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[54] **ANTIDANDRUFF SHAMPOO COMPOSITIONS**

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[51] Int. Cl.⁵ **A61K 7/75**

[52] U.S. Cl. **424/70; 424/DIG. 4; 252/DIG. 13; 252/106; 252/174.21; 252/174.22; 252/174.17; 252/174.15; 514/852**

[58] Field of Search **424/70, DIG. 4, 78; 252/106, 174.15, 174.17, 174.21, 174.22, DIG. 13; 514/852**

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[57] **ABSTRACT**

Antidandruff shampoos comprising a surfactant, platelet zinc pyridinethione active of specific particle size, a suspending agent, water, and a synergizer for the active. Said compositions have superior efficacy when compared with antidandruff shampoos known in the art.

23 Claims, No Drawings

ANTIDANDRUFF SHAMPOO COMPOSITIONS

TECHNICAL FIELD

The present invention relates to antidandruff shampoos. These shampoos exhibit excellent antidandruff activity.

BACKGROUND OF THE INVENTION

Antidandruff shampoos are well known in the art and rely upon various actives for their antidandruff effectiveness. Such compositions are not only designed to relieve the dandruff condition, but also to effectively clean the hair.

U.S. Pat. No. 3,917,817, Vanlerberghe et al., issued Nov. 5, 1975, discloses a shampoo composition comprising a piperazine based cationic polymer active, 10% sodium alkyl sulfate, 4% lauryl monoethanolamide and 3% glycol distearate. U.S. Pat. No. 4,013,787, Vanlerberghe et al., issued Mar. 22, 1977, discloses similar compositions.

Pyridinethione slats are known for use as dandruff control actives. Specifically, 1-hydroxypyridinethione salts have been taught as antidandruff actives in lotion form shampoos. Included in this group is 2-zinc pyrithion (ZPT) as disclosed in U.S. Pat. No. 2,809,971, Bernstein, issued Oct. 15, 1957; U.S. Pat. No. 3,236,733, Karsten, issued Feb. 22, 1966; U.S. Pat. No. 3,753,916, Parran, issued Aug. 21, 1973; Japanese Published Application 60810, published May 19, 1977 (Lion Fat and Oil); U.S. Pat. No. 4,323,683, Bolich et al., issued Apr. 6, 1982; U.S. Pat. No. 4,345,080, Bolich, issued Aug. 17, 1982; U.S. Pat. No. 4,379,753, Bolich, issued Apr. 12, 1983; U.S. Pat. No. 4,470,982, Winkler, issued Sept. 11, 1984; and European Published Patent Application No. 285,388, published Oct. 5, 1988 abandoned.

In the present invention it has been surprisingly found that when a pyridinethione metal salt in platelet form, with a specified particle size, is combined with any of a group of specific synergizers in a shampoo matrix, an unexpected substantial improvement in antidandruff efficacy is realized. Such compositions are stable, safe and effective in cleaning the hair while treating the scalp for dandruff.

SUMMARY OF THE INVENTION

The present invention relates to shampoo compositions comprising:

- (a) from about 5% to about 70% of a synthetic surfactant;
- (b) from about 0.3% to about 2% of pyridinethione metal salt in platelet particle form having a mean particle size of from about 2 microns to about 15 microns;
- (c) from about 0.5% to about 5% of a synergizer selected from the group consisting of polyethylene glycols containing from about 6 to about 22 ethylene oxide units, polypropylene glycols containing from about 6 to about 22 propylene oxide units, polyoxamer block polymers, polyethylene oxide fatty glycerides, polyethylenimines containing from about 6 to about 22 imine groups, polyethoxylated polyethylenimines, polyethylene oxide carbohydrates, ethoxylated nonylphenols, ethoxylated alcohols, and mixtures thereof (preferred synergizers include the polyethylene glycols, particularly PEG-12);

(d) from about 0.5% to about 6% of a suspending agent; and

(e) the remainder water.

These antidandruff shampoos are effective in cleansing the hair, as well as effectively treating dandruff. These compositions may also include additional antidandruff actives and/or silicone polymers to condition the hair without interrupting the treatment of said dandruff. The lotion form is particularly preferred for the shampoos.

All ratios, percentages and parts given herein are "by weight" unless otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

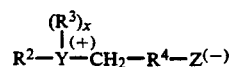
The essential components of the present invention as well as optional components, are set forth in the following paragraphs.

SURFACTANT

An essential component of the present compositions is a synthetic surfactant. The surfactant, which may be selected from any of a wide variety of synthetic anionic, amphoteric, zwitterionic and nonionic surfactants typically used in shampoos, is present at a level of from about 5% to about 70%, preferably from about 10% to about 30%, most preferably from about 10% to about 22%, of the composition.

Synthetic anionic surfactants can be exemplified by the alkali metal salts or organic sulfuric reaction products having in their molecular structure an alkyl radical containing from 8-22 carbon atoms and a sulfonic acid or sulfuric acid ester radical (included in the term alkyl is the alkyl portion of higher acyl radicals). Preferred are the sodium, ammonium, potassium or triethanolamine alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms), sodium coconut oil fatty acids monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and 1 to 12 moles of ethylene oxide; sodium or potassium slats of alkyl phenol ethylene oxide ether sulfate with 1 to 10 units of ethylene oxide per molecular and in which the alkyl radicals contain from 8 to 12 carbon atoms, sodium alkyl glyceryl ether sulfonates; the reaction product of fatty acids having from 10 to 22 carbon atoms esterified with isethionic acid and neutralized with sodium hydroxide; water soluble salts of condensation products of fatty acids with sarcosine; and others known in the art.

Zwitterionic surfactants can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



wherein R² contains an alkyl, alkenyl, or hydroxyalkyl radical of from about 8 to about 18 carbon atoms, from

0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms, x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom; R⁴ is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms; and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:

- 4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
- 5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;
- 3-[P,P-diethyl-P-3,6,9-trioxatetradecylphosphonio]-2-hydroxypropane-1-phosphate;
- 3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
- 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
- 4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
- 3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
- 3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
- 5-[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxypentane-1-sulfate.

Other zwitterionics, such as betaines, are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gammacarboxypropyl betaine, and lauryl bis-(2-hydroxypropyl) alphacarboxyethyl betaine. The sulfobetaines may be represented by, for example, coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, and lauryl bis-(2-hydroxyethyl) sulfopropyl betaine. Amido betaines and amidosulfobetaines, wherein the RCONH(CH₂)₃ radical is attached to the nitrogen atom of the betaine, are also useful in this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylamino-propane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Pat. No. 2,528,378.

Nonionic surfactants, which are preferably used in combination with an anionic, amphoteric or zwitter-

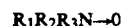
ionic surfactant, can be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Examples of preferred classes of nonionic surfactants are:

1. The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 60 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or nonane, for example.

2. Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

3. The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

4. Long chain tertiary amine oxide corresponding to the following general formula:



wherein R₁ contains an alkyl, alkenyl or monohydroxyalkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to 1 glyceryl moiety, and R₂ and R₃ contain from 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. The arrow in the formula is a conventional representation of a semipolar bond. Examples of amine oxides suitable for use in this invention include dimethyldodecylamine oxide, oleyldi(2-hydroxyethyl) amine oxide, dimethyloctylamine oxide, dimethyldodecylamine oxide, dimethyltetradecylamine oxide, 3,6,9-trioxaheptadecyldiethylamine oxide, di(2-hydroxyethyl)-tetradecylamine oxide, 2-dodecoxyethyl dimethylamine oxide, 3-dodecoxy-2-hydroxypropyldi(3-hydroxypropyl)amine oxide, dimethylhexadecylamine oxide.

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from 8 to 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety, and R' and R'' are each alkyl or monohydroxyalkyl groups containing from 1 to

3 carbon atoms. The arrow in the formula is a conventional representation of a semipolar bond. Examples of suitable phosphine oxides are: dodecyldimethylphosphine oxide, tetradecyldimethylphosphine oxide, tetradecylmethylethylphosphine oxide, 3,6,9-trioxaoc-
 5 tetradecyldimethylphosphine oxide, cetyltrimethylphosphine oxide, 3-dodecoxy-2-hydroxypropyl-di(2-hydroxyethyl)phosphine oxide, stearyldimethylphosphine oxide, stearyldimethylphosphine oxide, cetylethylpropyl-
 10 phosphine oxide, oleyldiethylphosphine oxide, dodecyl-diethylphosphine oxide, tetradecyldiethylphosphine oxide, dodecylpropylphosphine oxide, dodecyl-di(hydroxymethyl)phosphine oxide, dedecyl-di(2-hydroxyethyl)phosphine oxide, tetradecylmethyl-2-hydroxy-
 15 propylphosphine oxide, oleyldimethylphosphine oxide, 2-hydroxydedecyldimethylphosphine oxide.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxyalkyl radical of 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which contains alkyl, alkenyl, hydroxyalkyl,
 20 or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety. Examples include octadecyl methyl sulfoxide, 2-ketotridecyl methyl sulfoxide, 3,6,9-trioxaoctadecyl 2-hydroxyethyl
 25 sulfoxide, dodecyl methyl sulfoxide, oleyl 3-hydroxypropyl sulfoxide, tetradecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl methyl
 30 sulfoxide.

Many additional nonsoap surfactants, useful herein, are described in *McCutcheon's Detergents and Emulsifiers*, 1979 Annual, published by Allured Publishing Corporation, which is incorporated herein by reference.

The above-mentioned surfactants can be used alone
 35 or in combination in the shampoo compositions of the present invention. The anionic surfactants, particularly the alkyl sulfates, the ethoxylated alkyl sulfates and mixtures thereof, as well as the isethionates, are preferred for use herein. Most preferred are the mixtures of
 40 alkyl sulfate and ethoxylated alkyl sulfate, wherein the ratios of the former to the latter are from about 1:5 to about 5:1. Most preferred contains ammonium lauryl sulfate and ammonium laureth sulfate.

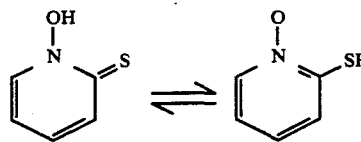
When these surfactants are introduced into the composition it is preferred they be introduced as mixtures
 45 having a surfactant concentration of about 28% in the case of ammonium laureth sulfate and about 25% in the case of ammonium lauryl sulfate. These concentrations allow for optimum processing of the shampoo compositions.
 50

ANTIDANDRUFF ACTIVE

In the present invention, the antidandruff active is a 1-hydroxy-2-pyridinethione salt in platelet particle
 55 form, wherein the particles have an average size of from 2 microns to about 15 microns, preferably from about 5 microns to about 9 microns. The active is used at a level of from about 0.3% to about 2%, preferably about 1%, of the shampoo composition. The 1-hydroxy-2-
 60 pyridinethione salts are disclosed for use in antidandruff shampoos in U.S. Pat. No. 2,809,971, Bernstein, issued Oct. 15, 1957; U.S. Pat. No. 3,236,733, Karsten et al., issued Feb. 22, 1966; U.S. Pat. No. 3,753,196, Parran, issued Aug. 21, 1973; U.S. Pat. No. 3,761,418, Parran,
 65 issued Sept. 25, 1973; U.S. Pat. No. 4,345,080, Bolich, issued Aug. 17, 1982; U.S. Pat. No. 4,323,683, Bolich et al., issued Apr. 6, 1982; U.S. Pat. No. 4,379,753, Bolich

issued Apr. 12, 1983; and U.S. Pat. No. 4,470,982, Winkler, issued Sept. 11, 1984; all incorporated herein by reference.

The pyridinethione salts useful herein can generally be defined as water-insoluble salts of 1-hydroxy-2-pyridinethione which has the following structural formula in tautomeric form, the sulfur being attached to the No. 2 position in the pyridine ring.



The salts result from substitution of the hydrogen of one of the tautomeric forms by the appropriate salt cation. Depending, of course, on the valence of the salt cation involved there may be more than one of the pyridinethione rings in the compound.

Preferred salts are formed from metals such as zinc, tin, cadmium, magnesium, aluminium and zirconium. The most preferred metal herein is zinc which forms 2-zinc pyridinethione or ZPT. Other cations such as sodium are also suitable.

The pyridinethione salts useful herein take the form of water-insoluble flat platelet particles which have a mean sphericity of less than about 0.65, preferably from about 0.20 to about 0.54, and a median particle size of from about 2 μ to about 15 μ , preferably from about 5 μ to about 9 μ , the particle size being expressed as the median equivalent diameter of a sphere of equal volume. The median diameters are on a mass basis with
 50 50% of the mass of particles falling on either side of the value given.

The diameter of a sphere of equivalent volume for a particle can be determined by a variety of sedimentation techniques which are based on Stokes' Law for the settling velocity of a particle in a fluid. Such techniques are described in Stockham, J. D. and Fochtam, E. G., *Particles Size Analysis*, Ann Arbor Science, 1978, incorporated herein by reference. An approach for determining the median equivalent spherical diameter based on volume, d_v , is shown in U.S. Pat. No. 4,345,080, Bolich,
 55 issued Aug. 17, 1982, Example II, incorporated herein by reference.

The sphericity of a particle is also described by Stockham and Fochtmann, supra, at page 113, as $(d_v/d_s)^2$, where d_v is the diameter of a sphere of equivalent volume, supra, and d_s is the diameter of a sphere of equivalent area. As used herein, however, the mean sphericity is $(d_v/d_s)^2$ or the surface area of spheres having equivalent volume distribution divided by the actual surface area of particles as measured. A technique for determining actual surface area is shown in the examples using the BET technique described by Stockham and Fochtam, supra, at page 122.

From the viewpoint of antidandruff efficacy, the BET surface area herein preferably falls in the range of from about 0.5 to about 3.5 m^2/g , more preferably from about 1.0 to about 3.0 m^2/g .

The platelet 2-zinc pyridinethione crystals preferred herein are made in the manner disclosed in U.S. Pat. No. 4,323,683, Bolich et al., issued Apr. 6, 1982; U.S. Pat. No. 4,345,080, Bolich, issued Aug. 17, 1982; and U.S. Pat. No. 4,379,753, Bolich, issued Apr. 12, 1983; all of which are incorporated herein by reference.

In addition to the 1-hydroxy-2-pyridinethione salts, the shampoo composition disclosed herein may include other known antidandruff actives. Such antidandruff actives, when used, are included at levels of from about 0.1% to about 1% of the composition, and are selected from the group consisting of hydroxypyridone salts, selenium disulfide, and mixtures thereof.

Hydroxypyridone salts are known antimicrobials. See *Cosmetics and Drug Preservation, Principles and Practice*, p 742 (edited by J. Kabura, 1984), incorporated herein by reference. The hydroxypyridone salts used herein can generally be described as 1-hydroxy-4-methyl-(1H)-pyridones having an aliphatic or aromatic moiety (R) at the 6 position thereof, wherein R has a π factor of at least 1:3, preferably from 2 to 6, more preferably from 3 to 5.5. The π factor is a measure of the lipophilicity/hydrophilicity of the substituent and is defined in detail in the paper by W. Dittmar, E. Druckrey and H. Urbach, *J. Med. Chem.* 17(7), 753-6(1974) and references cited therein; all of which are incorporated herein by reference.

In structural terms, preferred R substituents are selected from linear and branched C₃-C₁₁, preferably C₆-C₁₁, alkyl and alkenyl groups, C₅-C₈ cycloalkyl groups, and C₅-C₈ aryl groups. The cyclic moieties, discussed above, can also be substituted with one or more alkyl or alkenyl groups up to C₄. The R groups can further be substituted with halogen atoms. Of the above, preferred R moieties are cyclohexyl and 2,4,4-trimethyl pentyl, the latter being highly preferred.

The above mentioned compounds can be used both in the free form and as salts, for example, salts with organic bases or inorganic cations. Low molecular weight alkanolamines are especially preferred organic bases. The preferred hydroxypyridone salt for use herein is monoethanolamine salt known as piroctone olamine or Octopirox; see *Cosmetic and Drug Preservation*, supra.

Piroctone olamine is described for use in deodorant compositions in Japanese Patent Application Sho 57-104,313, published Dec. 23, 1983; Japanese Patent Application Sho 58-127,893 published Feb. 5, 1985 (both to Lion) and U.S. patent application Ser. No. 314,627, Melanson and Sturm, filed Feb. 23, 1989. Japanese Patent Application Sho 57-080,644 (Lion), published Nov. 18, 1983, discloses the use of a broad group of hydroxypyridone compounds for dandruff control. All above cited references are incorporated herein by reference.

The combination of pyridinethione and hydroxypyridone compounds for use in antidandruff shampoos is known in the art. Japanese Patent Application Sho 58-198, 413 (Lion), published Nov. 18, 1983, incorporated herein by reference, discloses antidandruff shampoo compositions which include a combination of zinc pyridinethione and piroctone olamine at a level from 0.05 to 5% by weight, wherein the ratio of zinc pyridinethione to piroctone olamine is from 9:1 to 1:9.

The pyridinethione/hydroxypyridone mixtures specified herein are generally used at levels of from about 0.4% to about 3% of the compositions. The weight ratio of pyridinethione salt to hydroxypyridone is generally from about 1:1 to about 5:1, preferably from about 2:1 to about 3:1, most preferred is about 2.5:1.

Selenium disulfide is a medicine used in medicated shampoos for treatment of seborrhea. U.S. Pat. No. 2,694,668, Baldwin et al., issued Nov. 16, 1954; U.S. Pat. No. 3,152,046, Kapral, issued Oct. 6, 1984; U.S. Pat. No. 4,089,945, Brinkman, issued May 16, 1978; and U.S. Pat.

No. 4,885,107, Wetzel, issued Dec. 12, 1989, all incorporated herein by reference, discloses selenium disulfide as the active ingredient in antidandruff shampoo compositions.

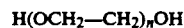
The pyridinethione/selenium disulfide mixtures specified herein are generally used at levels of from about 1.25% to about 3% of the composition. The ratio of pyridinethione salt to selenium disulfide is generally from about 1:4 to about 2:1, preferred is about 1:1.

SYNERGIZER

When a synergizer component, defined below, is combined with the specified size platelet pyridinethione salts in a shampoo, the shampoo's antidandruff efficacy is unexpectedly enhanced. These synergizers are used at levels from about 0.5% to about 5%, preferably from about 1% to about 3% and most preferably about 2%, of the composition, and are selected from the group consisting of specific polyethylene glycols (PEG), polypropylene glycols (PPG), polyethoxy/polypropoxy copolymers (polyoxamers), polyethylenimines, polyethoxylated polyethylenimines, polyethylene oxide fatty glycerides, ethoxylated nonylphenyl, ethoxylated alcohols, polyethylene oxide carbohydrates, and mixtures thereof. Preferred synergizers herein are the polyethylene glycols containing from about 6 to about 22 ethoxy groups, particularly those having a molecular weight from about 280 to about 1000. An especially preferred synergizer is PEG-12, with a molecular weight of about 546.

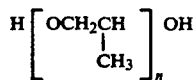
PEG and PPG are known for use in shampoos as viscosity modifiers. See Goldemberg, *Advances in Cosmetic Technology*, Vol. 1 p. 70-71 (1978), incorporated herein by reference.

The PEG for use in the present invention has the formula



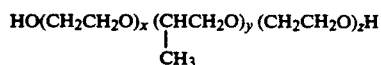
wherein n is from about 6 to about 22; preferably from about 6 to about 18. Most preferred is PEG-12 wherein n has the average value of 12, available as Carbowax 600, from Union Carbide; Polyglycol E-600, from Dow Chemical U.S.A.; and Pluracol E-600, from BASF-Wyandotte.

The PPG used in the present invention has the formula



wherein n is from about 6 to about 22, preferably from about 6 to about 18. Most preferred is PPG-12 wherein n has the average value of 12, available as Pluracol P-710, from BASF-Wyandotte.

Polyoxamers are polyoxyethylene/polyoxypropylene block polymers, which are useful herein as synergizers. An example of such a block polymer has the formula



wherein the total of x+z is from about 38 to about 156, and y is from about 30 to about 54. The block polymers

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