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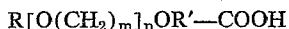
SHAMPOO COMPOSITION

Hugo Martin de Jong, Bodegraven, Jacobus Adrianus Brenkman, Gouda, and Johan Gerhard Aalbers, Bodegraven, Netherlands, assignors to N.V. Chemische Fabriek "Andrélon," Bodegraven, Netherlands
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This invention relates to a novel type of shampoo. In recent years formerly prevailing alkaline soap constituents in shampoos have been superseded completely by synthetic detergents (see for instance "Neue Erkenntnisse der Haarforschung," by Hirsch, published in Bern, 1955, page 142). Shampoos containing the commonly used synthetic detergents such as synthetic sulfates and sulfonates suffer from the drawback that they exert an excessive defatting action on the hair treated with the shampoo, whereby too many nutrient substances are withdrawn from the hair. On the other hand, hair is more easily washed with these detergents than with soaps, because use of the latter requires that they be removed as thoroughly as possible from the hair by a subsequent prolonged rinsing treatment with water, which may still leave behind an undesirable degree of alkalinity on the scalp.

The above mentioned drawback of a strong defatting action of the synthetic sulfate and sulfonate detergents which is mentioned, for instance, in "Das Haar und seine Krankheiten," Cologne, 1954, pages 198 and 199, leads to a further drawback of leaving the shampooed hair rigid and, consequently, difficult to comb. Furthermore, hair thus treated has a tendency to show electrostatic charges. The art has, therefore, tried to find other detergent compositions suitable for shampoos. In "Textilhilfsmittel und Waschrohstoffe" by Lindner (1954), pages 324-327, mixtures of synthetic detergents with soaps are described which seem, however, to have little value as shampoos. For instance, when such mixtures are brought into contact with calcium ions in the water, lime soaps are formed which must, in turn, be dispersed by the synthetic detergent. Consequently, not only is a part of the soap lost by binding to calcium, when the ions of the latter are present, but also part of the synthetic detergent is consumed as a dispersing agent for the lime soap formed and thereby lost to the detergent action of the shampoo. It must be borne in mind that in washing hair, even a professional hairdresser normally uses tap water.

It is, therefore, an object of the present invention to provide for a novel shampoo consisting of synthetic detergents and of such properties that the shampooed hair is not rigid and, therefore, can be easily combed, is free from strong electrostatic charges and is defatted to a lesser degree than with the known shampoos. This object is attained and the drawbacks of the known shampoos avoided by a new shampooing composition which contains as the detergent component therein a mixture of (A) one or more salts between a monovalent inorganic or organic base and at least one organic acid having the general formula:



in which R is an alkyl or cycloalkyl radical containing at least 8 and up to 18 carbon atoms or an aryl or alkylaryl radical or a mixture of the aforesaid radicals and wherein R' is an alkylene group containing maximally 3 carbon atoms, m is one of the integers 2 or 3, and n is one of the integers 1 to 10, and (B) at least one compound having the general formula:



in which R and m have the same definition as in general

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Formula A, while n' is 0 to 10 and may be different from n, and wherein X is a sulfate or a sulfonate group.

We have found by extensive experiments that certain detergents of the alkyl polyoxyalkylene carboxylic type, in which the alkyl group contains more than 8 carbon atoms, are very suitable as shampoo constituents due to the fact that they exhibit a more limited defatting action than the hitherto used synthetic detergents of the sulfate and sulfonate type.

These alkyl polyoxyalkylene carboxylic acids can be produced, for instance, as described in U.S. Patent 2,183,853, by reacting a high molecular alcohol with a polyoxyalkylene carboxylic acid or by condensing higher alcohols with alkylene oxides and reacting the resulting intermediate product with a halo-carboxylic acid or by oxidizing its terminal alcoholic group to a carboxylic group. It has been stated in the art that these compounds may be used as detergents generally in the form of their alkali metal salts.

However, this group of detergents has never been used as shampoo constituents. One reason for this fact may be seen in the relatively high price of their production; furthermore, carboxylic acid derivatives generally possess a less pronounced foaming power than the corresponding sulfonates and sulfates while an abundant foam formation is a primary requirement in the use of a detergent as a shampoo constituent as compared with other uses, for instance, industrial uses.

We have now found by further extended research that excellent shampoos of fully satisfactory foaming properties are obtained by incorporating in the shampoo as the active detergent agent a mixture of the two components (A) and (B) described hereinbefore, of which components one consists of the above mentioned salt or salts of one or more alkyl polyoxyethylene or polyoxypropylene carboxylic acids of the type described, while the other component consists of a sulfate or sulfonate.

In the first of the above stated general formulas, i.e., in the carboxylic acid component (A), m is preferably the integer 2, i.e. the carboxylic acid is preferably a polyoxyethylene carboxylic acid. The optimum value of n depends on the size of radical R. The larger R, the higher should be the value of n. If, for instance, m equals 2, R represents the group C₁₂H₂₅ and R' is CH₂, the value of n varies preferably between 2 and 4. In practice, it is convenient to use mixtures of compounds having different values of n as starting materials so that the mixed product obtained by epoxyalkylation does not have to be separated but has an average value of n falling broadly within the range from 2 to 4.

The monovalent cation in the salt or salts formed with the aforesaid carboxylic acid or acids can be any suitable monovalent inorganic or organic bases. In particular, sodium and potassium ions and organic ammonium derivatives, such as, for instance, isopropanolamine, have been found to be perfectly suitable.

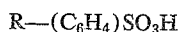
In several of the examples to be given hereinafter, the isopropanolamine salts of carboxylic acids having a formula:



isopropanolamine are used in the form of 8.8% aqueous solutions and are referred to in these examples, according to the number of oxygen atoms contained per molecule other than that of the carboxyl group as "(n+1) EO acids," i.e., if n is 1, the acid is referred to as "2 EO acid," if n is 2, the acid is referred to as "3 EO acid," etc. If the component consists of a mixture of acids, n may be a fraction such as, for instance, 3.7 or the like.

Apart from the aforementioned alkyl compounds, the component B may also consist of an aryl or an alkylaryl sulfonic acid salt, or a mixture of several such salts with

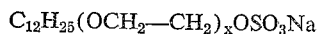
each other, or a mixture of aryl or alkylaryl sulfonic acid salts with alkylsulfonic acid salts. In a number of examples given hereinafter, we have used the triethylamine salt of an alkyl benzene sulfonic acid of the general formula:



in which R is C_6H_{17} .

This salt will be referred to in the examples as ABS for the sake of brevity.

The second component in the detergent composition, according to the invention, constituting the detergent agent in the novel shampoo which is the sulfate or sulfonate component, according to the general Formula B may vary greatly in its structure within the range set forth by that formula. Thus, a mixture of sodium sulfate derivatives having the formula:



in which x has an average value in the range of from 2 to 3 has led to most satisfactory results. The 8.8% solution of this mixture in water was used for carrying out a number of examples to be given hereinafter and shall be referred to therein as "EO 20" for the sake of brevity.

In the case that R is an alkylaryl group, the remainder of the molecule of the carboxylic sulfonic or sulfuric acid according to the invention is linked to the aryl part of R, and not to the alkyl part. Preferably the linkage of the remaining part of the molecule to the aryl part, for instance, $-C_6H_4-$, is in para-position to the alkyl part of R.

The minimum concentration of the detergent mixture when under an aqueous solution depends, of course, on the desired cleaning action. The desired amount of the detergent mixture should not be contained in a greater amount of aqueous mixture than can be applied to the head in a first and second washing. For practical purposes the concentration should at least be about 1%. The upper limit of the concentration, for practical purposes, is in the first place dependent on the solubility of the detergents. In some cases the solubility is quite high. For example, the isopropanolamine salt of lauryl 4 EO-acid gives at room temperature clear aqueous solutions in concentrations up to 30%, although the viscosity increases enormously. However, the maximum concentration is not absolutely limited by the solubility. It is indeed possible to prepare pasty shampoos containing the synergistic mixture according to the invention, which shampoos can be diluted by the user.

The detergent mixture to be introduced as the detergent agent into a novel shampoo composition can be obtained, according to the method of our invention, by treating an alcohol containing at least 8 carbon atoms with alkylene oxide, partially converting the product, either in bulk or into separate portions, into a corresponding carboxylic acid and partially into the corresponding sulfuric or sulfonic acid; preparing the desired salts of both types of acids and admixing the two resulting salts in a determined ratio.

We have found that this mixing ratio of the carboxylic acid salt component with the sulfate or sulfonic component may vary within relatively wide limits, while it must always be understood that a mixture must be obtained which is free from excessive defatting action, while at the same time showing excellent foaming properties and leaving the shampooed hair smooth and easily to be combed and substantially free from a tendency to accumulate electrostatic charges. Keeping these points in mind, we have found that for best results the ratio between the two components (A) and (B) may vary between 30 to 70% by weight of the carboxylic acid salt component to 70 to 30% by weight of the sulfate or sulfonate component.

In judging the advantageous features of a shampoo

containing the detergent mixture according to our invention, the following factors must be considered:

(1) The amount of shampoo required for obtaining a sufficient amount of foam on the scalp of a person treated therewith depends both on the state of the hair of that person and on the nature of the shampoo. The difference between the quantities of two different shampoos necessary to form a sufficient amount of foam on the scalp of the same person may amount to as much as 20% by weight. We have found that the mixture of components A and B shows a higher degree of foam formation than the average of the components when applied alone so that a synergistic effect must be assumed in using the mixture.

(2) The stability of the foam formed by applying the new shampoo. We have found that the stability of the foam is greater when using carboxylic acid derivatives alone than in the case of sulfates and sulfonates used alone, while a mixture containing a ratio of about 50:50 of both components, yields a foam which is about as stable as that of the carboxylic acid derivative, while the shampoo shows the other advantages not obtained with the carboxylic acid derivative alone. Again, this indicates a synergistic effect of the mixture.

(3) The ease with which the freshly shampooed hair may be combed while still in wet condition. Washing with the conventionally used sulfates and sulfonates alone leaves the hair rigid and difficult to comb, which drawback is assumed to be due to an excessive defatting action of the detergent. When using the carboxylic acid derivative alone, the hair can be easily combed and shows practically no rigidity while, after shampooing with a mixture according to our invention, hardly any rigidity can be perceived either.

(4) Accumulation of electrostatic charges on the hair after drying. After washing with sulfates or sulfonates, the treated hair shows a very strong tendency to become charged electrostatically, while such charges are practically absent when using the carboxylic acid derivatives alone and the tendency to accumulate electrostatic charges is only very slight after shampooing with the mixture according to our invention.

(5) The amount of dust gathered on the comb when combing the hair after shampooing and drying. When sulfates and sulfonates are used as in the conventional shampoos, the amount of dust formed and subsequently gathered on a comb is practically negligible. Use of carboxylic acid derivatives alone, however, leads to a much greater undesirable dust accumulation on the hair. On the contrary, hair shampooed with a mixture according to the invention, shows only a very slight accumulation of dust which may only be detected by very close examination, for instance, under a microscope, and is practically as negligible as that accumulated by the treatment with sulfates or sulfonates. Again, in this regard, one may speak of a synergistic effect of the mixture containing both sulfates or sulfonates and carboxylic acid derivatives.

Our invention will be further illustrated with the aid of comparative examples in which the following procedure was followed:

A number of persons who had pledged not to have their hair washed between two successive experiments, were subjected at determined intervals to test shampooings. The interval between two successive shampooings amounted to either 18 or 28 days, as stated in the examples. The shampooings were carried out by a professional hairdresser and part of the experiments was carried out according to the so-called "half-head" procedure, in which the hair on the head was parted in a right and a left half and each half treated differently. All shampooings in the Examples I-XXXIII were carried out with a shampoo concentrate of 8.8% by weight in aqueous solution. Since the amounts of shampoo required differ from person to person, the specific amount required by each

person to obtain a satisfactory foam formation was determined by a preliminary test prior to treating a test person with a shampoo containing only one of the two components of the mixture according to the invention. When carrying out tests with this mixture, the sum of the respective amounts required for the half head tests of the separate components was used.

In certain of the examples the shampooing treatment was divided into a first washing, in which the hair was cleansed thoroughly, while foam formation was still limited or practically non-existent and a subsequent second washing in which abundant foam formation occurred. The first washing required about one-third of the total amount of shampoo to be used in the particular experiment. In the remaining experiments, a single shampooing treatment was applied. The results of the shampooing tests were judged independently by two experts, and in those cases in which there was a difference of opinion between them, the decision was made by the hairdresser who had carried out the shampooing.

About 18-20 days prior to each pair of experiments, the tested persons had received a shampooing with EO-20 as defined above, so as to establish expert starting conditions for all.

EXAMPLES I-VII

Mutual Comparison of EO-20, 2 EO-Acid and the Mixtures thereof

EXAMPLE I.—(TEST PERSON A)

First experiment:

Left—12 cc. 2 EO-acid.

Result—Amplly sufficient formation of foam, which is very stable; the hair is easily combed in wet condition and it possesses no static charge in dry condition; some white dust, however, remains in the comb.

Right—10 cc. EO 20.

Result—Sufficient foam, which is somewhat limp.

Wet—the hair is difficult to comb and brittle and it tangles.

Dry—Large static effect, but a much smaller amount of white dust in the comb.

Second experiment (18 days after first):

The whole head was washed with a mixture of 12 cc. 2 EO-acid and 10 cc. EO 20.

Result—Amplly sufficient foam, exceedingly stable; may be increased by the addition of some cc. water; after a while this may be repeated until 5 to 6 times before the amount of foam decreases.

Wet—The hair is easily combed, feels soft and has not strongly been defatted.

Dry—The hair exhibits a slight static charge and gives little dust in the comb.

EXAMPLE II.—(TEST PERSON B)

First experiment:

Left—9 cc. 2 EO-acid.

Result—Foams but not abundantly; the hair is rather soft.

Wet—Is easily combed.

Dry—No static effect, some white dust.

Right—9 cc. EO 20.

Result—More foam than on the left side, but the foam is less stable; the hair feels rigid and is difficult to comb in wet condition.

Dry—Strong electrostatic effect; some white dust.

Second experiment (28 days after first):

The whole head is washed with 9 cc. 2 EO-acid and 9 cc. EO 20.

Result—The dose appeared to be too low; 2 cc. 2 EO-acid and 2 cc. EO 20 were therefore added. An abundant amount of foam is now formed which may yet be increased by the addition of some water.

Wet—The hair is easily combed.

Dry—The hair exhibits substantially no static charge and gives some white dust in the comb.

Remark—In view of the fact that this experiment was carried out 28 days instead of 18 days after the first, it is clear that a small increase of the dose should be made.

EXAMPLE III.—(TEST PERSON D)

10 First experiment:

Left—11 cc. EO 20.

Result—The dose is too small, yields too little foam.

Wet—The hair is rigid.

Dry—Static charge, some dust.

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Right—14 cc. 2 EO-acid.

Result—Solid foam, which may be increased with water.

Wet—The hair is coarse.

Dry—No static effect though dust.

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Second experiment (28 days after first):

The whole head is washed with 11 cc. EO 20 and 14 cc. 2 EO-acid. This quantity appeared not to be sufficient, yet 2 cc. EO 20 and 2 cc. 2 EO-acid were therefore added. An abundant amount of foam is now formed.

Wet—The hair feels soft and is easily combed.

Dry—Very slight amount of dust, substantially no static charge.

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Remark—The increased dose is in this case again to be ascribed to the fact that the second experiment was carried out 28 days instead of 18 days after the first experiment.

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EXAMPLE IV.—(TEST PERSON E)

35 First experiment:

Left—20 cc. 2 EO acid.

Result—Sufficient amount of foam.

Wet—The hair is soft and not strongly defatted.

Dry—No static charge; almost no white dust.

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Right—16 cc. EO 20.

Result—A sufficient amount of foam.

Wet—Feels somewhat more rigid, tangles less than on the left half.

Dry—Static charge; almost no white dust.

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Second experiment (18 days after first):

20 cc. 2 EO-acid and 16 cc. EO 20 on the whole head. This amount is amplly sufficient for the test person.

Wet—The hair is easily combed.

Dry—Yields a very slight amount of dust and possesses substantially no charge.

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EXAMPLE V.—(TEST PERSON G)

First experiment:

Left—First washing: 5 cc. 2 EO-acid; foams a little; second washing: 10 cc. 2 EO-acid; forms foam but somewhat limp; upon the addition of water more foam is formed.

Wet—Easily combed.

Dry—The hair exhibits a slight static charge and yields white dust.

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Right—First washing: 4 cc. EO 20; no foam; second washing: 8 cc. EO 20; more foam than on the left half but more loose; the foam disappears upon the addition of water.

Wet—The hair feels rigid.

Dry—A strong static charge; some dust.

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Second experiment (18 days after first):

First washing—The whole head is treated in the first washing with 5 cc. 2 EO-acid and 4 cc. EO 20; foams a little.

Second washing—10 cc. 2 EO-acid and 8 cc. EO 20; foams but it could be better; the formation of foam may be increased somewhat by the addition of water.

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Wet—Is easily combed.

Dry—No white dust; slight static charge.

EXAMPLE VI.—(TEST PERSON H)

First experiment:

Left—First washing: 4 cc. EO 20; foams a little; second washing: 8 cc. EO 20; foaming rather sufficient, but feels rigid.

Dry—Large static effect.

Right—First washing: 5 cc. 2 EO-acid; foams a little; second washing: 10 cc. 2 EO-acid; foams very sufficiently but feels slightly fatty when combing.

Dry—No static effect; some dust.

Second experiment (18 days after first):

First washing—The whole head is washed with 4 cc. EO 20 and 5 cc. 2 EO-acid; foams a little.

Second washing—8 cc. EO 20 and 10 cc. 2 EO-acid; foams abundantly; beautiful, white and solid foam; the hair is very easily combed.

Dry—A slight amount of white dust; low electrostatic charge.

EXAMPLE VII.—(TEST PERSON I)

First experiment:

Left—11 cc. 2 EO-acid; foams sufficiently; the hair has a solid feel; no electrostatic charge; some dust.

Right—8½ cc. EO 20; foams sufficiently; the hair becomes more rigid.

Dry—A smaller amount of dust, but static charge.

Second experiment (18 days after first):

The whole head is washed with 11 cc. 2 EO-acid and 8½ cc. EO 20.

Result—Foams very abundantly; may be increased several times with water.

Wet—Is easily combed.

Dry—No dust, slight static charge.

It appears from the foregoing Examples I–VII, that as regards the five above mentioned properties, the mixture according to the invention is more satisfying than the individual components so that it is better suited as a shampoo.

The following examples illustrate by comparison the foaming properties of 2 EO-acid, used singly, with those of some other EO acids, also used singly, and the superior effect of mixtures of 3 EO-acid with some sulfates and sulfonates as compared with the components when used singly.

EXAMPLES VIII–XIV

(A) Comparison of 2 EO-Acid With 3 EO-Acid

EXAMPLE VIII.—(TEST PERSON G)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
2 EO-acid.	3 EO-acid.
First washing—5 cc. foams a little.	5 cc. foams better than on the left half.
Second washing — 10 cc. foams, but not abundantly.	10 cc. foams more than on the left half; foam is more stable.

EXAMPLE IX.—(TEST PERSON D)

15 cc. 2 EO-acid.	3 EO-acid 15 cc. in total.
Amply sufficient foam which feels soft.	At the outset less and later on more foam than on the left half; feels very soft.

EXAMPLE X.—(TEST PERSON F)

13 cc. 3 EO-acid in total.	13 cc. 2 EO-acid in total.
Foams sufficiently; feels very soft; exhibits great stability.	Foams somewhat more foam than on the left half and reaches sooner the maximum quantity.

EXAMPLE XI.—(TEST PERSON A)

13 cc. 2 EO-acid.	13 cc. 3 EO-acid.
Amply sufficient foam that is formed very quickly.	Much more foam than on the left half; feels softer.

EXAMPLE XII.—(TEST PERSON J)

12 cc. 2 EO-acid.	12 cc. 3 EO-acid.
Yields a sufficient amount of stable foam.	Yields more foam than on the left half and has a somewhat stronger defatting effect.

EXAMPLE XIII.—(TEST PERSON K)

First washing—5 cc. 3 EO-acid; foams well.	5 cc. 2 EO-acid; foams well.
Second washing—10 cc. 3 EO-acid; amply sufficient solid foam.	10 cc. 2 EO-acid; more foam than on the left half, but somewhat more loose.

EXAMPLE XIV.—(TEST PERSON H)

12 cc. 3 EO-acid.	12 cc. 2 EO-acid.
Sufficient amount of solid foam.	Very abundant amount of solid foam.

From the results of Examples VIII–XIV, it is apparent that the amount of foam formed by 2 EO-acid and 3 EO-acid is substantially the same. The maximum amount of foam is formed sooner with 2 EO-acid than with 3 EO-acid. The stability of the foam, however, is greater with 3 EO-acid than with 2 EO-acid. The foam feels more fatty and is more rigid.

EXAMPLES XV–XVII

(B) Comparison of 2 EO-Acid With 4 EO-acid

EXAMPLE XV.—(TEST PERSON H)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
15 cc. 2 EO-acid.	15 cc. 4 EO-acid.
Foams very well and the maximum amount is formed very quickly.	Foams well but less quickly; more foam is formed upon the addition of water than on the left half.

EXAMPLE XVI.—(TEST PERSON L)

15 cc. 4 EO-acid.	15 cc. 2 EO-acid.
Foams, but not strongly.	More than the sufficient amount of foam which is formed quickly.

EXAMPLE XVII.—(TEST PERSON C)

11 cc. 2 EO-acid.	11 cc. 4 EO-acid.
Foams well; is formed quickly and is stable.	Foams well; more foam is formed upon the addition of water.

In view of the above it would appear that the amount of foam with 2 EO-acid is somewhat larger than with 4 EO-acid, whereas the stability of the foam would seem to be somewhat higher with 4 EO-acid than with 2 EO-acid.

EXAMPLES XVIII–XX

(C) Comparison of 2 EO-Acid With 5 EO-Acid

EXAMPLE XVIII.—(TEST PERSON G)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
13 cc. 2 EO-acid.	13 cc. 5 EO-acid.
Foams, but not abundantly.	Foams less than on the left, half but may be strongly increased upon the addition of water.

EXAMPLE XIX.—(TEST PERSON I)

11 cc. 2 EO-acid.	11 cc. 5 EO-acid.
Foams well and is formed very quickly.	Foams well; yields more foam than on the left half of the head upon the addition of extra water.

EXAMPLE XX.—(TEST PERSON J)

11 cc. 5 EO-acid.	11 cc. 2 EO-acid.
Foams well; foam is formed slowly and is somewhat more limp than on the right half.	Foam is formed quickly and is more abundant than on the left half.

From the above data it appears that as regards the amount of foam and the stability thereof 2 EO-acid and 5 EO-acid are practically equivalent.

EXAMPLES XXI–XXVII

(D) Comparison of 3 EO-Acid With Mixtures of 3 EO-Acid and EO 20 According to the Invention

EXAMPLE XXI.—(TEST PERSON B)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
9 cc. 3 EO-acid.	6 cc. 3 EO-acid + 3 cc. EO 20.
Foams, but not much. The amount of foam may be increased somewhat with water.	Foams quickly and yields more foams too; which may be strongly increased by the addition of water.
Wet—Is easily combed.	A characteristic difference is present with respect to the left half.
Dry—White dust in the comb almost no electrostatic charge.	Wet—Is easily combed.
	Dry—Much smaller amount of white dust, slight charge.

EXAMPLE XXII.—(TEST PERSON A)

8 cc. 3 EO-acid+3.3 cc. EO 20.
A sufficient amount of foam, which may be increased with water.
Wet—Is easily combed.
Dry—Slight charge and a slight amount of white dust.

12 cc. 3 EO-acid.
The same amount of foam as on the left half, which may be increased with water but is more limp.
Wet—Is easily combed.
Dry—Somewhat more dust than on the left half, but less than with test person B; slight electrostatic charge.

EXAMPLE XXIII.—(TEST PERSON F)

12 cc. 3 EO-acid.
Foams well, the amount of foam may be increased with water; becomes more abundant and well stable.
Wet—Is easily combed.
Dry—More dust than on the right half, no electrostatic charge.

7 cc. 3 EO-acid+4.2 cc. EO 20.
Yields more quickly a solid foam than on the left half, but becomes somewhat more limp upon the addition of water.
Wet—Is easily combed.
Dry—Some white dust, no electrostatic charge.

EXAMPLE XXIV.—(TEST PERSON C)

11 cc. 3 EO-acid.
Abundant amount of foam; is increased upon the addition of water, but somewhat more limp than on the right half.
Wet—Is easily combed.
Dry—Some white dust, no electrostatic charge.

6 cc. 3 EO-acid+4.1 cc. EO 20
20 is formed more quickly and yields more foam; upon the addition of water foam remains, which is more stable than on the left half.
Wet—Is easily combed.
Dry—Smaller amount of dust than on the left half, some electrostatic charge.

EXAMPLE XXV.—(TEST PERSON H)

12 cc. 3 EO-acid.
Foams, but not abundantly; may be increased with water but becomes somewhat more limp.
Wet—Is easily combed.
Dry—Slight amount of white dust, no electrostatic charge.

8 cc. 3 EO-acid+3.3 cc. EO 20.
Foams somewhat more, and may be increased with water; more foam is formed which is more stable.
Wet—Is easily combed.
Dry—Less dust than on the left half, some electrostatic charge.

EXAMPLE XXVI.—(TEST PERSON M)

18 cc. 3 EO-acid.
Foams well, but foam is formed somewhat later especially if some water is yet added later on; feels soft and is very abundant.
Wet—Is easily combed.
Dry—No white dust; no electrostatic charge.

12 cc. 3 EO-acid+5 cc. EO 20.
Foam is formed quickly and yields a more abundant amount of foam than on the left half; upon the addition of water a very solid stable foam is formed.
Wet—Is easily combed.
Dry—No white dust, slight electrostatic charge.

EXAMPLE XXVII.—(TEST PERSON L)

15 cc. 3 EO-acid.
Foams formed quickly, may be increased with water but not as solid in that case.
Wet—Is easily combed.
Dry—More white dust than on the right half.

10 cc. 3 EO-acid+4.3 cc. of EO 20.
Foams very quickly, is solid and may be increased with water; more stable than on the left half and also much more.
Wet—Is easily combed.
Dry—Clearly less dust than on the left half. No electrostatic charge.

Again, in these Examples XXI-XXVII, the advantages of the mixture with respect to the separate components stated in the introductory part are evident. The mixture yields a larger amount of foam than the components, which is, moreover, somewhat more stable. The hair in wet condition may as easily be combed as upon washing with 3 EO-acid per se, whereas it yields less white dust in dry condition than after the use of 3 EO-acid per se and possesses less or no electrostatic charge. Furthermore, it may be remarked that the combination of 3 EO-acid with EO 20 has even a better effect than the mixture of 2 EO-acid with EO 20.

EXAMPLES XXVIII-XXX

(E) Comparison of the Isopropanolamine Salt of Lauryl Sulfate with Mixtures Thereof With 3 EO-Acid

EXAMPLE XXVIII.—(TEST PERSON P)

5 LEFT HALF OF THE HEAD
13 cc. lauryl sulfate.
Foams well, more foam upon the addition of water, solid foam in a sufficient amount.
10 Dry—Strong electrostatic charge, whole lock lifts, rather large amount of dust.

RIGHT HALF OF THE HEAD
10 cc. lauryl sulfate+3 cc. 3 EO-acid.
Foams coarsely; yields a very abundant amount of solid foam upon the addition of water.
Dry—Very slight electrostatic charge, no dust.

EXAMPLE XXIX.—(TEST PERSON Q)

11 cc. lauryl sulfate.
15 Foams sufficiently; not much better upon the addition of water; limp foam.
Dry—No static charge, much dust.

7 cc. lauryl sulfate+4 cc. 3 EO-acid.
Foams more coarsely than on the left half, is formed better, upon the addition of water a very abundant amount of solid foam.
Dry—No electrostatic charge, no dust.

EXAMPLE XXX.—(TEST PERSON R)

14 cc. lauryl sulfate.
Foams, but not well, does not become better upon the addition of water, limp foam.
25 Dry—No electrostatic charge, some dust.

8 cc. lauryl sulfate+6 cc. 3 EO-acid.
Foam is formed somewhat later, but is more abundant, may be increased somewhat upon the addition of water, limp foam.
Dry—No electrostatic charge, no dust.

The isopropanolamine salt of lauryl sulfate in these Examples XXVIII-XXX, foams little per se and yields when used as a shampoo much dust and sometimes also a strong electrostatic charge. From the foregoing experiments, it appears that a general improvement is obtained by the addition of 3 EO-acid.

EXAMPLES XXXI-XXXIII

(F) Comparison of 3 EO-Acid With Mixtures Thereof With the Triethanolamine Salt of Alkyl Benzene Sulfonic Acid (ABS)

EXAMPLE XXXI.—(TEST PERSON S)

LEFT HALF OF THE HEAD
12 cc. 3 EO-acid+3 cc. ABS.
Foams more coarsely at the outset and yields also more foam; abundant but limp.
45 Dry—Electrostatic charge on the loose locks of hair, slight amount of dust.

RIGHT HALF OF THE HEAD
15 cc. 3 EO-acid.
Foams well immediately, but yields a limp foam; the amount is somewhat sparingly.
Dry—Practically no electrostatic charge, some more dust than on the left half.

EXAMPLE XXXII.—(TEST PERSON T)

50 6 cc. 3 EO-acid+2 cc. ABS.
Foams well, upon the addition of water more foam, which is solid and amply sufficient.
Dry—More dust than on the right half.

8 cc. 3 EO-acid.
Foams well, upon the addition of water a solid and abundant foam is formed, foam is formed somewhat later, but is more than on the left half.
Dry—More static charge than on the left half.

EXAMPLE XXXIII.—(TEST PERSON U)

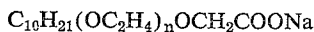
8 cc. 3 EO-acid+5 cc. ABS.
Foams sufficiently, is formed well, increases upon the addition of water, solid foam.
60 Wet:
Dry—No dust.

13 cc. 3 EO-acid.
Foams sufficiently, but is formed later, may be increased with water, solid foam. Somewhat more rigid than on the left half.
Dry—More electrostatic charge than on the left half, no dust.

In the Examples XXXI-XXXIII, the triethanolamine salt of alkyl benzene sulfonic acid per se scarcely foams. The mixtures thereof with the 3 EO-acid, however, do not form less foam than the latter used alone. Furthermore, the calcium resistency of alkyl benzene sulfonate is not so great so that it was to be expected that the hair, after washing with the mixture, would contain more dust than after washing with 3 EO-acid used alone. However, we found that, surprisingly, the accumulation of dust in the hair was less when using the mixture according to our invention. Furthermore, after washing with that mix-

ture, the shampooed hair exhibits a much slighter electrostatic charge than after washing with EO-acid alone. Consequently, in this case a general synergistic effect of the components of the mixture according to our invention is also to be noticed.

The following example illustrates the synergistic effect of a mixture of compounds of the formula

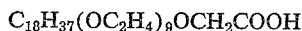


wherein n has an average value of 0.8 (hereinafter called 1.8 EO-acid) with the mono-ethanolamine salt of benzenesulfonic acid (hereinafter called sulfonate). 1.8 EO-acid 14%; concentration of the sulfonate 5%.

EXAMPLE XXXIV.—(TEST PERSON H)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
First experiment: 9.5 cc. 1.8 EO-acid. Foams sufficiently, rather solid foam. Wet—Soft feel. Dry—Very little static charge, virtually no dust.	First experiment: 30 cc. sulfonate. Foams badly, coarse and limp foam. Wet—Hair tangles. Dry—The hair is not clean and has to be washed again.
Second experiment: The whole head is washed with 9.5 cc. 1.8 EO-acid and 30 cc. sulfonate. Amply sufficient and solid foam. Wet—Soft feel. Dry—Virtually no static charge and little dust.	

The following example illustrates the synergistic effect of a mixture of the diethylamine salt of the acid having the formula



(hereinafter called 10 EO-acid) with the monoethanolamine salts of compounds having the formula

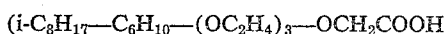


wherein x has an average value of 3.3 (hereinafter called 3.3 EO sulfate). Concentration of the 10 EO-acid 6%; concentration of the 3.3 EO sulfate 15%.

EXAMPLE XXXV.—(TEST PERSON P)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
First experiment: 38 cc. 10 EO-acid. Sufficient, rather coarse foam, can be increased with water. Wet—Soft and not strongly defatted. Dry—Some white dust, no static charge.	First experiment: 11 cc. 3.3 EO sulfate. Solid foam, but less than left side, can be increased with water. Wet—The hair is rigid and is difficultly combed. Dry—No dust, great static charge.
Second experiment: The whole head is washed with 38 cc. 10 EO-acid and 11 cc. 3.3 EO sulfate. Amply sufficient and solid foam, can be increased with water. Wet—The hair is soft and very easily combed. Dry—No dust, nearly no static charge.	

The following example illustrates the synergistic effect of a mixture of the sodium salt of iso-octyl cyclohexyl 4 EO-acid



hereinafter called CH 4 EO acid) used in a concentration of 15% and decylsulfate (sodium salt), concentration 12%.

EXAMPLE XXXVI.—(TEST PERSON V)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
First experiment: 10 cc. CH 4 EO-acid. Solid foam, but is formed slowly, can be increased with water. Wet—The hair is soft and easily combed. Dry—No static charge, little dust.	First experiment: 8 cc. decylsulfate. Rather limp foam, but sufficient. Wet—Hair tangles and is difficultly combed. Dry—Strong static charge, no dust.

Second experiment: The whole head is washed with 10 cc. CH 4 EO-acid and 8 cc. decylsulfate. Sufficient and solid foam.
Wet—Hair is soft and easily combed.
Dry—Virtually no static charge and dust.

The following Examples XXXVII and XXXVIII show a convenient method for preparing a mixture of the invention and the synergistic effect of the so obtained mixture.

EXAMPLE XXXVII

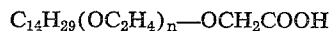
Starting from di-isobutylene and phenol and using borontrifluoride as a catalyst the corresponding alkylphenol is made according to the method disclosed in the C.I.O.S. report item No. 22, file XXVI-2, page 15 ff. The product is ethoxylated with the aid of ethylene oxide in the manner also disclosed in the above mentioned report.

One-half of the thus obtained oxyethylated phenol containing 4 oxyethylene groups is treated in a known manner with metallic sodium and chloroacetic acid to prepare the corresponding carboxylic acid. This acid is hereinafter referred to as alkyl phenol 5 EO-acid and the sodium salt of this acid is used. The other half of the product is treated in a known way with chlorosulfonic acid and the sodium salt of 4 EO-sulfate is made. The two aforesaid end products are compared in the following experiments:

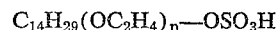
EXAMPLE XXXVIII.—(TEST PERSON J)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
First experiment: 19 cc. of an 8% aqueous solution of alkyl phenol 5 EO-acid. Rather solid foam, amount can be increased with water. Wet—Hair is rather soft. Dry—No static charge, some dust.	First experiment: 20 cc. of an 8% aqueous solution of 4 EO sulfate. Coarse foam, amount cannot be increased with water. Wet—Hair is somewhat rigid. Dry—No dust, some static charge.
Second experiment: The whole head is washed with a mixture of the above mentioned solutions, i.e. 19 cc. 8% alkyl phenol 5 EO acid and 20 cc. 8% 4 EO sulfate. Solid abundant foam having a soft feel. Wet—The hair has a soft feel and does not tangle. Dry—Virtually no static charge and virtually no dust.	

The following example shows the synergistic effect of a mixture of the isopropanolamine salts of acids of the formula



wherein n has an average value of 2.5 (hereinafter called myristyl 3.5 EO acid) with isopropanolamine salts of compounds of the formula



wherein n also has an average value of 2.5 (hereinafter called 2.5 EO sulfate). The myristyl 3.5 EO acid was used in a concentration of 21% and the 2.5 EO sulfate was used in a concentration of 24%.

EXAMPLE XXXIX.—(TEST PERSON T)

LEFT HALF OF THE HEAD	RIGHT HALF OF THE HEAD
First experiment: 7 g. myristyl 3.5 EO-acid, in the form of a paste. Sufficient foam. Wet—Hair is soft. Dry—No static charge, little dust.	First experiment: 5.3 g. 2.5 EO sulfate in the form of a solution. Sufficient foam. Wet—Hair is rigid. Dry—Great static charge, no dust.
Second experiment: The whole head is washed with 7 g. of myristyl 3.5 EO-acid and 5.3 g. of 2.5 EO sulfate. Amply sufficient foam of a very good structure, can be increased with water. Wet—Hair is soft and is very well combed. Dry—Nearly no dust, no static charge.	

EXAMPLE XL

Although shampooing according to the "half-head" procedure, as described in the foregoing examples, enables the expert to observe differences in foaming properties of two shampoos visually in a satisfactory way, quantitative tests were run for comparing the foaming properties of the isopropanolamine salt of lauryl 3 EO-acid, the sodium lauryl 2.2 EO-sulfate and the 50:50 mixture of these compounds. The tests were carried out according to Ross and Miles in substantially the same way and using substantially the same apparatus as described in the standard method of test for foaming properties of surface active agents, A.S.T.M. designation D1173.

In the first test 1 g. of each detergent was dissolved in dehardened water (0° DH). The following table gives

the heights of foam in millimeters at the beginning of the test and 5 minutes thereafter.

	0'	5'
Isopropanolamine salt of lauryl 3 EO-acid.....	140	125
Sodium salt of lauryl 2.2 EO-sulfate.....	140	125
50:50 mixture.....	147	128

In order to compare the foaming properties in the presence of greasy substances a second test was run in which 1 g. of the detergent to be tested was dissolved in a mixture of 950 g. of water, 5 g. of paraffin oil and 45 g. of dioxan. The results are shown in the following table.

	0'	5'	10'	15'
Isopropanolamine salt of lauryl 3 EO-acid....	165	144	141	139
Sodium salt of lauryl 2.2 EO-sulfate.....	160	138	136	133
50:50 mixture.....	166	144	141	138

As appears from the above results the foaming properties of the mixture are as good as or better than the best of the two components.

It should be noted moreover that a normal shampooing takes considerably less than 5 minutes.

It will be understood that while there have been given herein certain specific examples of the practice of this invention, it is not intended thereby to have this invention limited to or circumscribed by the specific details of materials, proportions or conditions herein specified, in view of the fact that this invention may be modified according to individual preference or conditions without necessarily departing from the spirit of this disclosure and the scope of the appended claims.

What we claim is:

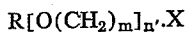
1. A shampoo composition for treatment of hair consisting essentially of a mixture of components (A) and (B), in a weight ratio of 7:3-3:7 said components being as follows—

(A) at least one water soluble salt of a monovalent base with an organic acid of the formula



wherein R is a radical selected from the group consisting of alkyl, alkylaryl and aryl radicals containing from 8 to 20 carbon atoms, and mixtures thereof, *m* is an integer of from 2 to 3; *n* is an integer from 1 to 10 inclusive; and R' is an alkylene radical containing from 1 to 3 carbon atoms; and

(B) at least one water soluble compound of the formula



wherein R and *m* are the same as defined in component

(A), *n'* is a value between 0 and 10 inclusive, and X is a radical selected from the group consisting of —OSO₃P and —SO₃P wherein P is a cation.

2. The shampoo composition of claim 1, wherein component (A) is a monovalent salt of carboxylic acid of the aforesaid formula in which *m*=2.

3. The shampoo composition of claim 1 wherein component (A) is a monovalent salt of carboxylic acid of the aforesaid formula in which R is a dodecyl radical and in which *n* has a value ranging from 2 to 4.

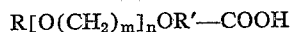
4. The shampoo composition of claim 1, wherein component (A) is a mixture of salts of at least two carboxylic acids of the aforesaid general formula.

5. The shampoo composition of claim 1, wherein component (A) is the isopropanolamine salt of a carboxylic acid having the aforesaid general formula.

6. The shampoo composition of claim 1, wherein component (A) is a sodium salt of a carboxylic acid having the aforesaid general formula.

7. The shampoo composition of claim 1, wherein component (A) is a potassium salt of a carboxylic acid having the aforesaid general formula.

8. In a method for shampooing hair with a shampoo composition comprising at least one water-soluble salt of a monovalent base with an organic acid of the formula



wherein R is a radical selected from the group consisting of alkyl, alkylaryl and aryl radicals containing from 8 to 18 carbon atoms, and mixtures thereof; *m* is an integer of from 2 to 3; *n* is an integer from 1 to 10 inclusive; and R' is an alkylene radical containing from 1 to 3 carbon atoms, the improvement which comprises adding to said shampoo composition a sufficient amount of at least one water-soluble compound of the formula



wherein R and *m* are the same as defined for the organic acid; *n'* is a value between 0 and 10 inclusive; and X is a radical selected from the group consisting of —OSO₃P and —SO₃P wherein P is a cation, to substantially increase the foaming power and to substantially eliminate the dust accumulating power of said water-soluble salt.

References Cited in the file of this patent

UNITED STATES PATENTS

2,183,853 Haussmann et al. Dec. 19, 1939
2,213,477 Steindorff et al. Sept. 3, 1940

OTHER REFERENCES

Drug and Cosmetic Industry, "Lauryl Ether Sulfate Shampoos," June 1956: 78, 6, page 819.
Lesser: "Shampoos," Soap and Sanitary Chemicals, January 1951, pages 38-41, 115, 117 and 119.