, and

(II) A water soluble nonionic surfactant comprising a polyoxyethylenated derivative of a hydrophobic base, said derivative being a member of the group consisting of:

(a) 9-18 carbon atom fatty acid monesters and diesters of aliphatic polyhydric alcohols, the polyhydric alcohols containing at least 3 hydroxyls, reacted with at least 10 moles of ethylene oxide and having a cloud point of at least 85° C. determined at 2% concentration in distilled water, and

(b) A member of the group consisting of the reaction

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products of 9-18 carbon atom alcohols, acids, amides and mercaptans, 12-24 carbon atom alkyl phenols and alkyl cyclohexanols, and polypropylene glycols having a molecular weight of about 800-2500, with at least 20 moles of ethylene oxide, said reaction products having a cloud point of at least 100° C. determined at 2% concentration in distilled water.

Optionally there may be included a hair conditioner, such as a fatty acid ester of a cyclized carbohydrate; a glycol ester; a glyceryl ester; lecithin; and lanolin.

In each ampholyte preparation, the starting material is composed of the condensation product of a fatty acid (e.g., lauric acid) and an appropriate amine (e.g., 2-hydroxyethylethylenediamine). The amino content of this condensation product is determined by titration to give the weight of product containing one weight equivalent of titratable amino. A given weight of the condensation product divided by this equivalent weight expresses the amino content in terms of moles. This value, when carried through the ampholyte solution, expresses the active amino content of that ampholyte solution as total moles of amino group. Thus, in a combination with the appropriate anionic modifier, the "moles of amino" of the ampholyte solution will determine the number of moles of anionic to be combined into salt form, and in practice at least 90% of the active amino content of any ampholyte solution is contributed by the ampholyte and aminoamide.

The following examples are presented for the purpose of illustrating the invention and not as a limitation. Parts and percentages are expressed on the basis of weight of active material unless otherwise indicated.

### EXAMPLE 1

#### Part A

In a reaction vessel capable of withstanding at least 15 p.s.i. pressure, having a corrosion resistant inner surface (e.g., glass, stainless steel, or the like), equipped with an agitator, reactant inlet means, indirect heating means (e.g., a steam coil, electrical heater, or the like), evacuating means (e.g., a conventional vacuum pump), and a condenser, there are charged: 15.27 parts (0.1316 mole) of sodium chloroacetate (in 40 parts of aqueous solution having a pH of 8.5) and 40 parts (0.1316 mole) of an aminoamide,



(which may be prepared by the method of Morgan et al., 2,344,260), and the mixture is heated and maintained at 50° C. with agitation for about 15 to 20 minutes, then 2.63 parts (0.0658 mole) of sodium hydroxide (in the form of 14.9 N aqueous solution) is added gradually over a period of about 9 to 10 minutes, and the resulting mixture heated at about 70 to 80° C., with agitation, for about two hours.

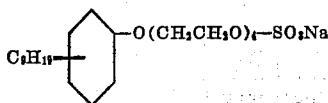
Optionally, during this period, 15 parts of isopropanol is added to reduce the viscosity of the mixture and facilitate agitation. The resulting product is a clear, light amber liquid having a pH of about 8 and weighs 98 parts.

An aqueous solution containing 0.5 to 5% or more of this material remains clear at pH range of about 2 to 6 and at pH range about 8 to 12 but is strongly turbid at about pH 6.5 to 8.9, the pH changes being made by adding aqueous sodium hydroxide or aqueous hydrochloric acid, as required.

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## Part B

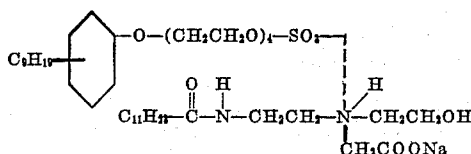
In a suitable reaction vessel, such as of the above type, there are charged: 20 parts of the above clear, light amber product of A (containing about 0.027 mole of amino, principally the carboxymethylated derivative of the aminoamide) 49.5 parts (0.027 mole) of an anionic surfactant (commercially available in the form of about 25 to 30% aqueous solution) of the following structure:



and the mixture is heated at about 70 to 80° C. for two hours with agitation. During this period all the isopropanol is distilled off (no odor of isopropanol is discernible in the vapor rising from the reaction mixture at the end of this period). The resulting mixture is a paste weighing about 45.5 parts.

This mixture is diluted with 60 parts of water, and the final product is an amber-colored liquid of pH 8.2 and containing about 25% dry solids and weighs about 105.5 parts.

It has the following structure:



with a minor part of the corresponding sulfate salt of the following aminoamide:



## Part C

In a suitable vessel, such as of the above type, there are mixed:

14 parts by weight of a polyoxyethylenated sorbitan ester (commercially available sorbitan monolaurate containing about 20 oxyethylene groups per molecule)  
11.2 parts of active surfactant B (having a pH of 8.2)  
72.74 parts of water

and the pH is adjusted to about 7 by adding aqueous hydrochloric acid or caustic solution, as required.

This product shows very low irritation to the human eye and eyelid surface and 1% and 5% concentrations thereof in water foam copiously on shaking. It is eminently suitable as a shampoo for washing human hair.

In this example the molar ration of unmodified ampholyte plus aminoamide to modifier is 1:1.

The polyoxyethylene derivative of sorbitan monolaurate used in this example had a cloud point above 100° C. when determined at 2% concentration in distilled water, as defined hereinafter.

In another such composition, there are included:

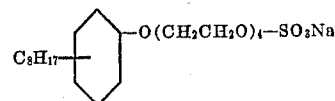
1.25 to 1.5 parts fatty ester hair conditioner (commercially available sorbitan monolaurate)  
0.5 part boric acid (optionally)  
0.06 part perfume.

and the resulting material is equally good as to non-irritation and as to foaming properties; but is superior as a shampoo, inasmuch as it leaves the hair conditioning agent on the hair.

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## EXAMPLE 2

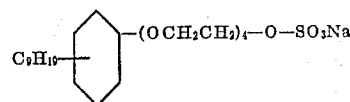
The procedure of the above example is followed, except using in part B an anionic surfactant of the formula:



in the same molar ratio, and comparable results are obtained.

## EXAMPLE 3

Fifty-three and seventy-hundredths parts of a solution containing 8.44 parts (0.023 mole) of N-lauroyl-N'-sodium carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine and 1.56 parts (0.0055 mole) of N-lauroyl-N'-(2-hydroxyethyl)ethylenediamine was mixed with 51.30 parts of a solution containing 15.04 parts (0.03 mole) of the following anionic surface active agent:

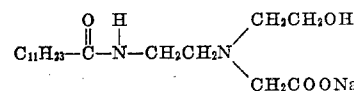


giving a molar ratio of unmodified ampholyte plus aminoamide to modifier of about 0.95:1. The mixture was heated with stirring for about two hours at 85-90° C. The resulting amber-colored solution weighed 92.2 parts and had a pH of 8.8. The solution contained 26.5% of the anionic sulfate ester salts of N-lauroyl-N'-(2-hydroxyethyl)ethylenediamine and the corresponding carboxymethyl containing ampholyte. Eleven parts of the above solution was mixed with 14 parts of the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide. The mixture was neutralized to pH 7 with hydrochloric acid and diluted to 100 parts with water.

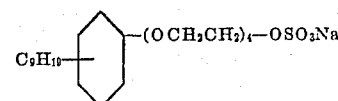
The product was an excellent shampoo. A dilution of 1 part shampoo in 3 parts of water gave little or no sting when it accidentally came into contact with the eyes.

## EXAMPLE 4

Two hundred eighty and nine-tenths parts of an aqueous solution containing 57.2 parts (0.156 mole) of N-lauroyl-N'-sodium carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine:



and 32.6 parts (0.114 mole) of N-lauroyl-N'-(2-hydroxyethyl)ethylenediamine, was mixed with 460 parts of an aqueous solution which contained 0.270 mole of an anionic surfactant having the following structure:



The molar ration of unmodified ampholyte plus aminoamide to modifier is about 1:1. The resulting solution was heated on the steam bath in an open vessel for 30 minutes. There was obtained 736.4 parts of clear, amber-colored solution containing 29.9% of organic surface active material.

Forty-four and fourteen hundredths parts of the above solution was mixed with 16.8 parts of the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide. The solution was neutralized to pH 7 with hydro-

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chloric acid and then made up to 100 parts with distilled water.

The final product gives copious foam and excellent cleansing when used as a shampoo. When some of the shampoo accidentally gets into the eyes during use it causes little or no sting if the concentration of surface active material is less than 5%.

#### EXAMPLE 5

Example 4 was carried out, except that an equal weight of the reaction product of lauryl alcohol and 23 moles of ethylene oxide was substituted for the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide. The nonionic used had a cloud point above 100° C. when determined at 2% concentration in distilled water.

The resulting product is mild to the skin and has a good cleansing and foaming action when used with hard or distilled water.

#### EXAMPLE 6

One hundred and thirty-two and two tenths parts of an aqueous solution containing 0.136 mole of N-lauroyl-N'-carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine and 232.5 parts of an aqueous solution containing 0.136 mole of nonylphenoxytriethyleneoxyethyl sulfate sodium salt were mixed and stirred on the steam bath for 30 minutes in an open vessel. Water was added as needed to reduce viscosity. The final weight of product was 622 parts, having 18.7% content of organic surface active materials. The molar ratio of unmodified ampholyte to modifier is 1:1. Fifty-eight and eighty-three hundredths parts of the above solution was mixed with 14 parts of the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide. The solution was neutralized to pH 7 with hydrochloric acid.

The resulting product is mild to the skin and gives copious foam and strong cleansing action when used with hard or distilled water.

#### EXAMPLE 7

One hundred and eighty parts of an aqueous solution containing 48.4 parts (0.132 mole) of N-lauroyl-N'-sodium carboxy-methyl-N'-(2-hydroxyethyl)ethylenediamine and 17.6 parts (0.062 mole) of N-lauroyl-N'-(2-hydroxyethyl)ethylenediamine was mixed with 337 parts of an aqueous solution containing 100 parts (0.2 mole) of nonylphenoxytriethyleneoxyethyl sulfate sodium salt. The mixture was stirred in an open container for 1 hour at 60-70° C. The solution, which weighed 468 parts, contained 166 parts of active material. The molar ratio of unmodified ampholyte plus aminoamide to modifier is about 0.97:1. Twenty-nine and forty-nine hundredths parts of the above solution containing 10.48 parts of active surfactant (polyether sulfate ester salts of the above amphoteric and aminoamide), was mixed with 14 parts of the reaction product of sorbitan monolaurate and 98 moles of ethylene oxide. This polyoxyethylene derivative of sorbitan monolaurate had a cloud point above 100° C. when determined at 2% concentration in distilled water.

The above product gives excellent foam when used as a shampoo and gives little or no sting if aqueous solutions, of 3.5% active surfactant basis, come into contact with the eyes or mucous membranes.

#### EXAMPLE 8

Example 7 was repeated, except that an equal quantity of the reaction product of lauryl alcohol and 103 moles of ethylene oxide was substituted for the reaction product of sorbitan monolaurate and 98 moles of ethylene oxide. This reaction product of lauryl alcohol and ethylene oxide had a cloud point above 100° C. when determined at 2% concentration in distilled water.

A product was obtained which had similar foaming action and did not give appreciable sting to the eyes or

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mucous membranes when the concentration of surfactants in water was 2.7% or less.

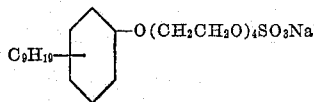
#### EXAMPLE 9

Example 3 was repeated, except that 14 parts of the reaction product of nonylphenol and 30 moles of ethylene oxide was substituted for 14 parts of the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide. The mixture was neutralized to pH 7 with hydrochloric acid. This reaction product of nonylphenol and ethylene oxide had a cloud point above 100° C. when determined at 2% concentration in distilled water.

The neutral product gave excellent foam and was useful as a mild detergent for cleansing skin.

#### EXAMPLE 10

Four hundred and twelve parts of an aqueous solution, containing 66.6 parts (0.179 mole) of N-lauroyl-N'-sodium carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine and 10.4 parts (0.0362 mole) of N-lauroyl-N'-(2-hydroxyethyl)ethylenediamine was mixed with 304.9 parts of a solution containing 89.5 parts (0.179 mole) of the following surface active agent:



The mixture is heated with stirring for about 30 minutes at 85-90° C. The resulting amber-colored solution weighs 705.2 parts and contains about 24.1% surface active materials. Twenty-two and eighty-two hundredths parts of the above solution is mixed with 7 parts of the reaction product of t-dodecyl mercaptan and 19.85 moles of ethylene oxide. This nonionic had a cloud point of about 102° C. when determined at 2% concentration in distilled water, where the solution was a superheated refluxing liquid.

The mixture is neutralized to pH 7 with hydrochloric acid and diluted to 50 parts with water.

The resulting product is mild to the skin and has good cleansing and foaming action when used with hard or distilled water.

#### EXAMPLE 11

Example 4 was repeated, except that the 16.8 parts of the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide was increased to 66 parts.

The product gave good foam and cleansing action when used as a shampoo.

#### EXAMPLE 12

Example 4 was repeated, except that the 16.8 parts of the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide was reduced to 5.27 parts.

The product gave copious foam and was useful for cleansing skin.

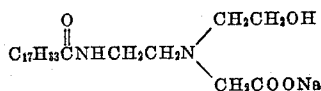
#### EXAMPLE 13

(A) In a 3-liter three-necked flask, fitted with a thermometer, stirrer and dropping funnel, there is placed 256.5 parts (0.761 mole) of 1-(2-hydroxyethyl)-2-heptadecenyl-2-imidazoline (commercially available Amine 220 from Union Carbide and Carbon Corp.) and 1000 parts of water. The mixture is heated with stirring to 70-80° C. over a two-hour period. Then, 10 parts by volume of concentrated hydrochloric acid solution is added to reduce the pH of the mixture from 10.4 to 8.2.

In a separate container, 89.8 parts (0.95 mole) of monochloroacetic acid dissolved in 180 parts of water is neutralized below 50° C. with a 25% solution of sodium hydroxide to a pH of 6.5. About 10 parts of this sodium

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chloracetate solution is quickly added to the imidazoline mixture to facilitate stirring, and thereafter the sodium chloracetate solution is added dropwise at 75–80° C. over a period of 1.5 hours. When the addition is complete, 1.07 moles of sodium hydroxide as a 25% solution is added dropwise over a period of 1 hour, and the reaction mixture is heated for a final 3 hours, all at 75–80° C. The product weighs 1844.8 parts, and consists essentially of amphoteric material having the following structure:



with a minor amount of unreacted aminoamide having the structure:



(B) Two hundred and thirty-two and eight-tenths parts (0.1695 mole) of dinonylphenoxypolyoxyethylene ethanol (having a polyoxyethylene chain length corresponding to 23.4 moles of ethylene oxide) in a 500 ml. three-necked flask fitted with a thermometer, stirrer, and condenser is heated with stirring to 95° C. Then 18.9 parts (0.195) mole of sulfamic acid is added in portions over about 30 minutes, during which time the reaction temperature rises to 122° C. When the solution is complete, the mixture is heated for an additional 2 hours at 111–121° C. The reaction mixture is allowed to cool, and the viscosity is decreased by addition of a quantity of aqueous ethanol (50%) sufficient to allow a smooth stirring rate. Sixteen parts of 50% sodium hydroxide solution is added dropwise over a period of 30 minutes. Heating and stirring are continued until the evolution of ammonia and ethanol has ceased (about 8.5 hours). The product weighs 263 parts and consists of about 68.7 parts of active anionic material.

(C) One hundred and eighty-three parts (0.0755 mole of amino) of the amphoteric surface active solution in part A and 160 parts (0.0755 mole) of anionic surface active material of part B are placed in a widemouthed open vessel and heated on the steam bath with stirring for 15–30 minutes. The resulting opaque product weighs 339.3 parts, containing 42.3 parts of surface active material. The molar ratio of unmodified ampholyte plus aminoamide to modifier is about 1:1.

(D) Twenty-six parts of part C, containing 11 parts of surface active materials, is mixed with 14 parts of the reaction product of 1 mole of sorbitan monolaurate and 20 moles of ethylene oxide. The solution is neutralized to pH 7 with hydrochloric acid.

The product is a good foaming mild shampoo.

#### EXAMPLE 14

Example 3 is repeated, except that an equal weight of the reaction product of hydrogenated tallow amide and 50 moles of ethylene oxide is substituted for the reaction product of sorbitan monolaurate and 20 moles of ethylene oxide. The reaction product of hydrogenated tallow amide and ethylene oxide had a cloud point above 100° C. when determined at 2% concentration in distilled water.

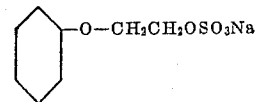
The product produces copious foam and excellent cleansing action in the presence of hard and distilled water when used as a hair shampoo.

#### EXAMPLE 15

Five hundred and six parts of the surface active amphoteric solution used in Example 3, containing 78.8

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parts (0.215 mole) of N-lauroyl-N'-sodium carboxymethyl-N'-(2-hydroxyethyl)ethylenediamine and 15.4 parts (0.054 mole) of N-lauroyl-N'-(2-hydroxyethyl)ethylenediamine, is mixed with 183.7 parts of a solution containing 67.9 parts (0.283 mole) of sodium 2-phenoxyethyl sulfate,



The mixture is heated on the steam bath in an open vessel with stirring for 5 hours. The product is partially neutralized (pH 8.8) with hydrochloric acid, weighs 646.0 parts, and contains about 25.5% active organic materials. The molar ratio of unmodified ampholyte plus aminoamide to modifier is about 0.95:1.

One hundred twenty-nine and four tenths parts of the above solution is mixed with 42.0 parts of the reaction product of coconut fatty acids and 50 moles of ethylene oxide, and neutralized to pH 7 with hydrochloric acid. The reaction product of coconut fatty acids and ethylene oxide had a cloud point above 100° C. when determined at 2% concentration in distilled water.

The product is mild to the skin and shows excellent cleansing action when used as a hair shampoo.

#### EXAMPLE 16

Example 4 was repeated except that the acid portions of the N-acyl-N'-sodium carboxymethyl-N'-(2-hydroxyethyl) fatty ethylenediamine and the N-acyl-N'-(2-hydroxyethyl) ethylenediamine were derived from an approximately 1:1 mixture by weight of lauric and coconut fatty acids. 11 parts (active basis) of the resulting amphoteric anionic products are mixed with 14 parts of the reaction product of 136–160 moles of ethylene oxide with one mole of a polypropylene glycol having a molecular weight of from 1501–1800.

After neutralization to pH 7 with hydrochloric acid and adding distilled water to make 100 parts, a product is obtained which gives copious foam and excellent cleansing and low sting when used as a shampoo.

#### EXAMPLE 17

Example 16 was repeated, except that the same amount of the reaction product of sorbitan monolaurate and 10 moles of ethylene oxide was substituted for the polyoxyethylenated polypropylene glycol. The polyoxyethylenated sorbitan monolaurate had a cloud point of 85° C. when determined at 2% concentration in distilled water.

The resulting shampoo gave similar results to that of Example 16.

TABLE 1

In the table below "percent active" signifies percent by weight of the indicated ingredient. The Amphoteric Ingredient column and Amphoteric-Nonionic column include not only the indicated surfactant but also anionic surfactant. The anionic is combined with the amphoteric in salt form. "d" denotes foam tests carried out in distilled water and "h" signifies that the foam tests were carried out in distilled water containing 300 p.p.m. calcium chloride.

All solutions were adjusted to pH 7, but it has been found that there is no substantial difference in foam when measured at small variations therefrom.

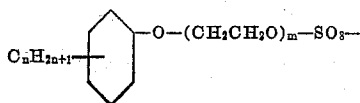
Not all compositions which show synergism will show it at exactly the same concentration. Some, however, show synergism at all of the concentrations tested. In the use of a shampoo best cleaning is generally obtained in the concentration range of 1 to 10%. However, good foaming is desirable even at lesser concentrations.

| Example | Water Used in Foam Test | Conc., Percent Active | mm. of Foam by Ross-Miles Method |                     |                               |
|---------|-------------------------|-----------------------|----------------------------------|---------------------|-------------------------------|
|         |                         |                       | Amphoteric Ingredient            | Nonionic Ingredient | Combination of Amph.-Nonionic |
| 1-----  | h                       | 0.1                   | 180                              | 55                  | 157                           |
|         |                         | 0.5                   | 210                              | 114                 | 207                           |
|         |                         | 1.0                   | 210                              | 130                 | 202                           |
|         |                         | 5.0                   | 24                               | 179                 | 191                           |
| 1-----  | d                       | 0.1                   | 187                              | 80                  | 155                           |
|         |                         | 0.5                   | 211                              | 135                 | 193                           |
|         |                         | 1.0                   | 210                              | 150                 | 203                           |
|         |                         | 5.0                   | 123                              | 174                 | 197                           |
| 2-----  | h                       | 1.0                   | 213                              | 130                 | 206                           |
|         |                         | 2.5                   | 203                              | 148                 | 205                           |
| 2-----  | d                       | 5.0                   | 168                              | 179                 | 196                           |
|         |                         | 5.0                   | 168                              | 174                 | 199                           |
| 3-----  | h                       | 5.0                   | 69                               | 179                 | 209                           |
|         |                         | 7.5                   | 33                               | 164                 | 192                           |
| 4-----  | h                       | 1.0                   | 180                              | 130                 | 211                           |
|         |                         | 5.0                   | 72                               | 179                 | 210                           |
|         |                         | 10.0                  | 100                              | 154                 | 175                           |
| 5-----  | h                       | 1.0                   | 180                              | 150                 | 212                           |
|         |                         | 5.0                   | 72                               | 156                 | 209                           |
|         |                         | 10.0                  | 100                              | 156                 | 175                           |
|         |                         | 1.0                   | 211                              | 130                 | 212                           |
| 6-----  | h                       | 2.5                   | 204                              | 148                 | 204                           |
|         |                         | 5.0                   | 180                              | 179                 | 191                           |
|         |                         | 7.5                   | 113                              | 167                 | 190                           |
|         |                         | 10.0                  | nil                              | 154                 | 181                           |
| 7-----  | h                       | 5.0                   | 110                              | 12                  | 187                           |
|         |                         | 7.5                   | nil                              | 8                   | 172                           |
| 8-----  | h                       | 5.0                   | 110                              | 139                 | 185                           |
|         |                         | 7.5                   | nil                              | 144                 | 167                           |
| 9-----  | h                       | 1.0                   | 205                              | 140                 | 206                           |
|         |                         | 5.0                   | 69                               | 147                 | 198                           |
| 10----- | h                       | 5.0                   | 45                               | 173                 | 193                           |
|         |                         | 7.5                   | 22                               | 161                 | 176                           |
| 11----- | d                       | 1.0                   | 216                              | 150                 | 185                           |
|         |                         | 5.0                   | 70                               | 174                 | 197                           |
| 12----- | d                       | 1.0                   | 216                              | 150                 | 221                           |
|         |                         | 5.0                   | 70                               | 174                 | 191                           |
|         |                         | 0.1                   | 120                              | 55                  | 130                           |
| 13----- | h                       | 0.5                   | 150                              | 114                 | 160                           |
|         |                         | 1.0                   | 165                              | 130                 | 170                           |
|         |                         | 5.0                   | 69                               | 119                 | 195                           |
| 14----- | h                       | 7.5                   | 33                               | 10                  | 177                           |
|         |                         | 5.0                   | 94                               | 119                 | 216                           |
|         |                         | 7.5                   | 51                               | 60                  | 190                           |
| 15----- | h                       | 5.0                   | 127                              | 96                  | 170                           |
|         |                         | 7.5                   | 124                              | 81                  | 165                           |
|         |                         | 10.0                  | 109                              | 89                  | 168                           |
| 16----- | h                       | 0.1                   | 38                               | 60                  | 175                           |
|         |                         | 0.5                   | 175                              | 124                 | 184                           |
|         |                         | 1.0                   | 190                              | 155                 | 195                           |
| 17----- | h                       | 5.0                   | 127                              | 145                 | 158                           |

In addition to having foam synergism in distilled or hard water, it is desirable that the composition possess good foaming properties in the presence of grease.

The example data show that the amount of foam obtained with the mixture of organic surface active material from the amphoteric solution and polyoxyethylene cyclized carbohydrate ester of the invention is greater than, and is unpredictable from, the foam obtainable with either of these compounds alone.

Although the para-alkylphenoxy modification of the anionic component



is preferred because of commercial availability, the ortho or the meta, or mixtures thereof, give equally satisfactory results, as do di- or tri-alkyl modifications. Suitable examples are p-1,1,3,3-tetramethylbutylphenoxy-, p-nonylphenoxy-, 2,4,6-trihexylphenoxy-, 2,4-dibutylphenoxy-, 2,4-dinonylphenoxy-, 2,4,6-tripropylphenoxy- and p-decylphenoxy-polyoxyethyl sulfate.

In any of the formulae herein the sodium may be replaced wholly or in part by other alkali metal or substituted alkanol ammonium (such as triethanol ammonium), or replaced in part by hydrogen, depending on the pH.

The amount of polyoxyethylenated material may be in the range of about 2 to about 600 or more, per 100 parts of the nitrogen containing surfactant, and preferably the amount that gives a mixture having major foam-

ing and detergent action. Typical polyoxyethylenated materials, in addition to those in the specific examples, which may be used in the present synergistic compositions include the following: sucrose dipalmitate, sorbitan caprate, sorbitan distearate, sorbitan dipelargonate, oleyl alcohol, nonyl alcohol, tertiary hexadecyl mercaptan, dinonyl phenol, hexyl phenol, and nonyl cyclohexanol.

A preferred hair conditioning agent is a moacylated sorbitan, wherein the acyl group contains 5 to 18 carbon atoms, and preferably 10 to 18. Those containing acyls of fewer carbon atoms are too soluble for the present purposes, and those containing more than 18 carbon atoms tend to be so insoluble as to give turbid or unattractive mixtures. Other conditioners which may be used include fatty acid esters of glycerol or the glycols, lanolin or lecithin. Generally, the amount of conditioning agent is in the range of about 0.5 to 2.0% based on the weight of the total mixture.

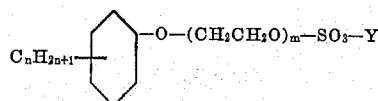
From the above discussion it will be apparent that we have developed a group of compositions which make excellent shampoos, and in which the foam produced by a combination of alkyl phenoxy-polyoxyethylene alkali metal sulfate modified ampholytes, in a molar ratio of unmodified ampholyte (and aminoamide if any) to modifier of from about 0.95:1 to 1.2:1, and certain nonionic surfactants having a cloud point of at least about 85° C., determined at 2% concentration in distilled water, is unexpectedly greater than the foam produced by either of these components alone.

This application is a continuation-in-part of Serial No. 343,516, filed March 19, 1953 (now abandoned); Serial No. 414,874, filed March 8, 1954; Serial No. 414,876, filed March 8, 1954 (now abandoned); Serial No. 489,798, filed February 21, 1955 (now abandoned); Serial No. 489,799, filed February 21, 1955 (now abandoned); and Serial No. 551,724, filed December 8, 1955.

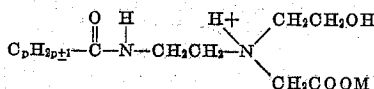
It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof; and, therefore, it is not intended to be limited except as indicated in the appended claims.

We claim:

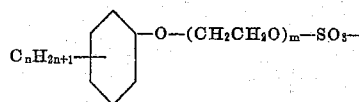
1. A substantially neutral aqueous composition consisting essentially of (I) a compound which is represented by the formula:



where Y is a member of the group which consists of the ampholyte



and a mixture of that compound ampholyte with the corresponding aminoamide in which the  $\text{CH}_2\text{COOM}$  is replaced by H, the molar amount of aminoamide in all cases being less than the molar amount of that ampholyte, and the ratio of Y to



being not over 1.2 to 1 and not less than 19 to 20, M is a member of the group consisting of alkali metals, triethanol ammonium, mixtures of an alkali metal with hydrogen, and mixtures of triethanol ammonium with hydrogen, n is a whole number from 0 to 9, inclusive, m is a number from 1 to 23, inclusive, and p is a whole number from 11 to 17, inclusive, and (II) a water soluble nonionic surface active agent comprising a polyoxy-

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ethylenated derivative of a hydrophobic base, said derivative being a member of the group consisting of:

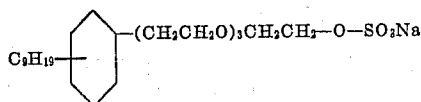
- (a) 9-18 carbon atom fatty acid monoesters and diesters of aliphatic polyhydric alcohols, the polyhydric alcohols containing at least 3 hydroxyls, reacted with 10 to 98 moles of ethylene oxide and having a cloud point of at least 85° C. determined at 2% concentration in distilled water, and
- (b) a member of the group consisting of the reaction products of 9-18 carbon atom alcohols, acids, amides and mercaptans, 12-24 carbon atom alkyl phenols and alkyl cyclohexanols, and polypropylene glycols having a molecular weight of about 800-2500, with 20 to 103 moles of ethylene oxide, said reaction products having a cloud point of at least 100° C. determined at 2% concentration in distilled water.

components (II) and (I) being present in a ratio of 2-600 parts of (II) per 100 parts of (I).

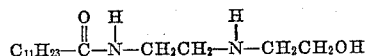
2. A composition of claim 1, wherein  $n$  is 8 to 9, inclusive,  $m$  is 3 to 5, inclusive,  $C_pH_{2p+1}$  is  $C_{11}H_{23}$ .

3. A composition of claim 2 containing the reaction product of sorbitan monolaurate and 10 to 98 moles of ethylene oxide, and having a cloud point of at least 85° C. determined at 2% concentration in distilled water.

4. A composition of claim 1, in which the component (I) comprises the neutralized reaction product of substantially equal molar quantities of

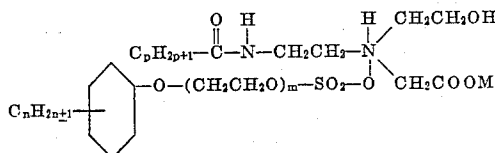


and the reaction product of



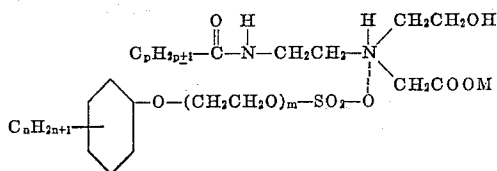
sodium chloracetate and sodium hydroxide.

5. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of

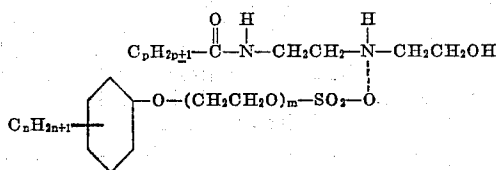


wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of sorbitan monolaurate containing about 10 to 98 oxyethylene groups and having a cloud point of at least about 85° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

6. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of a mixture



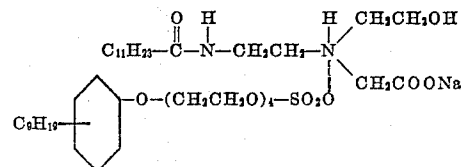
and



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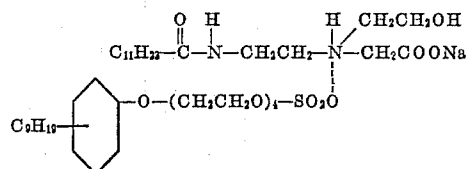
wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of sorbitan monolaurate containing about 10 to 98 oxyethylene groups and having a cloud point of at least about 85° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

7. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of

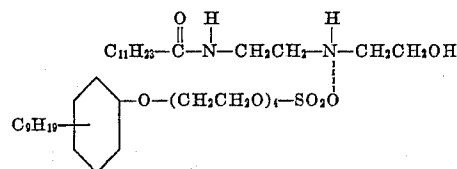


and (2) a polyoxyethylene derivative of sorbitan monolaurate containing about 10 to 98 oxyethylene groups and having a cloud point of at least about 85° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

8. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of a mixture of

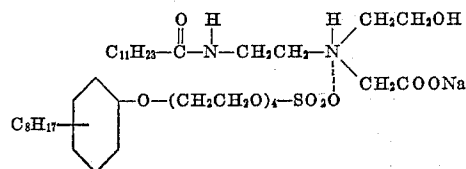


and



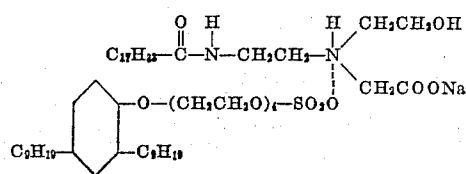
laureate containing about 10 to 98 oxyethylene groups and having a cloud point of at least about 85° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

9. A substantially neutral aqueous composition consisting essentially of (1)



and (2) a polyoxyethylene derivative of sorbitan monolaurate containing about 10 to 98 oxyethylene groups and having a cloud point of at least about 85° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

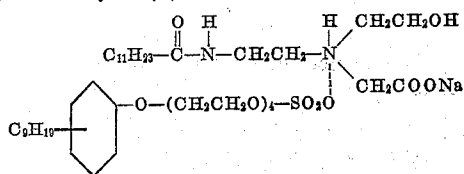
10. A substantially neutral aqueous composition consisting essentially of (1)



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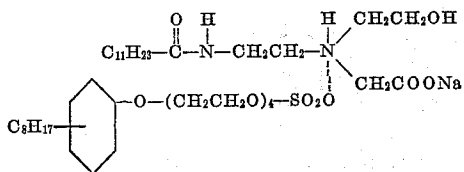
and (2) a polyoxyethylene derivative of sorbitan mono-laureate containing about 10 to 98 oxyethylene groups and having a cloud point of at least about 85° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

11. A substantially neutral aqueous composition consisting essentially of (1)



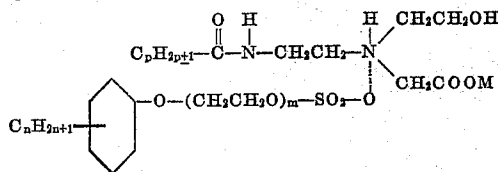
and (2) the reaction product of lauryl alcohol and 23 moles of ethylene oxide, having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

12. A substantially neutral aqueous composition consisting essentially of (1)



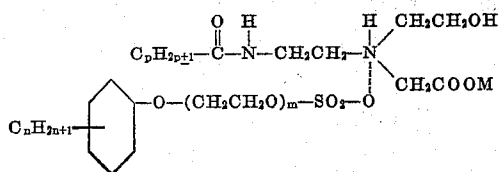
and (2) the reaction product of lauryl alcohol and 23 moles of ethylene oxide, having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

13. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of

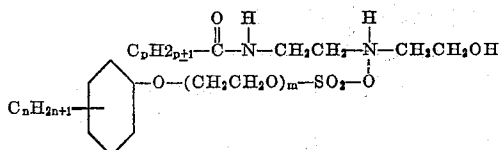


wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of 9-18 carbon atom fatty monoamides containing 20 to 50 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

14. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of a mixture of



and

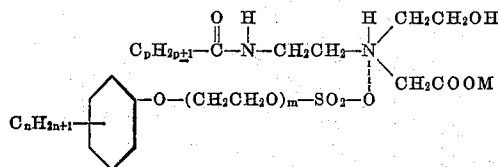


wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and

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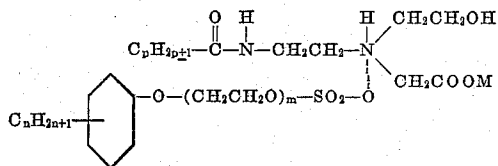
(2) a polyoxyethylene derivative of 9-18 carbon atom fatty monoamides containing 20 to 50 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

15. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of

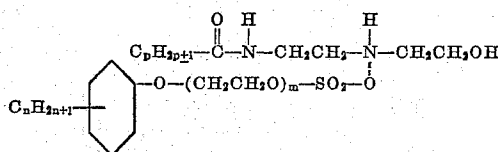


wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of 9-18 carbon atom fatty monoamides containing 20 to 50 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

16. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of a mixture of

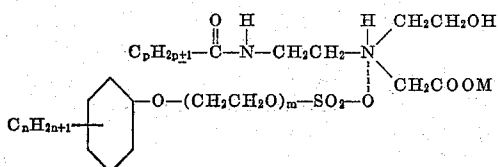


and



wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of 9-18 carbon atom fatty monoamides containing 20 to 50 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

17. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of

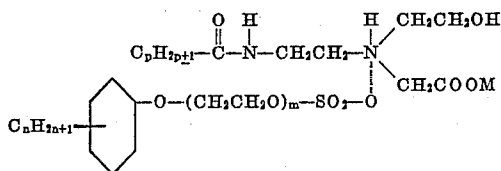


wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of 9-18 carbon atom aliphatic mercaptans containing about 20 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

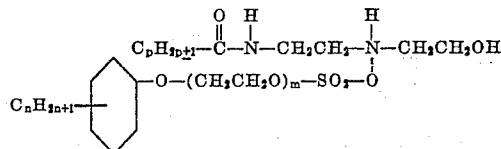
18. A substantially neutral aqueous composition con-

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sisting essentially of (1) a detergent which consists of a mixture of

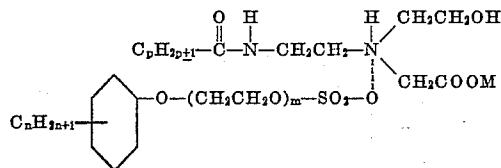


and



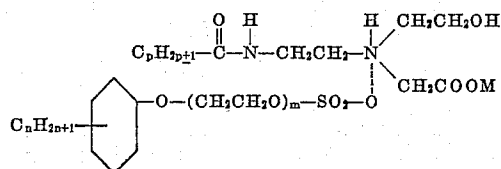
wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of 9-18 carbon atom aliphatic mercaptans containing about 20 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

19. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of

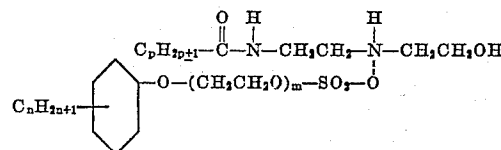


wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of a polypropylene glycol of a molecular weight of about 800 to 2500 containing 20 to 160 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

20. A substantially neutral aqueous composition consisting essentially of (1) a detergent which consists of a mixture of



and

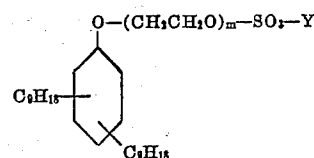


wherein  $n$  is a whole number from 0 to 9, inclusive,  $m$  is a number from 1 to 23, inclusive,  $p$  is a whole number from 11 to 17, inclusive, and  $M$  is an alkali metal, and (2) a polyoxyethylene derivative of a polypropylene glycol of a molecular weight of about 800 to 2500 containing 20 to 160 moles of ethylene oxide and having a cloud point of at least about 100° C., determined at 2% concentration in distilled water, components (2) and (1) being present in a ratio of 2-600 parts of (2) per 100 parts of (1).

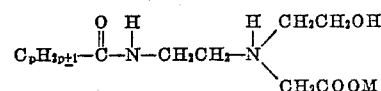
21. A substantially neutral aqueous composition con-

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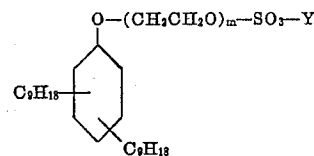
sisting essentially of (I) a compound which is represented by the formula:



10 where  $Y$  is a member of the group which consists of the ampholyte



and a mixture of that ampholyte with the corresponding aminoamide in which the  $\text{CH}_2\text{COOM}$  is replaced by  $\text{H}$ , the molar amount of aminoamide in all cases being less than the molar amount of that ampholyte, and the ratio of  $Y$  to



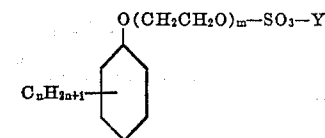
being not over 1.2 to 1 and not less than 19 to 20,  $M$  is a member of the group consisting of alkali metals, triethanol ammonium, mixtures of an alkali metal with hydrogen, and mixtures of triethanol ammonium with hydrogen,  $m$  is a number from 1 to 23, inclusive, and  $p$  is a whole number from 11 to 17, inclusive, and (II) a water soluble nonionic surface active agent comprising a polyoxyethylenated derivative of a hydrophobic base, said derivative being a member of the group consisting of:

(a) 9-18 carbon atom fatty acid monoesters and diesters of aliphatic polyhydric alcohols, the polyhydric alcohols containing at least 3 hydroxyls, reacted with 10 to 98 moles of ethylene oxide and having a cloud point of at least 85° C. determined at 2% concentration in distilled water, and

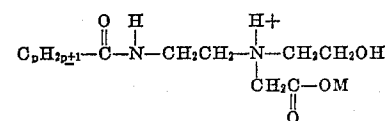
(b) a member of the group consisting of the reaction products of 9-18 carbon atom alcohols, acids, amides and mercaptans, 12-24 carbon atom alkyl phenols and alkyl cyclohexanols, and polypropylene glycols having a molecular weight of about 800-2500, with 20 to 103 moles of ethylene oxide, said reaction products having a cloud point of at least 100° C. determined at 2% concentration in distilled water,

components (II) and (I) being present in a ratio of 2-600 parts of (II) per 100 parts of (I).

22. A detergent composition consisting essentially of: (1) a compound which is represented by the formula:



where  $Y$  is:

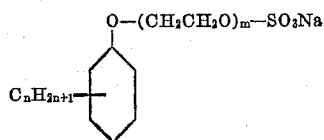


$n$  is 8 to 9,  $m$  is a whole number from 3 to 5, inclusive, and  $p$  is 11, and

(2) a water soluble polyoxyethylenated sorbitan ester of a fatty acid, said ester containing about 20 oxyethylene groups, and  $M$  being a member of the group consisting

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of hydrogen, alkali metals, and ammonium and substituted ammonium ions, the

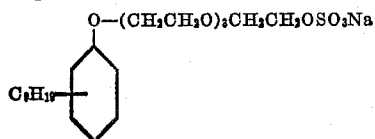


and Y being present in substantially equal molar amounts, and compounds (1) and (2) being present in a ratio of 100 to 2-600.

23. The composition of claim 22 containing sorbitan monolaurate.

24. The neutral composition of claim 22, in which the component

(1) comprises the reaction product of substantially equal molar quantities of

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and the reaction product of an aminoamide



5 at least an equal molar amount of sodium chloracetate, and sodium hydroxide.

#### References Cited in the file of this patent

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|    |           |            |               |
|----|-----------|------------|---------------|
| 10 | 2,619,467 | Isbell     | Nov. 25, 1952 |
|    | 2,781,376 | Mannheimer | Feb. 12, 1957 |

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15 Schwartz and Perry: Surface Active Agents, Interscience Publishers Inc., N.Y. (1949), pp. 218 and 219.

# UNITED STATES PATENT OFFICE

## CERTIFICATION OF CORRECTION

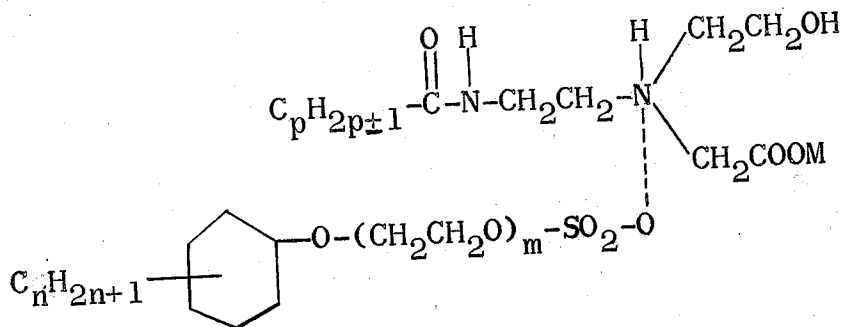
Patent No. 2,999,069

September 5, 1961

Joseph N. Masci et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 22, after "reaction" insert -- product --; column 2, line 66, for "8.9" read -- 8.0 --; column 10, line 8, for "moacylated" read -- monacylated --; line 57, strike out "compound"; column 11, lines 41 to 48, the formula should appear as shown below instead of as in the patent:



column 12, line 47, strike out "and (2) a polyoxyethylene derivative of sorbitan mono-" and insert the same before "laureate" in line 45, same column 12; column 14, line 74, for "1-00" read -- 100 --.

Signed and sealed this 3rd day of April 1962.

(SEAL)  
Attest:

ERNEST W. SWIDER  
Attesting Officer

DAVID L. LADD  
Commissioner of Patents