United States Patent Office 3,769,398
Patented Oct. 30, 1973

3,769,398

POLYETHYLENIMINE SHAMPOO COMPOSITIONS

Gordon Trent Hewitt, Upper Montclair, N.J., assignor to Colgate-Palmolive Company, New York, N.Y.

No Drawing. Filed May 25, 1970, Ser. No. 40,385
Int. Cl. A61k 7/06
U.S. Cl. 424—70 8 Claims

ABSTRACT OF THE DISCLOSURE

Clear, viscous, homogeneous shampoo compositions which have excellent conditioning characteristics and are effective against *Pityrosporum ovale* containing as the active ingredients a detergent selected from the group consisting of betaines, sulfobetaines, amine oxides, and mixtures thereof, a water-soluble polymer selected from the group consisting of polyethylenimines, ethoxylated polyethylenimines, and propoxylated polyethylenimines having a molecular weight from about 1,800 to about 500,000, and an aqueous vehicle.

This invention relates to clear, viscous, homogeneous shampoo compositions which have outstanding hair conditioning characteristics and are effective against *Pityrosporum ovale*. The instant shampoo compositions have all of the basic characteristics of commercially acceptable shampoos—they clean but maintain hair luster, are clear, viscous, and homogeneous, condition hair and leave it easy to manage (no static flyaway or tangles), and form copious lather even in hard water.

The inventive compositions are also suitable for cleaning and conditioning the human hair which is used to make hairpieces such as wigs and toupees. It is considered that the hair in such hairpieces should be free of the *P. ovale* yeast in order to eliminate or minimize the problems associated with migration of such yeast to the scalp of the hairpiece wearer. Since the described compositions effectively inhibit the growth of *P. ovale*, they are particularly suitable for cleaning the hair prior to or after its fabrication into hairpieces.

It is, therefore, an object of this invention to provide clear, stable, homogeneous shampoo compositions which have excellent hair conditioning characteristics, and inhibit the growth of *P. ovale*.

In general the preferred compositions of this invention are comprised of from about 5 to about 25 percent by weight of a betaine, sulfobetaine, or amine oxide detergent, and mixtures thereof, from about 0.1 to about 3.0 percent by weight of a water-soluble polyethylenimine (PEI), and an aqueous medium and minor ingredients to make the balance of the composition. Additionally, an imidazoline or oxazoline foam booster may be added in an amount of from about 1.0 to about 6.0 percent by weight of the total composition.

The pH of the composition ranges from about 5.0 to about 9.0 but is preferably adjusted to the near neutral range of 6.5 to 8.0. A lower pH will help solubilize the imidazoline or oxazoline foam booster and enhance their cationic nature; however, too low a pH means that free fatty acids in the natural hair oils will be more tenacious and not as readily removed by the surfactant. A pH of about 7.5 is most preferred.

It has been found that PEI in a free and uncomplexed form is an outstandingly good antimicrobial agent having both inhibitory activity [1] against *P. ovale* (MIC [2] of 3.9 μg./ml.) and substantivity to the hair and scalp. PEI, however, is a cationic polyamine and has been found to complex strongly with the usual anionic-acting shampoo surfactants, including amphoterics at their useful alkaline pH values and soaps. When PEI is present in a shampoo along with an anionic-acting surfactant, the PEI loses its antimicrobial characteristics; the complex of PEI with the anionic surfactant seems to destroy this extremely valuable property. However, PEI can be formulated into a superior shampoo composition and still maintain its valuable antimicrobial characteristics provided that the shampoo compositions contain carefully selected groups of detergents which do not complex with PEI and which themselves exhibit some inhibitory activity toward *P. ovale*. The useful detergents are the zwitterionic detergents such as the betaines and sulfobetaines and the semi-polar amine oxide detergents. In such non-anionic compositions the PEI is uncomplexed and thus free to act as an antimicrobial agent.

Moreover, as was stated previously, all of the ingredients in these shampoos were chosen on the basis of their own distinct inhibitory action toward *P. ovale*. Myristyl and palmityl betaine both have MIC's against *P. ovale* of about 250 μg./ml., lauryl betaine of about 500 μg./ml., 1-hydroxyethyl-2-coco imidazoline of about 250 μg./ml., and lauryl dimethyl amine oxide of about 1250 μg./ml. Thus all of the active ingredients in the shampoo are effective to a greater or lesser degree against *P. ovale*.

In order to determine the substantivity of PEI on the hair the Rubine Dye Test is used. In this test a 0.5-percent aqueous solution of Direct Fast Rubine WS dye is adjusted to a pH of 3.5 with acetic acid. Then approximately 0.5 gram of white hair (or wool) is immersed or rubbed (to produce a lather) for 3 minutes in a shampoo solution. The shampoo concentration is approximately 10 parts shampoo to 90 parts water at room temperature to simulate hair shampooing. After thorough rinsing with water the damp hair sample is immersed for 5 minutes in the dye solution at 100° F. The hair is then rinsed thoroughly with room temperature water. The presence of a deep red color indicates that the hair or wool has deposited on its some cationic active substance. In the absence of such an absorbed cationic, the hair color is essentially unchanged, that is, there is no takeup of the Rubine dye.

It was found that the deposits from the instant non-anionic shampoo solutions formed a very strong, very difficult to remove attachment of Rubine dye indicating excellent substantivity of PEI. PEI, per se, does not deposit from shampoo solutions containing anionics, such as lauryl sulfates and fatty alcohol ether sulfates.

The PEI polymers which can be used in the shampoos of this invention can be prepared by polymerizing ethyl-

[1] In a standard laboratory test to determine antimicrobial activity PEI offered almost no general antimicrobial properties as it was ineffective against *S. aureus* (MIC greater than 500 μg./ml.), *Str. mitis* (MIC greater than 500 μg./ml.), *E. coli* (MIC greater than 1000 μg./ml.), *Ps. aeruginosa* (MIC greater than 1000 μg./ml.), *C. albicans* (MIC of 1000 μg./ml.), and *A. niger* (MIC greater than 1000 μg./ml.). Against *T. mentagrophytes* PEI was very modestly inhibitory (MIC of 500 μg./ml.).

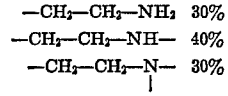
[2] Minimum Inhibitory Concentration (MIC) of an individual substance or formulation needed to inhibit the growth of a particular organism.

enimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods of preparation are described in U.S. Pats. Nos. 2,182,306, Ulrich et al., granted Dec. 5, 1939; 3,033,746, Moyle et al., granted May 8, 1962; 2,208,095, Esselmann et al., granted July 16, 1940; 2,806,839, Crowther, granted Sept. 17, 1957; and 2,553,969, Wilson, granted May 21, 1951.

Similarly, alkoxylated PEI's can be prepared, for example, by reacting one part by weight ethylene oxide or propylene oxide with one part by weight PEI prepared as described above and having a molecular weight greater than about 1,800. Preferably, the weight ratio of PEI to alkylene oxide is at least about 1:1, but ratios as low as about 1:4 are acceptable.

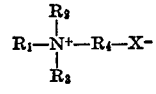
It is believed that the general structure of the PEI polymer is:

wherein x represents a whole number of sufficient magnitude to yield a polymer of molecular weight greater than about 1800. Generally, x may vary from 14 to about 1500, and preferably x is from 45 to 5,000. Branch chains occur along the polymeric backbone and the relative proportions of primary, secondary, and tertiary amino groups present in the polymer will vary, depending on the manner of preparation. The distribution of amino groups in a typical PEI is approximately as follows:



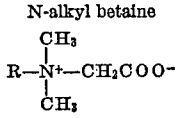
The polymers suitable for use in this invention have viscosities (in 1 percent by weight aqueous solutions) ranging from about 1.0 to about 3.0 centipoises (absolute viscosity) when measured by an Ostwald viscometer at 100° F. The molecular weight of the PEI polymers includes the entire range of dermatologically-safe materials. The preferred polymers have an average molecular weight within the range of about 1800 to about 200,000 with the most preferred polymer having an average molecular weight of about 100,000. The molecular weight may range as high as 500,000 for ethoxylated and propoxylated polymers.

The useful zwitterionic detergents are betaines and sulfobetaines having the following general formula:

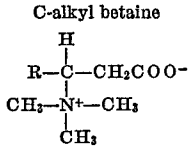


where R_1 is an alkyl group having 10 to about 20 carbon atoms, preferably 12 to 16 carbon atoms, R_2 and R_3 are each alkyl groups having 1 to 3 carbon atoms, R_4 is an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms, and X is an anion selected from the group consisting of $SO_3^=$ and $COO^=$. The preferred betaines and sulfobetaines have the following formulas:

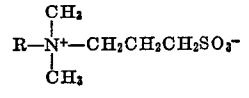
N-alkyl betaine



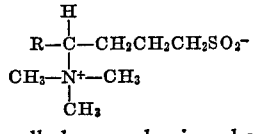
C-alkyl betaine



N-alkyl sulfobetaine



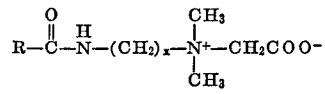
C-alkyl sulfobetaine



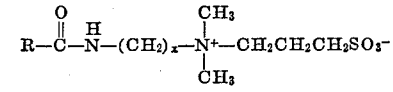
where R in each formula is an alkyl group having about 10 to about 20 carbon atoms.

Amido betaines and amido sulfobetaines having the following structure may also be used:

Amido betaine



Amido sulfobetaine



where R in both formulas is an alkyl group having about 10 to about 20 carbon atoms.

The preferred compound from the group of zwitterionic detergents is coco [3] dimethyl betaine.

The useful semi-polar amine oxide detergents have the following general formula:

Amine oxide

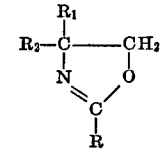
$$R_1R_2R_3N\rightarrow O$$

where R_1 is an alkyl, alkenyl, or monohydroxyalkyl group having 10 to about 20 carbon atoms, and R_2 and R_3 are each selected from the group consisting of methyl, ethyl, propyl, ethanol, and propanol groups.

The preferred amine oxide detergent is myristyl dimethyl amine oxide.

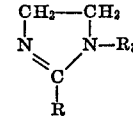
The useful foam boosters are the imidazoline and oxazoline materials having the following general formulas:

Oxazoline



where R is an alkyl group having about 9 to about 17 carbon atoms, and R_1 and R_2 are selected from the group consisting of hydrogen and alkyl and hydroxyalkyl groups containing from 1 to 2 carbon atoms.

Imidazoline



where R is an alkyl group having about 9 to about 17 carbon atoms, and R_3 is selected from the group consisting of hydroxy methyl, hydroxyethyl, hydroxypropyl and $CH_2CH_2OCH_2CH_2OH$.

In the preparation of the imidazoline and oxazoline foam booster, the carboxyl carbon of the fatty acid reactant becomes part of the ring, and thus the resultant alkyl group contains one less carbon than the corresponding fatty acid.

The preferred imidazoline foam booster is 1-hydroxyethyl-2-coco imidazoline; the preferred oxazoline foam booster is 2-coco-4,4 dihydroxymethyl oxazoline.

A water-soluble, nonionic synthetic detergent may be substituted for the preferred zwitterionic and amine oxide detergents; however, the resultant shampoo compositions are non-preferred due to the lower foaming properties of the nonionic detergents. Suitable nonionic synthetic organic detergents are generally the condensation product of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups or the polyhydration product thereof, i.e., polyethylene glycol.

[3] The term "coco" as used herein refers to the mixture of alkyl groups found in the alcohols obtained by hydrogenating the mixture of fatty acids obtained upon hydrolysis of coconut oil, that is, C_8–8%; C_{10}–7%; C_{12}–48%; C_{14}–17%; C_{16}–15%; and C_{18}–5%.

Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide to form a nonionic detergent. Suitable nonionic detergents include the polyethylene oxide condensate of one mole of alkyl phenol containing from about 6 to about 12 carbon atoms in a straight or branched chain configuration with about 5 to 30 moles of ethylene oxide, e.g., nonyl phenol condensed with 9 moles of ethylene oxide; the condensation product of a higher alcohol containing about 8 to 22 carbon atoms in a straight or branched chain configuration with about 5 to 30 moles of ethylene oxide, e.g., lauryl-myristyl alcohol condensed with 16 moles of ethylene oxide; the condensation product of ethylene oxide on a hydrophobic base formed by the condensation of propylene oxide on propylene glycol wherein the molecular weight of the hydrophobe ranges from about 1,500 to 1,800 and the polyethylene oxide content may comprise up to 50% of the total weight of the condensate; and the ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof with higher fatty acids containing about 10 to 20 carbon atoms, e.g., sorbitan monolaurate, sorbitan mono-oleate, and mannitan monopalmitate. Alternatively, such nonionic detergents may be used in addition to the preferred betaine, sulfobetaine, and amine oxide detergents in concentrations of about 3% to 10% by weight of the shampoo composition.

The aqueous vehicle may contain an organic solvent such as monohydric and dihydric alcohols containing 2 to 3 carbon atoms. The solvent may be present in an amount of from about 5 to 30 percent by weight and preferably from about 10 to 20 percent.

In the most preferred shampoo compositions, the betaine, sulfobetaine, and amine oxide detergents are present in an amount of 10% to about 20% by weight; the PEI is present in an amount of about 1% to 2% by weight; the imidazoline and oxazoline foam booster is present in an amount of about 3% to 5% by weight; and the aqueous medium or vehicle is the balance. When a mixture of detergents is used, the preferred concentration of the individual detergents is reduced because the total amount of detergent present in the most preferred compositions ranges from about 10% to about 20% by weight.

Various conventional shampoo additives may also be present, for example, compatible nonionic thickeners, perfumes, pH adjusters, sequestering agents, opacifiers, compatible antimicrobial compounds, etc. Such additives are present in their conventional amounts ranging from about 0.4 to about 10 percent by weight. More specifically, coconut mono- or diethanolamides and strongly ionizing salts such as sodium chloride and sodium sulfate may be used up to about 5 percent of the formula weight. These compounds serve to aid in the compatibilization of the polymer-detergent composition; however, they are not essential.

EXAMPLE I

Shampoo compositions were prepared having the following composition:

EXAMPLE I

	A	B	C
Coco dimethyl betaine	10.0	10.0	10.0
Myristyl dimethyl amine oxide	5.0		
1-hydroxyethyl-2-coco imidazoline		5.0	
2-coco-4,4-dihydroxymethyl oxazoline			5.0
Polyethylenimine (M.W. 50,000)	1.0	1.0	1.0
HCl (pH adjustment to about 7.5)	1.0	1.0	1.0
Propylene glycol		5.0	5.0
Perfume	0.4	0.4	0.4
Deionized water	(1)	(1)	(1)

[1] Balance.

These compositions were clear, stable liquids which yielded copious lather, left hair free from tangles and static flayaway, and showed inhibitory action against the growth of *P. ovale.*

EXAMPLE II

Coco dimethyl sulfobetaine	10.0
1-hydroxyethyl-2-coco imidazoline	5.0
Polyethylenimine (M.W. 1800)	2.0
HCl (to adjust pH to about 7.5)	1.0
Deionized water	Balance

EXAMPLE III

Myristyl dimethyl betaine	15.0
1-hydroxyethyl-2-coco imidazoline	2.0
Polyethylenimine (M.W. 100,000)	1.0
HCl (to adjust pH to about 7.5)	1.0
Ethanol	10.0
Deionized water	Balance

EXAMPLE IV

Palmityl dimethyl amido betaine	15.0
Polyethylenimine (M.W. 50,000)	2.0
HCl (to adjust pH to about 7.5)	1.0
NaCl	3.0
Deionized water	Balance

EXAMPLE V

Myristyl dimethyl amine oxide	10.0
Polyethylenimine (M.W. 1800)	3.0
HCl (pH adjustment to about 7.5)	1.0
Perfume	0.4
Deionized water	Balance

In order to determine the conditioning effect of PEI on the hair the following test was conducted.

Clean hair samples (washed in a nonionic surfactant and rinsed in distilled water and in ethanol) were dipped in a 2-percent oleic acid-alcohol solution to provide free fatty acid such as is present on the scalp. After drying the various tresses were shampooed with:

(A) Composition A of Example I
(B) Composition A with PEI omitted
(C) Shampoo containing 19% triethanolamine lauryl sulfate and 5% lauryl-myristyl diethanolamide in an aqueous medium.

The shampoo solutions were diluted with water to 10 parts shampoo to 90 parts water to simulate dilution in actual shampooing. The shampooed tresses were rinsed well and dried. As a control tress one of the clean tresses was not treated with oleic acid but was washed with Composition A of Example I.

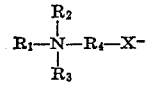
The results of this test revealed that the tress which had oleic acid on it and washed with Composition A of Example I was low in friction during dry combing, was low in static "fly" when combed, and felt smooth. However, the tress having no oleic acid present which was shampooed with Composition A of Example I was difficult to comb and gave static "fly." Further, Composition A without PEI also was difficult to comb and gave static "fly." These results indicate that the conditioning effects of Composition A of Example I are probably due to the fact that PEI deposits on the hair and also redeposits the natural oils. Composition A also gave superior conditioning results as compared to the conventional anionic/alkanolamide shampoo whose washed tress also gave static "fly" and was difficult to comb.

Percentage values employed in the specification and claims refer to percent by weight of the total composition unless otherwise stated.

What is claimed is:

1. A clear, homogeneous shampoo composition particularly suitable for conditioning hair and for inhibiting the growth of *Pityrosporum ovale* which consists essentially of about 5 to 25 percent by weight of a water-soluble

detergent selected from the group consisting of betaines and sulfobetaines having the formula



wherein R_1 is alkyl of 10 to 20 carbons, R_2 and R_3 are each alkyl of 1 to 3 carbons, R_4 is alkylene or hydroxyalkylene of 1 to 4 carbons, and X is $SO_3^=$ or $CO_2^=$, C-alkyl betaines of the formula

$$(CH_3)_3N^+CH(R)CH_2CO_2^-$$

wherein R is an alkyl of 10 to 20 carbons, C-alkyl sultaines of the formula

$$(CH_3)_3N^+CH(R)CH_2CH_2CH_2SO_3^-$$

wherein R is an alkyl of 10 to 20 carbons, amine oxides of the formula $R_1R_2R_3N\rightarrow O$ wherein R_1 is an alkyl, alkenyl, or monohydroxyalkyl of 10 to 20 carbons, and R_2 and R_3 are each methyl, ethyl, propyl, ethanol, or propanol, and mixtures of the foregoing detergents; 0.1 to 3 percent by weight of a water-soluble polymer selected from the group consisting of polyethylenimine having a molecular weight from about 1,800 to about 200,000 and the reaction product of said polyethylenimine with either ethylene oxide or propylene oxide in a weight ratio of polyethylenimine to alkylene oxide of at least 1:4, said reaction product having a molecular weight of up to 500,000, said polymer exhibiting inhibitory activity against *Pityrosporum ovale;* and an aqueous vehicle, said composition being free of anionic-acting surfactants.

2. The shampoo composition as set forth in claim **1** wherein said detergent is a mixture of said betaine or sulfobetaine corresponding to the formula

$$R_1N(CH_3)_2R_4—X^-$$

and said amine oxide and said mixture is present in an amount of 10 to 20 percent by weight of the composition.

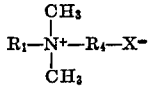
3. The shampoo composition as set forth in claim **1** wherein said detergent is said amine oxide.

4. The shampoo composition as set forth in claim **1** wherein said aqueous vehicle contains from about 10 to 20 percent by weight of the total composition of an organic solvent selected from the group consisting of monohydric and dihydric alcohols containing 2 to 3 carbons.

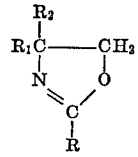
5. The shampoo composition as set forth in claim **1** wherein said aqueous medium is water.

6. The shampoo composition as set forth in claim **1** wherein said polymer is said polyethylenimine having a molecular weight of about 1,800 to 100,000.

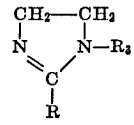
7. The shampoo composition as set forth in claim **1** wherein said detergent is said betaine or sulfobetaine corresponding to the formula



8. The shampoo composition as set forth in claim **1** which contains in addition from about 1 to 6 percent by weight of the total composition of foam boosting compound selected from the group consisting of an oxazoline having the following structure



wherein R is alkyl containing 9 to 17 carbons and R_1 and R_2 are each selected from the group consisting of hydrogen, alkyl containing 1 to 2 carbons, and hydroxyalkyl containing from 1 to 2 carbons and an imidazoline having the following structure



wherein R is alkyl containing 9 to 17 carbons and R_3 is selected from the group consisting of hydroxymethyl, hydroxyethyl, hydroxypropyl, and $CH_2CH_2OCH_2CH_2OH$.

References Cited

UNITED STATES PATENTS

3,033,746	5/1962	Moyle et al.	424—325
3,098,794	7/1963	Dohr et al.	424—70 X
3,206,512	9/1965	Koebner et al.	424—325 X
3,280,179	10/1966	Ernst	424—70 X
3,449,430	6/1969	Dohr et al.	424—70 X
3,470,102	9/1969	Heinz	424—70 X

FOREIGN PATENTS

451,412	5/1968	Switzerland	424—316
1,111,708	5/1968	Great Britain	424—325
1,078,075	8/1967	Great Britain.	

OTHER REFERENCES

Wells et al., Cosmetics and The Skin, p. 404, Reinhold Publishing Corp. New York, 1964.

American Perfumer and Cosmetics, vol. 84, pp. 37–39, December 1969.

ALBERT T. MEYERS, Primary Examiner

V. C. CLARKE, Assistant Examiner

U.S. Cl. X.R.

252—106; 424—DIG. 24, 78, 316, 325