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3,697,452  
SHAMPOO

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No Drawing. Continuation-in-part of abandoned appli-  
cation Ser. No. 558,266, June 17, 1966. This applica-  
tion May 19, 1969, Ser. No. 826,010

Int. Cl. A61k 7/08; C11d 1/32, 1/825  
U.S. Cl. 252—545 10 Claims

## ABSTRACT OF THE DISCLOSURE

A conditioning shampoo suitable for cleaning hair which has previously been treated with hairspray having a pH of 8.8 to 9.6 is disclosed which comprises an aqueous mixture of (a) a higher alkyl amine oxide surfactant, (b) a water-soluble, foaming amphoteric surfactant, and (c) a higher alkyl, quaternary ammonium salt surfactant, the total amount of said surfactants being about 12% to 30% by weight of the shampoo.

This application is a continuation-in-part of copending application, Ser. No. 558,266 (filed June 17, 1966), now abandoned.

This invention relates to the production of conditioning shampoos.

The production of a good conditioning shampoo, to be used without a subsequent creme rinse, has been a goal of chemists in the field of hair treatment for a long time. Shampoos which thoroughly clean the hair usually leave it in a statically electrified state, in which the individual hairs repel each other, or in a state in which simple combing produces this undesired electrification; in either case the hair is very difficult to manage. To overcome this defect, creme rinses containing antistatic agents have been employed after shampooing, but the use of these materials naturally requires additional time, effort and expense on the part of the user.

An effective conditioning shampoo, to be used without a creme rinse, must have a unique combination of properties. Aside from removing soil from the hair, it must yield a foam comparable to that of current commercial shampoos insofar as maintaining its body and remaining on the hair without running. It must rinse out easily, with water, and the rinsing process must not only cause the foam to disappear but also eliminate any undesirable residual soapy feel. It must leave the hair pleasant to the touch, and lustrous. It must reduce or entirely eliminate the snarling of wet hair which ordinarily results as the user's fingers become entangled with the hair during the shampooing process. It must promote easy wet-combing of the washed and rinsed hair, so that the hair strands slip easily on each other and slip easily past the comb. It must also promote easy dry-combing, i.e., there should be minimal drag on the comb and the strands of hair should not tend to fly apart and become disaligned as a result of the dry combing process. It must reduce static electrification of the hair; this can be tested, for example, by dry combing a tress containing several hundred hairs, using a given number of strokes (e.g. 15 strokes) at a given tempo, with a comb made of hard rubber or other insulating material, and then placing the back of the comb against the lower, free, end of the hair-tress and moving the comb upward; the number of strands which follow the comb and thereby become disaligned from the main body of the tress is an indication of the degree of static electrification of the hair. The conditioning shampoo must also be substantially non-irritating and non-damaging to the eyes of the user.

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From the foregoing it will be seen that there are a great many stringent requirements which must be met before a satisfactory conditioning shampoo can be produced. There are still other, unexpected, requirements which we have encountered in our efforts to develop such a shampoo. We found that some compositions gave disastrous results when used on hair which had previously been treated with certain common types of hairsprays; the use of the shampoo caused the hair to become gummy and uncombable, with the individual hairs being, in effect, glued together. The effect was particularly noticeable on hair which had previously been damaged, as by bleaching or permanent waving.

We have now determined that the undesirable gumming effect was due to an interaction between certain amine oxide materials in the shampoo and a commonly used hairspray resin, namely a copolymer of methylvinyl ether and monoethyl maleate.

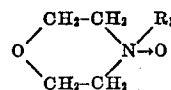
In accordance with one aspect of this invention, we have produced excellent conditioning shampoos which give the effect of a creme rinse without the need for using such a rinse. These conditioning shampoos are a combination of detergents consisting essentially of a cationic surfactant, an amphoteric surfactant, a higher alkyl amine oxide surfactant, and water, having a pH in the range of 8.8 to 9.6, preferably about 8.9 to 9.2. Such shampoos, despite their amine oxide content, have been found to be quite compatible with all the commonly used types of hairspray materials and entirely suitable for use on damaged hair. Even though the shampoos have a relatively high pH, they have been found to impart a marked antistatic, conditioned effect to the hair.

It was quite unpredictable that a combination of the foregoing ingredients at the high pH would have the unique combination of properties needed for an effective conditioning shampoo and, further, would be useable on hair which had been treated with the commercially available hairspray materials.

The suitable higher alkyl amine oxides are those having the formula:



wherein  $R_1$  is a higher alkyl group containing an average of about 12 to 20 carbon atoms, preferably about 13 to 16 carbon atoms, and  $R_2$  and  $R_3$  each represent a radical selected from the group consisting of alkyl and hydroxy-alkyl groups having one to four carbon atoms or  $R_2$  and  $R_3$  together with the oxygen linked nitrogen form a heterocyclic morpholino group, e.g.,



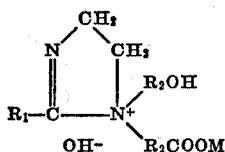
Typical higher alkyl groups which may be present include decyl, lauryl, myristyl, cetyl, stearyl, eicosyl or other higher alkyl groups of about 10-20 carbon atoms, derived for example from tallow, hydrogenated tallow, coconut oil, etc. The amine oxides in which the average number of carbon atoms in the higher alkyl groups is above about 15 have given compositions whose foams (produced during shampooing of the hair) have a creamier appearance, with a smaller bubble size. Most preferably both  $R_2$  and  $R_3$  are methyl groups, but other radicals, e.g., ethyl, hydroxyethyl or hydroxypropyl, may be used in place of one or both methyl groups.

The water-soluble, ampholytic or amphoteric detergents which can be used in the compositions of this invention generally contain a hydrophobic alkyl group of about 10

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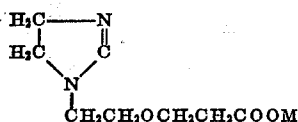
to 20 carbon atoms, at least one anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, or phosphono, and at least one cationic group, e.g., non-quaternary nitrogen, quaternary ammonium, or quaternary phosphonium group, in their molecular structure. The alkyl group may be straight chain or branched and the specific cationic atom may be part of a heterocyclic ring.

Examples of suitable ampholytic detergents include the alkyl beta-aminopropionates,  $R_1N(H)C_2H_4COOM$ ; the alkyl betal-iminodipropionates,  $R_1N(C_2H_4COOM)_2$ ; and the long chain imidazole derivatives sold under the trade name "Miranol" having the following formula:



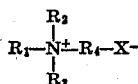
wherein  $R_1$  is an alkyl group of about 10 to 20 carbon atoms,  $R_2$  is an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms and M is a water-soluble cation, e.g. alkali metal, ammonium or alkylolammonium. The higher alkyl group of the aminopropionates and iminodipropionates may be, for example, derived from coco fatty alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, or blends of such alcohols; whereas, the higher alkyl group of the imidazole derivatives is derived from a higher fatty acid, e.g., the fatty acid mixture obtained from coconut oil or tallow. Preferred detergents are sodium N-lauryl beta-aminopropionate, disodium N-lauryl beta-iminodipropionate, and the sodium salt of 2-lauryl-cycloimidium-1-hydroxy, 1-hydroxy-ethanoic acid, 1-ethanoic acid.

Other suitable amphoteric, imidazole detergents have the following structure:



wherein  $R_1$  is a higher acyclic group of 7 to 17 carbon atoms and M is a water-soluble cation, e.g., sodium, potassium, ammonium, and mono-, di- or tri-alkylolammonium. The acyclic groups may be derived from coconut oil fatty acids (a mixture of fatty acids containing 8 to 18 carbon atoms), lauric fatty acid, and oleic fatty acid, and alkyl groups of 7 to 17 carbons are preferred acyclic groups.

Other suitable amphoteric detergents are the sultaine and betaine types having the following general structure:



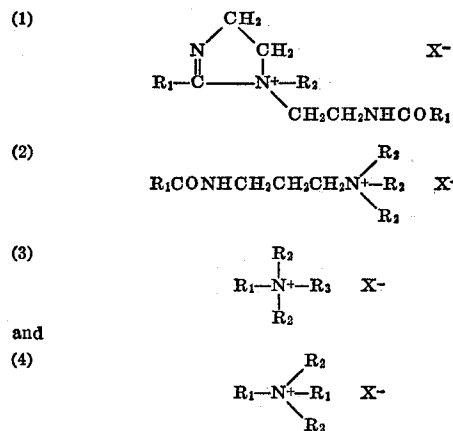
wherein  $R_1$  is an alkyl group containing about 8 to 18 carbon atoms,  $R_2$  and  $R_3$  are lower alkyl groups containing 1 to 3 carbon atoms,  $R_4$  is an alkylene or hydroxyalkylene group containing about 1 to 4 carbon atoms, and X is an anion selected from the group consisting of  $\text{SO}_3^-$  (sultaine)

and  $\text{COO}^-$  (betaine). Preferred components are 1-(myristyl dimethylammonio) acetate and 1-(myristyl dimethylammonio)-2-hydroxypropane-3-sulfonate.

With the exception of the internally neutralized betaine and sultaine amphoteric detergents, as stated above, the foregoing amphoteric detergents are usually supplied in the sodium, potassium, alkylol ammonium or other salt form. It is preferred to use those amphoteric detergents which dissolve and foam readily in water at the pH of 8.8-9.6 and the most preferred amphoteric detergents are the higher alkyl beta-aminopropionate salts and the higher alkyl beta iminodipropionate salts.

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Cationic detergents which may be used are the quaternary ammonium compounds having at least one long chain hydrophobic radical, e.g., alkyl radicals of 10-24 carbon atoms, in their molecular structure. The higher alkyl group may be directly attached to the quaternary nitrogen or indirectly attached thereto through an imidazole groups or an amidopropyl group. Suitable quaternary ammonium salts are selected from the group consisting of higher alkyl quaternary ammonium salts having the following formulas:



wherein  $R_1$  is a higher alkyl or alkenyl group containing an average of 10 to 24 carbon atoms,  $R_2$  is an alkyl or hydroxyalkyl group of 1 to 3 carbon atoms,  $R_3$  is an alkyl or hydroxyalkyl group of 1 to 3 carbon atoms or a benzyl group, and X is an anion selected from the group consisting of chloride, methosulfate, bromide, phosphate, dialkyl phosphate, and acetate. Preferred cationic compounds are 2-stearyl, 1-methyl or 1-hydroxyethyl, 1-stearyl-amidoethyl imidazolium methosulfate and tallowl amidopropyl, dimethyl, hydroxyethyl ammonium chloride. (Tallowyl describes the mixture of  $\text{C}_{14}$  to  $\text{C}_{18}$  fatty acids obtained from tallow.)

The quaternary ammonium compound is preferably one which is stable in aqueous solution or dispersion at pH 9 at room temperature and more preferably stable for at least a month at pH 9 at 120° F. The preferred quaternary ammonium compounds are free of ester linkages unstable under the foregoing conditions. (Preferably the other detergent components, and the entire composition, should meet this same stability requirement.) The water-soluble quaternary ammonium compound is most usually supplied as a chloride or methosulfate ( $-\text{OSO}_2\text{OCH}_3$ ) ion.

Best results have been thus far obtained with compositions whose proportions are in the following ranges (the ranges being in percent by weight of the shampoo composition): water-soluble quaternary ammonium detergent surfactant about 1/2-10%, preferably about 1-6%; water-soluble amphoteric detergent surfactant about 2-20%, preferably about 3-12% (calculated as the acidic form of the amphoteric material); water-soluble amine oxide detergent surfactant about 1-8%, preferably about 4-15%. Generally the total amount of the detergents in the mixture is in the range of about 12-30%, preferably about 15-25%. It will be appreciated, of course, that the composition may be supplied in more highly concentrated form, for subsequent dilution with water.

The pH of the composition may be adjusted to the level previously mentioned by the use of an alkaline material. A water-soluble amine, e.g. a substantially non-volatile amine such as an alkanolamine, preferably triethanolamine, may be used for this purpose, as may inorganic bases such as sodium hydroxide or potassium hydroxide. Typically the pH of the composition remains

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substantially constant on considerable dilution with water; in one typical case the pH (measured electrically) was 9.05 at 20% concentration, 9.01 at 10%, 9.00 at 5%, 8.98 at 2%, and 8.97 at 1% concentration.

Compositions of a wide range of viscosities have been produced from the combination of the foregoing ingredients. It is often desirable to add viscosity-adjusting ingredients. As viscosity-increasing materials there may be used long chain fatty amides, e.g. a monoethanolamide, diethanolamide or dimethylamide of a fatty acid of about 10 to 16 carbon atoms such as lauric-myristic monoethanolamide or diethanolamide. As viscosity decreasing ingredients which also serve to lower the cloud point of the composition there may be used water-soluble solvents, such as polyhydric alcohols, e.g. propylene glycol or ethoxylated polypropylene glycol or lower alkyl ethers of such glycols. The proportion of such ingredients is generally less than 5% of the total composition, e.g. about 1/2-4%.

Another aspect of this invention is the use of a water-soluble protein in the composition. It has been found that this ingredient in the compositions described above has given improved curl retention to the shampooed hair, while substantially retaining, or improving the other desirable effects previously discussed. Chemically, this ingredient is a low molecular weight polypeptide obtained by hydrolysis of protein materials such as human and animal hair, horns, hides, hoofs, gelatin, collagen, and the like. During hydrolysis the proteins are gradually broken down into their constituent polypeptides and amino acids by prolonged heating with acids, e.g., sulfuric acid, or alkalis, e.g., sodium hydroxide, or treatment with enzymes, e.g., peptidases. In hydrolysis, high molecular weight polypeptides are formed first and as hydrolysis proceeds these are converted progressively to simpler and simpler polypeptides, to tripeptides, dipeptides, and finally to amino acids. It is obvious that the polypeptides derived from proteins are complex mixtures and in practice the average molecular weight of the hydrolysate will vary from 120 (amino acids) to about 20,000. All satisfactory hydrolyzed polypeptides are characterized by water solubility. It is preferred to use hydrolyzed collagen of such low molecular weight as to be completely soluble in water, non-gelling, and non-denaturing with an average molecular weight below 15,000, preferably in the range of about 500 to 10,000. The amount of protein is preferably in the range of about 1/2-3%, most preferably about 1 to 2%, based on the total weight of the composition.

The following examples are given to illustrate this invention further.

#### EXAMPLE 1,

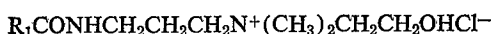
A shampoo is prepared from the following components:

3 parts of a higher alkyl dimethylamine oxide containing 95% cetyl dimethylamine oxide, 3% lauryl dimethylamine oxide and 2% myristyl dimethylamine oxide;

9 parts of a higher alkyl dimethylamine oxide mixture containing 60-65% lauryl dimethylamine oxide, 25-30% myristyl dimethylamine oxide and 10-15% cetyl dimethylamine oxide;

3 parts of a blend of N-higher alkyl  $\beta$ -aminopropionic acid and the corresponding N-higher alkyl  $\beta$ -iminodipropionate (the ratio of the former, monocarboxylic acid, to the latter, dicarboxylic acid, being 10:1) in which the higher alkyl radicals are lauryl and myristyl in ratio of 2.3:1 (known as "Deriphat 170-C");

3 parts of an ethoxylated fatty quaternary ammonium chloride, of the formula



(Dimethylhydroxyethyl- $\alpha$ -alkyl amidopropyl ammonium chloride) where  $R_1$  is the alkyl residue of tallow fatty

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acid (46% oleic, 24% stearic, 4% palmitoleic, 25% palmitic and 1% myristic), said quaternary compound being supplied, in about 87% concentration, as "Culver-soft WS-90";

1.5 parts of water-soluble hydrolyzed pig collagen;  
5 parts of triethanolamine;

3 1/2 parts of lauric-myristic diethanolamide; together with minor amounts of perfumes, ultraviolet absorbers (e.g. 2,2'-dihydroxy 4,4'-dimethoxybenzophenone) and dyes, together with sufficient deionized water to make a total of 100 parts. The amine oxides and amphoteric detergent are supplied in aqueous solutions. The pH of the blend is 9.1.

The product is a clear solution at room temperature; its cloud point is about 40-50° F.

#### EXAMPLE 2

Example 1 is repeated but using twice the amount of the amphoteric detergent (i.e. 6 parts) and 3/4 the amount of the lauryl-rich amine oxide (i.e. 6 parts); the lauric-myristic diethanolamide is omitted, since the viscosity of the mixture is relatively high even without this ingredient. As in Example 1, the pH is adjusted to 9.1 by the incorporation of a sufficient amount of triethanolamine.

The product is a clear solution at room temperature.

#### EXAMPLE 3

Example 1 is repeated using twice the amount of the long chain quaternary ammonium compound (i.e. 6 parts), and two-thirds the amount of the lauryl-rich amine oxide (i.e. 6 parts); the lauric-myristic diethanolamide is omitted, since the viscosity of the mixture is relatively high even without this ingredient. As in Example 1, the pH is adjusted to 9.1 by the incorporation of a sufficient amount of triethanolamine.

The product is a clear solution at room temperature.

#### EXAMPLE 4

Example 1 is repeated using twice the amount of the amphoteric detergent (i.e. 6 parts), twice the amount of the long chain quaternary ammonium compound (i.e. 6 parts), and one-third the amount of the lauryl-rich amine oxide (i.e. 3 parts); the lauric-myristic diethanolamide is omitted, since the viscosity of the mixture is relatively high even without this ingredient. As in Example 1, the pH is adjusted to 9.1 by the incorporation of a sufficient amount of triethanolamine.

The product is a clear solution at room temperature.

The viscosity of the above mixture, and its cloud point, are lowered by the incorporation of (a) 3 parts of propylene glycol; or (b) 1/2 part of a monobutyl ether of poly-alkylene glycol of molecular weight about 2800 (viscosity 400 centistokes at 100° F.) having about equal weight of ethylene oxide and 1,2-propylene oxide in the polyalkylene oxide chain, made according to the process of U.S. Pat. 2,424,755.

#### EXAMPLE 5

Example 1 is repeated using twice the amount of the amphoteric detergent (i.e. 6 parts) and one-half the amount of the lauryl-rich amine oxide component (i.e. 4.5 parts), and omitting the cetyl-rich amine oxide component. As in Example 1, the pH is adjusted to 9.1 by the incorporation of a sufficient amount of triethanolamine.

The product is a clear solution at room temperature.

#### EXAMPLE 6

Example 1 is repeated using twice the amount of the amphoteric detergent (i.e. 6 parts) and 1 1/2 times the amount of the cetyl-rich amine oxide component while omitting the lauryl-rich amine oxide component and the lauric-myristic diethanolamide. The lauric-myristic diethanolamide is omitted, since the viscosity of the mixture is relatively high even without this ingredient. As in Example 1, the pH is adjusted to 9.1 by the incorporation of a sufficient amount of triethanolamine.

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The product is a clear solution at room temperature.

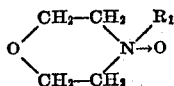
## EXAMPLE 7

Example 1 is repeated, substituting 3 parts of arachidyl-behenyl dimethyl benzyl ammonium chloride (supplied as Kemamine BQ 1902C) for the cationic detergent of Example 1; the lauric-myristic diethanolamide is omitted, since the viscosity of the mixture is relatively high even without this ingredient. As in Example 1, the pH is adjusted to 9.1 by the incorporation of a sufficient amount of triethanolamine.

The product is a clear solution at room temperature.

## EXAMPLE 8

Example 1 is repeated substituting, for both amine oxides, 12 parts of a long chain amine oxide of the formula



where  $\text{R}_1$  is lauryl (supplied as Ammonyx MAO) and omitting the lauric-myristic diethanolamide. As in Example 1, the pH is adjusted to 9.1 by the incorporation of a sufficient amount of triethanolamine.

The product is a clear solution at room temperature, having a relatively low viscosity.

## EXAMPLE 9

Example 1 is repeated, substituting 9 parts of the morpholino amine oxide of Example 8 for the lauryl-rich amine oxide of Example 1, and omitting the lauric-myristic diethanolamide.

Shampoos having good condition, cleansing and foaming properties are obtained when other amphoteric detergents, e.g., coco-dimethylglycine, sodium salt of 2-coco-1-(ethyl-beta-oxipropionic acid) imidazoline, and sodium 1-carboxy methyl-1-hydroxy-ethyl-2-coco imidazolium hydroxide, and other cationic quaternary ammonium salts, e.g., dicoco dimethyl quaternary ammonium chloride, stearyl dimethyl benzyl ammonium chloride and 1-methyl-1-oleyl-amidoethyl-2-oleyl imidazolium methosulfate, are substituted for the N-alkyl  $\beta$ -aminopropionate amphoteric detergent and the higher alkyl, dimethyl,  $\alpha$ -amido-propyl ammonium chloride cationic detergent in the compositions of Example 1.

What is claimed is:

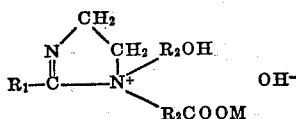
1. An aqueous hair conditioning shampoo suitable for cleaning hair which has previously been treated with hair-spray which consists essentially of an aqueous mixture having a pH of 8.8 to 9.6 of (a) about 4 to 15% by weight of a higher alkyl amine oxide having the structural formula:



wherein  $\text{R}_1$  is a higher alkyl group containing an average of about 12 to 20 carbon atoms,  $\text{R}_2$  and  $\text{R}_3$  each represent a radical selected from the group consisting of alkyl and hydroxyalkyl groups containing one to four carbon atoms or  $\text{R}_2$  and  $\text{R}_3$  together with the oxygen-linked nitrogen form a morpholino group; (b) about 3 to 12% by weight of a water-soluble, foaming amphoteric detergent selected from the group consisting of

- (1)  $\text{R}_1\text{N}(\text{H})\text{C}_2\text{H}_4\text{COOM}$ ,
- (2)  $\text{R}_1\text{H}(\text{C}_2\text{H}_4\text{COOM})_2$ , and

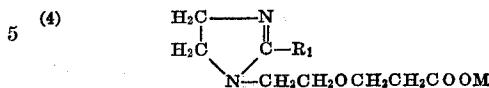
(3)



wherein  $\text{R}_1$  is an alkyl group of 10 to 20 carbon atoms,  $\text{R}_2$  is an alkylene or hydroxyalkylene group containing 1

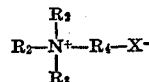
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to 4 carbon atoms, and M is a water-soluble cation selected from the group consisting of sodium, potassium, ammonium, and alkylammonium,



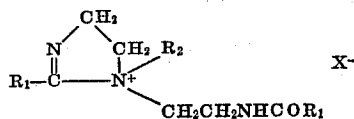
wherein  $\text{R}_1$  is a higher acyclic group of 7 to 17 carbon atoms and M is a water-soluble cation selected from the group consisting of sodium, potassium, ammonium, and alkylammonium, and

(5)

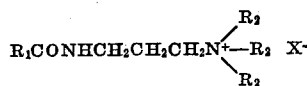


wherein  $\text{R}_1$  is an alkyl group containing about 8 to 18 carbon atoms,  $\text{R}_2$  and  $\text{R}_3$  are lower alkyl groups of 1 to 3 carbon atoms,  $\text{R}_4$  is an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms and X is  $\text{SO}_3^-$  or  $\text{CO}_2^-$ ; (c) about 1 to 6% by weight of a quaternary ammonium salt selected from the group consisting of

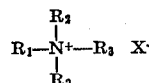
(1)



(2)

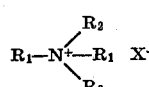


(3)



and

(4)



wherein  $\text{R}_1$  is a higher alkyl or alkenyl group containing an average of 10 to 24 carbon atoms,  $\text{R}_2$  is an alkyl or hydroxyalkyl group of 1 to 3 carbon atoms,  $\text{R}_3$  is an alkyl or hydroxyalkyl group of 1 to 3 carbon atoms or a benzyl group, and X is an anion selected from the group consisting of chloride, methosulfate, bromide, phosphate, dialkyl phosphate, and acetate, the total amount of (a), (b), and (c) in said shampoo being about 15 to 25% by weight; and  $\frac{1}{2}$  to 4% by weight of a fatty acid amide selected from the group consisting of monoethanolamides, diethanolamides, and dimethylamides of fatty acids of about 10 to 16 carbon atoms; said shampoo yielding a good foam with good cleansing power and leaving the hair in an easily combable condition on rinsing with water without the need for a subsequent antistatic creme rinse.

2. A shampoo as in claim 1 in which the pH is about 8.9-9.2.

3. A shampoo as in claim 1 in which said amine oxide is a higher alkyl dimethylamine oxide having an average of about 13 to 16 carbon atoms in its higher alkyl group.

4. A shampoo as in claim 1 in which said amine oxide is an N-higher alkyl morpholine oxide.

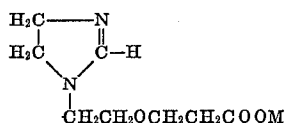
5. A shampoo as in claim 1 in which said amphoteric detergent is an N-higher alkyl  $\beta$ -aminopropionate.

6. A shampoo as in claim 1 in which said quaternary ammonium detergent is a water-soluble dimethylhydroxyethyl- $\gamma$ -higher alkylamidopropyl ammonium salt.

7. A shampoo as in claim 1 in which said quaternary ammonium salt having an average of at least 18 carbon atoms in the higher alkyl group.

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8. A shampoo as in claim 1 in which said amphoteric detergent has the following structure:



9. A shampoo as in claim 1 which contains in addition about ½ to 3% of dissolved, water-soluble polypeptides having a molecular weight in the range of about 120 to 20,000, said polypeptide having been produced by hydrolysis of a protein material selected from the group consisting of human and animal hair, horns, hides, hoofs, gelatin, and collagen.

10. A shampoo as in claim 9 in which said polypeptide has a molecular weight in the range of about 500 to 15,000 and is produced by hydrolysis of collagen.

## References Cited

## UNITED STATES PATENTS

|           |         |             |           |
|-----------|---------|-------------|-----------|
| 2,211,001 | 8/1940  | Chwala      | 260—309.6 |
| 2,267,965 | 12/1941 | Wilson      | 260—309.6 |
| 2,459,062 | 1/1949  | Cook et al. | 252—152 X |

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|              |         |                |           |
|--------------|---------|----------------|-----------|
| 2,820,043    | 1/1958  | Rainey et al.  | 260—309.6 |
| 2,950,255    | 8/1960  | Goff           | 252—152   |
| 3,086,943    | 4/1963  | Lang           | 252—152   |
| 3,296,145    | 1/1967  | Findlan et al. | 252—106   |
| 5 3,156,656  | 11/1964 | Libby          | 252—152   |
| 3,496,110    | 2/1970  | Shumway et al. | 252—152   |
| 3,507,796    | 4/1970  | Voss           | 252—106   |
| 3,533,955    | 10/1970 | Pader          | 252—152   |
| 2,468,012    | 4/1949  | Isbell         | 260—534   |
| 10 3,280,179 | 10/1966 | Ernst          | 252—117 X |

## OTHER REFERENCES

Burnett, Proteins in Cosmetics, Article in American Perfumer and Cosmetics, vol. 78, October 1963, pp. 69 to 72.

Shansky, Hair Conditioners, Article in American Perfumer and Cosmetics, vol. 80, June 1965, pp. 39 to 41.

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20 D. L. ALBRECHT, Assistant Examiner

U.S. Cl. X.R.

252—153, 546, 547, 548, DIG. 7, DIG. 13; 424—70

# UNITED STATES PATENT OFFICE

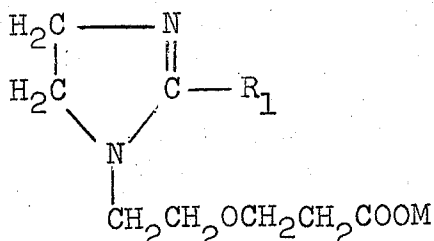
## CERTIFICATE OF CORRECTION

Patent No. 3,697,452 Dated October 10, 1972

Inventor(s) Frank Wesley Olson, Jr. and Karl Hutcheson Roberts

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 10, change "betal" to --beta--; in lines 39-42, the structural formula should read:

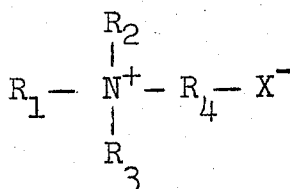


and line 64, change "myristly" to --myristyl--.

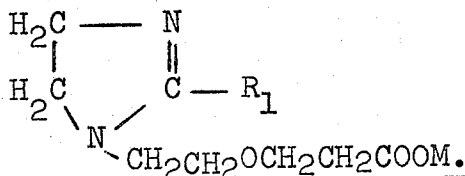
Column 4, line 63, change "8" to --18--.

Column 7, line 66, the structural formula should read:  $\text{R}_1\text{N}(\text{C}_2\text{H}_4\text{COOM})_2$ ; and line 74, change "R(" to --R<sub>1</sub>--.

Column 8, lines 14-16, the structural formula should read:



Column 9, lines 3-6, the structural formula should read:



Signed and sealed this 29th day of May 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents