



(86) Date de dépôt PCT/PCT Filing Date: 2017/03/03  
(87) Date publication PCT/PCT Publication Date: 2017/09/08  
(45) Date de délivrance/Issue Date: 2021/10/19  
(85) Entrée phase nationale/National Entry: 2018/08/16  
(86) N° demande PCT/PCT Application No.: US 2017/020604  
(87) N° publication PCT/PCT Publication No.: 2017/152020  
(30) Priorité/Priority: 2016/03/03 (US62/303,049)

(51) Cl.Int./Int.Cl. *A61K 8/46* (2006.01),  
*A61K 8/04* (2006.01), *A61K 8/49* (2006.01),  
*A61K 8/73* (2006.01), *A61Q 5/00* (2006.01)  
(72) Inventeurs/Inventors:  
RENOCK, SEAN MICHAEL, US;  
LANE, BRANDON SCOTT, US;  
JOHNSON, ERIC SCOTT, US  
(73) Propriétaire/Owner:  
THE PROCTER & GAMBLE COMPANY, US  
(74) Agent: TORYS LLP

(54) Titre : COMPOSITION ANTIPELLICULAIRE EN AEROSOL  
(54) Title: AEROSOL ANTIDANDRUFF COMPOSITION

(57) Abrégé/Abstract:

The present invention is directed to a foaming composition comprising: from about 18% to about 36% of one or more anionic surfactants; from 0.1 to about 5% of one or more viscosity modifiers with a molecular weight of from about 38 to about 2800; from about 0.1 to about 10% of an anti-dandruff particulate; from about 1% to about 10% of a blowing agent, and wherein the foam density is from about 0.05 to about 0.25g/ml.



## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
8 September 2017 (08.09.2017)

WIPO | PCT

(10) International Publication Number  
**WO 2017/152020 A1**

## (51) International Patent Classification:

*A61K 8/46* (2006.01) *A61K 8/73* (2006.01)  
*A61K 8/49* (2006.01) *A61K 8/04* (2006.01)  
*A61Q 5/00* (2006.01)

## (21) International Application Number:

PCT/US2017/020604

## (22) International Filing Date:

3 March 2017 (03.03.2017)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

62/303,049 3 March 2016 (03.03.2016) US

(71) Applicant: THE PROCTER & GAMBLE COMPANY  
[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).(72) Inventors: **RENOCK, Sean, Michael**; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US). **LANE, Brandon, Scott**; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US). **JOHNSON, Eric, Scott**; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).(74) Agents: **KREBS, Jay A.** et al.; c/o The Procter & Gamble Company, Global IP Services, One Procter & Gamble Plaza, C9, Cincinnati, Ohio 45202 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

## Published:

— with international search report (Art. 21(3))

## (54) Title: AEROSOL ANTIDANDRUFF COMPOSITION

(57) Abstract: The present invention is directed to a foaming composition comprising: from about 18% to about 36% of one or more anionic surfactants; from 0.1 to about 5% of one or more viscosity modifiers with a molecular weight of from about 38 to about 2800; from about 0.1 to about 10% of an anti-dandruff particulate; from about 1% to about 10% of a blowing agent, and wherein the foam density is from about 0.05 to about 0.25g/ml.



WO 2017/152020 A1

## AEROSOL ANTIDANDRUFF COMPOSITION

## FIELD OF THE INVENTION

The present invention relates to an aerosol antidandruff composition which is providing  
5 deposition of actives and a foam density that is maintaining composition efficacy.

## BACKGROUND OF THE INVENTION

Aerosol foams for the personal cleansing category have certain advantages compared to  
traditional product forms. One drawback to products delivered via the foam form is the dilution of  
10 the formula ingredients by the entrained air which can result in performance negatives versus their  
traditional liquid/gel form counterparts. For this reason it is necessary to significantly increase the  
levels of surfactant in the formula versus a traditional cleansing product to remain efficacious from a  
cleansing standpoint. This negative is further exacerbated for products containing insoluble active  
ingredients which can easily be diluted to levels that are no longer efficacious. For this reason it is  
15 imperative to accurately control the density of the delivered foam to ensure the reasonable delivery  
of effective amounts of said actives. By increasing the active concentrations based on their volume  
in the delivered foam we have found that we can drive significantly higher deposition of these  
actives from the foam form. To this end we have found that specific levels and combinations of  
formula ingredients and aerosol blowing agents can be leveraged to ensure that the foam density is  
20 kept in a range that remains high enough to maintain product efficacy.

## SUMMARY OF THE INVENTION

In an embodiment of the present invention, the present invention is directed to a foaming  
composition comprising: from about 18% to about 36% of one or more anionic surfactants; from 0  
0.1 to about 5% of one or more viscosity modifiers with a molecular weight of from about 38 to  
25 about 2800; from about 0.1 to about 10% of an anti-dandruff particulate; from about 1% to about  
10% of a blowing agent, and wherein the foam density is from about 0.05 to about 0.25g/ml.

## DETAILED DESCRIPTION OF THE INVENTION

While the specification concludes with claims particularly pointing out and distinctly  
claiming the invention, it is believed that the present invention will be better understood from the  
30 following description.

As used herein, the term "fluid" includes liquids and gels.

As used herein, the articles including "a" and "an" when used in a claim, are understood to mean one or more of what is claimed or described.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

As used herein, "mixtures" is meant to include a simple combination of materials and any compounds that may result from their combination.

As used herein, "molecular weight" or "Molecular weight" refers to the weight average molecular weight unless otherwise stated. Molecular weight is measured using industry standard method, gel permeation chromatography ("GPC").

As used herein, "personal care compositions" includes products such as shampoos, shower gels, liquid hand cleansers, hair colorants, facial cleansers, and other surfactant-based liquid compositions

As used herein, the terms "include," "includes," and "including," are meant to be non-limiting and are understood to mean "comprise," "comprises," and "comprising," respectively.

All percentages, parts and ratios are based upon the total weight of the 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.

Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

It should be understood that every maximum numerical limitation given throughout this specification includes every lower numerical limitation, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this specification will include every higher numerical limitation, as if such higher numerical limitations were expressly written herein. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

#### DETERSIVE SURFACTANT

The hair care composition may comprise greater than about 20% by weight of a surfactant

system which provides cleaning performance to the composition. The surfactant system comprises an anionic surfactant and/or a combination of anionic surfactants, with a co-surfactant selected from the group consisting of amphoteric, zwitterionic, nonionic and mixtures thereof. Various examples and descriptions of deterative surfactants are set forth in U.S. Patent No. 8,440,605; U.S. Patent  
 5 Application Publication No. 2009/155383; and U.S. Patent Application Publication No. 2009/0221463.

The hair care composition may comprise from about 18% to about 36%, from about 20% to about 32%, and/or from about 22% to about 28% by weight of one or more anionic surfactants.

The composition of the present invention can also include anionic surfactants selected from  
 10 the group consisting of:

- a)  $R_1 O(CH_2CHR_3O)_y SO_3M$ ;
- b)  $CH_3 (CH_2)_z CHR_2 CH_2 O (CH_2 CHR_3O)_y SO_3M$ ; and
- c) mixtures thereof,

where  $R_1$  represents  $CH_3 (CH_2)_{10}$ ,  $R_2$  represents H or a hydrocarbon radical comprising 1 to  
 15 4 carbon atoms such that the sum of the carbon atoms in  $z$  and  $R_2$  is 8,  $R_3$  is H or  $CH_3$ ,  $y$  is 0 to 7, the average value of  $y$  is about 1 when  $y$  is not zero (0), and  $M$  is a monovalent or divalent, positively-charged cation.

Anionic surfactants suitable for use in the compositions are the alkyl and alkyl ether sulfates. Other suitable anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction  
 20 products. Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. Other similar anionic surfactants are described in U.S. Patent Nos. 2,486,921; 2,486,922; and 2,396,278.

Exemplary anionic surfactants for use in the hair care composition include ammonium lauryl  
 25 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  
 30 sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine

lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium cocoyl isethionate, undecyl sulfate and combinations thereof. In a further embodiment, the anionic surfactant is sodium lauryl sulfate or sodium laureth sulfate.

Suitable anionic alkyl sulfates and alkyl ether sulfate surfactants include, but are not limited to, those having branched alkyl chains which are synthesized from C8 to C18 2-alkylbranched alcohols which may be selected from the group consisting of: Guerbet alcohols, aldol alcohols, oxo alcohols and mixtures thereof. Nonlimiting examples of the 2-alkyl branched alcohols include the Guerbet alcohols such as 2-methyl-1-undecanol, 2-ethyl-1-decanol, 2-methyl-1-dodecanol, 2-butyl 1-octanol, 2-butyl-1-nonanol, 2-ethyl-1-undecanol, 2-propyl-1-nonanol, 2-pentyl-1-octanol, 2-pentyl-1-heptanol, and those sold under the tradename ISOFOL® (Sasol), and oxo alcohols, e.g., those sold under the tradenames LIAL® (Sasol), ISALCHEM® (Sasol), NEODOL® (Shell),

The hair care composition may comprise a co-surfactant. The co-surfactant can be selected from the group consisting of amphoteric surfactant, zwitterionic surfactant, non-inonic surfactant and mixtures thereof. The co-surfactant can include, but is not limited to, lauramidopropyl betaine, cocoamidopropyl betaine, lauryl hydroxysultaine, sodium lauroamphoacetate, coco monoethanolamide and mixtures thereof.

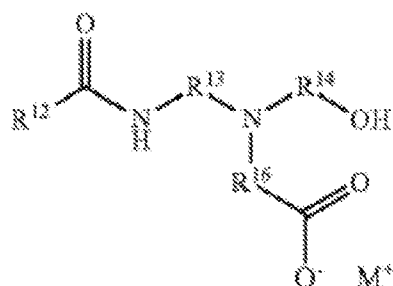
The hair care composition may further comprise from about 1% to about 5%, from about 2% to about 4%, from about 2.5 to about 3%% by weight of one or more amphoteric/zwitterionic, nonionic co-surfactants, or a mixture thereof.

Suitable amphoteric or zwitterionic surfactants for use in the hair care composition herein include those which are known for use in shampoo or other hair care cleansing. Non limiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Patent Nos. 5,104,646 and 5,106,609.

Amphoteric co-surfactants suitable for use in the composition include those surfactants described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate. Suitable amphoteric surfactant include, but are not limited to, those selected from the group consisting of: sodium cocaminopropionate, sodium cocaminodipropionate, sodium cocoamphoacetate, sodium cocoamphohydroxypropylsulfonate, sodium cocoamphopropionate, sodium cornamphopropionate, sodium lauraminopropionate, sodium lauroamphoacetate, sodium lauroamphohydroxypropylsulfonate, sodium lauroamphopropionate,

sodium cornamphopropionate, sodium lauriminodipropionate, ammonium cocaminopropionate, ammonium cocaminodipropionate, ammonium cocoamphoacetate, ammonium cocoamphohydroxypropylsulfonate, ammonium cocoamphopropionate, ammonium cornamphopropionate, ammonium lauraminopropionate, ammonium lauroamphoacetate, ammonium lauroamphohydroxypropylsulfonate, ammonium lauroamphopropionate, ammonium cornamphopropionate, ammonium lauriminodipropionate, triethanolamine cocaminopropionate, triethanolamine cocaminodipropionate, triethanolamine cocoamphoacetate, triethanolamine cocoamphohydroxypropylsulfonate, triethanolamine cocoamphopropionate, triethanolamine cornamphopropionate, triethanolamine lauraminopropionate, triethanolamine lauroamphoacetate, triethanolamine lauroamphohydroxypropylsulfonate, triethanolamine lauroamphopropionate, triethanolamine cornamphopropionate, triethanolamine lauriminodipropionate, cocoamphodipropionic acid, disodium caproamphodiacetate, disodium caproamphoadipropionate, disodium caprylamphodiacetate, disodium caprylamphodipropionate, disodium cocoamphocarboxyethylhydroxypropylsulfonate, disodium cocoamphodiacetate, disodium cocoamphodipropionate, disodium dicarboxyethylcocopropylenediamine, disodium laureth-5 carboxyamphodiacetate, disodium lauriminodipropionate, disodium lauroamphodiacetate, disodium lauroamphodipropionate, disodium oleoamphodipropionate, disodium PPG-2-isodecethyl-7 carboxyamphodiacetate, lauraminopropionic acid, lauroamphodipropionic acid, lauryl aminopropylglycine, lauryl diethylenediaminoglycine, and mixtures thereof

The amphoteric co-surfactant can be a surfactant according to the following structure:



wherein R12 is a C-linked monovalent substituent selected from the group consisting of substituted alkyl systems comprising 9 to 15 carbon atoms, unsubstituted alkyl systems comprising 9 to 15 carbon atoms, straight alkyl systems comprising 9 to 15 carbon atoms, branched alkyl systems comprising 9 to 15 carbon atoms, and unsaturated alkyl systems comprising 9 to 15 carbon atoms; R13, R14, and R15 are each independently selected from the group consisting of C-linked divalent

straight alkyl systems comprising 1 to 3 carbon atoms, and C-linked divalent branched alkyl systems comprising 1 to 3 carbon atoms; and M<sup>+</sup> is a monovalent counterion selected from the group consisting of sodium, ammonium and protonated triethanolamine. In an embodiment, the amphoteric surfactant is selected from the group consisting of: sodium cocoamphoacetate, sodium  
 5 cocoamphodiacetate, sodium lauroamphoacetate, sodium lauroamphodiacetate, ammonium lauroamphoacetate, ammonium cocoamphoacetate, triethanolamine lauroamphoacetate, triethanolamine cocoamphoacetate, and mixtures thereof.

The composition may comprises a zwitterionic co-surfactant, wherein the zwitterionic surfactant is a derivative of aliphatic quaternary ammonium, phosphonium, and sulfonium  
 10 compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. The zwitterionic surfactant can be selected from the group consisting of: cocamidoethyl betaine, cocamidopropylamine oxide, cocamidopropyl betaine, cocamidopropyl dimethylaminohydroxypropyl hydrolyzed collagen,  
 15 cocamidopropyldimonium hydroxypropyl hydrolyzed collagen, cocamidopropyl hydroxysultaine, cocobetaineamido amphopropionate, coco-betaine, coco-hydroxysultaine, coco/oleamidopropyl betaine, coco-sultaine, lauramidopropyl betaine, lauryl betaine, lauryl hydroxysultaine, lauryl sultaine, and mixtures thereof. A suitable zwitterionic surfactant is lauryl hydroxysultaine. The zwitterionic surfactant can be selected from the group consisting of: lauryl hydroxysultaine,  
 20 cocamidopropyl hydroxysultaine, coco-betaine, coco-hydroxysultaine, coco-sultaine, lauryl betaine, lauryl sultaine, and mixtures thereof.

The co-surfactant can be a zwitterionic surfactant, wherein the zwitterionic surfactant is selected from the group consisting of: lauryl hydroxysultaine, cocamidopropyl hydroxysultaine, coco-betaine, coco-hydroxysultaine, coco-sultaine, lauryl betaine, lauryl sultaine, and mixtures  
 25 thereof.

The co-surfactant can be a non-ionic surfactant selected from the group consisting of: Cocamide, Cocamide Methyl MEA, Cocamide DEA, Cocamide MEA, Cocamide MIPA, Lauramide DEA, Lauramide MEA, Lauramide MIPA, Myristamide DEA, Myristamide MEA, PEG-20 Cocamide MEA, PEG-2 Cocamide, PEG-3 Cocamide, PEG-4 Cocamide, PEG-5 Cocamide, PEG-6  
 30 Cocamide, PEG-7 Cocamide, PEG-3 Lauramide, PEG-5 Lauramide, PEG-3 Oleamide, PPG-2 Cocamide, PPG-2 Hydroxyethyl Cocamide, and mixtures thereof.

Non limiting examples of other anionic, zwitterionic, amphoteric, and non-ionic additional

surfactants suitable for use in the hair care composition are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Patent Nos. 3,929,678, 2,658,072; 2,438,091; 2,528,378.

## 5 VISCOSITY REDUCING AGENT

The hair care composition comprises from about 1% to about 5%, alternatively from about 2% to about 4%, alternatively from about 1% to about 3%, of one or more viscosity reducing agents, by weight of the hair care composition.

The viscosity reducing agents may be selected from the group consisting of The viscosity  
 10 reducing agents may be selected from the group consisting of, ethanol, dipropylene glycol, sodium xylene sulfonate,, alkoxyated silicone/ethoxylated silicone/propoxylated silicone/polyoxyethylene silicone/polyoxypropylene silicone/polyethyleneglycol silicone/PEG-8 silicone/PEG-9  
 silicone/PEG-n silicone/silicone ether (n could be another integer), non-limiting examples include PEG8-dimethicone A208) MW 855, PEG 8 Dimethicone D208 MW2706 , Silsurf and combinations  
 15 thereof.

The hair care composition described herein may have a liquid phase viscosity of from about 8 centipoise to about 15,000 centipoise, alternatively from about 9 centipoise to about 12,000 centipoise, alternatively from about 10 centipoise to about 11,000 centipoise, The concentrated hair composition viscosity values may be measured using a TA Instruments AR-G2 Rheometer with a  
 20 concentric cylinder attachment at a shear rate of 2 reciprocal seconds at 25°C. In an embodiment of the present invention, a hair care composition may have a viscosity in a range that allows for ease of dispensing from a package configuration.

## WATER MISCIBLE SOLVENTS

25 The compositions can include water miscible glycols and other diols. Non-limiting examples include dipropylene glycol, tripropylene glycol, diethylene glycol, ethylene glycol, propylene glycol, 1,3-propane diol, 2,2-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 1-Propene, 1,3,3,3 Tetrafluoro- (1E), and 2-methyl-2,4-pentanediol.

### **Anti-dandruff Actives**

30 The compositions of the present invention may also contain an anti-dandruff agent. Suitable, non-limiting examples of anti-dandruff particulates include: pyridinethione salts, , selenium sulfide, particulate sulfur, and mixtures thereof. Such anti-dandruff particulate should be physically and

chemically compatible with the essential components of the composition, and should not otherwise unduly impair product stability, aesthetics or performance.

### **1. Pyridinethione salts**

Pyridinethione anti-dandruff particulates, especially 1-hydroxy-2-pyridinethione salts, are one embodiment of a particulate anti-dandruff agents for use in compositions of the present invention. The concentration of pyridinethione anti-dandruff particulate typically ranges from about 0.1% to about 10%, by weight of the composition. In an embodiment, the concentration of pyridinethione anti-dandruff particulate ranges from about 0.1% to about 8%, and in a further embodiment, ranges from from about 0.3% to about 5%. In an embodiment of the present invention, pyridinethione salts include those formed from heavy metals such as zinc, copper, tin, cadmium, magnesium, aluminum and zirconium. In an embodiment of the present invention, a pyridinethione salts formed from a heavy metal zinc, and in a further embodiment, the zinc salt of 1-hydroxy-2-pyridinethione (known as “zinc pyridinethione” or “ZPT”), and yet a further embodiment of 1-hydroxy-2-pyridinethione salts in platelet particle form, wherein the particles have an average size of up to about 20 $\mu$ . In an embodiment of the present invention, the particles have an average size up to about 5 $\mu$ , and in a further embodiment up to about 2.5 $\mu$ . Salts formed from other cations, such as sodium, may also be suitable. Pyridinethione anti-dandruff agents are described, for example, in U.S. Pat. No. 2,809,971; U.S. Pat. No. 3,236,733; U.S. Pat. No. 3,753,196; U.S. Pat. No. 3,761,418; U.S. Pat. No. 4,345,080; U.S. Pat. No. 4,323,683; U.S. Pat. No. 4,379,753; and U.S. Pat. No. 4,470,982. It is contemplated that when ZPT is used as the anti-dandruff particulate in the compositions herein, that the growth or re-growth of hair may be stimulated or regulated, or both, or that hair loss may be reduced or inhibited, or that hair may appear thicker or fuller.

### **2. Other Anti-microbial Actives**

In addition to the anti-dandruff active selected from polyvalent metal salts of pyrrithione, the present invention may further comprise one or more anti-fungal or anti-microbial actives in addition to the metal pyrrithione salt actives. Suitable anti-microbial actives include coal tar, sulfur, whitfield's ointment, castellani's paint, aluminum chloride, gentian violet, octopirox (piroctone olamine), ciclopirox olamine, undecylenic acid and it's metal salts, potassium permanganate, selenium sulphide, sodium thiosulfate, propylene glycol, oil of bitter orange, urea preparations, griseofulvin, 8-Hydroxyquinoline ciloquinol, thiobendazole, thiocarbamates, haloprogin, polyenes, hydroxypyridone, morpholine, benzylamine, allylamines (such as terbinafine), tea tree oil, clove leaf oil, coriander, palmarosa, berberine, thyme red, cinnamon oil, cinnamic aldehyde, citronellic acid,

hinokitol, ichthyol pale, Sensiva SC-50, Elestab HP-100, azelaic acid, lyticase, iodopropynyl butylcarbamate (IPBC), isothiazalinones such as octyl isothiazalinone and azoles, and combinations thereof. In an embodiment of the present invention, anti-microbials include itraconazole, ketoconazole, selenium sulphide and coal tar.

5       **a. Azoles**

Azole anti-microbials include imidazoles such as benzimidazole, benzothiazole, bifonazole, butaconazole nitrate, climbazole, clotrimazole, croconazole, eberconazole, econazole, clubiol, fenticonazole, fluconazole, flutimazole, isoconazole, ketoconazole, lanoconazole, metronidazole, miconazole, neticonazole, omoconazole, oxiconazole nitrate, sertaconazole, sulconazole nitrate, tioconazole, thiazole, and triazoles such as terconazole and itraconazole, and combinations thereof. When present in the composition, the azole anti-microbial active is included in an amount from about 0.01% to about 5%. In an embodiment of the present invention, the azole anti-microbial active is included in an amount from about 0.1% to about 3%, and in a further embodiment, from about 0.3% to about 2%, by weight of the composition. In an  
10       embodiment of the present invention, the azole anti-microbial is ketoconazole.

15       **b. Selenium Sulfide**

Selenium sulfide is a particulate anti-dandruff agent suitable for use in the anti-microbial compositions of the present invention, effective concentrations of which range from about 0.1% to about 4%, by weight of the composition, and in an embodiment of the present invention, from about  
20       0.3% to about 2.5%, and in a further embodiment from about 0.5% to about 1.5%. 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 that conforms to the general formula  $Se_xS_y$ , wherein  $x + y = 8$ . Average particle diameters for the selenium sulfide are typically less than 15 $\mu$ m, as measured by forward laser light scattering device (e.g. Malvern 3600 instrument), and in an embodiment of the  
25       present invention, less than 10  $\mu$ m. Selenium sulfide compounds are described, for example, in U.S. Pat. No. 2,694,668; U.S. Pat. No. 3,152,046; U.S. Pat. No. 4,089,945; and U.S. Pat. No. 4,885,107.

30       **c. Sulfur**

**d. Keratolytic Agents**

**e. Additional Anti-microbial Actives**

Additional anti-microbial actives of the present invention may include extracts of melaleuca (tea tree) and charcoal. The present invention may also comprise combinations of anti-microbial actives. Such combinations may include octopirox and zinc pyrithione combinations, pine tar and

sulfur combinations, salicylic acid and zinc pyrithione combinations, octopirox and climbazole combinations, and salicylic acid and octopirox combinations, zinc pyrithione and climbazole and mixtures thereof. These actives, when used herein, are used at levels of from about 1% to about 4%, and in an embodiment of the present invention, from about 2% to about 4%.

5 In an embodiment, the composition comprises an effective amount of a zinc-containing layered material. In an embodiment, the composition comprises from about 0.001% to about 10%, or from about 0.01% to about 7%, or from about 0.1% to about 5% of a zinc-containing layered material, by total weight of the composition.

Zinc-containing layered materials may be those with crystal growth primarily occurring in two dimensions. It is conventional to describe layer structures as not only those in which all the atoms are incorporated in well-defined layers, but also those in which there are ions or molecules between the layers, called gallery ions (A.F. Wells "Structural Inorganic Chemistry" Clarendon Press, 1975). Zinc-containing layered materials (ZLMs) may have zinc incorporated in the layers and/or be components of the gallery ions. The following classes of ZLMs represent relatively common examples of the general category and are not intended to be limiting as to the broader scope of materials which fit this definition.

Many ZLMs occur naturally as minerals. In an embodiment, the ZLM is selected from the group consisting of: hydrozincite (zinc carbonate hydroxide), basic zinc carbonate, aurichalcite (zinc copper carbonate hydroxide), rosasite (copper zinc carbonate hydroxide), and mixtures thereof. Related minerals that are zinc-containing may also be included in the composition. Natural ZLMs can also occur wherein anionic layer species such as clay-type minerals (e.g., phyllosilicates) contain ion-exchanged zinc gallery ions. All of these natural materials can also be obtained synthetically or formed *in situ* in a composition or during a production process.

Another common class of ZLMs, which are often, but not always, synthetic, is layered double hydroxides. In an embodiment, the ZLM is a layered double hydroxide conforming to the formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} A^{m-}_{x/m} \cdot nH_2O$  wherein some or all of the divalent ions ( $M^{2+}$ ) are zinc ions (Crepaldi, EL, Pava, PC, Tronto, J, Valim, JB *J. Colloid Interfac. Sci.* 2002, 248, 429-42).

Yet another class of ZLMs can be prepared called hydroxy double salts (Morioka, H., Tagaya, H., Karasu, M, Kadokawa, J, Chiba, K *Inorg. Chem.* 1999, 38, 4211-6). In an embodiment, the ZLM is a hydroxy double salt conforming to the formula  $[M^{2+}_{1-x}M^{2+}_{1+x}(OH)_{3(1-y)}]^{+} A^{n-}_{(1=3y)/n} \cdot nH_2O$  where the two metal ions ( $M^{2+}$ ) may be the same or different. If they are the same and represented by zinc, the formula simplifies to  $[Zn_{1+x}(OH)_2]^{2x+} 2x A^{-} \cdot nH_2O$ . This latter formula

represents (where  $x=0.4$ ) materials such as zinc hydroxychloride and zinc hydroxynitrate. In an embodiment, the ZLM is zinc hydroxychloride and/or zinc hydroxynitrate. These are related to hydrozincite as well wherein a divalent anion replace the monovalent anion. These materials can also be formed *in situ* in a composition or in or during a production process.

5 In an embodiment, the composition comprises basic zinc carbonate. Commercially available sources of basic zinc carbonate include Zinc Carbonate Basic (Cater Chemicals: Bensenville, IL, USA), Zinc Carbonate (Shepherd Chemicals: Norwood, OH, USA), Zinc Carbonate (CPS Union Corp.: New York, NY, USA), Zinc Carbonate (Elementis Pigments: Durham, UK), and Zinc Carbonate AC (Bruggemann Chemical: Newtown Square, PA, USA). Basic zinc carbonate, which  
10 also may be referred to commercially as "Zinc Carbonate" or "Zinc Carbonate Basic" or "Zinc Hydroxy Carbonate", is a synthetic version consisting of materials similar to naturally occurring hydrozincite. The idealized stoichiometry is represented by  $Zn_5(OH)_6(CO_3)_2$  but the actual stoichiometric ratios can vary slightly and other impurities may be incorporated in the crystal lattice.

In embodiments having a zinc-containing layered material and a pyrithione or polyvalent  
15 metal salt of pyrithione, the ratio of zinc-containing layered material to pyrithione or a polyvalent metal salt of pyrithione is from about 5:100 to about 10:1, or from about 2:10 to about 5:1, or from about 1:2 to about 3:1.

#### CATIONIC POLYMERS

The hair care composition also comprises a cationic polymer. These cationic polymers can  
20 include at least one of (a) a cationic guar polymer, (b) a cationic non-guar galactomannan polymer, (c) a cationic tapioca polymer, (d) a cationic copolymer of acrylamide monomers and cationic monomers, and/or (e) a synthetic, non-crosslinked, cationic polymer, which may or may not form lyotropic liquid crystals upon combination with the deterative surfactant (f) a cationic cellulose polymer. Additionally, the cationic polymer can be a mixture of cationic polymers.

25 The hair care composition may comprise a cationic guar polymer, which is a cationically substituted galactomannan (guar) gum derivatives. 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, which is branched at regular intervals with single membered galactose units on alternative mannose units. The mannose units are linked to each  
30 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

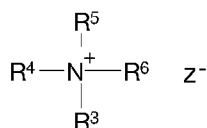
substitution of the cationic groups onto the guar structure should be sufficient to provide the requisite cationic charge density described above.

According to one embodiment, the cationic polymer, including but not limited to a cationic guar polymer, has a molecular weight of less than 1.0 million g/mol, or from about 10 thousand to about 1 million g/mol, or from about 25 thousand to about 1 million g/mol, or from about 50 thousand to about 1 million g/mol, or from about 100 thousand to about 1 million g/mol. In one embodiment, the cationic guar polymer has a charge density of from about 0.2 to about 2.2 meq/g, or from about 0.3 to about 2.0 meq/g, or from about 0.4 to about 1.8 meq/g; or from about 0.5 meq/g to about 1.7 meq/g.

According to one embodiment, the cationic guar polymer has a weight average molecular weight of less than about 1.0 million g/mol, and has a charge density of from about 0.1 meq/g to about 2.5 meq/g. In an embodiment, the cationic guar polymer has a weight average molecular weight of less than 950 thousand g/mol, or from about 10 thousand to about 900 thousand g/mol, or from about 25 thousand to about 900 thousand g/mol, or from about 50 thousand to about 900 thousand g/mol, or from about 100 thousand to about 900 thousand g/mol. In one embodiment, the cationic guar polymer has a charge density of from about 0.2 to about 2.2 meq/g, or from about 0.3 to about 2.0 meq/g, or from about 0.4 to about 1.8 meq/g; or from about 0.5 meq/g to about 1.5 meq/g.

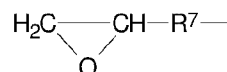
The hair care composition can comprise from about 0.05% to less than about 1%, from about 0.05% to about 0.9%, from about 0.1% to about 0.8%, or from about 0.2% to about 0.7% of cationic polymer (a), by total weight of the composition.

The cationic guar polymer may be formed from quaternary ammonium compounds. In an embodiment, the quaternary ammonium compounds for forming the cationic guar polymer conform to the general formula 1:

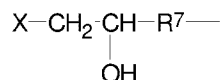


wherein where  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are methyl or ethyl groups;  $\text{R}^6$  is either an epoxyalkyl group of the general formula 2:

13

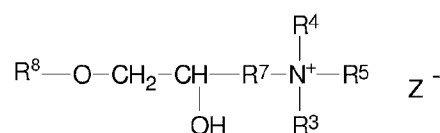


or R<sup>6</sup> is a halohydrin group of the general formula 3:

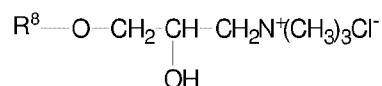


wherein R<sup>7</sup> is a C<sub>1</sub> to C<sub>3</sub> alkylene; X is chlorine or bromine, and Z is an anion such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or HSO<sub>4</sub><sup>-</sup>.

In an embodiment, the cationic guar polymer conforms to the general formula 4:



wherein R<sup>8</sup> is guar gum; and wherein R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are as defined above; and wherein Z is a halogen. In an embodiment, the cationic guar polymer conforms to Formula 5:



Suitable cationic guar polymers include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride. In an embodiment, the cationic guar polymer is a guar hydroxypropyltrimonium chloride. Specific examples of guar hydroxypropyltrimonium chlorides include the Jaguar<sup>®</sup> series commercially available from Rhone-Poulenc Incorporated, for example Jaguar<sup>®</sup> C-500, commercially available from Rhodia. Jaguar<sup>®</sup> C-500 has a charge density of 0.8 meq/g and a molecular weight of 500,000 g/mol. Other suitable guar hydroxypropyltrimonium chloride are: guar hydroxypropyltrimonium chloride which has a charge density of about 1.1 meq/g and a molecular weight of about 500,000 g/mol is available from ASI, a charge density of about 1.5 meq/g and a molecular weight of about 500,000 g/mole is available from ASI. Other suitable guar hydroxypropyltrimonium chloride are: Hi-Care 1000, which has a charge density of about 0.7 meq/g and a Molecular weight of about 600,000 g/mole and is available from Rhodia; N-Hance 3269 and N-Hance 3270, which has a charge density of about 0.7 meq/g and a molecular weight of about 425,000 g/mol and is available from ASIAquaCat CG518 has a charge density of about 0.9 meq/g and a Molecular weight of about 50,000 g/mol and is available from ASI. BF-13, which is a borate

(boron) free guar of charge density of about 1.1 meq/g and molecular weight of about 800,000 and BF-17, which is a borate (boron) free guar of charge density of about 1.7 meq/g and M. W.t of about 800,000 both available from ASI.

The hair care compositions may comprise a galactomannan polymer derivative having a mannose to galactose ratio of greater than 2:1 on a monomer to monomer basis, the galactomannan polymer derivative selected from the group consisting of a cationic galactomannan polymer derivative and an amphoteric galactomannan polymer derivative having a net positive charge. As used herein, the term "cationic galactomannan" refers to a galactomannan polymer to which a cationic group is added. The term "amphoteric galactomannan" refers to a galactomannan polymer to which a cationic group and an anionic group are added such that the polymer has a net positive charge.

Galactomannan polymers are present in the endosperm of seeds of the Leguminosae family. Galactomannan polymers are made up of a combination of mannose monomers and galactose monomers. The galactomannan molecule is a straight chain mannan branched at regular intervals with single membered galactose units on specific 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. The ratio of mannose monomers to galactose monomers varies according to the species of the plant and also is affected by climate. Non Guar Galactomannan polymer derivatives can have a ratio of mannose to galactose of greater than 2:1 on a monomer to monomer basis. Suitable ratios of mannose to galactose can be greater than about 3:1, and the ratio of mannose to galactose can be greater than about 4:1. Analysis of mannose to galactose ratios is well known in the art and is typically based on the measurement of the galactose content.

The gum for use in preparing the non-guar galactomannan polymer derivatives is typically obtained as naturally occurring material such as seeds or beans from plants. Examples of various non-guar galactomannan polymers include but are not limited to Tara gum (3 parts mannose/1 part galactose), Locust bean or Carob (4 parts mannose/1 part galactose), and Cassia gum (5 parts mannose/1 part galactose).

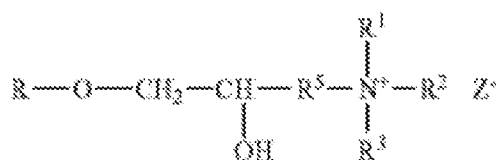
In one embodiment of the invention, the non-guar galactomannan polymer derivatives have a M. Wt. from about 1,000 to about 1,000,000, and/or from about 5,000 to about 900,000.

The hair care compositions of the can also include galactomannan polymer derivatives which have a cationic charge density from about 0.5 meq/g to about 7 meq/g. In one embodiment, the galactomannan polymer derivatives have a cationic charge density from about 1 meq/g to about 5

meq/g. The degree of substitution of the cationic groups onto the galactomannan structure should be sufficient to provide the requisite cationic charge density.

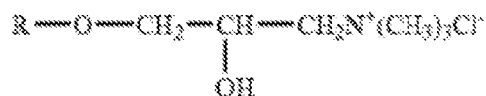
The galactomannan polymer derivative can be a cationic derivative of the non-guar galactomannan polymer, which is obtained by reaction between the hydroxyl groups of the polygalactomannan polymer and reactive quaternary ammonium compounds. Suitable quaternary ammonium compounds for use in forming the cationic galactomannan polymer derivatives include those conforming to the general formulas 1-5, as defined above.

Cationic non-guar galactomannan polymer derivatives formed from the reagents described above are represented by the general formula 6:



10

wherein R is the gum. The cationic galactomannan derivative can be a gum hydroxypropyltrimethylammonium chloride, which can be more specifically represented by the general formula 7:



15

Alternatively the galactomannan polymer derivative can be an amphoteric galactomannan polymer derivative having a net positive charge, obtained when the cationic galactomannan polymer derivative further comprises an anionic group.

The cationic non-guar galactomannan can have a ratio of mannose to galactose is greater than about 4:1, a molecular weight of about 50,000g/mol to about 1,000,000g/mol, and/or from about 100,000 g/mol to about 900,000 g/mol and a cationic charge density from about 1 meq/g to about 5 meq/g, and/or from 2 meq/ g to about 4 meq/ g and can also be derived from a cassia plant.

The hair care compositions can comprise at least about 0.05% of a galactomannan polymer derivative by weight of the composition, alternatively from about 0.05% to about 2%, by weight of the composition, of a galactomannan polymer derivative.

The hair care compositions can comprise water-soluble cationically modified starch polymers. As used herein, the term "cationically modified starch" refers to a starch to which a

25

cationic group is added prior to degradation of the starch to a smaller molecular weight, or wherein a cationic group is added after modification of the starch to achieve a desired molecular weight. The definition of the term "cationically modified starch" also includes amphoterically modified starch. The term "amphoterically modified starch" refers to a starch hydrolysate to which a cationic group and an anionic group are added.

The hair care compositions can comprise cationically modified starch polymers at a range of about 0.01% to about 10%, and/or from about 0.05% to about 5%, by weight of the composition.

The cationically modified starch polymers disclosed herein have a percent of bound nitrogen of from about 0.5% to about 4%.

The cationically modified starch polymers for use in the hair care compositions can have a molecular weight about 50,000 g/mol to about 1,000,000 g/mol and/or from about 100,000 g/mol to about 1,000,000 g/mol.

The hair care compositions can include cationically modified starch polymers which have a charge density of from about 0.2 meq/g to about 5 meq/g, and/or from about 0.2 meq/g to about 2 meq/g. The chemical modification to obtain such a charge density includes, but is not limited to, the addition of amino and/or ammonium groups into the starch molecules. Non-limiting examples of these ammonium groups may include substituents such as hydroxypropyl trimmonium chloride, trimethylhydroxypropyl ammonium chloride, dimethylstearylhydroxypropyl ammonium chloride, and dimethyldodecylhydroxypropyl ammonium chloride. See Solarek, D. B., Cationic Starches in Modified Starches: Properties and Uses, Wurzburg, O. B., Ed., CRC Press, Inc., Boca Raton, Fla. 1986, pp 113-125. The cationic groups may be added to the starch prior to degradation to a smaller molecular weight or the cationic groups may be added after such modification.

The cationically modified starch polymers generally have a degree of substitution of a cationic group from about 0.2 to about 2.5. As used herein, the "degree of substitution" of the cationically modified starch polymers is an average measure of the number of hydroxyl groups on each anhydroglucose unit which is derivatized by substituent groups. Since each anhydroglucose unit has three potential hydroxyl groups available for substitution, the maximum possible degree of substitution is 3. The degree of substitution is expressed as the number of moles of substituent groups per mole of anhydroglucose unit, on a molar average basis. The degree of substitution may be determined using proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) methods well known in the art. Suitable <sup>1</sup>H NMR techniques include those described in "Observation on NMR Spectra of Starches in Dimethyl Sulfoxide, Iodine-Complexing, and Solvating in Water-

Dimethyl Sulfoxide", Qin-Ji Peng and Arthur S. Perlin, Carbohydrate Research, 160 (1987), 57-72; and "An Approach to the Structural Analysis of Oligosaccharides by NMR Spectroscopy", J. Howard Bradbury and J. Grant Collins, Carbohydrate Research, 71, (1979), 15-25.

5 The source of starch before chemical modification can be chosen from a variety of sources such as tubers, legumes, cereal, and grains. Non-limiting examples of this source starch may include corn starch, wheat starch, rice starch, waxy corn starch, oat starch, cassaya starch, waxy barley, waxy rice starch, glutenous rice starch, sweet rice starch, amioca, potato starch, tapioca starch, oat starch, sago starch, sweet rice, or mixtures thereof.

10 The cationically modified starch polymers can be selected from degraded cationic maize starch, cationic tapioca, cationic potato starch, and mixtures thereof. Alternatively, the cationically modified starch polymers are cationic corn starch and cationic tapioca.

The starch, prior to degradation or after modification to a smaller molecular weight, may comprise one or more additional modifications. For example, these modifications may include cross-linking, stabilization reactions, phosphorylations, and hydrolyzations. Stabilization reactions may  
15 include alkylation and esterification.

The cationically modified starch polymers may be incorporated into the composition in the form of hydrolyzed starch (e.g., acid, enzyme, or alkaline degradation), oxidized starch (e.g., peroxide, peracid, hypochlorite, alkaline, or any other oxidizing agent), physically/mechanically degraded starch (e.g., via the thermo-mechanical energy input of the processing equipment), or  
20 combinations thereof.

An optimal form of the starch is one which is readily soluble in water and forms a substantially clear (% Transmittance.gtoeq.80 at 600 nm) solution in water. The transparency of the composition is measured by Ultra-Violet/Visible (UV/VIS) spectrophotometry, which determines the absorption or transmission of UV/VIS light by a sample, using a Gretag Macbeth Colorimeter  
25 Color i 5 according to the related instructions. A light wavelength of 600 nm has been shown to be adequate for characterizing the degree of clarity of cosmetic compositions.

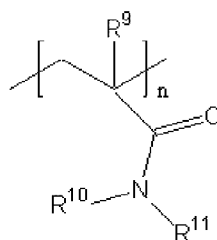
Suitable cationically modified starch for use in hair care compositions are available from known starch suppliers. Also suitable for use in hair care compositions are nonionic modified starch that can be further derivatized to a cationically modified starch as is known in the art. Other suitable  
30 modified starch starting materials may be quaternized, as is known in the art, to produce the cationically modified starch polymer suitable for use in hair care compositions.

Starch Degradation Procedure: a starch slurry can be prepared by mixing granular starch in water. The temperature is raised to about 35°C. An aqueous solution of potassium permanganate is then added at a concentration of about 50 ppm based on starch. The pH is raised to about 11.5 with sodium hydroxide and the slurry is stirred sufficiently to prevent settling of the starch. Then, about a 30% solution of hydrogen peroxide diluted in water is added to a level of about 1% of peroxide based on starch. The pH of about 11.5 is then restored by adding additional sodium hydroxide. The reaction is completed over about a 1 to about 20 hour period. The mixture is then neutralized with dilute hydrochloric acid. The degraded starch is recovered by filtration followed by washing and drying.

The hair care composition can comprise a cationic copolymer of an acrylamide monomer and a cationic monomer, wherein the copolymer has a charge density of from about 1.0 meq/g to about 3.0 meq/g. The cationic copolymer can be a synthetic cationic copolymer of acrylamide monomers and cationic monomers.

The cationic copolymer can comprise:

(i) an acrylamide monomer of the following Formula AM:

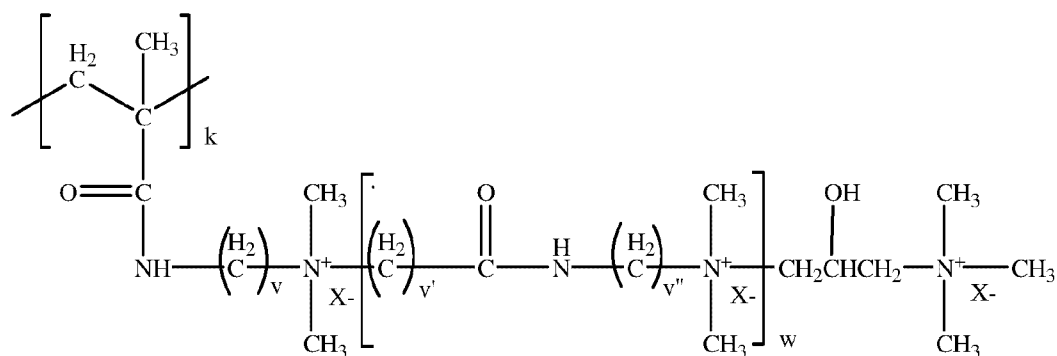


Formula AM

where  $\text{R}^9$  is H or  $\text{C}_{1-4}$  alkyl; and  $\text{R}^{10}$  and  $\text{R}^{11}$  are independently selected from the group consisting of H,  $\text{C}_{1-4}$  alkyl,  $\text{CH}_2\text{OCH}_3$ ,  $\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_3)_2$ , and phenyl, or together are  $\text{C}_3$ -cycloalkyl; and

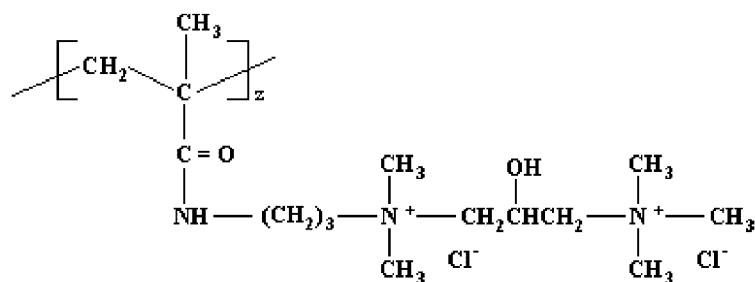
(ii) a cationic monomer conforming to Formula CM:

19

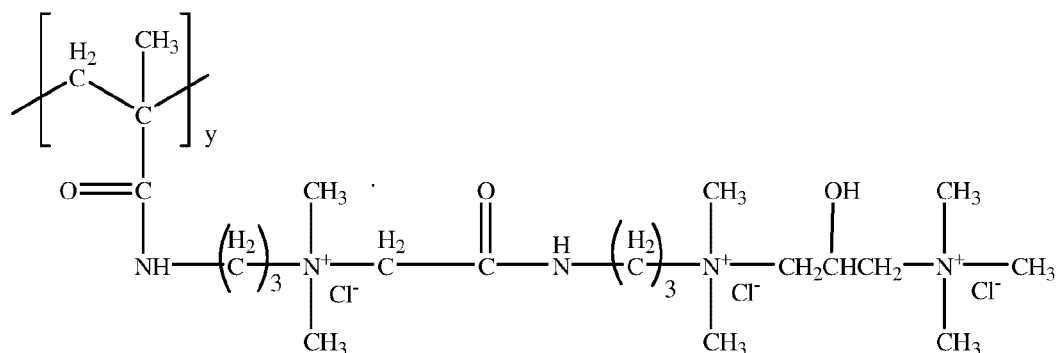
Formula CM

where  $k = 1$ , each of  $v$ ,  $v'$ , and  $v''$  is independently an integer of from 1 to 6,  $w$  is zero or an integer of from 1 to 10, and  $X^-$  is an anion.

- 5 The cationic monomer can conform to Formula CM and where  $k = 1$ ,  $v = 3$  and  $w = 0$ ,  $z = 1$  and  $X^-$  is  $Cl^-$  to form the following structure:



The above structure may be referred to as diquat. Alternatively, the cationic monomer can conform to Formula CM and wherein  $v$  and  $v''$  are each 3,  $v' = 1$ ,  $w = 1$ ,  $y = 1$  and  $X^-$  is  $Cl^-$ , such as:



10

The above structure may be referred to as triquat.

Suitable acrylamide monomer include, but are not limited to, either acrylamide or methacrylamide.

- 15 In an alternative embodiment, the cationic copolymer is of an acrylamide monomer and a cationic monomer, wherein the cationic monomer is selected from the group consisting of:

dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, ditertiobutylaminoethyl (meth)acrylate, dimethylaminomethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide; ethylenimine, vinylamine, 2-vinylpyridine, 4-vinylpyridine; trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbzyl dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido chloride, trimethyl ammonium propyl (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride, diallyldimethyl ammonium chloride, and mixtures thereof.

The cationic copolymer can comprise a cationic monomer selected from the group consisting of: cationic monomers include trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbzyl dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido chloride, trimethyl ammonium propyl (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride, and mixtures thereof.

The cationic copolymer can be water-soluble. The cationic copolymer is formed from (1) copolymers of (meth)acrylamide and cationic monomers based on (meth)acrylamide, and/or hydrolysis-stable cationic monomers, (2) terpolymers of (meth)acrylamide, monomers based on cationic (meth)acrylic acid esters, and monomers based on (meth)acrylamide, and/or hydrolysis-stable cationic monomers. Monomers based on cationic (meth)acrylic acid esters may be cationized esters of the (meth)acrylic acid containing a quaternized N atom. In an embodiment, cationized esters of the (meth)acrylic acid containing a quaternized N atom are quaternized dialkylaminoalkyl (meth)acrylates with C1 to C3 in the alkyl and alkylene groups. Suitable cationized esters of the (meth)acrylic acid containing a quaternized N atom can be selected from the group consisting of: ammonium salts of dimethylaminomethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, diethylaminomethyl (meth)acrylate, diethylaminoethyl (meth)acrylate; and diethylaminopropyl (meth)acrylate quaternized with methyl chloride. In an embodiment, the cationized esters of the (meth)acrylic acid containing a quaternized N atom is dimethylaminoethyl acrylate, which is quaternized with an alkyl halide, or with methyl chloride or benzyl chloride or dimethyl sulfate (ADAME-Quat). the cationic monomer when based on (meth)acrylamides can be quaternized dialkylaminoalkyl(meth)acrylamides with C1 to C3 in the alkyl and alkylene groups, or dimethylaminopropylacrylamide, which is quaternized with an alkyl halide, or methyl chloride or benzyl chloride or dimethyl sulfate.

Suitable cationic monomer based on a (meth)acrylamide include quaternized dialkylaminoalkyl(meth)acrylamide with C1 to C3 in the alkyl and alkylene groups. The cationic monomer based on a (meth)acrylamide can be dimethylaminopropylacrylamide, which is quaternized with an alkyl halide, especially methyl chloride or benzyl chloride or dimethyl sulfate.

5 The cationic monomer can be a hydrolysis-stable cationic monomer. Hydrolysis-stable cationic monomers can be, in addition to a dialkylaminoalkyl(meth)acrylamide, all monomers that can be regarded as stable to the OECD hydrolysis test. The cationic monomer can be hydrolysis-stable and the hydrolysis-stable cationic monomer can be selected from the group consisting of: diallyldimethylammonium chloride and water-soluble, cationic styrene derivatives.

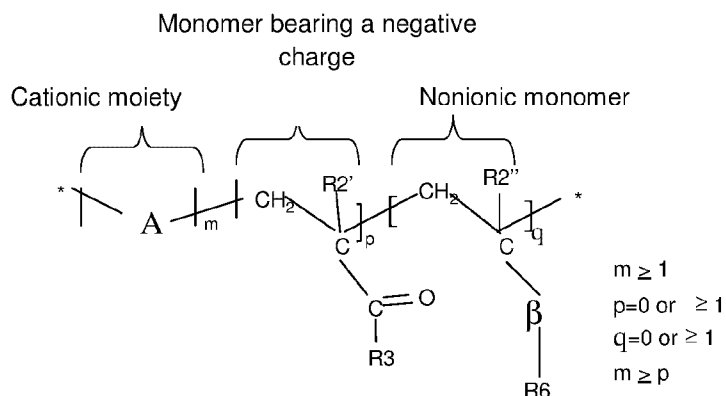
10 The cationic copolymer can be a terpolymer of acrylamide, 2-dimethylammoniumethyl (meth)acrylate quaternized with methyl chloride (ADAME-Q) and 3-dimethylammoniumpropyl(meth)acrylamide quaternized with methyl chloride (DIMAPA-Q). The cationic copolymer can be formed from acrylamide and acrylamidopropyltrimethylammonium chloride, wherein the acrylamidopropyltrimethylammonium chloride has a charge density of from  
15 about 1.0 meq/g to about 3.0 meq/g.

The cationic copolymer can have a charge density of from about 1.1 meq/g to about 2.5 meq/g, or from about 1.1 meq/g to about 2.3 meq/g, or from about 1.2 meq/g to about 2.2 meq/g, or from about 1.2 meq/g to about 2.1 meq/g, or from about 1.3 meq/g to about 2.0 meq/g, or from about 1.3 meq/g to about 1.9 meq/g.

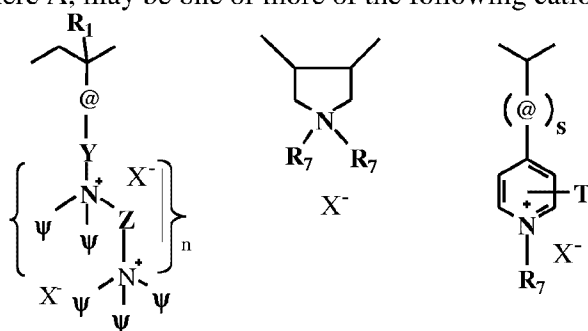
20 The cationic copolymer can have a molecular weight from about 10 thousand g/mol to about 1 million g/mol, or from about 25 thousand g/mol to about 1 million g/mol, or from about 50 thousand g/mol to about 1 million g/mol, or from about 100 thousand g/mol to about 1.0 million g/mol, or from about 150 thousand g/mol to about 1.0 million g/mol.

The hair care composition can comprise a cationic synthetic polymer that may be formed  
25 from one or more cationic monomer units, and optionally one or more monomer units bearing a negative charge, and/or a nonionic monomer, wherein the subsequent charge of the copolymer is positive. The ratio of the three types of monomers is given by “m”, “p” and “q” where “m” is the number of cationic monomers, “p” is the number of monomers bearing a negative charge and “q” is the number of nonionic monomers

30 The cationic polymers can be water soluble or dispersible, non-crosslinked, and synthetic cationic polymers having the following structure:



where A, may be one or more of the following cationic moieties:



where @ = amido, alkylamido, ester, ether, alkyl or alkylaryl;

10 where Y = C1-C22 alkyl, alkoxy, alkylidene, alkyl or aryloxy;

where  $\psi$  = C1-C22 alkyl, alkyloxy, alkyl aryl or alkyl arylox;

where Z = C1-C22 alkyl, alkyloxy, aryl or aryloxy;

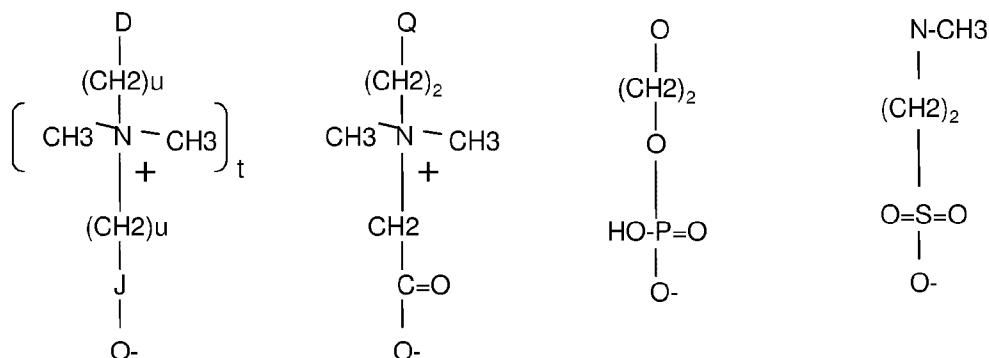
where R1 = H, C1-C4 linear or branched alkyl;

where s = 0 or 1, n = 0 or  $\geq 1$ ;

15 where T and R7 = C1-C22 alkyl; and

where X- = halogen, hydroxide, alkoxide, sulfate or alkylsulfate.

Where the monomer bearing a negative charge is defined by R2' = H, C1-C4 linear or branched alkyl and R3 as:



where D = O, N, or S;

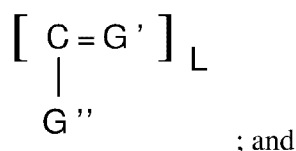
where Q = NH<sub>2</sub> or O;

where u = 1-6;

where t = 0-1; and

- 5 where J = oxygenated functional group containing the following elements P, S, C.

Where the nonionic monomer is defined by R2'' = H, C1-C4 linear or branched alkyl, R6 = linear or branched alkyl, alkyl aryl, aryl oxy, alkyloxy, alkylaryl oxy and β is defined as



where G' and G'' are, independently of one another, O, S or N-H and L = 0 or 1.

- 10 Examples of cationic monomers include aminoalkyl (meth)acrylates, (meth)aminoalkyl (meth)acrylamides; monomers comprising at least one secondary, tertiary or quaternary amine function, or a heterocyclic group containing a nitrogen atom, vinylamine or ethylenimine; dialyldialkyl ammonium salts; their mixtures, their salts, and macromonomers deriving from therefrom.

- 15 Further examples of cationic monomers include dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, ditertiobutylaminoethyl (meth)acrylate, dimethylaminomethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, ethylenimine, vinylamine, 2-vinylpyridine, 4-vinylpyridine, trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbzyl dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido chloride, trimethyl ammonium propyl (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride, dialyldimethyl ammonium chloride.
- 20

Suitable cationic monomers include those which comprise a quaternary ammonium group of formula  $-NR_3^+$ , wherein R, which is identical or different, represents a hydrogen atom, an alkyl group comprising 1 to 10 carbon atoms, or a benzyl group, optionally carrying a hydroxyl group, and comprise an anion (counter-ion). Examples of anions are halides such as chlorides, bromides, sulphates, hydrosulphates, alkylsulphates (for example comprising 1 to 6 carbon atoms), phosphates, citrates, formates, and acetates.

Suitable cationic monomers include trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbzyl dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido chloride, trimethyl ammonium propyl (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride.

Additional suitable cationic monomers include trimethyl ammonium propyl (meth)acrylamido chloride.

Examples of monomers bearing a negative charge include alpha ethylenically unsaturated monomers comprising a phosphate or phosphonate group, alpha ethylenically unsaturated monocarboxylic acids, monoalkylesters of alpha ethylenically unsaturated dicarboxylic acids, monoalkylamides of alpha ethylenically unsaturated dicarboxylic acids, alpha ethylenically unsaturated compounds comprising a sulphonic acid group, and salts of alpha ethylenically unsaturated compounds comprising a sulphonic acid group.

Suitable monomers with a negative charge include acrylic acid, methacrylic acid, vinyl sulphonic acid, salts of vinyl sulfonic acid, vinylbenzene sulphonic acid, salts of vinylbenzene sulphonic acid, alpha-acrylamidomethylpropanesulphonic acid, salts of alpha-acrylamidomethylpropanesulphonic acid, 2-sulphoethyl methacrylate, salts of 2-sulphoethyl methacrylate, acrylamido-2-methylpropanesulphonic acid (AMPS), salts of acrylamido-2-methylpropanesulphonic acid, and styrenesulphonate (SS).

Examples of nonionic monomers include vinyl acetate, amides of alpha ethylenically unsaturated carboxylic acids, esters of an alpha ethylenically unsaturated monocarboxylic acids with an hydrogenated or fluorinated alcohol, polyethylene oxide (meth)acrylate (i.e. polyethoxylated (meth)acrylic acid), monoalkylesters of alpha ethylenically unsaturated dicarboxylic acids, monoalkylamides of alpha ethylenically unsaturated dicarboxylic acids, vinyl nitriles, vinylamine amides, vinyl alcohol, vinyl pyrrolidone, and vinyl aromatic compounds.

Suitable nonionic monomers include styrene, acrylamide, methacrylamide, acrylonitrile, methylacrylate, ethylacrylate, n-propylacrylate, n-butylacrylate, methylmethacrylate, ethylmethacrylate, n-propylmethacrylate, n-butylmethacrylate, 2-ethyl-hexyl acrylate, 2-ethyl-hexyl methacrylate, 2-hydroxyethylacrylate and 2-hydroxyethylmethacrylate.

5       The anionic counterion ( X<sup>-</sup> ) in association with the synthetic cationic polymers may be any known counterion so long as the polymers remain soluble or dispersible in water, in the hair care composition, or in a coacervate phase of the hair care composition, and so long as the counterions are physically and chemically compatible with the essential components of the hair care composition or do not otherwise unduly impair product performance, stability or aesthetics. Non limiting  
10       examples of such counterions include halides (e.g., chlorine, fluorine, bromine, iodine), sulfate and methylsulfate.

The concentration of the cationic polymers ranges about 0.025% to about 5%, from about 0.1% to about 3%, and/or from about 0.2% to about 1%, by weight of the hair care composition.

Suitable cationic cellulose polymers are salts of hydroxyethyl cellulose reacted with  
15       trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10 and available from Dow/ Amerchol Corp. (Edison, N.J., USA) in their Polymer LR, JR, and KG series of polymers. Other suitable types of cationic cellulose include the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide referred to in the industry (CTFA) as Polyquaternium 24. These materials are available  
20       from Dow/ Amerchol Corp. under the tradename Polymer LM-200. Other suitable types of cationic cellulose include the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide and trimethyl ammonium substituted epoxide referred to in the industry (CTFA) as Polyquaternium 67. These materials are available from Dow/ Amerchol Corp. under the tradename SoftCAT Polymer SL-5, SoftCAT Polymer SL-30, Polymer  
25       SL-60, Polymer SL-100, Polymer SK-L, Polymer SK-M, Polymer SK-MH, and Polymer SK-H.

#### BLOWING AGENT

The hair care composition described herein may comprise from about 1% to about 10% blowing agent, alternatively from about 2% to about 8% Blowing Agent, and alternatively from about 2.5% to about 7% blowing agent, by weight of the hair care composition.

30       The blowing agent may comprise one or more volatile materials, which in a gaseous state, may carry the other components of the hair care composition in particulate or droplet form. The blowing agent may have a boiling point within the range of from about -45° C. to about 5° C. The

blowing agent may be liquefied when packaged in convention aerosol containers under pressure. The rapid boiling of the blowing agent upon leaving the aerosol foam dispenser may aid in the atomization of the other components of the hair care composition.

Aerosol blowing agents which may be employed in the aerosol composition may include the chemically-inert hydrocarbons such as propane, n-butane, isobutane, cyclopropane, and mixtures thereof, as well as halogenated hydrocarbons such as dichlorodifluoromethane, 1,1-dichloro-1,1,2,2-tetrafluoroethane, 1-chloro-1,1-difluoro-2,2-trifluoroethane, 1-chloro-1,1-difluoroethylene, 1,1-difluoroethane, dimethyl ether, monochlorodifluoromethane, trans-1,3,3,3-tetrafluoropropene, and mixtures thereof. Non-limiting examples of a blowing agent may be Propellant A46 (Isobutane and Propane) (18, Diversified Cpc International (Channahon US) and HF0 (Trans 1,3,3,3 Tetrafluoropropene) (19) from Honey Well. The blowing agent may comprise hydrocarbons such as isobutane, propane, and butane—these materials may be used for their low ozone reactivity and may be used as individual components where their vapor pressures at 21.1° C. range from about 1.17 Bar to about 7.45 Bar, alternatively from about 1.17 Bar to about 4.83 Bar, and alternatively from about 2.14 Bar to about 3.79 Bar.

#### OPTIONAL INGREDIENTS

The hair care composition may further comprise one or more optional ingredients, including benefit agents. Suitable benefit agents include, but are not limited to conditioning agents, cationic polymers silicone emulsions, anti-dandruff actives, gel networks, chelating agents, and, natural oils such as sun flower oil or castor oil. Additional suitable optional ingredients include but are not limited to perfumes, perfume microcapsules, colorants, particles, anti-microbials, foam busters, anti-static agents, rheology modifiers and thickeners, suspension materials and structurants, pH adjusting agents and buffers, preservatives, pearlescent agents, solvents, diluents, anti-oxidants, vitamins and combinations thereof.

Such optional ingredients should be physically and chemically compatible with the components of the composition, and should not otherwise unduly impair product stability, aesthetics, or performance. The CTFA Cosmetic Ingredient Handbook, Tenth Edition (published by the Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C.) (2004) (hereinafter "CTFA"), describes a wide variety of nonlimiting materials that can be added to the composition herein.

#### Conditioning Agents

The conditioning agent of the hair care compositions can be a silicone conditioning agent. The silicone conditioning agent may comprise volatile silicone, non-volatile silicone, or combinations thereof. The concentration of the silicone conditioning agent typically ranges from about 0.01% to about 10%, by weight of the composition, from about 0.1% to about 8%, from about 0.1% to about 5%, and/or from about 0.2% to about 3%. Non-limiting examples of suitable silicone conditioning agents, and optional suspending agents for the silicone, are described in U.S. Reissue Pat. No. 34,584, U.S. Pat. No. 5,104,646, and U.S. Pat. No. 5,106,609.

The silicone conditioning agents suitable for use can have a viscosity, as measured at 25° C, from about 20 to about 2,000,000 centistokes ("csk"), of from about 1,000 to about 1,800,000 csk, from about 50,000 to about 1,500,000 csk, and/or from about 100,000 to about 1,500,000 csk.

The dispersed silicone conditioning agent particles typically have a volume average particle diameter ranging from about 0.01 micrometer to about 10 micrometer. For small particle application to hair, the volume average particle diameters typically range from about 0.01 micrometer to about 4 micrometer, from about 0.01 micrometer to about 2 micrometer, from about 0.01 micrometer to about 0.5 micrometer.

Additional material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, are found in *Encyclopedia of Polymer Science and Engineering*, vol. 15, 2d ed., pp 204-308, John Wiley & Sons, Inc. (1989).

20

Silicone emulsions suitable for use include, but are not limited to, emulsions of insoluble polysiloxanes prepared in accordance with the descriptions provided in U.S. Patent No. 4,476,282 and U.S. Patent Application Publication No. 2007/0276087. Accordingly, suitable insoluble polysiloxanes include polysiloxanes such as alpha, omega hydroxy-terminated polysiloxanes or alpha, omega alkoxy-terminated polysiloxanes having a molecular weight within the range from about 50,000 to about 500,000 g/mol. The insoluble polysiloxane can have an average molecular weight within the range from about 50,000 to about 500,000 g/mol. For example, the insoluble polysiloxane may have an average molecular weight within the range from about 60,000 to about 400,000; from about 75,000 to about 300,000; from about 100,000 to about 200,000; or the average molecular weight may be about 150,000 g/mol. The insoluble polysiloxane can have an average particle size within the range from about 30 nm to about 10 micron. The average particle size may

be within the range from about 40 nm to about 5 micron, from about 50nm to about 1micron, from about 75 nm to about 500 nm, or about 100 nm, for example.

The average molecular weight of the insoluble polysiloxane, the viscosity of the silicone emulsion, and the size of the particle comprising the insoluble polysiloxane are determined by methods commonly used by those skilled in the art, such as the methods disclosed in Smith, A. L. *The Analytical Chemistry of Silicones*, John Wiley & Sons, Inc.: New York, 1991. For example, the viscosity of the silicone emulsion can be measured at 30°C with a Brookfield viscometer with spindle 6 at 2.5 rpm. The silicone emulsion may further include an additional emulsifier together with the anionic surfactant,

Other classes of silicones suitable for use include but are not limited to: i) silicone fluids, including but not limited to, silicone oils, which are flowable materials having viscosity less than about 1,000,000 csk as measured at 25°C; ii) aminosilicones, which contain at least one primary, secondary or tertiary amine; iii) cationic silicones, which contain at least one quaternary ammonium functional group; iv) silicone gums; which include materials having viscosity greater or equal to 1,000,000 csk as measured at 25°C; v) silicone resins, which include highly cross-linked polymeric siloxane systems; vi) high refractive index silicones, having refractive index of at least 1.46, and vii) mixtures thereof.

The conditioning agent of the hair care compositions may also comprise at least one organic conditioning material such as oil or wax, either alone or in combination with other conditioning agents, such as the silicones described above. The organic material can be non-polymeric, oligomeric or polymeric. It may be in the form of oil or wax and may be added in the formulation neat or in a pre-emulsified form. Some non-limiting examples of organic conditioning materials include, but are not limited to: i) hydrocarbon oils; ii) polyolefins, iii) fatty esters, iv) fluorinated conditioning compounds, v) fatty alcohols, vi) alkyl glucosides and alkyl glucoside derivatives; vii) quaternary ammonium compounds; viii) polyethylene glycols and polypropylene glycols having a molecular weight of up to about 2,000,000 including those with CTFA names PEG-200, PEG-400, PEG-600, PEG-1000, PEG-2M, PEG-7M, PEG-14M, PEG-45M and mixtures thereof.

#### Emulsifiers

A variety of anionic and nonionic emulsifiers can be used in the hair care composition. The anionic and nonionic emulsifiers can be either monomeric or polymeric in nature. Monomeric examples include, by way of illustrating and not limitation, alkyl ethoxylates, alkyl sulfates, soaps, and fatty esters and their derivatives. Polymeric examples include, by way of illustrating and not

limitation, polyacrylates, polyethylene glycols, and block copolymers and their derivatives. Naturally occurring emulsifiers such as lanolins, lecithin and lignin and their derivatives are also non-limiting examples of useful emulsifiers.

#### Chelating Agents

5           The hair care composition can also comprise a chelant. Suitable chelants include those listed in A E Martell & R M Smith, Critical Stability Constants, Vol. 1, Plenum Press, New York & London (1974) and A E Martell & R D Hancock, Metal Complexes in Aqueous Solution, Plenum Press, New York & London (1996). When related to chelants, the term "salts and derivatives thereof" means the salts and derivatives comprising the same  
10 functional structure (e.g., same chemical backbone) as the chelant they are referring to and that have similar or better chelating properties. This term include alkali metal, alkaline earth, ammonium, substituted ammonium (i.e. monoethanolammonium, diethanolammonium, triethanolammonium) salts, esters of chelants having an acidic moiety and mixtures thereof, in particular all sodium, potassium or ammonium salts. The term "derivatives" also includes "chelating surfactant"  
15 compounds, such as those exemplified in U.S. Pat. No. 5,284,972, and large molecules comprising one or more chelating groups having the same functional structure as the parent chelants, such as polymeric EDDS (ethylenediaminedisuccinic acid) disclosed in U.S. Pat. No. 5,747,440.

Levels of the EDDS chelant in the hair care compositions can be as low as about 0.01 wt% or even as high as about 10 wt%, but above the higher level (i.e., 10 wt%) formulation and/or human  
20 safety concerns may arise. In an embodiment, the level of the EDDS chelant may be at least about 0.05 wt%, at least about 0.1 wt%, at least about 0.25 wt%, at least about 0.5 wt%, at least about 1 wt%, or at least about 2 wt% by weight of the hair care composition. Levels above about 4 wt% can be used but may not result in additional benefit.

#### Aqueous Carrier

25           The hair care compositions can be in the form of pourable liquids (under ambient conditions). Such compositions will therefore typically comprise a carrier, which is present at a level of from about 40 % to about 80 %, alternatively from about 45 % to about 75 %, alternatively from about 50 % to about 70 % by weight of the hair care composition. The carrier may comprise water, or a miscible mixture of water and organic solvent, and in one aspect may comprise water with minimal  
30 or no significant concentrations of organic solvent, except as otherwise incidentally incorporated into the composition as minor ingredients of other essential or optional components.

The carrier useful in the hair care compositions includes water and water solutions of lower alkyl alcohols and polyhydric alcohols. The lower alkyl alcohols useful herein are monohydric alcohols having 1 to 6 carbons, in one aspect, ethanol and isopropanol. Exemplary polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, and propane diol.

5

### AEROSOL FOAM DISPENSER

The aerosol foam dispenser may comprise a reservoir for holding the hair care composition. The reservoir may be made out of any suitable material selected from the group consisting of plastic, metal, alloy, laminate, and combinations thereof. In an embodiment, the reservoir may be for one-time use. In an embodiment, the reservoir may be removable from the aerosol foam dispenser. Alternatively, the reservoir may be integrated with the aerosol foam dispenser. In an embodiment, there may be two or more reservoirs.

In an embodiment, the reservoir may be comprised of a material selected from the group consisting of rigid materials, flexible materials, and combinations thereof. The reservoir may be comprised of a rigid material if it does not collapse under external atmospheric pressure when it is subject to an interior partial vacuum.

### TEST METHODS

#### Foam Density

Foam density is measured by placing a 100 ml beaker onto a mass balance, tarring the mass of the beaker and then dispensing product from the aerosol container into the 100 ml beaker until the volume of the foam is above the rim of the vessel. The foam is made level with the top of the beaker by scraping a spatula across it. The resulting mass of the 100 ml of foam is then divided by the volume (100) to determine the foam density in units of g/ml.

#### In vivo Scalp depo

The on-scalp deposition of the anti-dandruff active is measured by having the hair of individuals washed with a composition comprising an anti-dandruff active, for example a composition pursuant to the present invention, by trained a cosmetician according to a conventional washing protocol. The hair is then parted on an area of the scalp to allow an open-ended glass cylinder to be held on the surface while an aliquot of an extraction solution is added and agitated prior to recovery and analytical determination of anti-dandruff active content by conventional methodology, such as HPLC.

30

ViscosityCone/Plate Viscosity measurement:

The viscosities of formulations are measured by a Cone/Plate Controlled Stress Brookfield Rheometer R/S Plus, by Brookfield Engineering Laboratories, Stoughton, MA. The cone used (Spindle C-75-1) has a diameter of 75 mm and 1° angle. The viscosity is determined using a steady state flow experiment at constant shear rate of 2 s<sup>-1</sup> and at temperature of 26.5 °C. The sample size is 2.5ml and the total measurement reading time is 3 minutes.

#### METHOD OF MAKING

The following examples illustrate embodiments of the invention described herein. The exemplified hair care compositions may be made by mixing together water, polymer, and surfactants along with Sodium Xylene Sulfonate or rheology modifier to thin surfactant phase. Surfactants are pH'd to target 7. Zinc Pyrithione and Zinc Carbonate solids are dispersed via mixing into the neutralized surfactant phase. The ingredients are mixed thoroughly at ambient temperature. Additional ingredients, including blowing agent, electrolytes, silicone emulsions, preservatives and fragrances may be added to the product. It will be appreciated that other modifications of the hair care compositions within the skill of those in the formulation art can be undertaken without departing from the spirit and scope of this invention. All parts, percentages, and ratios herein are by weight unless otherwise specified. Some components may come from suppliers as dilute solutions. The amount stated reflects the weight percent of the active material, unless otherwise specified.

The following examples illustrate embodiments of the invention described herein. All parts, percentages, and ratios herein are by weight unless otherwise specified. Some components may come from suppliers as dilute solutions. The amount stated reflects the weight percent of the active material, unless otherwise specified. The below table are non-limiting examples of hair care compositions described herein:

| Example compositions               | A     | B     | C     | D     | E     | F     | G     | H     | I     | J     | K     |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Sodium Laureth Sulfate (SLE1S) (1) | 20.75 | 20.75 | 20.75 | 20.75 | 20.75 | 20.75 | 20.75 | 20.75 | 20.75 | 20.75 | 20.75 |
| Sodium Lauryl Sulfate (SLS) (2)    | 2.25  | 2.25  | 2.25  | 2.25  | 2.25  | 2.25  | 2.25  | 2.25  | 2.25  | 2.25  | 2.25  |
| Cocamidopropyl Betaine (3)         | 2     | 2     | 2     | 2     | 2     | 2     | 2     | 2     | 2     | 2     | 2     |
| Trihydroxystearin (4)              | 0.1   | 0.1   |       |       | 0.1   | 0.1   |       |       | 0.1   | 0.1   | 0.1   |

|                                                              |      |      |      |      |      |      |      |      |      |      |      |
|--------------------------------------------------------------|------|------|------|------|------|------|------|------|------|------|------|
| Glycol Distearate (5)                                        |      |      | 1.5  | 2.5  |      |      | 1.5  | 2.5  |      |      |      |
| Zinc Pyrithione (6)                                          | 4    | 4    | 4    | 4    | 8    | 8    | 8    | 8    | 4    | 1    | 8    |
| Selenium Sulfide (7)                                         |      |      |      |      |      |      |      |      |      |      |      |
| Octopirox (8)                                                |      |      |      |      |      |      |      |      |      |      |      |
| Zinc Carbonate (9)                                           | 1.61 | 1.61 | 1.61 | 1.61 | 1.61 | 1.61 | 1.61 | 1.61 | 3.22 | 1.61 | 3.22 |
| Fragrance (10)                                               | 1.7  | 1.7  | 1.7  | 1.7  | 1.7  | 1.7  | 1.7  | 1.7  | 1.7  | 1.7  | 1.7  |
| Guar Hyrdroxypropyltrimonium Chloride (LMW) (11)             | 0.4  | 0.4  | 0.4  | 0.4  | 0.4  | 0.4  | 0.4  | 0.4  | 0.4  | 0.4  | 0.4  |
| Dimethicone DM5500 (12)                                      | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    |
| Hydrochloric acid (13)                                       | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   |
| Preservative (14)                                            | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 |
| Sodium Chloride (15)                                         | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   |
| Sodium Xylene Sulfonate (16)                                 | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   |
| Sodium Benzoate (17)                                         | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 | 0.27 |
| Water and Minors (QS to 100%) (18)                           | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   | QS   |
| Blowing Agent A46 (Isobutane and Propane) (19)               | 4    |      | 4    |      | 4    |      | 4    |      | 4    | 4    |      |
| Blowing Agent HFO (Trans 1,3,3,3 Tetrafluoroprop 1 ene) (20) |      | 6    |      | 6    |      | 6    |      | 6    |      |      | 6    |

[illegible][illegible]

|                                                                       |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
|-----------------------------------------------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| (13)                                                                  |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
| Preservative (14)                                                     | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 | 0.0<br>5 |
| Sodium Chloride<br>(15)                                               | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       |
| Sodium Xylene<br>Sulfonate (16)                                       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       |
| Sodium Benzoate<br>(17)                                               | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 | 0.2<br>7 |
| Water and Minors<br>(QS to 100%) (18)                                 | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       | QS       |
| Blowing Agent<br>A46 (Isobutane<br>and Propane) (19)                  |          | 4        |          | 4        |          | 4        |          | 4        |          | 4        | 4        |          |          |          |
| Blowing Agent<br>HFO (Trans 1,3,3,3<br>Tetrafluoroprop 1<br>ene) (20) | 6        |          | 6        |          | 6        |          | 6        |          | 6        |          |          | 6        | 6        | 6        |
| PEG 8<br>Dimethicone A208<br>(21) MW855                               |          | 3        | 3        |          |          |          |          |          |          |          |          |          |          |          |
| Peg 8<br>Dimethicone D208<br>(22) MW2706                              |          |          |          | 3        | 3        |          |          |          |          |          |          |          |          |          |

|                                    |       |
|------------------------------------|-------|
| Example compositions               | Z     |
| Sodium Laureth Sulfate (SLE1S) (1) | 20.75 |
| Sodium Lauryl Sulfate (SLS) (2)    | 2.25  |
| Cocamidopropyl Betaine (3)         | 2     |
| Trihydroxystearin (4)              | 0.1   |
| Glycol Distearate (5)              |       |
| Zinc Pyrithione (6)                | 10    |

|                                                              |      |
|--------------------------------------------------------------|------|
| Selenium Sulfide (7)                                         |      |
| Octopirox (8)                                                |      |
| Zinc Carbonate (9)                                           | 1.61 |
| Fragrance (10)                                               | 1.7  |
| Guar Hydroxypropyltrimonium Chloride (LMW) (11)              | 0.4  |
| Dimethicone DM5500 (12)                                      | 1    |
| Hydrochloric acid (13)                                       | QS   |
| Preservative (14)                                            | 0.05 |
| Sodium Chloride (15)                                         | QS   |
| Sodium Xylene Sulfonate (16)                                 | QS   |
| Sodium Benzoate (17)                                         | 0.27 |
| Water and Minors (QS to 100%) (18)                           | QS   |
| Blowing Agent A46 (Isobutane and Propane) (19)               | 4    |
| Blowing Agent HF0 (Trans 1,3,3,3 Tetrafluoroprop 1 ene) (20) |      |
| PEG 8 Dimethicone A208 (21) MW855                            |      |
| Peg 8 Dimethicone D208 (22) MW2706                           |      |

1. Sodium Laureth-1 Sulfate from the Stepan Company
2. Sodium Lauryl Sulfate from Stepan Company
- 3.. Amphosol HCA from Stepan Company
4. Trihydroxystearin Elementis Specialties
5. Glycol Distearate from Golschmidt Chemical Company
6. U2 ZPT from Lonza
7. Selenium Sulfide from Eskay Fine Chemicals
8. Octopirox from Clariant
9. Zinc Carbonate from Bruggeman Group
10. Fragrance from P&G
11. Jaguar C500 from Solvay with a M. Wt of 500,000 g/mol and charge density of 0.8meq/g
12. Dimethicone DM5500, Wacker Silicone

13. Hydrochloric acid from Mallinckrodt Baker Inc.
14. Preservative Kathon CG from Akzo Nobel
15. Sodium Chloride USP (food grade) Supplier Morton
16. Sodium Xylene Sulfonate from Stepan Company
17. Sodium Benzoate from Kalama Chemical
18. Water from Misty Mountain Spring Water
19. Blowing Agent A46 (Isobutane and Propane) (18, Diversified Cpc International (Channahon US)
20. Blowing Agent HFO (Trans 1,3,3,3 Tetrafluoroprop 1 ene) (19) from Honey Well
21. PEG 8 Dimethicone A208 (20) (MW 855), from Siltech
22. PEG 8 Dimethicone D208 (20) (MW 2706), from Siltech

## RESULTS

|                                           | <b>Blowing Agent</b> | <b>Foam Density (g/ml)</b> | <b>Foam Specific Volume (ml/g)</b> | <b>Application amount by weight (g)</b> | <b>Application amount by volume (ml)</b> | <b>In-vivo ZPT Scalp Deposition Avg. (ug/cm2)</b> |
|-------------------------------------------|----------------------|----------------------------|------------------------------------|-----------------------------------------|------------------------------------------|---------------------------------------------------|
| Anti- dandruff liquid shampoo control (1) | n/a                  | n/a                        | n/a                                | 5.00                                    | 5.00                                     | 1.32                                              |
| Example A                                 | A-46                 | 0.084                      | 10.00                              | 2.50                                    | 25.00                                    | 2.49                                              |
| Example B                                 | HFO                  | 0.180                      | 5.56                               | 2.50                                    | 13.90                                    | 2.79                                              |
| Example E                                 | A-46                 | 0.100                      | 10.00                              | 2.50                                    | 25.00                                    | 4.58                                              |
| Example F                                 | HFO                  | 0.180                      | 5.56                               | 2.50                                    | 13.90                                    | 5.02                                              |

1) Anti-dandruff shampoo with 1% ZPT and 1.61% zinc carbonate

Results

- 5 The results of the table indicate a nearly twofold increase in the average deposition of ZPT from the aerosol foam which contains concentrated levels of ZPT. This increase in deposition is delivered at half of the weight dosage of the liquid form control shampoo product. Furthermore it can be observed that the foams having higher densities (examples B and F from the chart) have the

capacity to deliver still more ZPT when delivered on a volume basis compared to the lower density examples of A and E.

#### Examples/Combinations

5

A. A foaming composition comprising:

- i. From about 18% to about 36% of one or more anionic surfactants;
- ii. From 0.1 to about 5% of one or more viscosity modifiers with a molecular weight of from about 38 to about 2800;

10

iii. From about 0.1 to about 10% of an anti-dandruff particulate;

iv. From about 1% to about 10% of a blowing agent, and

wherein the foam density is from about 0.05 to about 0.25g/ml.

B. A foaming composition according to Paragraph A wherein the anti-dandruff deposition is equal to or greater than 0.8 microgram per cm<sup>2</sup>.

15

C. A foaming composition according to Paragraph A-B, wherein the foam density is 0.1% to about 0.2%.

D. A foaming composition according to Paragraph A-C, wherein the viscosity (measured at 25C) is less than 9000cps.

20

E. A foaming composition according to Paragraph A-D, wherein the composition further comprises from about 1% to about 5% of one or more amphoteric/zwitterionic or nonionic co-surfactants, and mixtures thereof.

25

F. A foaming composition according to Paragraph A-E, wherein the viscosity modifiers with a molecular weight of from about 75 to about 350

G. A foaming composition according to Paragraph A-F, wherein the anti-dandruff particulate is from about 1 to about 5% of an anti-dandruff particulate.

30

H. A foaming composition according to Paragraph A-G, wherein the blowing agent is from about 2% to about 8%.

I. A foaming composition according to Paragraph A-H, wherein the composition further comprises from 0.1% to 5% of a stabilizing agent.

J. A foaming composition according to Paragraph A-I, wherein the stabilizing agent is selected from the group consisting of trihydroxystearin, ethylene glycol distearate polymers, and mixtures thereof.

K. A foaming composition according to Paragraph A-J, wherein the viscosity modifier is selected from the group consisting of ethanol, dipropylene glycol, sodium xylene sulfonate, sodium chloride, alkoxylated silicone/ethoxylated silicone/propoxylated silicone/polyoxyethylene silicone/polyoxypropylene silicone/polyethyleneglycol silicone/PEG-8 silicone/PEG-9 silicone/PEG-n silicone/silicone ether (n could be another integer), and mixtures thereof.

L. A foaming composition according to Paragraph A-K, wherein the anti-dandruff particulate is selected from the group consisting of pyridinethione salts, selenium sulfide, particulate sulfur, and mixtures thereof.

M. A foaming composition according to Paragraph A-L, wherein the anti-dandruff particulate is zinc pyrithione.

N. A foaming composition according to Paragraph A-M, wherein the composition further comprises an anti-dandruff material selected from the group consisting of an azole, octopirox, and mixtures thereof,

O. A foaming composition according to Paragraph A-N, wherein the co-surfactant is selected from the group consisting of lauramidopropyl betaine, cocoamidopropyl betaine, lauryl hydroxysultaine, sodium lauroamphoacetate, coco monoethanolamide, and mixtures thereof.

- 5 P. A foaming composition according to Paragraph A-O, wherein the blowing agent is selected from the group consisting of propane, n-butane, isobutane, cyclopropane, and mixtures thereof, as well as halogenated hydrocarbons such as dichlorodifluoromethane, 1,1-dichloro-1,1,2,2-tetrafluoroethane, 1-chloro-1,1-difluoro-2,2-trifluoroethane, 1-chloro-1,1-difluoroethylene, 1,1-difluoroethane, dimethyl ether, monochlorodifluoromethane, trans-1,3,3,3-tetrafluoropropene, and mixtures thereof.
- 10 Q. A foaming composition according to Paragraph A-P, wherein the blowing agent is selected from the group consisting of propane and isobutene, trans-1,3,3,3-tetrafluoropropene, and mixtures thereof,
- 15 R. A foaming composition according to Paragraph A-Q, wherein the composition further comprises a cationic polymer.
- S. A foaming composition according to Paragraph A-R, wherein the composition further comprises a conditioning agent.
- 20 T. A foaming composition according to Paragraph A-S, wherein the conditioning agent is a silicone.

25 The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

30 The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests or discloses any such invention. Further, to the extent that any

meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document referenced herein, the meaning or definition assigned to that term in this document shall govern.

- 5 While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

## CLAIMS

What is claimed is:

1. A foaming composition comprising:
  - i. from 18% to 36% of one or more anionic surfactants, based upon the total weight of the foaming composition;
  - ii. from 0.1 to 5% of one or more viscosity modifiers with a molecular weight of from 38 to 2800, based upon the total weight of the foaming composition, wherein the viscosity modifier is selected from the group consisting of ethanol, dipropylene glycol, sodium xylene sulfonate, sodium chloride, alkoxylated silicone, ethoxylated silicone, propoxylated silicone, polyoxyethylene silicone, polyoxypropylene silicone, polyethyleneglycol silicone, PEG-8 silicone, PEG-9 silicone, PEG-n silicone where n is an integer other than 8 or 9, silicone ether, and mixtures thereof;
  - iii. from 0.1 to 10% of an anti-dandruff particulate, based upon the total weight of the foaming composition;
  - iv. from 1% to 10% of a blowing agent, wherein the blowing agent comprises one or more volatile materials, which in a gaseous state, carry the other components of the hair care composition in particulate or droplet form, wherein the composition further comprises from 0.1% to 5% of a stabilizing agent, based upon the total weight of the foaming composition, wherein the stabilizing agent is selected from the group consisting of trihydroxystearin, ethylene glycol distearate, and mixtures thereof, and wherein the foam density is from 0.05 to 0.25g/ml.
2. A foaming composition according to claim 1 wherein the anti-dandruff particulate is from 1 to 5%.
3. A foaming composition according to claim 1 or claim 2, wherein an anti-dandruff deposition is equal to or greater than 0.8 microgram per cm<sup>2</sup>.

4. A foaming composition according to any one of claims 1 to 3, wherein the foam density is 0.1% to 0.2%.
5. A foaming composition according to any one of claims 1 to 4, wherein the composition has a viscosity measured at 25°C of less than 9000cps.
6. A foaming composition according to any one of claims 1 to 5, wherein the composition further comprises from 1% to 5% of one or more amphoteric/zwitterionic or nonionic co-surfactants, and mixtures thereof.
7. A foaming composition according to any one of claims 1 to 6, wherein the viscosity modifiers have a molecular weight of from 75 to 350.
8. A foaming composition according to any one of claims 1 to 7, wherein the blowing agent is from 2% to 8%.
9. A foaming composition according to any one of claims 1 to 8, wherein the anti-dandruff particulate is selected from the group consisting of pyridinethione salts, selenium sulfide, particulate sulfur, and mixtures thereof.
10. A foaming composition according to claim 9 wherein the anti-dandruff particulate is zinc pyrithione.
11. A foaming composition according to any one of claims 1 to 10, wherein the composition further comprises an anti-dandruff material selected from the group consisting of an azole, octopirox, and mixtures thereof.
12. A foaming composition according to any one of claims 1 to 11, wherein the composition further comprises a co-surfactant selected from the group consisting of lauramidopropyl betaine, cocoamidopropyl betaine, lauryl hydroxysultaine, sodium lauroamphoacetate, coco monoethanolamide, and mixtures thereof.

13. A foaming composition according to any one of claims 1 to 12, wherein the blowing agent is selected from the group consisting of propane, n-butane, isobutane, cyclopropane, and mixtures thereof, and is also selected from halogenated hydrocarbons.
14. A foaming composition according to claim 13 wherein the halogenated hydrocarbons are selected from the group consisting of dichlorodifluoromethane, 1,1-dichloro-1,1,2,2-tetrafluoroethane, 1-chloro-1,1-difluoro-2,2-trifluoroethane, 1-chloro-1,1-difluoroethylene, 1,1-difluoroethane, dimethyl ether, monochlorodifluoromethane, trans-1,3,3,3-tetrafluoropropene, and mixtures thereof.
15. A foaming composition according to claim 14 wherein the blowing agent is selected from the group consisting of propane, isobutane, trans-1,3,3,3-tetrafluoropropene, and mixtures thereof.
16. A foaming composition according to any one of claims 1 to 15, wherein the composition further comprises a cationic polymer.
17. A foaming composition according to any one of claims 1 to 16, wherein the composition further comprises a conditioning agent.
18. A foaming composition according to claim 17 wherein the conditioning agent is a silicone.