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DETERGENT COMPOSITION

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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 posses 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 adversely affects hair manageability. Although measures have been taken in shampoo formulation to prevent or alleviate this undesirable effect, as far as is known, none of these measures have succeeded without loss or impairment of one or more 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 mentoned 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. 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."

It is an object of this invention to provide a stable aqueous detergent composition especially adapted for cleansing the hair which improves hair manageability and wave set retention.

It is a further 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 quaternary ammonium-containing polymers when employed in liquid detergent compositions containing a mixture of anionic and ampholytic 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 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 from about 0.1% to about 7.0% of a water-soluble polymer at least 30 mole percent of the structure of which is composed of monomeric units selected from the group consisting of quaternized vinylimidazole, quaternized diethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, quaternized p-dimethylaminomethylstyrene and combinations thereof, from about 0.1% to about 10.0% of an organic anionic detergent, from about 5.0% to about 20.0% of a detergent selected from the group consisting of polar nonionic detergents, ampholytic detergents, and mixtures thereof, and the balance substantially water, the weight ratio of anionic detergent to the polymeric component being not greater than about 10:1. 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 of this invention.

The polymeric compounds which can be used in the compositions of this invention are characterized by possessing a net positive charge which is imparted by the substantial proportions of quaternary ammonium groups contained therein. At least about 30 mole percent of the total polymeric structure must be composed of the herein described monomeric units containing such groups. If the polymer contains less than about 30 mole percent of these monomeric units, the net positive charge of the polymer will not be great enough to cause the polymer to precipitate and adhere to the hair with sufficient force to prevent removal by the detergent components. Preferably, the polymer will be comprised of monomeric units at least 50 mole percent of which are the quaternary ammonium-containing monomeric units disclosed herein.

It can be seen that polymers encompassed by the foregoing description can be either homopolymers of quaternizable units at least 30 mole percent of which are in fact quaternized, or copolymers containing at least 30 mole percent of quaternizable units, the balance of the polymer being composed of non-quaternizable units, at least 30 mole percent of the quaternizable units being quaternized.

The molecular weight of the polymeric component is not critical; however, the preferred polymers have an average molecular weight within the range from about 1000 to 5,000,000. Polymers having a molecular weight of less than about 1000 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 5,000,000 may not be sufficiently soluble to provide a stable homogenous product. Preferably the molecular weight

of the polymers employed in the compositions of this invention will be greater than about 4000.

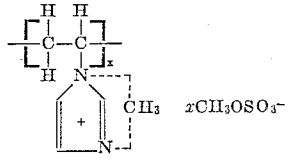
The concentration of the polymeric component can vary according to the amount of film deposition desired. Amounts below about 0.1% will not ordinarily yield improved manageability and wave set retention. Concentrations greater than about 7.0% yield an undesirably heavy and somewhat sticky film on the hair. Preferably, this component will be employed in a concentration of from about 0.5% to about 5.0% by weight of the total composition.

In general, the quaternary ammonium polymers employed in the compositions of this invention can be prepared by quaternizing the tertiary nitrogen-containing neutral polymer or copolymer to give a positively charged polymer neutralized by low molecular weight anions. Alternatively, these polymers can be prepared by quaternizing the tertiary nitrogen-containing monomer and then polymerizing the quaternized monomer, alone or with another suitable polymerizable unit as described hereinafter. The tertiary amine or quaternary ammonium-containing monomers are polymerized by reactions promoted by heat, with or without a catalyst present.

Any quaternizing agent which will not substantially change the nature of the finally resulting polymer (e.g. which does not greatly decrease its solubility or greatly increase its reactivity) can be employed in the preparation of suitable polymers. Those agents which provide a low molecular weight quaternizing group and anion are preferred from this standpoint. For example, benzyl halides such as benzyl chloride, and short chain alkyl halides such as methyl iodide, ethyl bromide and butyl chloride; short chain alkyl sulfates such as dimethyl sulfate; short chain alkyl sulfonates such as ethyl p-toluene sulfonate; alkyl phosphates such as triethyl phosphate; and alkyl phophites such as triethyl phosphite, are suitable quaternizing agents for preparing the quaternary ammonium-containing polymers to be employed in the compositions of this invention.

It should be understood that in the immediately following disclosure the identity of the anions which neutralize the charges of the quaternary ammonium polymers is not critical and depends upon the quaternizing agent employed and, in some cases, the conditions during and following quaternization (e.g. methyl sulfate may be entirely or partly hydrolyzed to sulfate, $SO_4^=$).

A preferred quaternary ammonium-containing polymer for the purpose of this invention is polyvinylimidazole quaternized, for example, with dimethyl sulfate, and having the following structural formula (a monomeric unit being represented within the brackets):

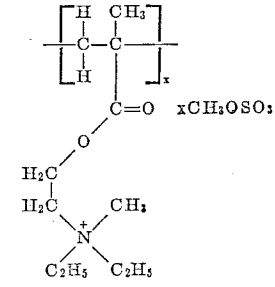


wherein x is preferably an integrer of sufficient magnitude to yield a polymer having a molecular weight within the range from about 1000 to 5,000,000. Such a polymer is prepared as follows:

86 parts of maleic acid diethyl ester and 47 parts of N-vinyl imidazole are dissolved in 200 parts of dioxane and mixed with 6 parts of 30% hydrogen peroxide. The polymerization is accomplished in the course of 15 hours at a temperature of 70° to 80° C. Then 63 parts of dimethyl sulfate are added dropwise to the solution of the resulting polymer. The product is a viscous precipitate which is separated from the supernatant dioxane by conventional means. Quaternization is essentially complete, thus substantially all of the polymer is composed of the monomeric units depicted above. The molecular weight of the polymer is between 5000 and 20,000.

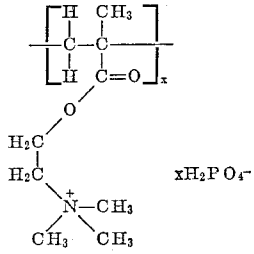
Methods of preparing polymers of this general structure are further disclosed in German patents 941,999, granted Apr. 26, 1956, and 847,347, granted Aug. 21, 1952.

Another polymer for use in the compositions of this invention is quaternized poly(diethylaminoethyl methacrylate) having the structural formula:



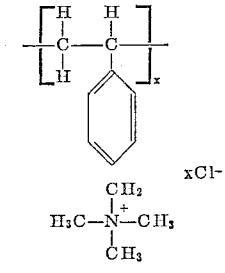
In the above structure x is preferably an integer of sufficient magnitude to yield a polymer having a molecular weight within the range from about 1000 to 5,000,000, the structure within the brackets representing a monomeric unit. Polymers of this structure and a method of preparation are disclosed in Hayek U.S. Patent 2,723,256, granted Nov. 8, 1955.

A closely related and similarly prepared quaternary ammonium-containing polymer is a quaternized poly(dimethylaminoethyl methacrylate) of the following structural formula (a monomeric unit being represented within the brackets):



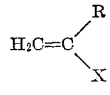
wherein x is preferably an integer of sufficient magnitude to yield a polymer having a molecular weight within the range from about 1000 to about 5,000,000.

Still another group of polymers which is suitable for use in the compositions of this invention is quaternized poly(p-dimethylaminomethylstyrene) which is comprised of units of the structural formula:



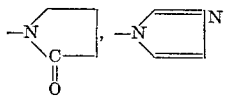
wherein x is preferably an integer of sufficient magnitude to yield a polymer having a molecular weight within the range from about 1000 to about 5,000,000, the bracketed structure being a monomeric unit.

In addition to the quaternary ammonium containing monomeric units described herein, the polymers can contain up to 70 mole percent of one or more non-quaternized monomeric units derived from monoethylenically unsaturated groups. Such groups conform to the structural formula

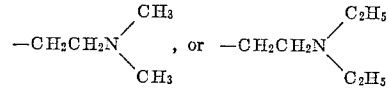


wherein R is hydrogen, methyl, ethyl or phenyl and X is

phenyl, substituted phenyl, —COOR', —$COONH_2$, —OH,



—OR'', or C≡N, wherein R' is alkyl,



and R'' is alkyl, including for example acrylonitrile, the vinyl aromatic compounds, more particularly the vinyl or other monoethylenically unsaturated substituted aromatic hydrocarbons (e.g., styrene, α-methylstyrene, the various dialkyl styrenes, etc.); other aliphatic compounds containing a CH_2=C= grouping, e.g., the various substituted acrylonitriles (e.g. methacrylonitrile, ethacrylonitrile, phenylacrylonitrile, etc.) acrylamide and the various substituted acrylamides (e.g., methacrylamide, ethyacrylamide); vinyl esters, e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, vinyl valerate, etc.; esters of an acrylic acid (including acrylic acid itself and the various α-substituted acrylic acids, e.g., methacrylic acid, ethacrylic acid, phenylacrylic acid, etc.), more particularly the alkyl esters of an acrylic acid, e.g., the ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, hexyl, heptyl, octyl, decyl, dodecyl, etc. esters of acrylic, methacrylic, ethacrylic, phenylacrylic, etc. acids; vinyl ethers, such as butyl vinyl ether; N-vinyl compounds such as N-vinyl pyrrolidone; and olefins, such as ethylene; fluorinated vinyl compounds, such as vinylidene fluoride, as well as other vinyl aromatic and vinyl aliphatic compounds, and others which will not substantially alter the nature of the resultant polymer.

A preferred copolymer for use in the present invention is a copolymer of approximately equimolar proportions of vinylbenzyltrimethyl ammonium chloride and acrylamide which can be prepared in accordance with the methods set forth in Canadian Patent 587,240, granted Nov. 17, 1959.

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 and sulfonic acid ester 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 glycerides of tallow or coconut oil; sodium or potassium alkylbenzene 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 alkylglycerylether 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 (e.g., 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 Byerley U.S. Patent 2,486,921, granted Nov. 1, 1949, and Strain, U.S. Patent 2,486,922, granted Nov. 1, 1949.

Preferably the non-soap anionic organic detergent will be of the high sudsing type as for example, the alkylglycerylether sulfonates, the sulfated fatty alcohols or the alkyl ether ethylene oxide sulfates wherein the ethylene oxide chain averages 3 units 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.

Soaps which may be used in the compositions of this invention include the sodium and potassium salts of the higher fatty acids of naturally occurring vegetable or animal fats and oils. For example, sodium and potassium salts of fatty acids occurring in coconut oil, soy bean oil, castor oil, tallow or synthetically produced fatty acids may be used.

The anionic organic detergent can be employed in concentrations ranging from about 0.1% to about 10% by weight of the total composition but must not exceed a weight ratio of 10:1 with respect to the quaternary ammonium-containing polymeric component. Preferably the organic anionic detergent will be employed in a weight ratio of about 4:1 to 1:4 to the quaternary ammonium-containing polymeric component. Because of the superior solubility and lathering properties of anionic detergents containing predominantly C_{12} and C_{14} alkyl chain lengths, 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 ampholytic detergents. This component 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 hydrophylic group contains a semi-polar bond directly between two atoms e.g., N→O, P→O, As→O, and S→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 ampholytic detergent includes 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 radical having from 10 to 16 carbon atoms. Desirable surface active properties are lost if R_1 is substantially less than 10 carbon atoms, and the compounds are insufficiently soluble if R_1 is greater than 16 carbon atoms. R_2 and R_3 are each selected from the group consisting of methyl and ethyl 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 dodecyldimethylamine oxide.

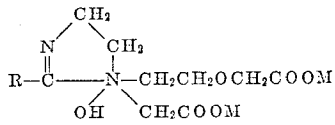
Other operable polar nonionic detergents are the phosphine oxides having the general formula

$$R_1R_2R_3P\rightarrow O$$

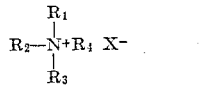
wherein R is an alkyl, alkenyl or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbon atoms, and R_2 and R_3 are each alkyl and monohydroxyalkyl radicals containing from 1 to 3 carbon atoms. A preferred phosphine oxide is dodecyldimethyl phosphine oxide. This and other phosphine oxides 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, ampholytic detergents can be used in conjunction with or in place of the polar nonionic detergents described above. Ampholytic 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 ampholytic detergents include, for example, alkyl beta-iminodipropionates, $RN(C_2H_4COOM)_2$; alkyl beta-amino propionates, $RN(H)C_2H_4COOM$; and long chain imidazole derivatives having the general formula:

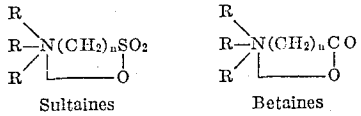


In each of the above formulae R is an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms and M is a cation to neutralize the charge of the anion. Specific operable ampholytic detergents include the disodium salt of lauroylcycloimidinium-1-ethoxyethionic acid-2-ethionic acid, dodecyl beta alanine, and the inner salt of 2-trimethylamino lauric acid. The substituted betaines, such as alkyl ammonio acetates wherein the alkyl radical contains from about 12 to about 18 carbon atoms can also be used. Several examples and a more complete description of this class of ampholytic detergents is set forth in the copending application of Smith, Ser. No. 80,991, filed Jan. 6, 1961. The betaine and sultaine types of ampholytic detergents are zwitterionic quaternary ammonium compound having the general formula:



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

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 "sultanes." The term "betains" is employed when the anion X is $COO^=$. The following structural formulae are illustrative of the two types and their inner salt character.



Sultaines Betaines

When one R in the above formulae is a high molecular alkyl radical having from about 10 to 18 carbon atoms, these compounds are surface active and have good detergency powers. If the high molecular alkyl radical contains less than about 10 carbon atoms, surface activity and detergency are inadequate. If this radical 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 radical 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 radicals 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 a betaine or sultaine having an alkyl group containing 16 carbon atoms in the compositions of this invention as will be illustrated infra. The alkyl radical can, of course, contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such as hydroxyl or halogen radicals which do not substantially affect the hydrophobic character of the radical.

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 group 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 ampholytic detergents are employed in the compositions of this invention, their concentration in the total composition will range from about 5% to about 20% by weight. Preferably this component will be employed at a concentration within the range of about 7% to about 15%.

Each of the forementioned components will be incorporated into an aqueous vehicle which may, in addition, include such materials as organic solvents, thickeners, perfumes, sequestering agents and opacifiers which are useful in enhancing the cosmetic properties of shampoo formulations.

The term "coconut" as used in the following examples refers to alkyl groups which are derived from middle cut 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:

	Percent
Dimethyl sulfate quaternized polyvinylimidazole [1]	1.6
Triethanolamine coconut sulfate	1.8
Coconut dimethylamine oxide	5.0
Water	Balance

[1] The polymer was water-soluble, had a molecular weight of from 5 to 20×10^3, and consisted substantially entirely of quaternized monomeric units.

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 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. The hair was then rinsed and placed into a curl configuration while still wet. After drying, the degree of curl retention was compared with the degree of curl retention attained with the same quantity of a conventional commercially available shampoo employed in like manner on a test switch of the same hair. The composition of this example was found to be markedly superior in this respect.

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 was prepared having the following composition:

	Percent
Dimethyl sulfate quaternized poly(diethylaminoethyl methacrylate) [1]	3.0
Triethanolamine coconut sulfate	2.5
Coconut dimethylamine oxide	10.0
Water	Balance

[1] Prepared in accordance with Example I of U.S. Patent 2,723,256. This polymer was water-soluble, and had a molecular weight within the range from about 1000 to about 5,000,000. The polymer consisted essentially entirely of quaternary ammonium-containing units.

This composition was found to be a clear stable liquid which possessed 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

were left in a highly manageable condition, i.e., easily combed and very little hair fly. The washed hair was tested for wave retention as in Example I. Curls formed after washing with the composition of this example were retained for a 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 fatty acids without a substantial loss of desired performance characteristics. Also, the polymeric component can be replaced with one in which quaternization has been limited so that only 50 mole percent of the monomeric units contain a quaternary ammonium group, without substantially altering product or performance characteristics.

Example III

	Percent
Dimethyl sulfate quaternized polyvinylimidazole [1]	2.0
Triethanolamine coconut sulfate	3.0
Lauroyl cycloimidinium-1-ethoxyethionic acid-2-ethionic acid, disodium	10.0
Water	Balance

[1] Same as Example I.

employed in this example can be replaced by a polymer of the same structure but having an average molecular weight of 100,000 or 750,000 without loss of the desired properties. So also, the concentration of the polymer employed in this example can be reduced to 0.5% by weight and the desired performance characteristics will still be observed.

Table I below sets forth several additional shampoo formulations which were prepared in accordance with the invention, exemplifying additional permissible variations in composition. The polymeric components designated A, B, C, and D are, respectively, polyvinylimidazole quaternized with dimethyl sulfate (same as Example I), poly(diethylaminoethyl methacrylate) quarternized with dimethyl sulfate (same as Example II), poly(dimethylaminoethyl methacrylate) quaternized with methyl phosphate (a water-soluble polymer having a molecular weight between 1000 and 5,000,000 and consisting substantially entirely of monomeric units containing a quaternary ammonium group), and the copolymer of equimolar proportions of vinylbenzyltrimethyl ammonium chloride and acrylamide (a water-soluble, polymer having a molecular weight of the order of 500,000 and containing approximately 50 mole percent of quaternary ammonium-containing monomeric units).

TABLE I

Component	Example							
	V	VI	VII	VIII	IX	X	XI	XII
Polymer A	2.5				2.0	2.0	2.0	3.0
Polymer B		3.0						
Polymer C			3.0					
Polymer D				3.0				
Lauroyl cycloimidinium-1-ethoxyethionic-acid-2-ethionic acid, disodium	10.0					10.0		
Coconutdimethylamine oxide		10.0	10.0	10.0				10.0
Cetyl betaine					10.0	10.0		
Triethanolammonium coconut sulfate	3.0							
Sodium salt of sulfated condensation product of 1 mole of coconut alcohol with 3 moles of ethylene oxide		5.0	5.0	5.0				5.0
Triethanolammonium alkyl [1]-benzene sulfonate							0.5	
Sodium coconut-alkylglycerylether sulfonate						0.5		
Sodium coconut monoglyceride sulfonate					0.5			
Alcohol		10.0	10.0	10.0				10.0
Water	[2]	[2]	[2]	[2]	[2]	[2]	[2]	[2]

[1] Alkyl group is a mixture of tri-, tetra- and penta-propylene and has an average carbon atoms content of about 12.
[2] Balance.

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

The disodium salt of lauroyl cycloimidinium-1-ethoxyethionic acid-2-ethionic acid employed in this example can be replaced in whole or in part with dodecyl beta-alanine, 2-trimethylamino lauric acid, or hexadecyldimethylamine oxide without substantially altering the product characteristics or performance.

Example IV

	Percent
Dimethyl sulfate quaternized polyvinylimidazole [1]	1.0
Sodium salt of sulfated condensation product of 1 mole of coconut alcohol with 3 moles of ethylene oxide	0.95
Coconut dimethylamine oxide	7.5
Water	Balance

[1] Same as Example I.

The above composition was a clear homogeneous liquid which remained stable after prolonged storage. Hair washed with this composition in the conventional manner was found to be highly manageable and retained a desired configuration for substantial periods of time.

The dimethyl sulfate quaternized polyvinylimidazole

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

Polymer D of Example VIII can be replaced by a quaternized poly(p-dimethylaminomethylstyrene) having a molecular weight of 250,000 and consisting essentially entirely of quaternized monomeric units with no substantial loss of desired product and performance characteristics.

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 ampholytic detergent, for example.

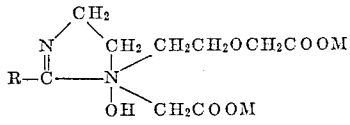
Percentage values employed in the specification and claims refer to percent by weight of the total composition unless otherwise stated.

What is claimed is:

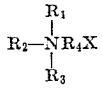
1. An aqueous detergent composition especially adapted for use in shampooing hair consisting essentially of (a) from about 0.1% to about 7.0% of a water-soluble polymer at least 30 mole percent of the molecular structure of which is composed of monomeric units selected

from the group consisting of quaternized vinylimidazole, quaternized diethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, quaternized p-dimethylaminomethylstyrene and combinations thereof, any balance of said polymer being composed of non-quaternized monomeric units derived from monoethylenically unsaturated groups, said polymer having a molecular weight within the range from about 1000 to about 5,000,000, (b) from about .1% to about 10% of a water-soluble salt of a higher fatty acid or an anionic organic sulfuric reaction product having in its molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a sulfuric acid or sulfonic acid ester radical, (c) from about 5% to about 20% of a member selected from the group consisting of polar nonionic detergents, ampholytic detergents 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 and M is a cation to neutralize the charge of the anion; or



wherein R_1 is an alkyl radical having from about 10 to about 18 carbon atoms, R_2 and R_3 are each alkyl radicals having from about 1 to about 3 carbon atoms, R_4 is an alkylene or hydroxyalkylene radical having from 1 to 4 carbon atoms and X is $SO_3^=$ or $COO^=$; and mixtures thereof, and the balance substantially (d) water, the weight ratio of component (b) to component (a) being not greater than about 10 to 1.

2. The composition of claim 1 wherein the polymer is a substantially completely quaternized polyvinylimidazole.

3. The composition of claim 1 wherein the polymer is a substantially completely quaternized poly(diethylaminoethyl methacrylate).

4. The composition of claim 1 wherein the polymer is a substantially completely quaternized poly(dimethylaminoethyl methacrylate).

5. The composition of claim 1 wherein the polymer is a substantially completely quaternized poly(p-dimethylaminomethylstyrene).

6. The composition of claim 1 wherein the polymer is a copolymer of equimolar quantities of vinylbenzyltrimethyl ammonium chloride and acrylamide.

7. An aqueous detergent composition especially adapted for use in shampooing hair consisting essentially of (a) from about 0.5% to about 5.0% of a water-soluble polymer at least 30 mole percent of the molecular structure of which is composed of monomeric units selected from the group consisting of quaternized vinylimidazole, quaternized diethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, quaternized p-dimethylaminomethylstyrene and combinations thereof, any balance of said polymer being composed of non-quaternized monomeric units derived from monoethylenically unsaturated groups, said polymer having a molecular weight within the range from about 1000 to about 5,000,000, (b) from about 0.1% to about 5.0% of a water-soluble salt of an anionic sulfuric reaction product having in its molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals, (c) from about 7% to about 15% of a polar nonionic detergent, and the balance substantially (d) water, the weight ratio of component (b) to component (a) being within the range from about 1:4 to about 4:1.

8. The composition of claim 7 wherein the water-soluble salt of an anionic sulfuric reaction product is an alkylglycerylether sulfonate, neutralized by an anion selected from the group consisting of sodium, potassium and triethanolammonium.

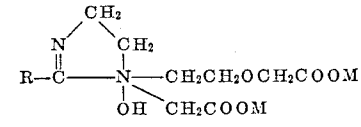
9. The composition of claim 7 wherein the water-soluble salt of an anionic sulfuric reaction product is a sulfated condensation product of 1 mole of coconut fatty acids and 3 moles of ethylene oxide, neutralized by an anion selected from the group consisting of sodium, potassium and triethanolammonium.

10. The composition of claim 7 wherein the water-soluble salt of an anionic sulfuric reaction product is an alkylbenzene sulfonate, neutralized by an anion selected from the group consisting of sodium, potassium and triethanolammonium.

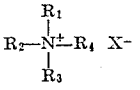
11. The composition of claim 7 wherein the polar nonionic detergent is an amine oxide of the general formula $R_1R_2R_3N\rightarrow O$ where R_1 is an alkyl radical having from 10 to 16 carbon atoms and R_2 and R_3 are each selected from the group consisting of methyl and ethyl radicals.

12. The composition of claim 7 wherein the polar nonionic detergent is a phosphine oxide of the general formula $R_1R_2R_3P\rightarrow O$ where R_1 is an alkyl radical having from 10 to 18 carbon atoms and R_2 and R_3 are each selected from the group consisting of alkyl and monohydroxyalkyl radicals having from 1 to 3 carbon atoms.

13. An aqueous detergent composition especially adapted for use in shampooing hair consisting essentially of (a) from about 0.5% to about 5.0% of a water-soluble polymer at least 30 mole percent of the molecular structure of which is composed of monomeric units selected from the group consisting of quaternized vinylimidazole, quaternized diethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, quaternized p-dimethylaminomethylstyrene and combinations thereof, any balance of said polymer being composed of non-quaternized monomeric units derived from monoethylenically unsaturated groups, said polymer having a molecular weight within the range from about 1000 to about 5,000,000, (b) from about 0.5% to about 5.0% of a water-soluble salt of an anionic organic sulfuric reaction product having in its molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals, (c) from about 7% to about 15% of an ampholytic 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 and M is a cation to neutralize the charge of the anion; or



wherein R_1 is an alkyl radical having from about 10 to about 18 carbon atoms, R_2 and R_3 are each alkyl radicals having from about 1 to about 3 carbon atoms, R_4 is an alkylene or hydroxyalkylene radical having from 1 to 4 carbon atoms and X is $SO_3^=$ or $COO^=$, and the balance substantially (d) water, the ratio of component (b) to component (a) being within the range from about 1:4 to about 4:1.

14. The composition of claim 13 wherein the ampholytic detergent is the disodium salt of lauroyl-cycloimidinium-1-ethoxyethionic acid-2-ethionic acid.

15. The composition of claim 13 wherein the ampholytic detergent is dodecyl beta alanine.

16. The composition of claim 13 wherein the ampholytic detergent is the inner salt of 2-trimethylamine lauric acid.

17. The composition of claim 13 wherein the anionic organic sulfuric reaction product is triethanolamine coconut sulfate.

18. The composition of claim 13 wherein the anionic organic sulfuric reaction product is the sodium salt of a sulfated condensation product of 1 mole of coconut alcohol with 3 moles of ethylene oxide.

References Cited by the Examiner

UNITED STATES PATENTS

2,723,256	11/1955	Hayek	260—79.3
2,741,568	4/1956	Hayek	252—8.8 X
2,965,594	12/1960	Maeder	252—8.8 X

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