SHAMPOO COMPOSITIONS WITH IMPROVED DEPOSITION OF ANTIMICROBIAL AGENTS

FIELD OF THE INVENTION

The present invention relates to shampoo compositions containing antimicrobial agents which provide antidandruff activity. In particular, the present invention relates to shampoo compositions containing antimicrobial agents, preferably particulate antimicrobial agents, in combination with a cationic guar polymer as an antimicrobial agent deposition aid.

BACKGROUND OF THE INVENTION

Various anti-dandruff shampoo compositions are commercially available or otherwise known in the shampoo art. These compositions typically comprise particulate, crystalline antimicrobial agents dispersed and suspended throughout the composition. Antimicrobial agents used for this purpose include sulfur, selenium sulfide and heavy metal salts of pyridinethione. During the shampooing process, these antimicrobial agents deposit on the scalp to provide anti-dandruff activity.

Many anti-dandruff shampoos, however, do no provide sufficient antimicrobial agent deposition during the shampooing process. Without such deposition, the antimicrobial agents simply rinse away during shampooing and therefore provide little or no anti-dandruff activity. In addition, the detersive surfactants in these shampoo compositions which are designed to remove oil, grease, dirt, and particulate matter will also carry away particulate antimicrobial agents during rinsing, thus further decreasing deposition and anti-dandruff activity.

Deposition of particulate antimicrobial agents is especially difficult in anti-dandruff shampoo compositions containing crystalline suspending agents. These suspending agents help disperse and suspend particulate antimicrobial agents in the shampoo composition. These suspending agents, however, adversely affect lathering performance. It has therefore become conventional practice to enhance the lathering performance of these shampoos by increasing detersive surfactant concentrations or by adding foam boosters, both of which further decrease deposition of particulate antimicrobial agents from the shampoo compositions.

It has now been found that select cationic deposition polymers are especially effective in providing enhanced deposition of antimicrobial agents, especially particulate antimicrobial agents, from a shampoo composition. The select polymers

are cationic derivatives of guar gum which have been found to be most effective when used in combination with crystalline suspending agents and high levels of anionic, amphoteric or zwitterionic surfactant in an anti-dandruff shampoo composition.

It is therefore an object of the present invention to provide an anti-dandruff shampoo composition with improved deposition of antimicrobial agents, especially particulate antimicrobial agents, and further to provide for such improved deposition in the presence of crystalline suspending agents and high concentrations of detersive surfactant. It is yet another object of the present invention to provide anti-dandruff shampoo compositions with excellent anti-dandruff activity and reduced concentration of antimicrobial agents.

SUMMARY OF THE INVENTION

The present invention is directed to high lathering, anti-dandruff shampoo compositions with improved deposition of antimicrobial agents, which compositions comprise (a) from about 7% to about 30% by weight of a detersive surfactant selected from the group consisting of anionic surfactant, amphoteric surfactant, zwitterionic surfactant, and combinations thereof; (b) from about 0.1% to about 10% by weight of an antimicrobial agent; (c) from about 0.5% to about 10% by weight of a suspending agent; (d) from about 0.01% to about 1.0% by weight of a cationic guar polymer having a charge density of from about 0.1 to about 3meq/gm, and (e) from about 40% to about 92% by weight of water; wherein at least about 50% by weight of the cationic guar polymer is in coacervate form, said coacervate comprising detersive surfactant and cationic guar polymer.

DETAILED DESCRIPTION OF THE INVENTION

The shampoo compositions of the present invention can comprise, consist of, or consist essentially of the essential elements and limitations of the invention described herein, as well any of the additional or optional ingredients, components, or limitations described herein.

All percentages, parts and ratios are based upon the total weight of the shampoo compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

Detersive Surfactant

The shampoo compositions of the present invention comprise a detersive surfactant selected from the group consisting of anionic surfactants, amphoteric surfactants, zwitterionic surfactants, and combinations thereof. The shampoo compositions preferably comprise an anionic surfactant. The detersive surfactant provides the shampoo compositions with cleaning performance.

Anionic surfactant

The detersive surfactant component of the shampoo compositions is preferably an anionic surfactant. Concentrations of anionic surfactant can range from about 7% to about 30%, preferably from about 10% to about 25%, more preferably from about 12% to about 22%, by weight of the shampoo compositions.

Anionic surfactants for use in the shampoo compositions include alkyl and alkyl ether sulfates. These materials have the respective formulae $ROSO_3M$ and $RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is an integer from 1 to 10, and M is a hydrogen, alkali metal (e.g., lithium, sodium, potassium), alkali earth metal (e.g., beryllium, magnesium, calcium, strontium, barium) ammonium or substituted ammonium.

Preferably, R has from about 10 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil are preferred. Such alcohols are reacted with between about 0 and about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which may be used in the shampoo compositions of the present invention are sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate; tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a combination of individual compounds, the combination having an average alkyl chain length of from about 10 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.

Other suitable anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction products of the general formula [R_1-SO_3-M] where R_1 is

selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radicals having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M hydrogen, alkali metal (e.g., lithium, sodium, potassium), alkali earth metal (e.g., beryllium, magnesium, calcium, strontium, barium) ammonium or substituted ammonium. Examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3, H_2SO_4, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{10-18} n-paraffins.

Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other similar anionic surfactants are described in U.S. Patent 2,486,921; U.S. Patent 2,486,922; and U.S. Patent 2,396,278, which descriptions are incorporated herein by reference.

Other anionic surfactants suitable for use in the shampoo compositions are the succinnates, examples of which include disodium N-octadecylsulfosuccinnate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinnate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; and dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2, etc., when used in the gaseous form.

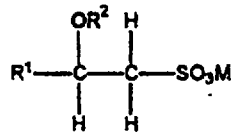
The alpha-olefins from which the olefin sulfonates are derived from mono-olefins having from about 12 to about 24 carbon atoms, preferably from about 14 to about 16 carbon atoms. Straight chain olefins are preferred.

In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other

materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process.

A specific alpha-olefin sulfonate mixture of the above type is described more fully in the U.S. Patent 3,332,880, which description is incorporated herein by reference.

Another class of anionic surfactants suitable for use in the shampoo compositions are the beta-alkyloxy alkane sulfonates. These compounds can be represented by the formula:



where R^1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R^2 is a lower alkyl group having from about 1 (preferred) to about 3 carbon atoms, and M hydrogen, alkali metal (e.g., lithium, sodium, potassium), alkali earth metal (e.g., beryllium, magnesium, calcium, strontium, barium) ammonium or substituted ammonium.

Many other anionic surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and in U.S. Patent 3,929,678, which descriptions are incorporated herein by reference.

Preferred anionic surfactants for use in the shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate and combinations thereof.

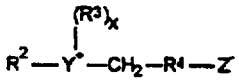
Amphoteric and zwitterionic surfactants

The detersive surfactant component of the shampoo compositions may comprise an amphoteric and/or zwitterionic surfactant. Concentrations of such

surfactants can range from about 0.5% to about 20%, preferably from about 1% to about 10%, by weight of the shampoo compositions.

Amphoteric surfactants for use in the shampoo compositions include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and 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.

Zwitterionic surfactants for use in the shampoo compositions include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. These compounds can be represented by the formula:



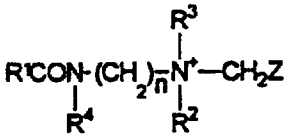
where R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing about 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; R^4 is an alkylene or hydroxyalkylene of from about 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 of amphoteric and zwitterionic surfactants also include sultaines and amidosultaines. Sultaines and amidosultaines can be used as foam enhancing surfactants that are mild to the eye in partial replacement of anionic surfactants. Sultaines, including amidosultaines, include for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl) propylsultaine and the like; and the amidosultaines such as cocoamidodimethylpropylsultaine, stearylamidododimethylpropylsultaine, laurylamidobis-(2-hydroxyethyl) propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C_{12}-C_{18} hydrocarbyl amidopropyl hydroxysultaines, especially C_{12}-C_{14} hydrocarbyl amido propyl hydroxysultaines, e.g., laurylamidopropyl hydroxysultaine and cocamidopropyl hydroxysultaine. Other sultaines are described in U.S. Patent 3,950,417, which descriptions are incorporated herein by reference.

Other suitable amphoteric surfactants are the aminoalkanoates of the formula $R\text{-}NH(CH_2)_nCOOM$, the iminodialkanoates of the formula $R\text{-}N[(CH_2)_mCOOM]_2$ and mixtures thereof; wherein n and m are integers from 1 to 4, R is C_8 - C_{22} alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Examples of suitable aminoalkanoates include n-alkylamino-propionates and n-alkyliminodipropionates, specific examples of which include N-lauryl--beta-amino propionic acid or salts thereof, and N-lauryl-beta-imino-dipropionic acid or salts thereof, and mixtures thereof.

Other suitable amphoteric surfactants include those represented by the formula :



where R^1 is alkyl or alkenyl having from about 8 to about 22 carbon atoms, preferably from about 12 to about 16 carbon atoms; R^2 is hydrogen or CH_2CO_2M; R^3 is CH_2CH_2OH or $CH_2CH_2OCH_2CH_2COOM$; R^4 is hydrogen, CH_2CH_2OH, or $CH_2CH_2OCH_2CH_2COOM$; Z is CO_2M or CH_2CO_2M; n is the integer 2 or 3, preferably 2; M is a hydrogen, alkali metal (e.g., lithium, sodium, potassium), alkali earth metal (e.g., beryllium, magnesium, calcium, strontium, barium) ammonium or substituted ammonium.

This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate.

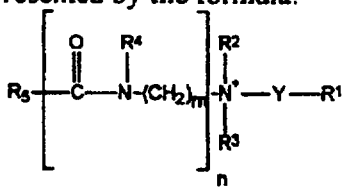
Suitable materials of this type are marketed under the trade name MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R^2. All such variations and species are meant to be encompassed by the above formula.

Examples of surfactants of the above formula are monocarboxylates and dicarboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P.,

MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

Betaine surfactants (zwitterionic) suitable for use in the shampoo compositions are those represented by the formula:



where R^1 is COOM or $CH(OH)CH_2SO_3M$;

R^2 is lower alkyl or hydroxyalkyl;

R^3 is lower alkyl or hydroxyalkyl;

R^4 is a member selected from the group consisting of hydrogen and lower alkyl;

R^5 is higher alkyl or alkenyl;

Y is lower alkyl, preferably methyl;

m is an integer from 2 to 7, preferably from 2 to 3;

n is the integer 1 or 0; and

M is a hydrogen, alkali metal, alkali earth metal, ammonium or substituted ammonium.

As used in this context, the term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about eight to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substitutents such as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

Examples of suitable surfactant betaines of the above formula wherein n is zero include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryl dimethyl-alpha-carboxyethylbetaine, cetyldimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)carboxymethyl-

betaine, stearyl-bis-(2-hydroxypropyl)carboxymethylbetaine, oleyl-dimethyl-gamma-carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)-alpha-carboxyethylbetaine, etc. Suitable sulfobetaines include cocodimethylsulfopropyl-betaine, stearyldimethylsulfopropylbetaine, and lauryl-bis-(2-hydroxyethyl)sulfopropylbetaine.

Suitable amido betaines and amidosulfo betaines for use in the shampoo compositions include the amidocarboxybetaines, such as cocoamidodimethylcarboxymethylbetaine, laurylamidodi-methylcarboxymethylbetaine, cetylamidodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, cocoamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. Amido sulfobetaines include cocoamidodimethylsulfopropylbetaine, stearylamidodimethylsulfopropylbetaine, and lauryl-amido-bis-(2-hydroxyethyl)-sulfopropylbetaine.

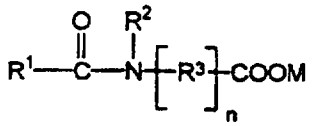
Highly solubilizing surfactants

The shampoo compositions of the present invention are preferably free of highly solubilizing surfactants such as N-acyl amino acid surfactants. As used in this context, "substantially free" means that the shampoo compositions preferably contain no more than about 1%, more preferably no more than about 0.5%, even more preferably no more than about 0.25%, most preferably essentially zero percent, of highly solubilizing surfactants by weight of the shampoo compositions.

Less preferably, the shampoo compositions may comprise N-acyl amino acid surfactants as a secondary optional surfactant or as the detersive surfactant component of the shampoo compositions.

N-acyl amino acid surfactants are well known surfactants for use in a variety of products. A description of these surfactants and their synthesis can be found, for example, in Anionic Suractants, Part II, Surfactant Science Series, Vol. III, edited by Warner M. Linfield, Marcel Dekker, Inc. (New York and Basel), pp 581-617 (1976), which description is incorporated herein by reference.

Suitable N-acyl amino acid surfactants for use in the shampoo compositions herein include N-acyl hydrocarbyl acids and salts thereof, which can be represented by the formula:



wherein R1 is a alkyl or alkenyl radical having from about 8 to about 24 carbon atoms, preferably from about 12 to about 18 carbons atoms; R^2 is hydrogen, alkyl having from about 1 to about 4 carbon atoms, phenyl, or CH_2COOM, preferably alkyl having from about 1 to about 4 carbon atoms, more preferably alkyl having from about 1 to about 2 carbon atoms; R3 is $(CR^4)_2$ or alkoxy having from about 1 or about 2 carbon atoms, wherein each R^4 is independently hydrogen or alkyl having from about 1 to about 6 carbon atoms or alkylester thereof; n is an integer from 1 to 4, preferably 1 or 2; and M a hydrogen, alkali metal (e.g., lithium, sodium, potassium), alkali earth metal (e.g., beryllium, magnesium, calcium, strontium, barium) ammonium or substituted ammonium. Especially preferred are N-acyl sarcosinates and acids thereof, examples of which include lauroyl sarcosinate, myristoyl sarcosinate, cocoyl sarcosinate, and oleoyl sarcosinate, preferably as sodium or potassium salts.

It has been found that the highly solubilizing surfactants described hereinabove, when used in combination with the guar cationic polymers described hereinafter, are less effective in providing improved deposition of the antimicrobial agent of the shampoo compositions herein. It has also been found that, by increasing the cationic charge density of the guar cationic polymer in the presence of these highly solubilizing surfactant, the less effective antimicrobial agent deposition can be improved substantially. In the presence of the highly solubilizing surfactants in the shampoo compositions herein, therefore, the cationic guar polymer should have a cationic charge density of from about 0.9meq/g to about 4meq/g, preferably between about 1.0 and 3meq/g.

Antimicrobial Agent

The shampoo compositions of the present invention comprise a safe and effective amount of an antimicrobial agent. The antimicrobial agent provides the shampoo compositions with antimicrobial activity. The antimicrobial agent is preferably a crystalline particulate that is insoluble in, and dispersed throughout, the shampoo compositions. Effective concentrations of such antimicrobial agents generally range from about 0.1% to about 5%, more preferably from about 0.3% to about 5%, by weight of the shampoo compositions. Suitable antimicrobial agents include sulfur, octopirox, selenium sulfide, and pyridinethione salts.

Selenium sulfide is a preferred particulate antimicrobial agent for use in the shampoo compositions, effective concentrations of which range from about 0.1% to

about 5.0%, preferably from about 0.3% to about 2.5%, more preferably from about 0.5% to about 1.5%, by weight of the shampoo compositions. Selenium sulfide is generally regarded as a compound having one mole of selenium and two moles of sulfur, although it may also be a cyclic structure, Se_xS_y, wherein $x + y = 8$. Average particle diameters for the selenium sulfide (selenium disulfide) are less than 15um, preferably less than 10 um, as measured by forward laser light scattering device, e.g., Malvern 3600 instrument. Selenium sulfide compounds are well known in the shampoo art, and are described, for example in U.S. Patent 2,694,668; U.S. Patent 3,152,046; U.S. Patent 4,089,945; and U.S. Patent 4,885,107, which descriptions are incorporated herein by reference.

Pyridinethione antimicrobial agents, especially 1-hydroxy-2-pyridinethione salts, are highly preferred particulate antimicrobial agents for use in the shampoo compositions, concentrations of which range from about 0.1% to about 3%, preferably about 0.3% to about 2%, by weight of the shampoo compositions. Preferred pyridinethione salts are those formed from heavy metals such as zinc, tin, cadmium, magnesium, aluminum and zirconium. Zinc salts are most preferred, especially the zinc salt of 1-hydroxy-2-pyridinethione (zinc pyridinethione, ZPT). Other cations such as sodium may also be suitable. Particularly preferred are 1-hydroxy-2-pyridinethione salts in platelet particle form, wherein the particles have an average size of up to about 20 microns, preferably up to about 8 microns, most preferably up to about 5 microns.

Pyridinethione antimicrobial agents are well known in the shampoo art, and are described, for example, in U.S. Patent 2,809,971; U.S. Patent 3,236,733; U.S. Patent 3,753,196; U.S. Patent 3,761,418; U.S. Patent 4,345,080; U.S. Patent 4,323,683; U.S. Patent 4,379,753; and U.S. Patent 4,470,982, which descriptions are incorporated herein by reference.

Sulfur may also be used as the particulate antimicrobial agent in the shampoo compositions herein. Effective concentrations of the particulate sulfur are generally from about 1% to about 5%, more preferably from about 2% to about 5%, by weight of the compositions.

Octopirox and related salts and derivatives may also be used as the antimicrobial agent in the shampoo compositions. Such antimicrobial agents are soluble in the shampoo composition and, therefore, do not disperse throughout the composition as crystalline particulates as do the other antimicrobial agents described hereinbefore.

Suspending or Thickening Agent

The shampoo compositions of the present invention comprise a suspending or thickening agent to help maintain dispersion of particulate antimicrobial agents throughout the composition. Any known suspending or thickening agent may be used in the shampoo compositions, provided that it is physically and chemically compatible with the essential components of the shampoo composition described herein, or does not otherwise unduly impair product stability, aesthetics or performance.

Crystalline suspending agents are preferred for suspending the particulate antimicrobial agent in the shampoo compositions. The selected suspending agent, at the selected concentration, should help maintain the suspension for at a period of at least one month, preferably at least three months, more preferably at least about twenty-four months, at ambient temperatures. In general, effective concentrations of the crystalline suspending agent range from about 0.5% to about 10%, preferably from about 0.5% to about 5%, more preferably about 1% to about 4%, most preferably about 1% to about 3%, by weight of the shampoo composition.

In general, concentrations of the crystalline suspending agent should be minimized to achieve only the desired property.

Preferred crystalline suspending agents are acyl derivatives and amine oxides, especially acyl derivatives, especially those which can be solubilized in a premix solution and then be recrystallized upon cooling. These materials comprise long chain (e.g., C_8-C_{22} preferably C_{14}-C_{22}, more preferably C_{16}-C_{22}) aliphatic groups, i.e., long chain acyl derivative materials and long chain amine oxides, as well as mixtures of such materials. Included are ethylene glycol long chain esters, alkanol amides of long chain fatty acids, long chain esters of long chain fatty acids, glyceryl long chain esters, long chain esters of long chain alkanolamides, and long chain alkyl dimethyl amine oxides, and combinations thereof.

Crystalline suspending agents are described, for example, in U.S. Patent 4,741,855, which description is incorporated herein by reference.

Suitable suspending agents for use in the shampoo compositions herein include ethylene glycol esters of fatty acids preferably having from about 14 to about 22 carbon atoms, more preferably 16-22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms. Preferred alkanol amides are

stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate); glyceryl esters (e.g., glyceryl distearate) and long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids, in addition to the preferred materials listed above, may be used as suspending agents.

Suspending agents also include long chain amine oxides such as alkyl (C_{16}-C_{22}) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide.

Other long chain acyl derivatives that can be used include N,N-dihydrocarbyl (C_{12}-C_{22}, preferably C_{16}-C_{18}) amido benzoic acid and soluble salts thereof (e.g., Na and K salts), particularly N,N-di(C_{16}-C_{18}, and hydrogenated tallow) amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

The crystalline suspending agent can be incorporated into the shampoo compositions herein by solubilizing it into a solution containing water and the anionic sulfate surfactant at a temperature above the melting point of the suspending agent. The suspending agent is then recrystallized, typically by cooling the solution to a temperature sufficient to induce crystallization.

Other suitable suspending agents for use in the shampoo compositions include that can be used include polymeric thickeners, such as carboxyvinyl polymers, examples of which are described in U.S. Patent 2,798,053, and U.S. Patent 4,686,254, which descriptions are incorporated herein by reference. Examples of suitable carboxyvinyl polymers include Carbopol® 934, -940, -941, -956, -980, -981, -1342, and -1382, all commercially available from B. F. Goodrich Company

Other suitable suspending agents include those which impart a gel-like viscosity to the composition, such as water soluble or colloidally water soluble polymers like cellulose ethers (e.g., hydroxyethyl cellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, xanthan gum and combinations thereof.

Other suitable suspending agents are described in U.S. Patent 4,788,006, which description is incorporated herein by reference.

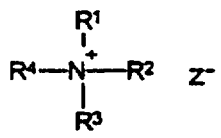
Cationic Guar Polymer

The shampoo compositions of the present invention comprise a cationic guar polymer having a select charge density. The cationic guar polymer, in combination with the essential components of the compositions, provides improved deposition of the antimicrobial agent onto the scalp and other areas of the skin. Concentrations of the cationic deposition polymer range from about 0.01% to about 1.0%, preferably from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.25%, by weight of the shampoo compositions.

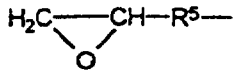
The cationic guar polymer for use in the shampoo composition is further defined as having a cationic charge density of from about 0.01meq/g to about 3meq/g, preferably from about 0.1meq/g to about 2meq/g, more preferably from about 0.8 to about 1.8meq/g, wherein at least about 50%, preferably about 100%, by weight of the cationic guar polymer forms coacervates with detersive surfactant in the shampoo compositions. The formed coacervates are in the form of hydrated, dispersed colloids that are insoluble in the shampoo compositions.

The cationic guar polymers for use in the shampoo compositions are cationically substituted galactomannan (guar) gum derivatives. The molecular weight of such derivatives ranges generally from about 2,000 to about 3,000,000. Guar gum for use in preparing these guar gum derivatives is typically obtained as a naturally occurring material from the seeds of the guar plant. The guar molecule itself is a straight chain mannan branched at regular intervals with single membered galactose units on alternative mannose units. The mannose units are linked to each other by means of beta (1-4) glycosidic linkages. The galactose branching arises by way of an alpha (1-6) linkage. Cationic derivatives of the guar gums are obtained by reaction between the hydroxyl groups of the polygalactomannan and reactive quaternary ammonium compounds. The degree of substitution of the cationic groups onto the guar structure must be sufficient to provide the requisite cationic charge density described hereinbefore.

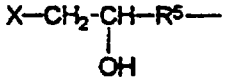
Suitable quaternary ammonium compounds for use in forming the guar cationic polymers include



wherein where R1, R2 and R3 are methyl or ethyl groups and R4 is an epoxyalkyl group of the formula

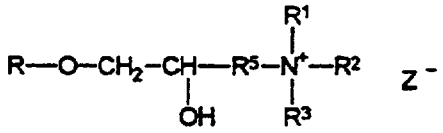


or R4 is a halohydrin group of the formula

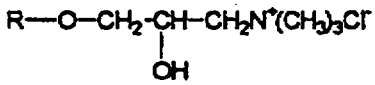


where R5 is C1-C3 alkylene and X is chlorine or bromine, and Z is an anion such as Cl^-, Br^-, I^- or HSO_4^-.

Cationic guar polymers (cationic derivatives of guar gum) formed from the reagents described hereinbefore are represented by the formula



wherein R is guar gum. Preferably, the cationic guar polymer is guar hydroxypropyltrimethylammonium chloride, which can be more specifically represented by the formula



specific examples of which include Jaguar® C-13-S (cationic charge density 0.8meq/g) and Jaguar C-17 (cationic charge density 1.6meq/g) commercially available from Rhone-Poulenc Surfactants and Specialties, Cranbury N..J. U.S.A.

Other suitable cationic guar polymers include hydroxypropylated cationic guar derivatives.

Water

The shampoo compositions of the present invention are aqueous systems which comprise from about 40% to about 92%, preferably from about 50% to about 85%, more preferably from about 60% to about 80%, water by weight of the compositions.

The pH of the shampoo compositions ranges, in general, from about 2 to about 10, preferably from about 3 to about 9, more preferably from about 4 to about 8, most preferably from about 5.5 to about 7.5. For zwitterionic or amphoteric surfactant systems, the pH should be adjusted according to the isoelectric point of the selected surfactant to maintain an anionic species on the selected surfactant prior to forming a coacervate with the cationic guar polymer described herein.

Optional Components

The shampoo compositions of the present invention may further comprise one or more optional components known for use in shampoo compositions, provided that the optional components are physically and chemically compatible with the essential components described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Concentrations of such optional components typically range from about 0.001% to about 10% by weight of the shampoo compositions.

Optional components include preservatives, conditioning agents, styling polymers, organic solvents, pearlescent aids, foam boosters, nonionic surfactants, pH adjusting agents, perfumes, proteins, dyes, skin active agents, sunscreens, vitamins, and viscosity adjusting agents. This list of optional components is not meant to be exclusive, and other optional components can be used.

METHOD OF USE

The shampoo compositions of the present invention are used in a conventional manner for cleaning hair and controlling dandruff on the scalp. The shampoo compositions herein are also useful for cleansing the skin and other areas of the body such as underarm and groin areas. An effective amount of the composition, typically from about 1 g to about 20 g of the composition, for cleaning hair, skin or other area of the body, is applied to the hair, skin or other area that has preferably been wetted, generally with water, and then rinsed off. Application to the hair typically includes working the shampoo composition through the hair such that most or all of the hair is contacted with the shampoo composition.

EXAMPLES

The compositions illustrated in Examples I-XX illustrate specific embodiments of the shampoo compositions of the present invention, but are not intended to be limiting thereof. Other modifications can be undertaken by the skilled artisan without departing from the spirit and scope of this invention. These exemplified embodiments of the shampoo compositions of the present invention provide excellent cleansing of hair and dandruff control.

All exemplified compositions can be prepared by conventional formulation and mixing techniques. Component amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components.

Examples I - XVI

Component	Example I	Example II	Example III	Example IV	Example V
Ammonium Laureth Sulfate	15.00	15.00	15.00	15.00	7.50
Ammonium Lauryl Sulfate	5.00	5.00	5.00	5.00	2.50
Sodium Lauroyl Sarcosinate	1.50	1.50	1.50	1.50	0.75
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Zinc Pyrithione	1.00	1.00	1.00	---	1.00
Selenium Disulfide	---	---	---	1.00	---
Jaguar C17S	0.10	0.05	0.50	0.10	0.10
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.	q.s.	q.s.
pH adjustment (Mono/Di sodium Phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.
viscosity adjustment (Sodium Chloride,	q.s.	q.s.	q.s.	q.s.	q.s.
preservative (DMDM Hydantoin); Water	q.s.	q.s.	q.s.	q.s.	q.s.

Component	Example VI	Example VII	Example VIII	Example IX	Example X
Ammonium Laureth Sulfate	7.50	15.00	15.00	10.00	10.00
Ammonium Lauryl Sulfate	2.50	5.00	5.00	2.50	2.50
Cocamidopropyl Betaine	---	---	---	2.50	2.50
Sodium Lauroyl Sarcosinate	0.75	---	---	---	---
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Zinc Pyrithione	1.00	1.00	1.00	1.00	1.00
Jaguar C13S	---	0.10	---	0.10	---
Jaguar C17S	0.05	---	0.10	---	0.10
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.	q.s.	q.s.
pH adjustment (Mono/Di sodium Phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.
Sodium Sulfate, PEG-600, Ammonium Xylene Sulfonate)	q.s.	q.s.	q.s.	q.s.	q.s.
preservative (DMDM Hydantoin) Water	q.s.	q.s.	q.s.	q.s.	q.s.

Component	Example XI	Example XII	Example XIII	Example XIV	Example XV	Example XVI
Ammonium Laureth Sulfate	15.00	15.00	15.00	15.00	15.00	15.00
Ammonium Lauryl Sulfate	5.00	5.00	5.00	5.00	5.00	5.00
Cocamidopropyl Betaine	2.00	---	---	---	---	---
Sodium Lauroyl Sarcosinate	---	1.50	1.50	---	---	---
Sodium Cocoyl Glutamate	---	---	---	---	---	1.50
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50	1.50

Stearyl Alcohol	---	---	---	---	---	---
Zinc Pyrithione	1.00	0.30	0.30	0.30	0.30	1.00
Jaguar C13S	0.20	---	---	0.10	0.05	---
Jaguar C17S	---	0.10	0.05	---	---	0.10
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
pH adjustment (Mono/Di sodium Phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
viscosity adjustment (Sodium Chloride,)	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
preservative (DMDM Hydantoin)	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.

In preparing each of the compositions described in Examples I to XVI, about one-third of the ammonium laureth sulfate (added as 25wt% solution) is added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. Salts (sodium chloride) and pH modifiers (disodium phosphate, monosodium phosphate) are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS) is added to the mixing vessel and allowed to melt. After the EGDS is melted and dispersed (e.g., after about 5-20 minutes), preservative and additional viscosity modifier are added to the surfactant solution. The resulting mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the EGDS crystallizes to form a crystalline network in the product. The remainder of the ammonium laureth sulfate and other components are added to the finishing tank with agitation to ensure a homogeneous mixture. Cationic guar polymer is dispersed in water as a 0.5-2.5% aqueous solution before addition to the final mix. Once all components have been added, viscosity and pH modifiers are added to the mixture to adjust product viscosity and pH to the extent desired.

Each exemplified composition provides excellent hair cleansing, lathering, antimicrobial agent deposition on the scalp and dandruff control.

Component	Example XVII	Example XVIII	Example XIX
Ammonium Laureth Sulfate	14.00	14.00	14.00
Cocamidopropyl Betaine	---	2.50	2.50
Cocoamphodiacetate	2.50	---	---
Cocamide MEA	1.00	1.00	1.00
Ethylene Glycol Distearate	1.50	1.50	1.50
Cetyl Alcohol	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18
Zinc Pyrithione	1.00	1.00	1.00
Jaguar C13S	0.15	0.15	---
Jaguar C17S	---	---	0.15
Fragrance	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.
pH adjustment (Mono/Di sodium Phosphate)	q.s.	q.s.	q.s.
viscosity adjustment (Sodium Chloride,	q.s.	q.s.	q.s.
preservative (DMDM Hydantoin); Water	q.s.	q.s.	q.s.

In preparing each of the compositions described in Examples XVII to XIX, from 50% to 100% by weight of the detersive surfactants are added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. If used, pH modifiers (monosodium phosphate, disodium phosphate) are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS) and fatty alcohols (cetyl alcohol, stearyl alcohol) are then added to the mixing vessel and allowed to melt. After the EGDS is melted and dispersed (usually about 5-10 minutes), preservative (if used) is added and mixed into the surfactant solution. Additional viscosity modifier are added to the surfactant solution if necessary. The resulting mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the EGDS crystallizes to form a crystalline network in the product. Any remaining surfactant and other components are added to the finishing tank with agitation to ensure a homogeneous mixture. Cationic guar polymer is dispersed in water as a 0.5-2.5% aqueous solution before addition to the final mix. Once all components have been added, viscosity and pH modifiers are added to the mixture to adjust product viscosity and pH to the extent desired.

Each exemplified composition provides excellent hair cleansing, lathering, antimicrobial agent deposition on the scalp, and dandruff control.

Example XX

Component	Example XX
Ammonium Laureth Sulfate	15.00
Ammonium Lauryl Sulfate	5.00
Cocamide MEA	1.00
Ethylene Glycol Distearate	1.50
Zinc Pyrithione	1.00
Jaguar C13S	0.20
Color	q.s.
pH adjustment (Mono/Di sodium Phosphate)	q.s.
viscosity adjustment (sodium Chloride,	q.s.
preservative (DMDM Hydantoin); Water	q.s.

In preparing the composition described in Examples XX, about one-third to all of the total surfactant are added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. Salts are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS) is then added to the mixing vessel and allowed to melt. After the EGDS is melted and dispersed (usually after about 5-20 minutes), preservative (DMDM hydantoin) if used is added to the surfactant solution. The resulting mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the EGDS crystallizes to form a crystalline network in the product. The remainder of the detersive surfactant and other components are added to the finishing tank with agitation to ensure a homogeneous mixture. Cationic guar polymer is dispersed in water as a 0.5-2.5% aqueous solution before addition to the final mix. Once all components have been added, viscosity and pH modifiers are added to the mixture to adjust product viscosity and pH to the extent desired.

The resulting composition provides excellent hair cleansing, lathering, antimicrobial agent deposition on the scalp and dandruff control.

WHAT IS CLAIMED IS:

1. A shampoo composition with improved deposition of antimicrobial agents, said composition comprising:
   (a) from 7% to 30% by weight of a detersive surfactant selected from the group consisting of anionic surfactants, amphoteric surfactants, zwitterionic surfactants, and combinations thereof, preferably anionic surfactant;
   (b) from 0.1% to 10% by weight of an antimicrobial agent;
   (c) from 0.5% to 10% by weight of a suspending agent;
   (d) from 0.01% to 1.0% by weight of a cationic guar polymer having a charge density of from 0.01meq/g to 3meq/gm; and
   (e) from 40% to 92% by weight of water;

   wherein at least 50% by weight of the cationic guar polymer is in coacervate form, said coacervate comprising detersive surfactant and cationic guar polymer.

2. The shampoo composition of Claim 1 wherein the antimicrobial agent is a crystalline, particulate material selected from the group consisting of sulfur, selenium sulfide, pyridinethione salts, and combinations thereof, preferably the zinc salt of 1-hydroxy-2-pyridinethione.

3. The shampoo composition of any one of the preceding claims wherein the composition is substantially free of N-acyl amino acid surfactants.

4. The shampoo composition of any one of the preceding claims wherein the cationic guar polymer has a cationic charge density of from 0.1meq/g to 2meq/g.

5. The shampoo composition of any one of the preceding claims wherein the concentration of the anionic detersive surfactant is from 12% to 22% by weight of the composition.

6. The shampoo composition any one of the preceding claims wherein the detersive surfactant comprises an N-acyl amino acid surfactant, and the cationic guar polymer has a cationic charge density of from 0.9meq/g to 3meq/g.

7. A shampoo composition with improved deposition of particulate antimicrobial agents, said composition comprising:
   (a) from 10% to 25% by weight of an anionic detersive surfactant;
   (b) from 0.1% to 10% by weight of a crystalline, particulate antimicrobial agent selected from the group consisting of sulfur, selenium sulfide, pyridinethione salts, and combinations thereof, preferably the zinc salt of 1-hydroxy-2-pyridinethione;
   (c) from 0.5% to 10% by weight of a crystalline suspending agent;
   (d) from 0.01% to 0.5% by weight of a cationic guar polymer having a charge density of from 0.1meq/g to 2meq/gm; and
   (e) from 50% to 85% by weight of water;

   wherein at least 50% by weight of the cationic guar polymer is in coacervate form, said coacervate comprising detersive surfactant and cationic guar polymer, and wherein the composition is substantially free of N-acyl amino acid surfactants.

8. The shampoo composition of any one of the preceding claims wherein the cationic guar polymer is guar hydroxypropyltrimethylammonium chloride.

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CORRECTED VERSION*

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(54) Title: SHAMPOO COMPOSITIONS WITH IMPROVED DEPOSITION OF ANTIMICROBIAL AGENTS

(57) Abstract

Disclosed are antidandruff shampoo compositions with improved deposition of antimicrobial agents, which compositions comprise (a) from about 7 % to about 30 % by weight of a detersive surfactant selected from the group consisting of anionic surfactant, amphoteric surfactant, zwitterionic surfactant, and combinations thereof; (b) from about 0.1 % to about 10 % by weight of an antimicrobial agent; (c) from about 0.5 % to about 10 % by weight of a suspending agent; (d) from about 0.01 % to about 1.0 % by weight of a cationic guar polymer having a charge density of from about 0.01 meq/g to about 3 meq/gm; and (e) from about 40 % to about 92 % by weight of water; wherein at least about 50 % by weight of the cationic guar polymer is in coacervate form, said coacervate comprising detersive surfactant and cationic guar polymer.

* (Referred to in PCT Gazette No. 45/1997, Section II)