United States Patent Office 3,808,311 Patented Apr. 30, 1974

3,808,311

AMINE OXIDE-AMPHOTERIC SURFACTANT-CATIONIC SURFACTANT-OIL CONTAINING HAIR CONDITIONING SHAMPOO

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No Drawing. Continuation-in-part of abandoned application Ser. No. 845,586, July 28, 1969. This application June 4, 1970, Ser. No. 43,599

Int. Cl. A61k 7/06

U.S. Cl. 424—70 4 Claims

ABSTRACT OF THE DISCLOSURE

A hair conditioning shampoo for improving the combing properties and luster of hair washed therein comprising a single phase aqueous detergent composition suitable for shampooing hair which contains a higher alkyl amine oxide, an amphoteric surfactant, a cationic surfactant, and an oil from the group consisting of mineral oil, vegetable oil, animal oil, and synthetic oil, in proper proportions.

This application is a continuation-in-part of copending application Ser. No. 845,586 filed July 28, 1969, now abandoned.

The present invention relates to a hair conditioning shampoo for improving the combing properties and luster of all colors of hair which comprises a single phase aqueous detergent composition suitable for use in shampooing hair which contains a higher alkyl amine oxide, an amphoteric surfactant, a cationic surfactant, and an oil from the group consisting of mineral, vegetable, animal, and synthetic oils in proper proportions.

There have been suggestions in the prior art to use mineral oil in champoos. One such suggestion proposed the use of up to about 3% of mineral oil in a shampoo containing sulfonates of fatty oils as the surfactant but, in effect, condemned this proposal on the ground that it is difficult to wash out. Another suggestion was to form a two phase shampoo by the use of at least 5% liquid oil material in an aqueous detergent composition in which an oil phase floats on the top of an aqueous phase as a sharply defined clear, separate layer and an essential ingredient in this composition was an emulsion breaker in sufficient proportion to insure the rapid and sharp separation of the two phases after they had been emulsified by shaking. In general, the consumer's reaction to such shampoo has not been favorable.

Shampoos containing amine oxides, amphoteric detergents and cationic detergents have been proposed for hair conditioning effects but it has been found that the degree of hair conditioning effects obtainable by the use of these ingredients is limited and that when hair is combed wet after shampooing with such a composition an undesirable foam is produced which is particularly noticeable on the comb.

It has now been discovered that improved combing properties, particularly the absence or substantially reduced amount of foam produced in wet combing, an improved degree of hair conditioning and an observable and highly desirable shine or luster and other properties mentioned hereinafter can be imparted to hair of all colors by shampoo compositions which contain proper proportions of a higher alkyl amine oxide, an amphoteric surfactant, a cationic surfactant and a non-volatile oil from the group consisting of mineral, vegetable, animal, and synthetic oils, and mixtures thereof.

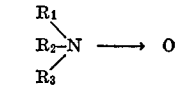
The mineral oil used in compositions made in accordance with the invention may be any oil that dissolves in

the detergent composition in sufficient proportions to function as described herein. The preferred oil is a mineral oil, and it may be a light to heavy hydrocarbon oil but is preferably a light mineral oil such as a water-clear, completely saturated, mineral oil having a Saybolt viscosity of about 50–80, desirably 55–65 cps. at 100° F., a specific gravity compared with water when the oil and water are at 25° C. of 0.831 to 0.871, a flash point of 280° F. minimum and a fire point of 305° F. minimum, as obtained by the Cleveland open cup method. The preferred mineral oil may be replaced in whole or part by olive oil or other comparable non- or semi-drying vegetable and animal oils having an iodine number less than 105, such as linseed oil, castor oil, cotton seed oil, safflower oil, almond oil, peanut oil, coconut oil, soya bean oil, sesame oil, avocado oil, and mineral oil soluble lanolin derivatives, such as lanolin esters, lanolin alcohols and ethylene oxide adducts thereof. Synthetic oils, i.e., esters of fatty acids having from about 10 to 20 carbon atoms such as isopropyl myristate, palmitate and stearate may also be used.

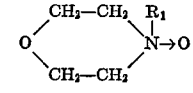
The proportion of oil, whether mineral, vegetable, animal or synthetic in the composition should be sufficient to produce the desired effect, usually at least about 0.5% but not enough to produce a separate phase on standing. In other words, the oil should be taken into the aqueous system, whether by dissolution or otherwise, so as to appear to the eye to be a single phase. The upper limit may vary, depending on the nature of the oil and the ingredients and proportions of the aqueous system. The upper limit is less than 5%, often less than 3%, and an effective maximum is about 2%.

In the description and claims where percentages are given, they are by weight of the entire composition.

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



where 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 hydroxyalkyl 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.,

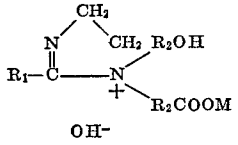


Typical higher alkyl groups which may be present include decyl, lauryl, myristyl, cetyl, stearyl, eicosyl or other higher alkyl groups of about 10–20 carbon atoms, derived for example from tallow, hydrogenated tallow, coconut oil, etc. The amine oxides in which the average number of carbon atoms in the higher alkyl groups is 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 the invention generally contain a hydrophobic alkyl group of about 10 to 20 carbon atoms attached directly or indirectly to at least one cationic group, e.g., non-quaternary nitrogen, quaternary nitrogen, or quaternary phosphorous, and at least one anionic water-solubilizing group, e.g., carboxylic, sulfonic, sulfuric, or phosphonic acids or salts thereof, in their molecular structure. The alkyl group may

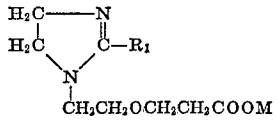
be straight chain or branched, and the specific cationic atom may be part of a heterocyclic ring.

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



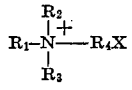
wherein R_1 is an alkyl group of about 10 to 20 carbon atoms, R_2 is an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms and M is a water-soluble cation, e.g., alkali metal, ammonium or alkylolammonium. The higher alkyl group of the aminopropionates and iminodipropionates may be, for 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 derivative is derived 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-hydroxyl, 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-alkylammonium. The acylic 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. Such detergents can be prepared by dehydrating the reaction product of a higher fatty acid and a hydroxyalkyl alkylene polyamine, e.g., beta-hydroxyethyl ethylene diamine as described in U.S. Pat. 2,267,965, and then reacting the resultant imidazoline with acrylic acid as shown in French Pat. 1,412,921 followed by neutralization.

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

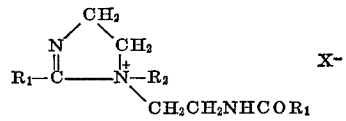


wherein R_1 is an alkyl group containing about 8 to 18 carbon atoms, R_2 and R_3 are lower alkyl groups containing 1 to 3 carbon atoms, R_4 is an alkylene or hydroxyalkylene group containing about 1 to 4 carbon atoms, and X is an anion selected from the group consisting of $SO_3^=$ (sultaine) and $COO^=$(betaine). Preferred compounds are 1-(myristyl dimethylammonio) acetate and 1-(myristyl dimethylammonio)-2-hydroxypropane-3-sulfonate.

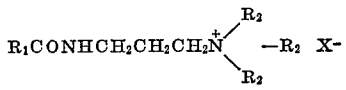
With the exception of the internally neutralized betaine and sultaine amphoteric detergents, as stated above, the foregoing amphoteric detergents are usually applied in the sodium, potassium, alkylol ammonium or other salt form. It is preferred to use those amphoteric detergents which dissolve and foam 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-iminodiproprionate salts.

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 group or an amidopropyl group. Suitable quaternary ammonium salts are selected from the group consisting of higher alkyl quaternary ammonium salts having the following formulas:

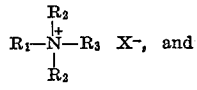
(1)



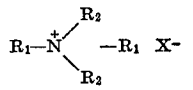
(2)



(3)



(4)



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-stearylamido-ethyl imidazolinium methosulfate and tallowyl amidopropyl, dimethyl, hydroxyethyl ammonium chloride (tallowyl describes the mixture of C_{14} to 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

$$(—OSO_2OCH_3)$$

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 0.1–10%, 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 1–18%, 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 compositions may be supplied in more highly concentrated form, for subsequent dilution with water.

The pH of the composition should be at least about 5, generally above 7, desirably about 8.8 to 9.6, preferably about 8.9 to 9.2. When the pH is below 7, M as defined above may include hydrogen. The pH may be adjusted to the level desired by the use of an acidic and/or an alkaline material. For this purpose acidic materials such as citric acid and basic materials, e.g., a water-soluble sub-

stantially non-volatile amine such as an alkanolamine, preferably tri-ethanolamine, may be used for this purpose, as may inorganic bases such as sodium hydroxide or potassium hydroxide. Citric acid also serves as a sequestering and buffering agent and is frequently added for this purpose even if not needed for pH adjustment. Generally speaking minor proportions, up to a maximum of about 2%, of each of these ingredients is sufficient to obtain the desired pH adjustment. Typically the pH of the composition remains 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 may be 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 monohydric alcohols containing 2 to 3 carbon atoms, polyhydric alcohols, e.g., propylene glycol or ethoxylated poly-propylene 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 ½–4%.

Water-soluble protein may also be present in the compositions. This ingredients in the compositions described above gives 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 enzyme, 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 hydrolysis will vary from 120 (amino acids) to about 20,000. All satisfactory hydrolyzed polypeptides are characterized by water solubility. In compositions which contain soluble protein 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 used is preferably in the range of about ½–3% most preferably about 1 to 2%.

It is desired in many cases to color the shampoo composition a desirable shade such as yellow, green, amber, blue, etc. For this purpose any suitable dyes may be incorporated in the solution. For example, D & C yellow No. 1, in a 1% solution, may be added to a shampoo composition of the above type at a level of about 0.05% to produce a desirable yellow color. A very attractive green color can be obtained by using about 0.2% FD & C yellow No. 5 (1% solution) and a 0.1% FD & C blue No. 1 (1% solution). An amber color is obtained by using about 0.075% D & C orange No. 4 (1% solution) with 0.025% red No. 2 (0.1% solution). An attractive blue color can be obtained by using 0.25% FD & C blue No. 1 (1% solution) and 0.050% D & C red No. 19 (0.1% solution).

Where dyes are added to the composition it is preferred to include a color preservative, e.g., a compound which absorbs ultraviolet light, e.g., a mixture of 2,2'-dihydroxy-4,4'-dimethoxy benzophenone and other tetra-substituted benzophenones, referred to hereafter as Preservative X, and 2,4-dihydroxy benzophenone, referred to hereafter as Preservative Y, and mixtures thereof. These materials are very effective in small proportions and in general about 0.025% adequately protects the composition from color change on exposure of the composition to light during storage and use. They may be used, however, within broader ranges of about 0.01 to 0.1%. Preservative X is preferred for all the above colors except blue for which Preservative Y is preferred.

It is also preferred to include a material which inhibits bacterial growth in the detergent compositions, e.g., formaldehyde USP, which is effective when about 0.1% is present. Other preservatives may also be used.

In general it is preferred to include a perfume of a suitable type and odor in the composition for its cosmetic appeal to the user. Perfume may be present within the range of 0–2%.

The liquid vehicle in which the foregoing ingredients are carried, primarily in solution, is water which may be replaced in part by a lower aliphatic monohydric alcohol, e.g., ethyl, propyl, and isopropyl alcohols. In some formulations lower aliphatic polyhydric alcohols such as propylene glycol and glycerine may be used. Alcohol may be present within the range of about 0–10% but never in such high proportion with reference to the oil content that a separate oil phase is formed. In making up the composition it is preferred to use deionized water so as to avoid discoloration and other adverse effects of the water hardness.

Examples I, II and III set forth satisfactory compositions of hair conditioning shampoos formulated in accordance with the present invention.

	Percent		
Example	I	II	III
Myristyl dimethyl amine oxide	12.0	12.0	6.0
Tallow amidopropyl dimethyl hydroxy-ethyl ammonium chloride	3.0	3.0	0.5
N-lauryl-myristyl beta-alanine	3.0	3.0	8.0
Lauric-myristic diethanolamide	3.0	4.0	1.6
Soluble protein	1.5	1.5	------
Citric acid (anhydrous)	0.25	0.25	0.25
Mineral oil-extra light	0.5	------	2.0
Olive oil	------	1.5	------
Caustic soda (to adjust to pH 9)	q.s.	q.s.	q.s.
Deionized water (with and without additives such as dyes, perfumes stabilizers, preservatives)	q.s.	q.s.	q.s
Total	100.00	100.00	100.00

The shampoos of the present invention are quite compatible with materials used on hair, particularly resin-type hair sprays, and they are entirely suitable for use on hair that has been damaged by bleaches, hair waving and straightening compositions, exposure to sun and sea water, etc. On combing the wet hair after shampooing there is either no observable foam on the comb or, if present at all, the amount thereof is greatly reduced as compared with the amount produced by a shampoo of the same formulation without the oil. The hair conditioning effect is also raised to a new level above that obtainable in these compositions without it.

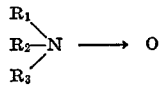
The hair conditioning effect of a shampoo is difficult to measure accurately because it is a combination of a number of properties or characteristics of the hair after it has been shampooed, both in wet condition and dry. A

useful but somewhat arbitrary scale of hair conditioning effects is as follows:

Value on scale	Characteristics of hair
0	Those obtained by washing with a shampoo based on an anionic sulfate and/or sulfonate only. There are no good combing effects dry or wet. Snarls and snags are hard to comb out, there is a raspiness on dry combing and the dry combed hair is strongly charged with static electricity.
1	Those obtained by washing with a shampoo having some ingredients present that make wet and dry combing easier than without such ingredients but still leave dry combed hair electrified.
2	Those obtained by washing with a shampoo having further ingredients present that eliminate static on dry combing but do not entirely eliminate snarls.
3	Those obtained by washing with a shampoo such as Examples I and II without oil which leaves the washed hair fairly soft and easy to comb wet or dry without snarls and without static on dry combing.
4	Those obtained by washing with a shampoo such as Examples I, II and III which leaves the hair still easier to comb because it has greater softness and weight and is more slippery than value 3.

What is claimed is:

1. A single phase liquid shampoo for improving combing properties and luster of hair consisting essentially of 1 to 18% by weight of a water-soluble higher alkyl amine oxide having the formula



wherein R_1 is a higher alkyl group containing an average of about 12 to 20 carbon atoms and R_2 and R_3 each represent a member selected from the group consisting of alkyl and hydroxyalkyl having one to four carbon atoms or R_2 and R_3 together with the oxygen linked nitrogen form a morpholino group; 2–20% by weight of a water-soluble amphoteric surfactant having a hydrophobic alkyl group of about 10 to 20 carbon atoms attached directly or indirectly to a non-quaternary nitrogen or quaternary nitrogen, and at least one anionic water-solubilizing group selected from the group consisting of carboxylic and sulphonic acids or salts thereof in its molecular structure, said salt being selected from the group consisting of sodium, potassium, ammonium, and alkylolammonium; 0.5–10% by weight of a water-soluble cationic quaternary ammonium surfactant having a long-chain hydrophobic radical of 10 to 24 carbon atoms directly or indirectly attached to the quaternary nitrogen; and at least about 0.5% and less than 5% by weight of a non-volatile oil selected from the class consisting of a mineral oil, a non- and semi-drying vegetable oil, an isopropyl ester of a C_{10}–C_{20} fatty acid, and mixtures thereof in an aqueous vehicle containing 0–10% by weight of a lower monohydric or polyhydric alcohol containing from 2 to 3 carbon atoms; the total content of said amine oxide, said amphoteric surfactant, and said cationic detergent being about 12–30% by weight of said shampoo.

2. A liquid shampoo according to claim **1** wherein said oil is extra light mineral oil or olive oil and is present in an amount from 0.5 to 2% by weight.

3. A liquid shampoo in accordance with claim **1** which contains in addition from ½ to 3% by weight of a water-soluble non-gelling protein material selected from the group consisting of hydrolysis products of human and animal hair, horns, hides, hoofs, gelatin, and collagen, and having a molecular weight in the range of about 500 to 10,000.

4. A single phase liquid shampoo for improving combing properties and luster of hair consisting essentially of 6 to 12% by weight of C_{10}–C_{20} high alkyl dimethyl amine oxide, 0.5 to 3% by weight of tallowyl amidopropyl dimethyl hydroxyethyl ammonium chloride, 1.6 to 4% by weight of lauric-myristic diethanolamide, 3 to 8% by weight of N-lauryl-myristyl beta-alanine, 0.5 to 2% by weight of oil selected from the class consisting of extra light mineral oil and olive oil, and water.

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U.S. Cl. X.R.

252—Dig. 2, 7, 13, 14, 542, 547, 153; 424—359