

1

3,400,198

WAVE SET RETENTION SHAMPOO CONTAINING POLYETHYLENIMINE POLYMERS

Edward W. Lang, Wyoming, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

No Drawing. Continuation-in-part of application Ser. No. 305,204, Aug. 28, 1963. This application Oct. 12, 1966, Ser. No. 586,013

19 Claims. (Cl. 424—71)

This application is a continuation-in-part of copending application Ser. No. 305,204, filed Aug. 28, 1963, and now abandoned.

This invention relates to an aqueous detergent composition especially adapted for cleansing hair. More specifically, it relates to a homogeneous aqueous shampoo composition characterized by its outstanding capacity to improve the condition of hair.

A shampoo composition in order to be commercially acceptable must possess certain basic characteristics. For example, it must clean without unduly diminishing the natural lustre of the hair, as by precipitation of dulling insoluble soap films. It must be a stable, homogeneous product which will not separate under ordinary conditions of storage and usage. Further, it must yield a copious lather and must work well in hard water.

With the advent of synthetic detergents, shampoo formulators have largely overcome the more basic problems of shampoo development and are now concerned with the provision of compositions which leave the hair in a manageable condition, since the removal of substantial proportions of the natural oil from the hair in the course of shampooing with such detergents adversely affects hair manageability. Although measures have been taken to prevent or alleviate this undesirable effect, as far as is known none of these measures have succeeded without loss or impairment of one of the forementioned basic characteristics of cleaning, lathering, stability, etc.

Hair conditioning agents such as polyglycols, fatty acid esters of glycols, natural or synthetic waxes and lanolin derivatives, for example, have been added to shampoo formulations as a means of counteracting the detrimental effects of natural oil loss caused by shampooing the hair. Such materials can cause the hair to have an unpleasant oily appearance and feel. Further, certain hair conditioning agents, especially those of the oily nature mentioned above, inhibit sudsing of the shampoo. Consumers have come to expect copious lather from shampoo and are dissatisfied if it is not formed.

Products are, of course, available for application to the hair subsequent to shampooing which are intended to counteract the undesirable effects of the shampoo on hair manageability and to improve the condition of the hair in various respects. Hair rinses, sets and sprays have been developed which improve manageability and wave set retention. Such products often contain polymeric substances which form a film on the hair upon drying, thereby holding the hair in a desired preformed configuration, i.e., increase wave set retention. As far as is known, however, none of these polymeric materials have been incorporated into a satisfactory shampoo formulation because generally these substances, if soluble enough to be included in a homogeneous shampoo product, are not of such a nature that they become substantively attached to the hair fiber to a degree sufficient to prevent removal in the course of washing and rinsing.

The term "hair manageability" as used herein refers to the relative ease with which the hair can be placed in a desired coiffure. Factors influencing hair manageability are hair lubricity and entanglement, i.e., "combability," and electrostatic charge causing hair "fly."

2

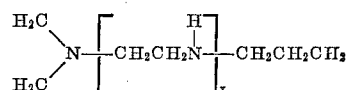
It is an object of this invention to provide a stable aqueous shampoo composition which improves the wave set retention of the washed hair but which also possesses excellent cleansing and lathering characteristics.

It has now been found that certain polyethylenimine polymers when employed in liquid detergent compositions containing a mixture of anionic and amphoteric or polar nonionic detergents, form clear homogeneous liquids while in a concentrated product form, but precipitate on the hair fiber when the product is diluted with water in the course of usage. Upon drying, this precipitate improves the wave retention of the hair and hair manageability. These concentrated formulations are stable and possess excellent cleaning and sudsing characteristics when diluted with water.

In general the compositions of this invention are comprised of (A) from about 0.1% to about 4.0% of a water-soluble polyethylenimine, (B) from about 4.0% to about 20.0% of an organic anionic detergent, (C) from about 4.0% to about 20.0% of a detergent selected from the group consisting of polar nonionic detergents, amphoteric detergents, and mixtures thereof, and the balance, (D) water and minor ingredients, the ratio by weight of B to C ranging from about 2:1 to about 1:2, said composition being at a pH between about 7 and about 10. Formulations encompassed by this invention are stable, homogeneous compositions which as hereinbefore indicated yield a fine precipitate of the polymer component upon dilution with water. The precipitate adheres firmly to the hair shaft in the course of lathering and rinsing and does not appreciably change the appearance of the hair on drying. The adherent material produces the improved hair manageability and wave set retention characteristics of this invention.

The polyethylenimine polymers which can be used in the compositions of this invention can be prepared by polymerizing ethylenimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and etc. Specific methods of preparation are described in U.S. Patent 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 2,553,696, Wilson, granted May 21, 1951.

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



wherein x represents a whole number preferably greater than 100. However, branch chains are possible along the polymer chain and, depending on the manner of preparation, there may be more tertiary and primary amines present than is apparent in this formula.

The polymers suitable for use in this invention have viscosities, in 1% by weight aqueous solutions, ranging from about 1.0 to about 3.0 centipoises (absolute viscosity) when measured by an Ostwald viscosimeter at 100° F. The viscosities of the polyethylenimines increase as the degree of polymerization increases; thus, polymers of higher molecular weight will, in general, have higher viscosities.

The molecular weight of the polymeric component is not critical; however, the preferred polymers have an average molecular weight within the range from about 5,000 to about 200,000 with the most preferred polymers having an average molecular weight of about 100,000. Polymers having a molecular weight of less than about 5,000 may not precipitate from the compositions of this

invention in the course of shampooing to impart the desired wave set retention properties. Polymers having molecular weights in excess of about 200,000 may not be sufficiently soluble to provide a stable homogeneous product. Preferably, the molecular weight of the polymers employed in the compositions of this invention will be greater than about 10,000 but less than about 150,000.

The concentration of the polymeric component can vary according to the amount of film deposition desired. Amounts below about 0.1% will not ordinarily yield improved manageability and wave set retention. Concentrations greater than about 4.0% yield an undesirably heavy and somewhat sticky film on the hair. Preferably, this component will be employed in a concentration of from about 0.1% to about 2.0% by weight of the total composition.

The polyethylenimine component is not compatible with normally used anionic detergents at pH's below about 10 because it has tendency to precipitate out of solution in the shampoo composition. It has been surprisingly found, however, that when an amphoteric or polar nonionic detergent is used in conjunction with the conventional anionic detergent, the polymer remains in solution within the pH range of about 7 to about 10 and will not precipitate out of solution until it is diluted with water when applied to the hair.

The organic anionic detergent which is employed in this invention includes both water-soluble soap and non-soap synthetic detergents. Operable non-soap anionic organic detergents include, for example, water-soluble salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a radical selected from the group consisting of sulfuric acid ester and sulfonic acid radicals. Important examples of this type of non-soap anionic synthetic detergent, include the sodium or potassium alkyl sulfates, especially those derived by sulfation of higher alcohols produced by reduction of tallow of coconut oil glycerides; sodium or potassium alkyl benzene sulfonates, especially those of the types described by Guenther et al. in U.S. Patent 2,220,099, granted Nov. 5, 1940, and by Lewis in U.S. Patent 2,477,383, granted July 26, 1949, in which the alkyl group contains from about 9 to about 15 carbon atoms; sodium alkylglyceryl ether sulfonates, especially those ethers of higher alcohols obtained from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (i.e., tallow or coconut oil alcohols) and about 3 moles of ethylene oxide; and others well known in the art, a number being specifically set forth in Byerly, U.S. Patent Nos. 2,486,921 and 2,486,922.

Additional non-soap anionic organic synthetic detergents which can be used in this invention include the salts of the condensation products of fatty acids with sarcosine, i.e., acyl sarcosinate, wherein the acyl radical has a chain length range from about 10 to 18 carbon atoms. An especially preferred acyl sarcosinate for the purpose of this invention is sodium lauroyl sarcosinate.

Preferably, the non-soap anionic organic detergent will be of the high sudsing type as for example, the alkylglyceryl-ether sulfonates, the sulfated fatty alcohols or the alkyl ether ethylene oxide sulfates wherein the ethylene oxide chain averages 3 units, and acyl sarcosinates, all as more fully set forth above. These and the foregoing detergents can be used in the form of their sodium, potassium or lower alkanolamine such as triethanolamine salts.

Conventional soaps may also be used as the anionic detergent component of this invention. Suitable soaps include the sodium, potassium, and lower alkanolamine salts of higher fatty acids of naturally occurring vegetable or animal fats and oils. For example, sodium, potassium and triethanolamine salts of fatty acids occurring in co-

conut oil, soybean oils, castor oil, tallow or synthetically produced fatty acids may be used. Because of its high natural alkalinity which requires a substantial portion of relatively expensive amphoteric detergent (relative to the anionic component) to compatibilize the soap and the polymer component within the pH range of the compositions of this invention, it is not desirable to use soap as the sole anionic detergent component.

If soap is to be used, it would desirably be used in small quantities, less than about 10%, and would be admixed with synthetic anionic detergents to form the anionic detergent component of the shampoo compositions of this invention. Preferably, the triethanolamine salt of coconut fatty acid would be used, since it is more readily soluble than the salts of higher alkyl chain length fatty acids. Other preferred soaps include the sodium and potassium salts of coconut fatty acid.

Mixture of any of the foregoing anionic detergents may also be used in the composition of this invention.

The anionic organic detergent can be employed in concentration ranging from about 4.0% to about 20.0% by weight of the total composition with the preferred range being from about 7% to about 15%. Because of the excellent solubility and lathering properties of anionic non-soap detergents containing predominantly C_{12} and C_{14} alkyl chain lengths and their ready availability, these are preferred for the purpose of this invention.

It is essential that the compositions of this invention contain at least one member selected from the group consisting of polar nonionic and amphoteric detergents. This component as mentioned herein serves to compatibilize the polymeric component and the anionic detergent. It further enhances the lathering and cleaning properties of the composition. By polar nonionic detergent is meant a detergent in which the hydrophilic group contains a semi-polar bond directly between two atoms, e.g., $N \rightarrow O$, $P \rightarrow O$, $As \rightarrow O$, and $S \rightarrow O$. There is charge separation between the two directly bonded atoms but the detergent molecule bears no net charge and does not dissociate into ions.

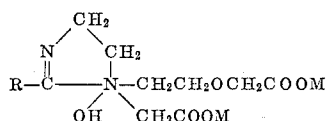
The polar nonionic detergents which can be used in conjunction with or as an alternative to the amphoteric detergent includes open-chain aliphatic amine oxides of the general formula $R_1R_2R_3N \rightarrow O$. The arrow is a conventional representation of a semi-polar bond. These compounds are generally prepared by the direct oxidation of the appropriate tertiary amine. When R_1 is a much longer chain than R_2 and R_3 , the amine oxides have surface activity. For the purpose of this invention R_1 is an alkyl, alkenyl, or monohydroxyalkyl radical having from about 10 to about 16 carbon atoms. Desirable surface active properties are lost if R_1 is substantially less than about 10 carbon atoms and the compounds are insufficiently soluble if R_1 is greater than about 16 carbon atoms. R_2 and R_3 are each selected from the group consisting of methyl, ethyl, propyl, ethanol and propanol radicals. Preferably R_1 is a dodecyl radical or a mixture of dodecyl with decyl, tetradecyl and hexadecyl such that at least 50% of the radicals are dodecyl radicals. R_2 and R_3 are preferably methyl radicals. A preferred amine oxide for the purpose of this invention is a dodecyl dimethylamine oxide.

Other operable polar nonionic detergents are the open-chain aliphatic phosphine oxides having the general formula $R_1R_2R_3P \rightarrow O$ wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbon atoms, and R_2 and R_3 are each alkyl and monohydroxyalkyl radicals containing from 1 to 3 carbon atoms. A preferred phosphine oxide is dodecyl dimethyl phosphine oxide. This and other phosphine oxides together with a method of preparation are fully described by Yoke et al. in copending application Ser. No. 173,834, filed Feb. 16, 1962.

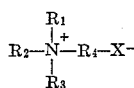
As hereinbefore stated, amphoteric detergents can be used in conjunction with or in place of the polar nonionic

5

detergents described above. As used herein the term "amphoteric" is interchangeable with the term "ampholytic." Amphoteric detergents are well known in the art and many operable detergents of this class are disclosed by A. M. Schwartz, J. W. Perry and J. Birch in "Surface Active Agents and Detergents," Interscience Publishers, New York, 1958, vol. 2. Examples of suitable amphoteric detergents include, for example, alkyl betainodipropionates, $RN(C_2H_4COOM)_2$; alkyl beta-amino propionates, $RN(H)C_2H_4COOM$; and long chain imidazole derivatives having the general formula:

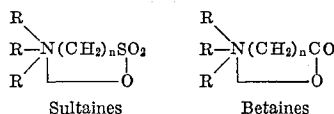


In each of the above formulae R is an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms and M is a cation to neutralize the charge of the anion. Specific operable amphoteric detergents include the disodium salt of lauroylcycloimidinium-1-ethoxyethionic acid-2-ethionic acid, dodecyl beta alanine, and the inner salt of 2-trimethylamino lauric acid. The substituted betaines and sultaines, such as alkyl ammonio acetates wherein the alkyl radical contains from about 12 to about 18 carbon atoms can also be used. The betaine and sultaine types of ampholytic detergents are zwitterionic quaternary ammonium compounds having the general formula:



wherein R_1 is an alkyl having from about 10 to about 18 carbon atoms, R_2 and R_3 are each alkyl having from about 1 to about 3 carbon atoms, R_4 is an alkylene or hydroxy-alkylene having from 1 to 4 carbon atoms, and X is an anion selected from the group consisting of SO_3^- and COO^- .

Compounds which conform to the above general formula are characterized by the presence of both positive and negative charges which are internally neutralized (i.e. zwitterionic). When the anion X is SO_3^- , these compounds are referred to as "sultaines." The term "betaines" is employed when the anion X is COO^- . The following structural formulae are illustrative of the two types and their inner salt character.



When one R in the above formulae is a high molecular alkyl having from about 10 to 18 carbon atoms, these compounds are surface active and have good detergency powers. If the high molecular alkyl contains less than about 10 carbon atoms, surface activity and detergency are inadequate. If this group contains more than about 18 carbon atoms, the compounds are not sufficiently soluble to be of utility in this invention. Preferably, the high molecular alkyl will contain from 12 to 16 carbon atoms or a mixture of dodecyl with decyl, tetradecyl, and hexadecyl radicals. A convenient source of a suitable mixture of alkyl groups is the middle cut of coconut fatty alcohol which has the approximate chain length composition: 2%— C_{10} , 66%— C_{12} , 23%— C_{14} , and 9%— C_{16} . Particular advantage can be gained by employing betaine or sultaine having an alkyl containing 16 carbon atoms in the compositions of this invention as will be illustrated infra. The alkyl can, of course, contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such as hydroxyl or halogen which do not substantially affect the hydrophobic character of the group.

6

Preferred compounds which fall within the above class include 1-(alkyldimethylammonio)acetate, 1-(alkyldimethylammonio) propane-3-sulfonate and 1-(alkyldimethylammonio)-2-hydroxy-propane-3-sulfonate wherein the alkyl contains from 12 to 16 carbon atoms.

The amine oxides are particularly advantageous for use in the present invention because of their superior capacity to compatibilize the other components of the compositions and their high lathering, cleaning and solubility characteristics.

Whether the polar nonionic detergents or amphoteric detergents are employed in the compositions of this invention, their concentration in the total composition will range from about 4% to about 20% by weight. Preferably, this component will be employed at a concentration within the range of about 7% to about 15%.

As hereinbefore explained the weight ratio of amphoteric and/or polar nonionic detergent can vary from about 2:1 to about 1:2 with good results. The preferred ratio is 1:1.

Each of the forementioned components will be incorporated into an aqueous vehicle which may, in addition, include such materials as organic solvents such as ethanol, thickeners such as carboxymethyl cellulose or methyl cellulose, perfumes, sequestering agents such as tetrasodium ethylenediamine tetraacetate, and opacifiers such as zinc stearate or magnesium stearate which are useful in enhancing the cosmetic properties of shampoo formulations.

Coconut mono- or diethanolamides and strongly ionizing salts such as sodium chloride and sodium sulfate may be used up to about 5% of the formula weight. The compounds serve to aid in the compatibilization of the polymer-detergent composition; however, they are not essential.

The term "coconut" as used in the following examples refers to alkyl groups which are derived from the middle cut of coconut alcohol having the following approximate chain length distribution: 2%— C_{10} , 66%— C_{12} , 23%— C_{14} , and 9%— C_{16} .

EXAMPLE I

A liquid detergent composition was prepared having the following composition:

	By weight, percent
Polyethylenimine ¹	1.0
Coconut monoethanol amide	5.0
Triethanolamine coconut sulfate	10.0
Coconut dimethylamine oxide	10.0
Ethanol	10.0
Water, NaOH to adjust pH	Balance
pH=8.5.	

¹ A water-soluble polymer having an average molecular weight of 100,000 and viscosity of 2.5 centipoises (absolute viscosity) a 1% by weight aqueous solution measured with an Ostwald viscosimeter at 100° F.

This composition was a clear stable liquid which yielded copious lather in the course of normal usage in shampooing the hair and left the hair in a highly manageable state after washing. In order to evaluate the hair set retention characteristics imparted by the shampoo, a 2 g. test switch of hair was washed with 1 g. of this composition and 5 g. water. The hair was then rinsed and placed into a curl configuration while still wet by winding the switch around a mandrel. The curl was placed in a constant humidity room and allowed to dry. After the curl had dried, the mandrel was removed and the curl was suspended to allow it to unwind. The time required for the curl to unwind was measured and compared with the time required for a test switch of the same hair to unwind which had been washed with the same quantity of a conventional commercially available shampoo and treated in an identical manner as the first mentioned test switch. The "conventional commercially available shampoo" referred to above and referred to hereinafter either as a "conventional shampoo" or a

"commercially available shampoo" comprises essentially triethanolamine alkyl sulfate where the alkyl group is derived from a mixture of coconut alcohols, coconut diethanolamide where the acyl radical is derived from coconut fatty acid, ethyl alcohol, and water. The time required for the curl to unwind is a measure of the curl retention of the hair switch.

The curl washed with the shampoo composition of this invention took considerably longer to unwind than did the curl washed with a conventional shampoo, thus demonstrating that hair washed with the compositions of this invention has markedly superior curl retention characteristics.

The coconut dimethylamine oxide employed in this example can be replaced with dodecyldimethylphosphine oxide with no substantial change in product characteristics or results achieved in use.

EXAMPLE II

An additional shampoo formulation is prepared having the following composition:

	By weight, percent
Polyethylenimine ¹	3.0
Ethanol	10.0
Triethanolamine coconut sulfate	10.0
Coconut beta-iminodipropionate, disodium	6.0
Water, NaOH to adjust pH 8.6	Balance

¹ Same as Example I.

This composition is a clear stable liquid which possesses the same excellent cleaning and lathering characteristics of a commercially available shampoo when used to wash hair in the conventional manner. In addition, test switches of hair washed with this composition are left in a highly manageable condition, i.e., easily combed and very little hair fly. The washed hair is tested for wave retention as in Example I. Curls formed after washing with the composition of this example are retained for much greater length of time than curls formed after washing test switches of the same hair with a conventional shampoo.

The triethanolamine coconut sulfate can be replaced with the potassium salt of coconut alkyl glyceryl ether sulfonate without a substantial loss of desired performance characteristics.

The polyethylenimine used in the above composition can be replaced by a polyethylenimine, a 1% aqueous solution of which has a viscosity of 3.0 centipoises (absolute viscosity) measured with an Ostwald viscosimeter at 100° F., and similar results are achieved.

EXAMPLE III

	By weight, percent
Polyethylenimine ¹	2.0
Ethanol	10.0
Triethanolamine coconut sulfate	12.0
Lauroylcycloimidinium-1-ethoxy-ethionic acid-2-ethionic acid, disodium	6.0
Water, NaOH to adjust pH 8.0	Balance

¹ Same as Example I.

The characteristics of the above formulation and the results of its use in shampooing hair are substantially the same as those of Examples I and II.

The disodium salt of lauroylcycloimidinium-1-ethoxy-ethionic acid-2-ethionic acid employed in this example can be replaced in whole or in part with dodecyl betalanine, 2-trimethylamino lauric acid, 1(coconutdimethylammonio)acetate, 1(coconutdimethylammonio)-propane-3-sulfonate, or hexadecyl-dimethylamine oxide without substantially altering the product characteristics or performance.

In the above formula, the polyethylenimine can be replaced by a polyethylenimine, the viscosity of a 1% aqueous solution being 1.0 centipoise (absolute viscosity—measured with an Ostwald viscosimeter at 100° F.), with substantially the same results.

EXAMPLE IV

Composition	By weight, percent
Polyethylenimine ¹	1.0
Ethanol	10.0
5 Sodium salt of sulfated condensation product of 1 mole of coconut alcohol with 3 moles of ethylene oxide	8.0
Coconut dimethylamine oxide	7.5
10 Water, NaOH to adjust pH	Balance
pH=9.3.	

¹ Same as Example I.

The above composition is a clear homogeneous liquid which remains stable after prolonged storage. Hair washed with this composition in the conventional manner is found to be highly manageable and retains a desired configuration for substantial periods of time. The concentration of the polymer employed in this example can be reduced to .1% by weight or increased to as much as 4.0% and desired performance characteristics will still be observed.

Additional examples of representative compositions of this invention are set forth hereafter. The invention is not to be limited thereby, however.

EXAMPLE V

Composition	By weight, percent
1 dodecyldimethylammonio) acetate	10
Triethanolamine coconut sulfate	10
30 Coconut monoethanolamide	5
Ethanol	10
Polyethylenimine ¹	1
Sodium chloride	5
35 Water	Balance
pH=7.2.	

¹ Average molecular weight of 100,000 and viscosity of 2.5 centipoises (a 1% by weight aqueous solution measured with an Ostwald Viscosimeter at 100° F.)

EXAMPLE VI

Composition	By weight, percent
1 dodecyldimethylammonio) acetate	6
Dodecyl dimethylphosphine oxide	6
Sodium coconut sulfate	6
45 Coconut monoethanolamide	5
Ethanol	7
Polyethylenimine ¹	0.5
Water	Balance
50 pH=8.3.	

¹ Viscosity of a 1% by weight aqueous solution being 1.0 centipoise measured with an Ostwald Viscosimeter at 100° F.

EXAMPLE VII

Composition	By weight, percent
55 Coconut beta-iminodipropionate, disodium	7.5
Triethanolamine coconut sulfate	7.5
Sodium lauroyl sarcosinate	3.0
Ethanol	7
Sodium chloride	3
60 Polyethylenimine ¹	1
Water	Balance
pH=8.6.	

¹ Same as Example VI.

EXAMPLE VIII

Composition	By weight, percent
1 (dodecyldimethylammonio) acetate	10
Sodium coconut (ethoxy) ₃ sulfate	10
70 Coconut monoethanolamide	5
Ethanol	10
Polyethylenimine ¹	0.5
Water	Balance
pH=7.0.	

¹ Same as Example VI.

EXAMPLE IX

Composition	By weight, percent
Lauroylcycloimidinium-1-ethoxy-ethionic acid-2-ethionic acid, disodium -----	10
Sodium coconut sulfate -----	7
Sodium lauroyl sarcosinate -----	5
Sodium chloride -----	4
Tetrasodium ethylenediaminetetraacetate -----	1
Ethanol -----	4
Polyethylenimine ¹ -----	1
Water -----	10
	Balance

pH=8.7.

¹ Viscosity of a 1% by weight aqueous solution being 3.0 centipoises measured with an Ostwald Viscosimeter at 100° F.

EXAMPLE X

Composition	By weight, percent
Dodecyl dipropylamine oxide	8.5
Sodium coconut sulfate	6.5
Triethanolamine salt of coconut fatty acid	4.0
Ethanol	5
Tetrasodium ethylenediaminetetraacetate	2
Sodium chloride	3
Polyethylenimine ¹	0.5
Water	Balance
pH=8.7.	

¹ Same as Example VI.

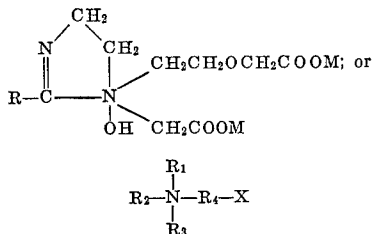
Each of the foregoing compositions is a stable homogeneous liquid. Each yields copious lather when used in normal concentration in water to wash test switches of hair. The test switches are wrapped upon a mandrel after washing and permitted to dry. The curl formed thereby is found to be retained, even under humid conditions, for substantial periods of time.

The precipitate which forms in the course of shampooing with the compositions of this invention may be removed if desired by shampooing the hair with an amphoteric detergent, for example.

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 shampoo composition adapted to promote wave set retention and hair manageability comprising (a) from about 0.1% to about 4.0% of a water-soluble polyethyl-
enimine polymer having a viscosity in 1% aqueous solu-
tion of from about 1.0 to about 3.0 centipoises at 100° F.;
(b) from about 4% to about 20% of a water-soluble salt
of a member selected from the group consisting of higher
fatty acids, anionic organic sulfuric reaction products
having in their molecular structure an alkyl containing
from about 8 to about 20 carbon atoms and a sulfonic
acid or sulfuric acid ester group, and acyl sarcosinates
wherein the acyl group is from fatty acids containing
about 10 to 18 carbon atoms; (c) from about 4% to about
20% of a detergent selected from the group consisting of
open-chain aliphatic amine oxides, open-chain aliphatic
phosphine oxides, amphoteric compounds having the struc-
tural formula $RN(C_2H_4COOM)_2$; $RN(H)C_2H_4COOM$; 60



wherein R is an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms, R₁ is an alkyl having from about 10 to about 18 carbon atoms, R₂ and 75

10

R₃ are each alkyl having from about 1 to about 3 carbon atoms, R₄ is alkylene or hydroxyalkylene having from 1 to 4 carbon atoms, M is a cation to neutralize the charge of the anion, and X is SO₃⁻ or COO⁻, and mixtures of said detergents; and the balance substantially (d) water, the ratio of (b) to (c) ranging from about 2:1 to about 1:2, said composition having a pH between about 7 and about 10.

2. The composition of claim 1 wherein component (a) has a molecular weight ranging from about 5,000 to about 200,000.

3. The composition of claim 1 wherein component (b) is triethanolamine coconut sulfate.

4. The composition of claim 1 wherein component
15 (c) is dimethyldodecylamine oxide.

5. The composition of claim 1 wherein component (c) is coconut beta-iminodipropionate.

6. The composition of claim 1 wherein component (b) is the sodium salt of a sulfated condensation product of coconut alcohol with 3 moles of ethylene oxide.

7. A shampoo composition adapted to promote wave set retention and hair manageability comprising (a) from about 0.1% to about 4.0% of a water-soluble polyethyl-enimine polymer having a viscosity in 1% aqueous solution of from about 1.0 to about 3.0 centipoises at 100° F.; (b) from about 7.0% to about 15.0% of a water-soluble salt of a member selected from the group consisting of anionic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester group, and acyl sarcosinates wherein the acyl group is from fatty acids containing about 10 to 18 carbon atoms; (c) from about 7% to about 15% of a polar nonionic detergent selected from the group consisting of open-chain aliphatic amine oxides and open-chain aliphatic phosphine oxides; and the balance substantially (d) water, the ratio of (b) to (c) ranging from about 2:1 to about 1:2, said composition having a pH of about 7 to about 10.

40 8. The composition of claim 7 wherein component (b) is alkylglycerylether sulfonate, neutralized by a cation selected from the group consisting of sodium, potassium and triethanolammonium.

9. The composition of claim 7 wherein component (b) is the sulfated condensation product of 1 mole of coconut fatty alcohol and 3 moles of ethylene oxide, neutralized by a cation selected from the group consisting of sodium, potassium and triethanolammonium.

10. The composition of claim 7 wherein component (b) is alkylbenzene sulfonate, neutralized by a cation selected from the group consisting of sodium, potassium and triethanolammonium.

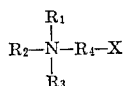
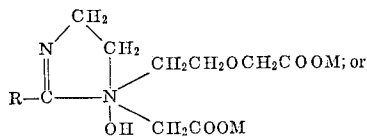
55 11. The composition of claim 7 wherein the component (c) is an amine oxide of the general formula $R_1R_2R_3N \rightarrow O$ where R_1 is selected from the group consisting of alkyl, alkenyl, and monohydroxyalkyl having from 10 to 16 carbon atoms and R_2 and R_3 are each selected from the group consisting of methyl, ethyl, propyl, ethanol and propanol.

60 **12.** The composition of claim 7 wherein component (c) is a phosphine oxide of the general formula $R_1R_2R_3P=O$ where R_1 is selected from the group consisting of alkyl, alkenyl, and monohydroxyalkyl having from 10 to 18 carbon atoms and R_2 and R_3 are each selected from the group consisting of alkyl and mono-hydroxyalkyl having
65 from 1 to 3 carbon atoms.

13. A shampoo composition adapted to promote wave set retention and hair manageability comprising (a) from about 0.1% to about 4.0% of a water-soluble polyethlenimine polymer having a viscosity in 1% aqueous solution of from about 1.0 to about 3.0 centipoises at 100° F.; (b) from about 4.0% to about 20.0% of a water-soluble salt of a member selected from the group consisting of anionic organic sulfuric reaction products having in their molecular structure an alkyl group containing from about

11

8 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group, and acyl sarcosinates wherein the acyl group is from fatty acids containing about 10 to 18 carbon atoms; (c) from about 7% to about 15% of an amphoteric detergent having the structural formula $RN(C_2H_4COOM)_2$; $RN(H)C_2H_4COOM$;



wherein R is an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms, R_1 is an alkyl having from about 10 to 18 carbon atoms, R_2 and R_3 are each alkyl having from about 1 to about 3 carbon atoms, R_4 is alkylene or hydroxyalkylene having from 1 to 4 carbon atoms, M is a cation to neutralize the charge of the anion, and X is SO_3^- or COO^- , and the balance substantially (d) water, the ratio of (b) to (c) ranging from about 2:1 to about 1:2, said composition having a pH within the range of about 7 to about 10.

14. The composition of claim 13 wherein the amphoteric detergent is the disodium salt of lauroylcycloimidium-1-ethoxyethionic acid-2-ethionic acid.

12

15. The composition of claim 13 wherein the amphoteric detergent is disodium coconut beta-imino-dipropionate.

16. The composition of claim 13 wherein the viscosity of a 1% aqueous solution of (a) is 2.5 centipoises measured at 100° F.

17. The composition of claim 13 wherein component (c) is 1(dodecyldimethylammonio)acetate.

18. The composition of claim 13 wherein component (b) is triethanolamine coconut sulfate.

19. The composition of claim 13 wherein component (b) is the sodium salt of the sulfated condensation product of 1 mole of coconut alcohol with 3 moles of ethylene oxide.

References Cited

UNITED STATES PATENTS

2,817,602	12/1957	Pardo	8—128 X
2,950,255	8/1960	Goff	167—87 X
2,999,068	9/1961	Pilcher et al.	252—137
3,085,982	4/1963	Steer et al.	252—137
3,098,794	7/1963	Dohr et al.	167—87

FOREIGN PATENTS

1,084,440	6/1960	Germany.
1,150,781	6/1963	Germany.

ALBERT T. MEYERS, *Primary Examiner.*

VERA C. CLARKE, *Assistant Examiner.*