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(54) Title: DELIVERY OF SURFACTANT SOLUBLE ANTI-DANDRUFF AGENT

(57) Abstract: A hair care composition directed to from about 14% to about 40% of one or more surfactants; from about 0.1% to 10% of one or more surfactant soluble antidandruff agents; wherein when the hair care composition is diluted to 1.3% surfactant concentration has a ratio of surfactant diffusion coefficient to soluble agent diffusion coefficient less than 0.6 or greater than 1.4.

## DELIVERY OF SURFACTANT SOLUBLE ANTI-DANDRUFF AGENT

## FIELD OF THE INVENTION

The present invention is directed to delivery of a surfactant soluble scalp agent from a  
5 hair care composition.

## BACKGROUND OF THE INVENTION

For years, anti-dandruff shampoos have been widely used to treat dandruff and clean hair  
and scalp, but there still remains a need for improved anti-dandruff shampoos. In general, anti-  
dandruff shampoos are formulated with anti-dandruff agents in combination with surfactants and  
10 aqueous systems that are intended to deposit the anti-dandruff agents on the scalp. The anti-  
dandruff agents can be insoluble particulates such as zinc pyrithione and/or surfactant soluble  
substances such as climbazole or octopirox. Many anti-dandruff shampoos use cationic  
polymers with anionic surfactants to form coacervate which aid in the deposition of insoluble  
particulate agents. However, generally coacervates do not impact soluble agents deposition as  
15 the soluble agents do not associate with the coacervates formed between the cationic polymers  
and anionic surfactants. Indeed it can prove difficult to deposit on scalp much more than 1-2%  
of the soluble agents present in anti-dandruff shampoos while the remaining 98-99% of the  
soluble agents in the formulas are rinsed away. As many of the anti-dandruff agents can be  
relatively expensive, allowing >97% of the soluble agents to rinse away is equivalent to pouring  
20 money down the drain, and so there remains a need for a shampoo that can more efficiently  
deposit soluble anti-dandruff agents. Also, as consumers continue to desire a shampoo that  
delivers superior anti-dandruff efficacy and lower agent deposition results in lower anti-dandruff  
efficacy, there remains a need for a shampoo that can deposit on scalp a higher percentage of the  
soluble agents present in anti-dandruff shampoos.

25 The association of many classes of surfactants into micellar aggregates is a well-known  
phenomenon. Micelles are often drawn as static structures of spherical aggregates, but in truth  
micelles are in dynamic equilibrium with individual surfactant molecules (monomers) that are  
constantly being exchanged between the bulk and the micelles. Additionally, the micelles  
themselves are continuously disintegrating and reassembling. There are two relaxation processes

involved in micellar solutions. The first is a fast relaxation process referred to as  $\tau_1$ , which is associated with the quick exchange of monomers between micelles and the surrounding bulk phase. The second relaxation time,  $\tau_2$ , is attributed to the micelle formation and dissolution process (i.e., the lifetime of the micelle). Extensive experimental research on the kinetics of micellization by Shah and co-workers (Patist, A., Jha, B.K., Oh, S.G., and Shah, D.O., *J. Surfactants Deterg.* **2**, 317, (1999); James-Smith, M.A., Shekhawat, D., and Shah, D.O., *Tenside Surf. Det.* **44**, 142 (2007)) showed a strong correlation of  $\tau_2$  with a number of detergency properties including oil solubilization in micellar solutions and droplet size in emulsions, as well as surfactant properties such as dynamic surface tension and micelle stability. Their research also showed a strong inverse correlation of  $\tau_2$  with other properties such as foamability and concentration of sub-micellar aggregates. Specifically, they showed that a maximal  $\tau_2$  and thus maximal micellar stability corresponded to both a maximal rate of oil solubilization and maximal amount of oil solubilized. Logic would therefore suggest that a cleansing composition with longer  $\tau_2$ , more stable micelles, and faster rate of solubilization would be preferred since such a system can clean better, more quickly solubilize larger quantities of oils or surfactant-soluble materials and should be more stable. Surprisingly however, it has been found that a composition with a surfactant system of shorter  $\tau_2$ , less stable micelles, and a slower rate of solubilization, as demonstrated in Figure 1, is preferred.

## SUMMARY OF THE INVENTION

In an embodiment of the present invention, it is directed to a hair care composition comprising from about 14% to about 40% of one or more surfactants; from about 0.1% to 10% of one or more surfactant soluble antidandruff agents; wherein when the hair care composition is diluted to 1.3% surfactant concentration has a ratio of surfactant diffusion coefficient to soluble agent diffusion coefficient less than 0.6 or greater than 1.4.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of the rate of octopirox solubilization as a function of surfactant composition.

## DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

All percentages and ratios used herein are by weight of the total composition, unless otherwise designated. All measurements are understood to be made at ambient conditions, where “ambient conditions” means conditions at about 25 °C, under about one atmosphere of pressure, and at about 50% relative humidity, unless otherwise designated. All numeric ranges are inclusive of narrower ranges; delineated upper and lower range limits are combinable to create further ranges not explicitly delineated.

The compositions of the present invention can comprise, consist essentially of, or consist of, the essential components as well as optional ingredients described herein. As used herein, “consisting essentially of” means that the composition or component may include additional ingredients, but only if the additional ingredients do not materially alter the basic and novel characteristics of the claimed compositions or methods.

“Apply” or “application,” as used in reference to a composition, means to apply or spread the compositions of the present invention onto keratinous tissue such as the hair.

“Dermatologically acceptable” means that the compositions or components described are suitable for use in contact with human skin tissue without undue toxicity, incompatibility, instability, allergic response, and the like.

“Safe and effective amount” means an amount of a compound or composition sufficient to significantly induce a positive benefit.

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 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").

Where amount ranges are given, these are to be understood as being the total amount of said ingredient in the composition, or where more than one species fall within the scope of the ingredient definition, the total amount of all ingredients fitting that definition, in the composition.

For example, if the composition comprises from 1% to 5% fatty alcohol, then a composition comprising 2% stearyl alcohol and 1% cetyl alcohol and no other fatty alcohol, would fall within this scope.

The amount of each particular ingredient or mixtures thereof described hereinafter can account for up to 100% (or 100%) of the total amount of the ingredient(s) in the hair care composition.

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.

While the  $\tau_2$  and micelle stability of a surfactant system and the solubility of surfactant-soluble agents in that system are important, of equal importance are the surfactant micelle stability and solubility and rate of solubilization of the agents in the system after dilution, such as when the cleansing composition is applied to the head during use. One way of understanding the solubility and associations of the soluble agent in the surfactant system upon dilution is to measure by NMR the diffusion coefficients of the surfactant and the surfactant-soluble agents in a diluted sample. If the diffusion coefficients of the surfactant and the agent are similar such that the ratio of the two coefficients is close to 1.0, one is able to infer that the surfactant-soluble agent is within or closely associated with the surfactant micelles. However if the diffusion coefficients of the surfactant and the agent are very different such that the ratio of the two coefficients is significantly more or less than 1.0, then one is able to infer that the surfactant-soluble agent is not within or associated with the surfactant micelles. This in turn implies that the surfactant-soluble agent is less soluble in the diluted surfactant of the latter case.

It has been found that a soluble anti-dandruff agent containing cleansing composition, which when diluted to 1.3% surfactant concentration has a ratio of surfactant diffusion coefficient to soluble agent diffusion coefficient less than 0.8 or greater than 1.2, can deposit that soluble agent with ~1.4X or greater efficiency than a soluble anti-dandruff agent containing composition whose ratio of diffusion coefficients is close to 1.0.

Without being bound by theory, the increased deposition efficiency exhibited by embodiments of the present invention can surprisingly be further increased by additionally incorporating an oil which phase separates upon dilution in combination with a cationic polymer which forms coacervate upon dilution. The coacervate aids in the deposition of the oil within

which the surfactant-soluble agent should be at least partially soluble, thus resulting in an incremental increase in the total percentage of soluble agent deposited.

Surfactant-soluble agents are defined as materials which are insoluble in water but soluble at a concentration of 0.1% or higher in an aqueous solution of 10% sodium laureth-1 sulfate. A conventional method may be used to determine solubility. Such method may include wherein solubility of a material of interest can be determined by first visually assessing that the material containing sodium laureth-1 sulfate mixture is homogeneous, followed by filling a glass jar with the material containing sodium laureth-1 sulfate mixture, then placing a Class 2 standard red laser pointer such as the Quartet Class 2 standard laser pointer (model MP-1202Q) against the side of the jar and shining the laser through the jar. If the material is soluble in the sodium laureth-1 solution the laser light will not be scattered, resulting in only an observable red dot appearing on the side of the jar opposite the laser pointer and no visible red laser beam will be observed passing through the solution.

### 15 **Soluble Anti-dandruff Agent**

Anti-dandruff agent may be one material or a mixture selected from the groups consisting of: azoles, such as climbazole, ketoconazole, itraconazole, econazole, and elubiol; hydroxy pyridones, such as octopirox (piroctone olamine), ciclopirox, rilopirox, and MEA-Hydroxyoctyloxypyridinone; kerolytic agents, such as salicylic acid and other hydroxy acids; strobilurins such as azoxystrobin and metal chelators such as 1,10-phenanthroline.

In an embodiment, the azole anti-microbials is an imidazole selected from the group consisting of: benzimidazole, benzothiazole, bifonazole, butaconazole nitrate, climbazole, clotrimazole, croconazole, eberconazole, econazole, elubiol, fenticonazole, fluconazole, flutimazole, isoconazole, ketoconazole, lanoconazole, metronidazole, miconazole, neticonazole, omoconazole, oxiconazole nitrate, sertaconazole, sulconazole nitrate, tioconazole, thiazole, and mixtures thereof, or the azole anti-microbials is a triazole selected from the group consisting of: terconazole, itraconazole, and mixtures thereof. In an embodiment, the azole anti-microbial agent is ketoconazole. In an embodiment, the sole anti-microbial agent is ketoconazole.

In an embodiment, the soluble anti-dandruff agent may be present in an amount from about 0.1% to 10%, in a further embodiment from about 0.25% to 8%, in yet a further embodiment from about 0.5% to 6%.

5                   A. DETERGENT SURFACTANT

The hair care composition may comprise greater than about 14% by weight of a surfactant system which provides cleaning performance to the composition, in an embodiment greater than 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  
10 anionic surfactants and/or a combination of anionic surfactants and co-surfactants selected from the group consisting of amphoteric, zwitterionic, nonionic and mixtures thereof. Various examples and descriptions of detergent surfactants are set forth in U.S. Patent No. 8,440,605; U.S. Patent Application Publication No. 2009/155383; and U.S. Patent Application Publication No. 2009/0221463, which are incorporated herein by reference in their entirety.

15                   In an embodiment, the hair care composition may comprise from about 14% to about 40%, from about 15% to about 36%, from about 18% to about 32%, and/or from about 20% to about 28% by weight of one or more surfactants.

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  
20 reaction 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, which are incorporated herein by reference in their entirety.

Exemplary anionic surfactants for use in the hair care composition include ammonium  
25 lauryl sulfate, ammonium laureth sulfate, ammonium C10-15 pareth sulfate, ammonium C10-15 alkyl sulfate, ammonium C11-15 alkyl sulfate, ammonium decyl sulfate, ammonium deceth sulfate, ammonium undecyl sulfate, ammonium undeceth 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, sodium C10-15 pareth sulfate, sodium C10-15 alkyl sulfate, sodium C11-15 alkyl sulfate, sodium decyl sulfate, sodium deceth sulfate, sodium undecyl sulfate, sodium undeceth sulfate, potassium lauryl sulfate, potassium laureth sulfate, potassium C10-15 pareth sulfate, potassium C10-15 alkyl sulfate, potassium C11-15 alkyl sulfate, potassium decyl sulfate, potassium deceth sulfate, potassium undecyl sulfate, potassium undeceth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium cocoyl isethionate and combinations thereof. In a further embodiment, the anionic surfactant is sodium lauryl sulfate or sodium laureth sulfate.

The composition of the present invention can also include anionic surfactants selected from 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 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.

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 branched alcohols which may be selected from the group consisting of: Guerbet alcohols, aldol condensation derived alcohols, oxo alcohols and mixtures thereof. Non-limiting examples of the 2-alkyl branched alcohols include oxo alcohols such as 2-methyl-1-undecanol, 2-ethyl-1-decanol, 2-propyl-1-nonanol, 2-butyl 1-octanol, 2-methyl-1-dodecanol, 2-ethyl-1-undecanol, 2-propyl-1-decanol, 2-butyl-1-nonanol, 2-pentyl-1-octanol, 2-pentyl-1-heptanol, and those sold

under the tradenames LIAL® (Sasol), ISALCHEM® (Sasol), and NEODOL® (Shell), and Guerbet and aldol condensation derived alcohols such as 2-ethyl-1-hexanol, 2-propyl-1-butanol, 2-butyl-1-octanol, 2-butyl-1-decanol, 2-pentyl-1-nonanol, 2-hexyl-1-octanol, 2-hexyl-1-decanol and those sold under the tradename ISOFOL® (Sasol) or sold as alcohol ethoxylates and alkoxyates under the tradenames LUTENSOL XP® (BASF) and LUTENSOL XL® (BASF).

The anionic alkyl sulfates and alkyl ether sulfates may also include those synthesized from C8 to C18 branched alcohols derived from butylene or propylene which are sold under the trade names EXXAL™ (Exxon) and Marlipal® (Sasol). This includes anionic surfactants of the subclass of sodium trideceth-n sulfates (STnS), where n is between about 0.5 and about 3.5. Exemplary surfactants of this subclass are sodium trideceth-2 sulfate and sodium trideceth-3 sulfate. The composition of the present invention can also include sodium tridecyl sulfate.

The composition of the present invention can also include anionic alkyl and alkyl ether sulfosuccinates and/or dialkyl and dialkyl ether sulfosuccinates and mixtures thereof. The dialkyl and dialkyl ether sulfosuccinates may be a C6-15 linear or branched dialkyl or dialkyl ether sulfosuccinate. The alkyl moieties may be symmetrical (i.e., the same alkyl moieties) or asymmetrical (i.e., different alkyl moieties). Nonlimiting examples include: disodium lauryl sulfosuccinate, disodium laureth sulfosuccinate, sodium bistridecyl sulfosuccinate, sodium dioctyl sulfosuccinate, sodium dihexyl sulfosuccinate, sodium dicyclohexyl sulfosuccinate, sodium diamyl sulfosuccinate, sodium diisobutyl sulfosuccinate, linear bis(tridecyl) sulfosuccinate and mixtures thereof.

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-ionic surfactant and mixtures thereof. The co-surfactant can include, but is not limited to, lauramidopropyl betaine, cocoamidopropyl betaine, lauryl hydroxysultaine, sodium lauroamphoacetate, disodium cocoamphodiacetate, cocamide monoethanolamide and mixtures thereof.

The hair care composition may further comprise from about 0.25% to about 15%, from about 2% to about 14%, from about 3% to about 13% 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, which are incorporated herein by reference in their entirety.

5 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,  
10 those selected from the group consisting of: sodium cocaminopropionate, sodium cocaminodipropionate, sodium cocoamphoacetate, sodium cocoamphodiacetate, sodium cocoamphohydroxypropylsulfonate, sodium cocoamphopropionate, sodium cornamphopropionate, sodium lauraminopropionate, sodium lauroamphoacetate, sodium lauroamphodiacetate, sodium lauroamphohydroxypropylsulfonate, sodium  
15 lauroamphopropionate, sodium cornamphopropionate, sodium lauriminodipropionate, ammonium cocaminopropionate, ammonium cocaminodipropionate, ammonium cocoamphoacetate, ammonium cocoamphodiacetate, ammonium cocoamphohydroxypropylsulfonate, ammonium cocoamphopropionate, ammonium cornamphopropionate, ammonium lauraminopropionate, ammonium lauroamphoacetate,  
20 ammonium lauroamphodiacetate, ammonium lauroamphohydroxypropylsulfonate, ammonium lauroamphopropionate, ammonium cornamphopropionate, ammonium lauriminodipropionate, triethanolamine cocaminopropionate, triethanolamine cocaminodipropionate, triethanolamine cocoamphoacetate, triethanolamine cocoamphohydroxypropylsulfonate, triethanolamine cocoamphopropionate, triethanolamine cornamphopropionate, triethanolamine  
25 lauraminopropionate, triethanolamine lauroamphoacetate, triethanolamine lauroamphohydroxypropylsulfonate, triethanolamine lauroamphopropionate, triethanolamine cornamphopropionate, triethanolamine lauriminodipropionate, cocoamphodipropionic acid, disodium caproamphodiacetate, disodium caproamphoadipropionate, disodium capryloamphodiacetate, disodium capryloamphodipropionate, disodium  
30 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,  
5 lauryl aminopropylglycine, lauryl diethylenediaminoglycine, 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  
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  
10 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, cocamidopropyldimonium hydroxypropyl  
hydrolyzed collagen, cocamidopropyl hydroxysultaine, cocobetaineamido amphopropionate,  
15 coco-betaine, coco-hydroxysultaine, coco/oleamidopropyl betaine, coco-sultaine,  
lauramidopropyl betaine, lauryl betaine, lauryl hydroxysultaine, lauryl sultaine, and mixtures  
thereof.

Suitable nonionic surfactants for use in the present invention include those described in  
McCutcheon's Detergents and Emulsifiers, North American edition (1986), Allured Publishing  
20 Corp., and McCutcheon's Functional Materials, North American edition (1992). Suitable  
nonionic surfactants for use in the personal care compositions of the present invention include,  
but are not limited to, polyoxyethylenated alkyl phenols, polyoxyethylenated alcohols,  
polyoxyethylenated polyoxypropylene glycols, glyceryl esters of alkanolic acids, polyglyceryl  
esters of alkanolic acids, propylene glycol esters of alkanolic acids, sorbitol esters of alkanolic  
25 acids, polyoxyethylenated sorbitol esters of alkanolic acids, polyoxyethylene glycol esters of  
alkanoic acids, polyoxyethylenated alkanolic acids, alkanolamides, N-alkylpyrrolidones, alkyl  
glycosides, alkyl polyglucosides, alkylamine oxides, and polyoxyethylenated silicones.

The co-surfactant can be a non-ionic surfactant selected from the alkanolamides group  
including: Cocamide, Cocamide Methyl MEA, Cocamide DEA, Cocamide MEA, Cocamide  
30 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 Cocamide, PEG-7 Cocamide, PEG-3 Lauramide, PEG-5 Lauramide, PEG-3 Oleamide, PPG-2 Cocamide, PPG-2 Hydroxyethyl Cocamide, PPG-2 Hydroxyethyl Isostearamide and mixtures thereof.

5           Representative polyoxyethylenated alcohols include alkyl chains ranging in the C9-C16 range and having from about 1 to about 110 alkoxy groups including, but not limited to, laureth-3, laureth-23, ceteth-10, steareth-10, steareth-100, beheneth-10, and commercially available from Shell Chemicals, Houston, Texas under the trade names Neodol® 91, Neodol® 23, Neodol® 25, Neodol® 45, Neodol® 135, Neodo®l 67, Neodol® PC 100, Neodol® PC 200, Neodol® PC 600,  
10 and mixtures thereof.

          Also available commercially are the polyoxyethylene fatty ethers available commercially under the Brij® trade name from Uniqema, Wilmington, Delaware, including, but not limited to, Brij® 30, Brij® 35, Brij® 52, Brij® 56, Brij® 58, Brij® 72, Brij® 76, Brij® 78, Brij® 93, Brij® 97, Brij® 98, Brij® 721 and mixtures thereof.

15           Suitable alkyl glycosides and alkyl polyglucosides can be represented by the formula (S)<sub>n</sub>-O-R wherein S is a sugar moiety such as glucose, fructose, mannose, galactose, and the like; n is an integer of from about 1 to about 1000, and R is a C8-C30 alkyl group. Examples of long chain alcohols from which the alkyl group can be derived include decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, and the like. Examples of  
20 these surfactants include alkyl polyglucosides wherein S is a glucose moiety, R is a C8-20 alkyl group, and n is an integer of from about 1 to about 9. Commercially available examples of these surfactants include decyl polyglucoside and lauryl polyglucoside available under trade names APG® 325 CS, APG® 600 CS and APG® 625 CS) from Cognis, Ambler, Pa. Also useful herein are sucrose ester surfactants such as sucrose cocoate and sucrose laurate and alkyl  
25 polyglucosides available under trade names Triton™ BG-10 and Triton™ CG-110 from The Dow Chemical Company, Houston, Tx.

          Other nonionic surfactants suitable for use in the present invention are glyceryl esters and polyglyceryl esters, including but not limited to, glyceryl monoesters, glyceryl monoesters of C12-22 saturated, unsaturated and branched chain fatty acids such as glyceryl oleate, glyceryl  
30 monostearate, glyceryl monopalmitate, glyceryl monobehenate, and mixtures thereof, and

polyglyceryl esters of C12-22 saturated, unsaturated and branched chain fatty acids, such as polyglyceryl-4 isostearate, polyglyceryl-3 oleate, polyglyceryl-2- sesquioleate, triglyceryl diisostearate, diglyceryl monooleate, tetraglyceryl monooleate, and mixtures thereof.

Also useful herein as nonionic surfactants are sorbitan esters. Sorbitan esters of C12-22 saturated, unsaturated, and branched chain fatty acids are useful herein. These sorbitan esters usually comprise mixtures of mono-, di-, tri-, etc. esters. Representative examples of suitable sorbitan esters include sorbitan monolaurate (SPAN® 20), sorbitan monopalmitate (SPAN® 40), sorbitan monostearate (SPAN® 60), sorbitan tristearate (SPAN® 65), sorbitan monooleate (SPAN® 80), sorbitan trioleate (SPAN® 85), and sorbitan isostearate.

Also suitable for use herein are alkoxyated derivatives of sorbitan esters including, but not limited to, polyoxyethylene (20) sorbitan monolaurate (Tween® 20), polyoxyethylene (20) sorbitan monopalmitate (Tween® 40), polyoxyethylene (20) sorbitan monostearate (Tween® 60), polyoxyethylene (20) sorbitan monooleate (Tween® 80), polyoxyethylene (4) sorbitan monolaurate (Tween® 21), polyoxyethylene (4) sorbitan monostearate (Tween® 61), polyoxyethylene (5) sorbitan monooleate (Tween® 81), and mixtures thereof, all available from Uniqema.

Also suitable for use herein are alkylphenol ethoxylates including, but not limited to, nonylphenol ethoxylates (Tergitol™ NP-4, NP-6, NP-7, NP-8, NP-9, NP-10, NP-11, NP-12, NP-13, NP-15, NP-30, NP-40, NP-50, NP-55, NP-70 available from The Dow Chemical Company, Houston, Tx.) and octylphenol ethoxylates (Triton™ X-15, X-35, X-45, X-114, X-100, X-102, X-165, X-305, X-405, X-705 available from The Dow Chemical Company, Houston, Tx).

Also suitable for use herein are tertiary alkylamine oxides including lauramine oxide and cocamine oxide.

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, which are incorporated herein by reference in their entirety.

Suitable surfactant combinations comprise an average weight % of alkyl branching of from about 0.5% to about 30%, alternatively from about 1% to about 25%, alternatively from about 2% to about 20%. The surfactant combination can have a cumulative average weight % of C8 to C12 alkyl chain lengths of from about 7.5% to about 25%, alternatively from about 10% to about 22.5%, alternatively from about 10% to about 20%. The surfactant combination can have an average C8-C12 / C13-C18 alkyl chain ratio from about 3 to about 200, alternatively from about 25 to about 175.5, alternatively from about 50 to about 150, alternatively from about 75 to about 125.

## B. CATIONIC POLYMERS

The hair care composition also comprises a cationic polymer. These cationic polymers can 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 detergent surfactant (f) a cationic cellulose polymer. Additionally, the cationic polymer can be a mixture of cationic polymers.

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 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.

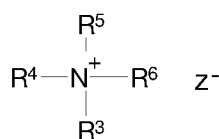
According to one embodiment, the cationic polymer, including but not limited to a cationic guar polymer, has a weight average Molecular weight of less than 1.5 million g/mol, or from about 150 thousand to about 1.5 million g/mol, or from about 200 thousand to about 1.5 million g/mol, or from about 300 thousand to about 1.2 million g/mol, or from about 750,000

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.

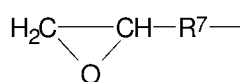
According to one embodiment, the cationic guar polymer has a weight average Molecular weight of less than about 1.5 million g/mol, and has a charge density of from about 0.1 meq/g to about 2.5 meq/g. In an embodiment, the cationic guar polymer has a weight average molecular weight of less than 900 thousand g/mol, or from about 150 thousand to about 800 thousand g/mol, or from about 200 thousand to about 700 thousand g/mol, or from about 300 thousand to about 700 thousand g/mol, or from about 400 thousand to about 600 thousand g/mol. from about 150 thousand to about 800 thousand g/mol, or from about 200 thousand to about 700 thousand g/mol, or from about 300 thousand to about 700 thousand g/mol, or from about 400 thousand to about 600 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:

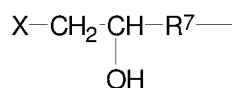


wherein where  $\text{R}^3$ ,  $\text{R}^4$  and  $\text{R}^5$  are methyl or ethyl groups;  $\text{R}^6$  is either an epoxyalkyl group of the general formula 2:



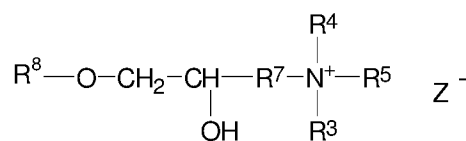


or R<sup>6</sup> is a halohydrin group of the general formula 3:

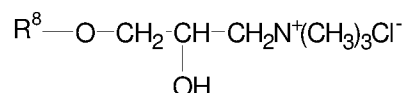


wherein R<sup>7</sup> is a C<sub>1</sub> to C<sub>3</sub> alkylene; X is chlorine or bromine, and Z is an anion such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or HSO<sub>4</sub><sup>-</sup>.

5 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:



10 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 Solvay, for example Jaguar<sup>®</sup> C-500, commercially available from Solvay. Jaguar<sup>®</sup> C-500 has a charge density of 0.8 meq/g and a  
 15 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  
 20 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 Solvay; N-Hance 3269 and N-Hance 3270, which have a charge density of about 0.7 meq/g and a molecular weight of about 425,000 g/mol and are available from ASI; N-Hance 3196, which has a charge

density of about 0.8 meq/g and a molecular weight of about 1,100,000 g/ mol and is available from ASI. AquaCat 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  
5 borate (boron) free guar of charge density of about 1.7 meq/g and M. Wt. of about 800,000 both available from ASI.

The hair care compositions of the present invention 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  
10 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  
20 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 of the present invention 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  
25 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

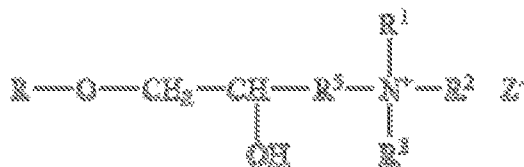
mannose/1 part galactose), Locust bean or Carob (4 parts mannose/1 part galactose), and Cassia gum (5 parts mannose/1 part galactose).

In one embodiment of the invention, the non-guar galactomannan polymer derivatives have a M. Wt. from about 1,000 to about 10,000,000, and/or from about 5,000 to about  
5 3,000,000.

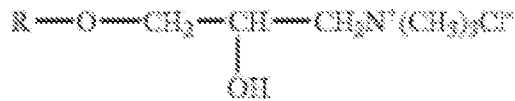
The hair care compositions of the invention can also include galactomannan polymer derivatives which have a cationic charge density from about 0.5 meq/g to about 7 meq/g. In one embodiment of the present invention, the galactomannan polymer derivatives have a cationic charge density from about 1 meq/g to about 5 meq/g. The degree of substitution of the cationic  
10 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  
15 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:



20 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:



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.

5           The cationic non-guar galactomannan can have a ratio of mannose to galactose is greater than about 4:1, a molecular weight of about 1,000 g/mol to about 10,000,000 g/mol, and/or from about 50,000 g/mol to about 1,000,000 g/mol, and/or from about 100,000 g/mol to about 900,000 g/mol, and/or from about 150,000 g/mol to about 400,000 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 be derived  
10 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  
15 polymers. As used herein, the term "cationically modified starch" refers to a starch to which a 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  
20 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  
25 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 850,000 g/mol to about 1,500,000 g/mol and/or from about 900,000 g/mol to about 1,500,000 g/mol.

The hair care compositions can include cationically modified starch polymers which have  
5 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,  
10 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.

15 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  
20 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-  
25 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.

The source of starch before chemical modification can be chosen from a variety of  
30 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, cassava 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.

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 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 combinations thereof.

An optimal form of the starch is one which is readily soluble in water and forms a substantially clear (% Transmittance of about 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 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 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

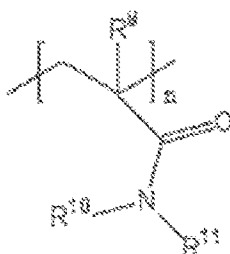
- to about 11.5 with sodium hydroxide and the slurry is stirred sufficiently to prevent settling of the starch. Then, about a 30% solution of hydrogen peroxide diluted in water is added to a level of about 1% of peroxide based on starch. The pH of about 11.5 is then restored by adding additional sodium hydroxide. The reaction is completed over about a 1 to about 20 hour period.
- 5 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.

10

The cationic copolymer can comprise:

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

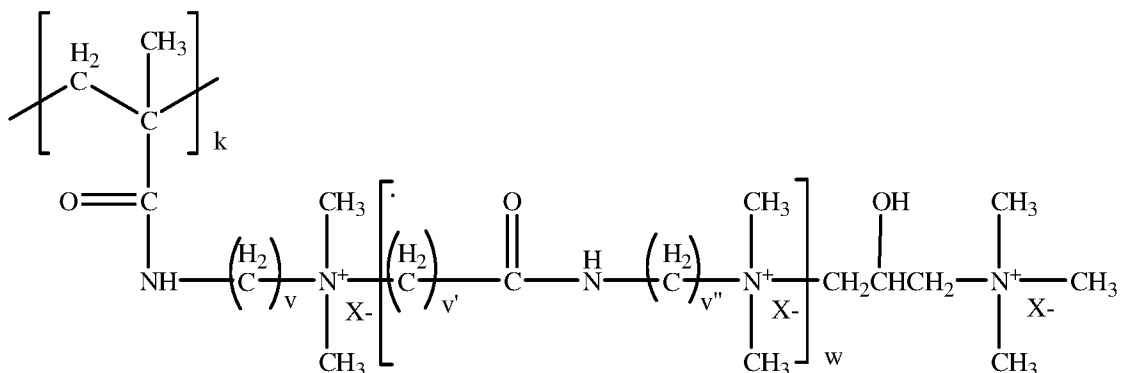


Formula AM

15

where  $R^9$  is H or  $C_{1-4}$  alkyl; and  $R^{10}$  and  $R^{11}$  are independently selected from the group consisting of H,  $C_{1-4}$  alkyl,  $CH_2OCH_3$ ,  $CH_2OCH_2CH(CH_3)_2$ , and phenyl, or together are  $C_{3-6}$ cycloalkyl; and

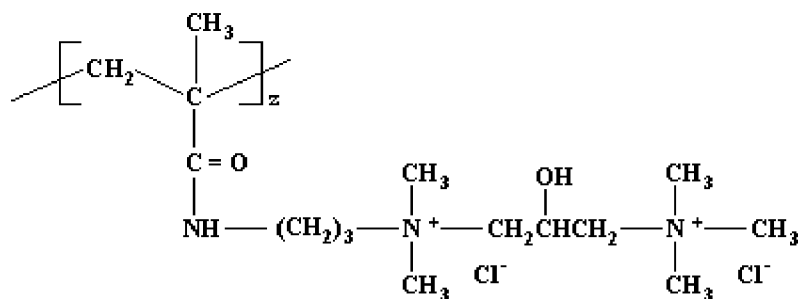
- (ii) a cationic monomer conforming to Formula CM:



Formula CM

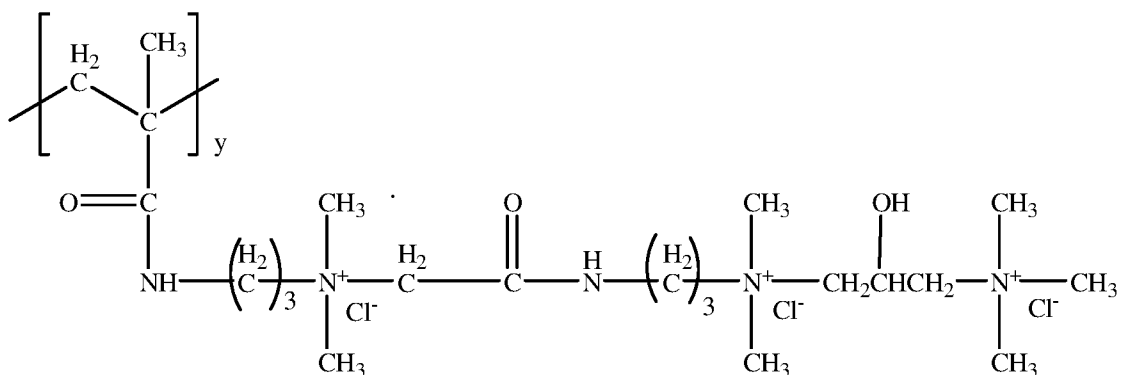
where  $k = 1$ , each of  $v$ ,  $v'$ , and  $v''$  is independently an integer of from 1 to 6,  $w$  is zero or an integer of from 1 to 10, and  $X^-$  is an anion.

- 5 The cationic monomer can conform to Formula CM and where  $k = 1$ ,  $v = 3$  and  $w = 0$ ,  $v' = 1$  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

- 10 as:





The above structure may be referred to as triquat.

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

The cationic copolymer (b) can be AM:TRIQUAT which is a copolymer of acrylamide  
5 and 1,3-Propanediaminium,N-[2-[[[dimethyl[3-[(2-methyl-1-oxo-2-propenyl)amino]propyl]ammonio]acetyl]amino]ethyl]2-hydroxy-N,N,N',N',N'-pentamethyl-, trichloride. AM:TRIQUAT is also known as polyquaternium 76 (PQ76). AM:TRIQUAT may have a charge density of 1.6 meq/g and a molecular weight of 1.1 million g/mol.

In an alternative embodiment, the cationic copolymer is of an acrylamide monomer and a  
10 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  
15 (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbenzyl 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  
20 consisting of: cationic monomers include trimethylammonium ethyl (meth)acrylate chloride, trimethylammonium ethyl (meth)acrylate methyl sulphate, dimethylammonium ethyl (meth)acrylate benzyl chloride, 4-benzoylbenzyl dimethylammonium ethyl acrylate chloride, trimethyl ammonium ethyl (meth)acrylamido chloride, trimethyl ammonium propyl (meth)acrylamido chloride, vinylbenzyl trimethyl ammonium chloride, and mixtures thereof.

25 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.

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.

The cationic copolymer can be a terpolymer of acrylamide, 2-dimethylammoniummethyl (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 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,  
5 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.

The cationic copolymer can have a molecular weight from about 100 thousand g/mol to about 1.5 million g/mol, or from about 300 thousand g/mol to about 1.5 million g/mol, or from about 500 thousand g/mol to about 1.5 million g/mol, or from about 700 thousand g/mol to about  
10 1.0 million g/mol, or from about 900 thousand g/mol to about 1.2 million g/mol.

The cationic copolymer can be a trimethylammoniopropylmethacrylamide chloride-N-Acrylamide copolymer, which is also known as AM:MAPTAC. AM:MAPTAC may have a charge density of about 1.3 meq/g and a molecular weight of about 1.1 million g/mol. The cationic copolymer can be AM:ATPAC. AM:ATPAC can have a charge density of about 1.8  
15 meq/g and a molecular weight of about 1.1 million g/mol.

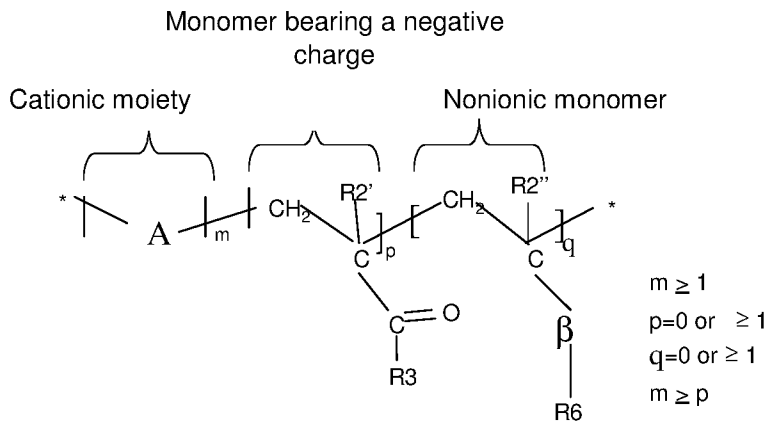
(a) Cationic Synthetic Polymers

The hair care composition can comprise a cationic synthetic polymer that may be formed from

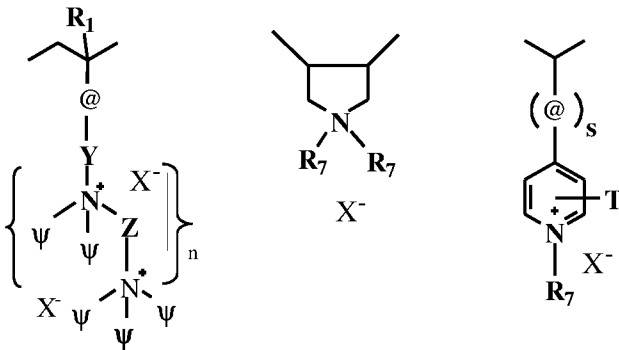
- i) one or more cationic monomer units, and optionally
- 20 ii) one or more monomer units bearing a negative charge, and/or
- iii) a nonionic monomer,

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

25 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:



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

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;

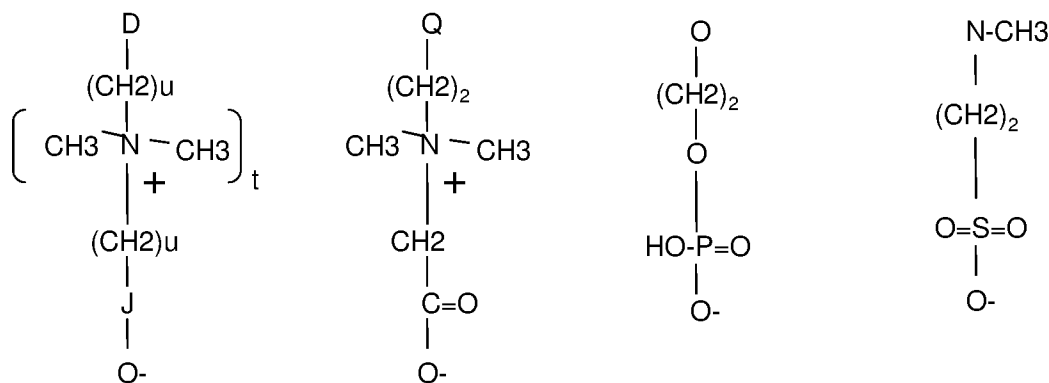
where R1 = H, C1-C4 linear or branched alkyl;

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

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;

5 where u = 1-6;

where t = 0-1; and

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.

15 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; diallyldialkyl ammonium salts; their mixtures, their salts, and macromonomers deriving from therefrom.

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, diallyldimethyl ammonium chloride.

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).

5           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  
10 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.

15           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.  
20 Non limiting examples of such counterions include halides (e.g., chlorine, fluorine, bromine, iodine), sulfate and methylsulfate.

The cationic polymer described herein can aid in providing damaged hair, particularly chemically treated hair, with a surrogate hydrophobic F-layer. The microscopically thin F-layer provides natural weatherproofing, while helping to seal in moisture and prevent further damage.  
25 Chemical treatments damage the hair cuticle and strip away its protective F-layer. As the F-layer is stripped away, the hair becomes increasingly hydrophilic. It has been found that when lyotropic liquid crystals are applied to chemically treated hair, the hair becomes more hydrophobic and more virgin-like, in both look and feel. Without being limited to any theory, it is believed that the lyotropic liquid crystal complex creates a hydrophobic layer or film, which  
30 coats the hair fibers and protects the hair, much like the natural F-layer protects the hair. The

hydrophobic layer returns the hair to a generally virgin-like, healthier state. Lyotropic liquid crystals are formed by combining the synthetic cationic polymers described herein with the aforementioned anionic detergent surfactant component of the hair care composition. The synthetic cationic polymer has a relatively high charge density. It should be noted that some synthetic polymers having a relatively high cationic charge density do not form lyotropic liquid crystals, primarily due to their abnormal linear charge densities. Such synthetic cationic polymers are described in WO 94/06403 to Reich et al. The synthetic polymers described herein can be formulated in a stable hair care composition that provides improved conditioning performance, with respect to damaged hair.

Cationic synthetic polymers that can form lyotropic liquid crystals have a cationic charge density of from about 2 meq/gm to about 7 meq/gm, and/or from about 3 meq/gm to about 7 meq/gm, and/or from about 4 meq/gm to about 7 meq/gm. In some embodiments, the cationic charge density is about 6.2 meq/gm. The polymers also have a M. Wt. of from about 1,000 to about 5,000,000, and/or from about 10,000 to about 1,500,000, and/or from about 100,000 to about 1,500,000.

In another embodiment of the invention cationic synthetic polymers that provide enhanced conditioning and deposition of benefit agents but do not necessarily form lyotropic liquid crystals have a cationic charge density of from about 0.7 meq/gm to about 7 meq/gm, and/or from about 0.8 meq/gm to about 5 meq/gm, and/or from about 1.0 meq/gm to about 3 meq/gm. The polymers also have a M. Wt. of from about 1,000 to about 1,500,000, from about 10,000 to about 1,500,000, and from about 100,000 to about 1,500,000.

Suitable cationic cellulose polymers are salts of hydroxyethyl cellulose reacted with 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. Non-limiting examples include: JR-30M, KG-30M, JP, LR-400 and mixtures thereof. 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 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 SL-60, Polymer SL-100, Polymer SK-L, Polymer SK-M, Polymer SK-MH, and Polymer SK-H.

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.

### C. VISCOSITY REDUCING AGENTS

In an embodiment, the hair care composition described herein may comprise from about 0.1% to about 35%, alternatively from about 0.25% to about 30%, and alternatively from about 0.5% to about 25% of a viscosity reducing agent, by weight of the hair care composition. Non-limiting examples of suitable viscosity reducing agents include Class A materials, Class B materials, water miscible solvents, hydrotropes, and mixtures thereof.

The hair care composition described herein may have a liquid phase viscosity of from about 1 centipoise to about 6,000 centipoise, alternatively from about 1 centipoise to about 4,500 centipoise, alternatively from about 1 centipoise to about 3,000 centipoise, and alternatively from about 5 centipoise to about 2,000 centipoise.

#### 1. CLASS A VISCOSITY REDUCING AGENTS

The Class A viscosity reducing agents may have a partition dispersion coefficient of from about -3.1 to about -0.7, alternatively from about -3 to about -0.85, and alternatively from about -2.92 to about -0.92. The Class A viscosity reducing agents may have a partition dispersion coefficient of from about -3 to about -1.9, alternatively from about -2.9 to about -2, wherein the one or more viscosity reducing agents has at least 2 polar groups, or has 1 polar group and less than 5 acyclic  $sp^3$  hybridized carbon atoms that are connected to each other in a contiguous group. The Class A viscosity reducing agents may have a partition dispersion coefficient of from about -3 to about -1.9, alternatively from about -2.9 to about -2, wherein the one or more viscosity reducing agents has 2 to 4 polar groups, or has 1 polar group and 1 to 3 acyclic  $sp^3$  hybridized carbon atoms that are connected to each other in a contiguous group. The Class A

viscosity reducing agents may have a partition dispersion coefficient of from about -3 to about -1, alternatively from about -2.9 to about -2, wherein the one or more viscosity reducing agents has 2 to 4 polar groups, or has 1 polar group and 2 acyclic sp<sup>3</sup> hybridized carbon atoms that are connected to each other in a contiguous group. The Class A viscosity reducing agents may provide unexpected viscosity reduction when used in the hair care composition described herein.

The partition dispersion coefficient (PDC) is defined by the following equation:

$$\text{PDC} = \log P - 0.3001 * (\Delta D)^2 + 10.362 * \Delta D - 93.251$$

wherein logP is the octanol water partitioning coefficient as computed by the Consensus algorithm implemented in ACD/Percepta version 14.02 by Advanced Chemistry Development, Inc. (ACD/Labs, Toronto, Canada), and wherein  $\Delta D$  is the Hansen solubility dispersion parameter in (MPa)<sup>1/2</sup> computed using Steven Abbott and Hiroshi Yamamoto's "HSPIP – Hansen Solubility Parameters in Practice" program, 4th Edition, version 4.1.07.

The viscosity reducing agents may be organic compounds comprising 1 polar group, alternatively at least 1 polar group, alternatively 2 to 4 polar groups, and alternative alternatively at least 2 polar groups. The polar groups may be selected from the group consisting of alcohols, aldehydes, esters, lactones, coumarins, ethers, ketones, phenol, phenyl, oxides, alkenyl, alkynyl, and combinations thereof. The viscosity reducing agents may have a molecular weight of between 100 daltons and 300 daltons, alternatively from about 125 daltons to about 300 daltons. Additionally, the viscosity reducing agents may have a water solubility at between 23 and 25 degrees Celsius of from about 900 to 50,000 mg/L.

The viscosity reducing agents may be selected from the group consisting of raspberry ketone, triethyl citrate, 5-methyl-3-heptanone oxime, hydroxycitronellal, camphor gum, 2-isopropyl-5-methyl-2-hexenal, eucalyptol, 1,1-dimethoxyoctane, isobutyl hexanoate, dihydro iso jasmonate, and combinations thereof. Alternatively, the viscosity reducing agents may be selected from the group consisting of raspberry ketone, triethyl citrate, hydroxycitronellal, camphor gum, and combinations thereof. Alternatively, the viscosity reducing agent may be selected from the group consisting of raspberry ketone, triethyl citrate, hydroxycitronellal, and combinations thereof.

## 2. CLASS B VISCOSITY REDUCING AGENTS

The Class B viscosity reducing agents may have a partition dispersion coefficient of from about 0.05 to about 5.1, alternatively from about 0.08 to about 4.5, alternatively from about 0.09 to about 4.4, alternatively from about 0.05 to about 2.0, alternatively from about 0.08 to about 1.8, alternatively from about 0.09 to about 1.7, and alternatively from about 0.095 to about 1.68. The Class B viscosity reducing agents may provide unexpected viscosity reduction when used in the hair care composition described herein.

The partition dispersion coefficient (PDC) is defined by the following equation:

$$\text{PDC} = \log P - 0.3001 * (\Delta D)^2 + 10.362 * \Delta D - 93.251$$

wherein  $\log P$  is the octanol water partitioning coefficient as computed by the Consensus algorithm implemented in ACD/Percepta version 14.02 by Advanced Chemistry Development, Inc. (ACD/Labs, Toronto, Canada), and wherein  $\Delta D$  is the Hansen solubility dispersion parameter in (MPa)<sup>1/2</sup> computed using Steven Abbott and Hiroshi Yamamoto's "HSPIP – Hansen Solubility Parameters in Practice" program, 4<sup>th</sup> Edition, version 4.1.07.

The viscosity reducing agents may be organic compounds comprising 1 polar group, alternatively at least 1 polar group, alternatively 2 to 4 polar groups, and alternative alternatively at least 2 polar groups. The polar groups may be selected from the group consisting of alcohols, aldehydes, esters, lactones, coumarins, ethers, ketones, phenol, phenyl, oxides, alkenyl, alkynyl, and combinations thereof. The viscosity reducing agents may have a molecular weight of between 100 daltons and 300 daltons, alternatively from about 125 daltons to about 300 daltons. Additionally, the viscosity reducing agents may have a water solubility at between 23 and 25 degrees Celsius of from about 10 to 900 mg/L.

The Class B viscosity reducing agents may be selected from the group consisting of veloutone, isoamyl salicylate, gamma-terpinene, linalyl iso butyrate, alpha-terpinene, limonene, dipentene, geranyl phenyl acetate, iso propyl myristate, hexadecane, and combinations thereof. Alternatively, the Class B viscosity reducing agents may be selected from the group consisting of veloutone, gamma-terpinene, linalyl iso butyrate, alpha-terpinene, limonene, dipentene, geranyl phenyl acetate, iso propyl myristate, hexadecane, and combinations thereof. Alternatively, the Class B viscosity reducing agents may be selected from the group consisting of veloutone,

isoamyl salicylate, gamma-terpinene, linalyl iso butyrate, alpha-terpinene, limonene, dipentene, geranyl phenyl acetate, and combinations thereof.

### 3. WATER MISCIBLE SOLVENTS

The carrier useful in embodiments of the hair care composition includes water and water  
5 solutions of lower alkyl alcohols, polyhydric alcohols, ketones having from 3 to 4 carbons atoms,  
C1-C6 esters of C1-C6 alcohols, sulfoxides, amides, carbonate esters, ethoxylated and  
propoxylated C1-C10 alcohols, lactones, pyrrolidones, and mixtures thereof. Non-limited lower  
alkyl alcohol examples are monohydric alcohols having 1 to 6 carbons, such as ethanol and  
isopropanol. Non-limiting examples of polyhydric alcohols useful herein include propylene  
10 glycol, dipropylene glycol, butylenes glycol, hexylene glycol, glycerin, propane diol and  
mixtures thereof.

In an embodiment of the present invention, the hair care composition may comprise a  
hydrotrope/viscosity modifier which is an alkali metal or ammonium salt of a lower alkyl  
benzene sulphonate such as sodium xylene sulphonate, sodium cumene sulphonate or sodium  
15 toluene sulphonate.

In a further embodiment of the present invention, the hair care composition may  
comprise 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 MW 2706.

20

### D. PROPELLANT OR BLOWING AGENT

The concentrated hair care composition described herein may comprise from about from  
about 1% to about 10% propellant or blowing agent, alternatively from about 2% to about 8%  
propellant, by weight of the concentrated hair care composition.

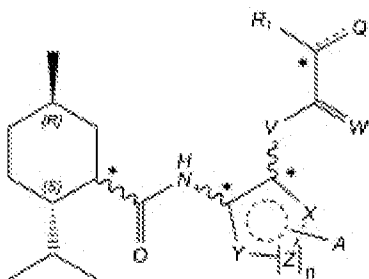
25 The propellant or blowing agent may comprise one or more volatile materials, which in a  
gaseous state, may carry the other components of the concentrated hair care composition in  
particulate or droplet form or as a foam. The propellant or blowing agent may have a boiling  
point within the range of from about  $-45^{\circ}$  C. to about  $5^{\circ}$  C. The propellant or blowing agent  
may be liquefied when packaged in convention aerosol containers under pressure. The rapid

boiling of the propellant or blowing agent upon leaving the aerosol foam dispenser may aid in the atomization or foaming of the other components of the concentrated hair care composition.

Aerosol propellants or 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. The propellant or 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.

#### E. SCALP HEALTH AGENTS

In an embodiment of the present invention, one or more scalp health agent may be added to provide scalp benefits in addition to the anti-fungal/anti-dandruff efficacy provided by the surfactant soluble anti-dandruff agents. This group of materials is varied and provides a wide range of benefits including moisturization, barrier improvement, anti-fungal, anti-microbial and anti-oxidant, anti-itch, and sensates, and additional anti-dandruff agents such as zinc pyrithione (ZPT) or selenium sulfide. Such scalp health agents include but are not limited to: vitamin E and F, salicylic acid, niacinamide, caffeine, panthenol, zinc oxide, zinc carbonate, glycols, glycolic acid, PCA, PEGs, erythritol, glycerin, triclosan, lactates, hyaluronates, allantoin and other ureas, betaines, sorbitol, glutamates, xylitols, menthol, menthyl lactate, iso cyclomone, benzyl alcohol, a compound comprising the following structure:



R<sub>1</sub> is selected from H, alkyl, amino alkyl, alkoxy;

Q = H<sub>2</sub>, O, -OR<sub>1</sub>, -N(R<sub>1</sub>)<sub>2</sub>, -OPO(OR<sub>1</sub>)<sub>x</sub>, -PO(OR<sub>1</sub>)<sub>x</sub>, -P(OR<sub>1</sub>)<sub>x</sub> where x = 1-2;

V = NR<sub>1</sub>, O, -OPO(OR<sub>1</sub>)<sub>x</sub>, -PO(OR<sub>1</sub>)<sub>x</sub>, -P(OR<sub>1</sub>)<sub>x</sub> where x = 1-2;

W = H<sub>2</sub>, O;

5 X, Y = independently selected from H, aryl, naphthyl for n=0;

X, Y = aliphatic CH<sub>2</sub> or aromatic CH for n ≥ 1 and Z is selected from aliphatic CH<sub>2</sub>, aromatic CH, or heteroatom;

A = lower alkoxy, lower alkylthio, aryl, substituted aryl or fused aryl; and stereochemistry is variable at the positions marked\*.

10 and natural extracts/oils including peppermint, spearmint, argan, jojoba and aloe.

## F. OPTIONAL INGREDIENTS

In accordance with embodiments of the present invention, 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 agents, 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.

### 1. 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, which descriptions are incorporated herein by reference.

The silicone conditioning agents for use in the compositions of the present invention can have a viscosity, as measured at 25° C, from about 20 to about 2,000,000 centistokes ("csk"), from about 1,000 to about 1,800,000 csk, from about 10,000 to about 1,500,000 csk, and/or from about 20,000 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 60 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), incorporated herein by reference.

Silicone emulsions suitable for use in the embodiments of the present invention include, but are not limited to, emulsions of insoluble polysiloxanes prepared in accordance with the descriptions provided in U.S. Patent No. 6,316,541 or U.S. Patent No. 4,476,282 or 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 an internal phase viscosity from about 5 csk to about 500,000 csk. For example, the insoluble polysiloxane may have an internal phase viscosity less than 400,000 csk, preferably less than 200,000 csk, more preferably from about 10,000 csk to about 180,000 csk. The insoluble polysiloxane can have an average particle size within the range from about 10 nm to about 10 micron. The average particle size may be within the range from about

15 nm to about 5 micron, from about 20nm to about 1 micron, or from about 25 nm to about 500 nm.

The average molecular weight of the insoluble polysiloxane, the internal phase viscosity of the insoluble polysiloxane, the viscosity of the silicone emulsion, and the size of the particle  
5 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  
10 surfactant,

Other classes of silicones suitable for use in compositions of the present invention 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  
15 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 of the present invention may also  
20 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)  
25 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.

30           2. Emulsifiers



A variety of anionic and nonionic emulsifiers can be used in the hair care composition of the present invention. 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  
5 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.

### 3. Chelating Agents

The hair care composition can also comprise a chelant. Suitable chelants include those  
10 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) both incorporated herein by reference. When related to chelants, the term "salts and derivatives thereof" means the salts and derivatives comprising the same functional structure (e.g., same chemical backbone) as the chelant they are referring to  
15 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  
20 "chelating surfactant" 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  
25 and/or human 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.

### 4. Aqueous Carrier

30 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 85%, alternatively from about 45% to about 80%, alternatively from about 50% to about 75% 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 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 embodiments of the hair care compositions of the present invention 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.

#### G. FOAM DISPENSER

The hair care composition described herein may be provided in a foam dispenser. The foam dispenser may be an aerosol foam dispenser. The aerosol foam dispenser may comprise a reservoir for holding the hair treatment 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.

The foam dispenser may also be a mechanical foam dispenser. The mechanical foam dispenser described may be selected from the group consisting of squeeze foam dispensers, pump foam dispensers, other mechanical foam dispensers, and combinations thereof. In an embodiment, the mechanical foam dispenser is a squeeze foam dispenser. Non-limiting examples of suitable pump dispensers include those described in WO 2004/078903, WO 2004/078901, and WO 2005/078063 and may be supplied by Albea (60 Electric Ave., Thomaston, CT 06787 USA) or Rieke Packaging Systems (500 West Seventh St., Auburn, Indiana 46706).

The mechanical foam dispenser may comprise a reservoir for holding the concentrated hair treatment composition. The reservoir may be made out of any suitable material selected from the group consisting of plastic, metal, alloy, laminate, and combinations thereof. The reservoir may be a refillable reservoir such as a pour-in or screw-on reservoir, or the reservoir  
5 may be for one-time use. The reservoir may also be removable from the mechanical foam dispenser. Alternatively, the reservoir may be integrated with the mechanical 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  
10 comprised of a rigid material if it does not collapse under external atmospheric pressure when it is subject to an interior partial vacuum.

#### H. PRODUCT FORM

The hair care compositions of the present invention may be presented in typical hair care formulations. They may be in the form of solutions, dispersion, emulsions, powders, talcs,  
15 encapsulated, spheres, spongers, solid dosage forms, foams, and other delivery mechanisms. The compositions of the embodiments of the present invention may be hair tonics, leave-on hair products such as treatment, and styling products, rinse-off hair products such as shampoos and personal cleansing products, and treatment products; and any other form that may be applied to hair.

#### 20 I. APPLICATOR

In an embodiment of the present invention, the hair care composition may be dispensed from an applicator for dispensing directly to the scalp area. Dispensing directly onto the scalp via a targeted delivery applicator enables deposition of the non diluted cleaning agents directly where the cleaning needs are highest. This also minimizes the risk of eye contact with the  
25 cleansing solution.

The applicator is attached or can be attached to a bottle containing the cleansing prodhair care composition. The applicator can consist of a base that holds or extends to a single or plurality of tines. The tines have openings that may be at the tip, the base or at any point

between the tip and the base. These openings allows for the product to be distributed from the bottle directly onto the hair and/or scalp.

Alternatively, the applicator can also consist of brush-like bristles attached or extending from a base. In this case product would dispense from the base and the bristles would allow for product distribution via the combing or brushing motion.

Applicator and tine design and materials can also be optimized to enable scalp massage. In this case it would be beneficial for the tine or bristle geometry at the tips to be more rounded similar to the roller ball applicator used for eye creams. It may also be beneficial for materials to be smoother and softer; for example metal or metal-like finishes, “rubbery materials”.

## 10 Viscosity Measurement

Shampoo viscosities can be measured on a 2.5 mL sample using a cone and plate Brookfield RS rheometer with cone C75-1 at  $2\text{ s}^{-1}$ ,  $27^{\circ}\text{C}$  at 3 mins.

### Measurement of Diffusion Coefficients by NMR

Surfactant-soluble agent containing cleansing compositions are diluted with de-ionized water to a surfactant concentration of about 1.3%. This dilution factor is believed to be representative of a cleansing composition when applied to a head during use. The diluted samples are introduced into 5mm NMR tubes with no further preparation. No deuterated solvents are present, therefore all experiments are run unlocked. Diffusion coefficients are determined using vendor-supplied pulse sequence (“ledbpgppr2s”, stimulated echo with bipolar gradients, longitudinal eddy current delay, presaturation and 2 spoil gradients) using a Bruker Avance 700 MHz NMR spectrometer equipped with a BBO z gradient probe. Gradient pulse durations ranged between 3000 - 6000 us, with diffusion periods set at 150 ms. 32 linearly-spaced gradient values are used ranging from 2%-95% of 10 A current from a GREAT 3/10 amplifier, with resulting gradient strengths given by 5 Gauss/cm/A. Data are processed using vendor supplied software.

The surfactant micelle diffusion coefficient is designated as  $D_S$  and the surfactant-soluble agent diffusion coefficient is designated as  $D_A$ . The ratio of the surfactant diffusion coefficient to the surfactant-soluble agent diffusion coefficient can be calculated using the following equation:

$$\text{Ratio of Diffusion Coefficients} = \frac{D_S}{D_A}$$

### Measurement of Surfactant-Soluble Agent Deposition

Surfactant-soluble agent deposition in-vivo on scalp can be determined by ethanol extraction of the agent after the scalp has been treated with a surfactant-soluble agent containing cleansing composition and rinsed off. The concentration of agent in the ethanol extraction solvent is measured by HPLC. Quantitation is made by reference to a standard curve. The concentration detected by HPLC is converted into an amount collected in grams by using the concentration multiplied by volume.

The percent agent deposited can be calculated using the following equation:

$$\begin{aligned} & \% \text{ agent deposited} \\ &= \frac{\frac{\text{grams of agent deposited}}{\text{area of scalp extracted}}}{\frac{(\text{wt. \% agent in shampoo}) \times (\text{grams of shampoo applied})}{\text{area of scalp treated}}} \times 100\% \end{aligned}$$

10

The deposition efficiency can be calculated using the following equation:

$$\text{Deposition efficiency} = \frac{\% \text{ agent deposited by example formula}}{\% \text{ agent deposited by control formula}}$$

### Preparation of Shampoo Compositions

The shampoo compositions are prepared by adding surfactants, anti-dandruff agents, perfume, viscosity modifiers, cationic polymers and the remainder of the water with ample agitation to ensure a homogenous mixture. The mixture can be heated to 50-75°C to speed the solubilization of the soluble agents, then cooled. Product pH may be adjusted as necessary to provide shampoo compositions of the present invention which are suitable for application to human hair and scalp, and may vary based on the selection of particular deterative surfactants and/or other components.

**Non-limiting Examples**

The shampoo compositions illustrated in the following examples are prepared by conventional formulation and mixing methods. All exemplified amounts are listed as weight percents on an active basis and exclude minor materials such as diluents, preservatives, color solutions, imagery ingredients, botanicals, and so forth, unless otherwise specified. All percentages are based on weight unless otherwise specified.

Ingredient	Examples, active wt%	
	1 (control)	2
Water	q.s.	q.s.
Sodium Laureth-1 Sulfate (SLE1S) <sup>1</sup>	14.00	-
Sodium Undecyl Sulfate <sup>2</sup>	-	28.00
Piroctone Olamine <sup>3</sup>	1.00	0.5
Sodium Chloride <sup>4</sup>	Up to 2%	Up to 2%
Preservatives, pH adjusters	Up to 1%	Up to 1%
Diffusion Coefficient of Surfactant, $D_S$ (m <sup>2</sup> /s)	8.06E-11	1.96E-10
Diffusion Coefficient of Surfactant-soluble agent, $D_A$ (m <sup>2</sup> /s)	7.94E-11	1.02E-10
Ratio of Diffusion Coefficients, $D_S/D_A$	1.0	1.9
% Piroctone Olamine deposited	1.3%	4.5%
Deposition Efficiency (vs control)	1.0X	3.5X

1 Sodium Undecyl Sulfate at 70% active, supplier: P&G

- 2 Sodium Laureth-1 Sulfate at 26% active, supplier: P&G
- 3 Octopirox, supplier: Clariant
- 4 Sodium Chloride, supplier: Morton

### Discussion of Results for Examples 1-2

For Example 1, the ratio of diffusion coefficients ( $D_S/D_A$ ) is close to 1.0 which indicates that the Piroctone Olamine is diffusing at the same rate as the SLE1S micelles, implying that the Piroctone Olamine is within the SLE1S micelles. However, the ratio ( $D_S/D_A$ ) for Example 2 is significantly greater than 1.0 which indicates that the Piroctone Olamine is diffusing at a different rate than the sodium undecyl sulfate micelles, implying that the Piroctone Olamine is not within the sodium undecyl sulfate micelles. The implications of the Piroctone Olamine not being within the surfactant micelles in Example 2 is reflected in the greatly increased deposition efficiency of Example 2 which is 3.6X that of Example 1 (control).

Ingredient	Examples, active wt%	
	3 (control)	4
Water	q.s.	q.s.
Sodium Laureth-1 Sulfate <sup>1</sup>	14.00	8.00
Piroctone Olamine <sup>2</sup>	1.00	1.00
Sodium Chloride <sup>3</sup>	Up to 2%	Up to 2%
Preservatives, pH adjusters	Up to 1%	Up to 1%
Viscosity (cps)	7300	1500
% Piroctone Olamine deposited	0.91%	1.1%

Deposition Efficiency (vs control)	1.0X	1.2X
------------------------------------	------	------

1 Sodium Laureth-1 Sulfate at 26% active, supplier: P&G

2 Octopirox, supplier: Clariant

3 Sodium Chloride, supplier: Morton

Ingredient	Examples, active wt%	
	7 (control)	8
Water	q.s.	q.s.
Sodium Laureth-1 Sulfate <sup>1</sup>	14.00	14.00
Piroctone Olamine <sup>2</sup>	1.00	1.00
Sodium Chloride <sup>3</sup>	Up to 2%	0.0
Preservatives, pH adjusters	Up to 1%	Up to 1%
Viscosity (cps)	10300	<50
% Piroctone Olamine deposited	1.3%	1.2%
Deposition Efficiency (vs control)	1.0X	0.9X

1 Sodium Laureth-1 Sulfate at 26% active, supplier: P&G

2 Octopirox, supplier: Clariant

3 Sodium Chloride, supplier: Morton

### Discussion of Results for Examples 3-8

Neither decreasing surfactant levels, such as in Examples 4 and 6, nor decreasing product  
 5 viscosity, such as in Example 8, significantly impact deposition efficiency versus their respective



controls, Examples 3, 5, and 7. In fact Examples 4, 6, and 8 demonstrates deposition efficiencies ranging 0.9-1.2X that of their respective controls.

Examples 9-13 below further exemplify embodiments of the present invention.

5

Ingredient	Examples, active wt%	
	9	10
Water	q.s.	q.s.
Sodium Undecyl Sulfate <sup>1</sup>	28.00	28.00
Piroctone Olamine <sup>2</sup>	0.5	0.5
Limonene <sup>3</sup>	7.00	-
Linalyl Isobutyrate <sup>4</sup>	-	7.00
Sodium Chloride <sup>5</sup>	Up to 2%	Up to 2%
Preservatives, pH adjusters	Up to 1%	Up to 1%
% Piroctone Olamine deposited	4.4%	4.2%
Deposition Efficiency (vs control)	3.3X	3.2X

1 Sodium Undecyl Sulfate at 70% active, supplier: P&G

2 Octopirox, supplier: Clariant

3 Limonene, supplier: Kerry

4 Linalyl Isobutyrate, supplier: Givaudan

5 Sodium Chloride, supplier: Morton

Ingredient	Examples, active wt %		
	11	12	13
Water	q.s.	q.s.	q.s.
Sodium Undecyl Sulfate <sup>1</sup>	24.00	28.00	24.00
Lauramidopropyl Betaine <sup>2</sup>	4.00	-	2.00
Piroctone Olamine <sup>3</sup>	0.5	1.00	1.00
Limonene <sup>4</sup>	7.00	7.00	7.00
Polyquaternium-6 <sup>5</sup>	0.2	-	0.2
Guar Hydroxypropyltrimonium Chloride <sup>6</sup>	-	0.2	-
Polyquaternium-10 <sup>7</sup>	-	0.2	-
Sodium Chloride <sup>8</sup>	Up to 1%	Up to 1%	Up to 1%
Fragrance	-	-	1.60
Preservatives, pH adjusters	Up to 1%	Up to 1%	Up to 1%

1 Sodium Undecyl Sulfate at 70% active, supplier: P&G

2 Lauramidopropyl Betaine at 35% active, supplier: Solvay

3 Octopirox, supplier: Clariant

4 Limonene, supplier: Kerry

5 Mirapol 100 (40% active solution), supplier: Solvay Novecare

6 Jaguar C-500, viscosity = 25-65 cps, % Nitrogen = 1.15-1.45%, supplier: Solvay Novecare

- 7 UCARE Polymer JP, 2% soln viscosity = 30000, % Nitrogen = 0.8-1.1%, supplier:  
Dow Chemicals
- 8 Sodium Chloride, supplier: Morton

#### Microscopy Sample Preparation Method

10:1 dilution sample preparation: Weigh out  $10.00 \pm 0.05$  g of tap water into a glass vial. Add  
1.00  $\pm$  0.02 g of shampoo to the tap water. Close vial cap tightly, and shake back and forth  
5 vigorously 20 times. Allow sample to sit for 5-24 hrs until milky phase has separated to the top.

5:1 dilution sample preparation: Weigh out  $10.00 \pm 0.05$  g of tap water into a glass vial. Add  
2.00  $\pm$  0.02 g of shampoo to the tap water. Close vial cap tightly, and shake back and forth  
vigorously 20 times. Allow sample to sit for 5-24 hrs until milky phase has separated to the top.

10 Microscope slide preparation: Use a 1 mL plastic bulb pipette to sample the top milky phase of  
the dilution sample and place one drop onto a microscopy slide, then place a glass microscope  
slide cover on top of the sample.

Dilution samples are evaluated under a 40X objective lens using differential interference contrast  
(DIC) microscopy. Images are captured by camera using imaging software AxioVs40 V 4.7.2.0  
available from Carl Zeiss Imaging Solutions.

#### 15 Discussion of Results for Examples 11-13

Microscopy of dilutions of Examples 11, 12 & 13 show the presence of limonene oil droplets  
trapped in coacervate. This is evidence that upon dilution of the shampoo, both the coacervate  
and the limonene oil phase separate.

Ingredient	Examples, active wt%	
	14 (control)	15
Water	q.s.	q.s.
Sodium Laureth-1 Sulfate (SLE1S) <sup>1</sup>	14.00	-

Sodium Undecyl Sulfate <sup>2</sup>	-	14.00
Piroctone Olamine <sup>3</sup>	1.00	1.00
Sodium Chloride <sup>4</sup>	Up to 2%	Up to 2%
Preservatives, pH adjusters	Up to 1%	Up to 1%
Diffusion Coefficient of Surfactant, $D_S$ ( $m^2/s$ )	1.15E-10	1.78E-10
Diffusion Coefficient of Surfactant-soluble agent, $D_A$ ( $m^2/s$ )	1.07E-10	1.18E-10
Ratio of Diffusion Coefficients, $D_S/D_A$	1.1	1.5
% Piroctone Olamine deposited	1.1%	1.9%
Deposition Efficiency (vs control)	1.0X	1.7X

1 Sodium Laureth-1 Sulfate at 26% active, supplier: P&G

2 Sodium Undecyl Sulfate at 70% active, supplier: P&G

3 Octopirox, supplier: Clariant

4 Sodium Chloride, supplier: Morton

### Discussion of Results for Examples 14-15

For Example 14 (control), the ratio of diffusion coefficients ( $D_S/D_A$ ) is close to 1.0 which indicates that the Piroctone Olamine is diffusing at the same rate as the SLE1S micelles, which allows one to infer that the Piroctone Olamine is within the SLE1S micelle. However, in Example 15 where the SLE1S is replaced with Sodium Undecyl Sulfate, the ratio ( $D_S/D_A$ ) is greater than 1.0. This change in  $D_S/D_A$  indicates that the Piroctone Olamine is diffusing at a different rate than the Sodium Undecyl Sulfate micelles, which allows one to infer that the Piroctone Olamine is not within those micelles. The implication of the Piroctone Olamine not

being within the surfactant micelles in Example 15 is reflected in the increased deposition efficiency of Example 15 vs. Example 14 (control).

Ingredient	Examples, active wt%		
	16 (control)	17	18
Water	q.s.	q.s.	q.s.
Sodium Laureth-1 Sulfate (SLE1S) <sup>1</sup>	14.00	-	-
Sodium Undecyl Sulfate <sup>2</sup>	-	14.00	28.00
Climbazole <sup>3</sup>	1.00	1.00	2.00
Sodium Chloride <sup>4</sup>	Up to 2%	Up to 2%	Up to 2%
Preservatives, pH adjusters	Up to 1%	Up to 1%	Up to 1%
Diffusion Coefficient of Surfactant, $D_S$ (m <sup>2</sup> /s)	8.50E-11	2.18E-10	2.05E-10
Diffusion Coefficient of Surfactant soluble agent, $D_A$ (m <sup>2</sup> /s)	7.26E-11	9.83E-11	1.02E-10
Ratio of Diffusion Coefficients, $D_S/D_A$	1.2	2.2	2.0
% Climbazole deposited	0.57%	1.1%	1.3%
Deposition Efficiency (vs control)	1.0X	1.9X	2.5X

1 Sodium Laureth-1 Sulfate at 26% active, supplier: P&G

2 Sodium Undecyl Sulfate at 70% active, supplier: P&G

3 Climbazole, supplier: Symrise

## 4 Sodium Chloride, supplier: Morton

**Discussion of Results for Examples 16-18**

For Example 16 (control), the ratio of diffusion coefficients ( $D_S/D_A$ ) is close to 1.0 which indicates that the Climbazole is diffusing at the same rate as the SLE1S micelles, which allows one to infer that the Climbazole is within the SLE1S micelle. However, in Example 17-18 where the SLE1S is replaced with Sodium Undecyl Sulfate, the ratio ( $D_S/D_A$ ) is significantly greater than 1.0. This change in  $D_S/D_A$  indicates that the Climbazole is diffusing at a different rate than the Sodium Undecyl Sulfate micelles, which allows one to infer that the Climbazole is not within those micelles. Consequently, Examples 17-18 are representative of the present invention and exhibit significantly greater deposition efficiency which is 1.9X-2.5X that of Example 16 (control). This demonstrates that the present invention can be broadly applied to a variety of soluble anti-dandruff agents.

Ingredient	Examples, active wt%				
	19 (control)	20	21	22	23 (comparative)
Water	q.s.	q.s.	q.s.	q.s.	q.s.
Sodium Laureth-1 Sulfate (SLE1S) <sup>1</sup>	14.00	16.00	16.00	-	21.60
Sodium Trideceth-2 Sulfate <sup>2</sup>	-	-	-	16.00	-
Sodium Undecyl Sulfate <sup>3</sup>	-	8.00	-	-	2.40
Sodium Decyl Sulfate <sup>4</sup>	-	-	8.00	8.00	-
Piroctone Olamine <sup>5</sup>	1.00	2.00	2.00	2.00	2.00

Sodium Chloride <sup>6</sup>	Up to 2%	Up to 2%	Up to 2%	Up to 2%	Up to 2%
Preservatives, fragrance, pH adjusters	Up to 2.5	Up to 2.5%	Up to 2.5%	Up to 2.5%	Up to 2.5%
Diffusion Coefficient of Surfactant, $D_S$ (m <sup>2</sup> /s)	1.10E-10	1.21E-10	1.55E-10	2.89E-10	1.21E-10
Diffusion Coefficient of Surfactant-soluble agent, $D_A$ (m <sup>2</sup> /s)	9.05E-11	8.57E-11	1.07E-10	1.36E-10	1.03E-10
Ratio of Diffusion Coefficients, $D_S/D_A$	1.2	1.4	1.4	2.1	1.2
% Piroctone Olamine deposited	2.1%	3.1%	3.0%	4.2%	2.4%
Deposition Efficiency (vs control)	1.0X	1.5X	1.4X	2.0X	1.1X

- 1 Sodium Laureth-1 Sulfate at 26% active, supplier: P&G
- 2 Sodium Trideceth-2 Sulfate at 65% active, supplier: Tianjin Tianzhi Fine Chemical Co
- 3 Sodium Undecyl Sulfate at 70% active, supplier P&G
- 4 Sodium Decyl Sulfate at 70% active, supplier: P&G
- 5 Octopirox, supplier: Clariant
- 6 Sodium Chloride, supplier: Morton

### Discussion of Results for Examples 19-23

This set of examples demonstrates that achieving diffusion coefficient ratios ( $D_S/D_A$ ) greater than 1.2 is key to achieving the desired increased deposition efficiencies. Examples 20-22 are representative of the present invention and demonstrate that it is possible to achieve diffusion coefficient ratios ( $D_S/D_A$ ) greater than 1.2 with a variety of surfactants. Consequently, Examples  
5 20-22 exhibit greater deposition efficiencies (1.4-2.0X) than that of Example 19 (control). Example 23 is a comparative example and shows that even when a formula contains Sodium Undecyl Sulfate, if  $D_S/D_A$  is close 1.0 the deposition efficiency will be low and similar to that of the control (Example 19).

In the examples, all concentrations are listed as weight percent, unless otherwise  
10 specified and may exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components. As is apparent to one of ordinary skill in the art, the selection of these minors will vary depending on the physical and chemical characteristics of the particular ingredients selected to make the hair care composition.

15 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."

20 Every document cited herein, including any cross referenced or related patent or application and any patent application or patent to which this application claims priority or benefit thereof, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. 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  
25 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 incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

30 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 hair care composition comprising:
  - a) from 14% to 40% of one or more surfactants;
  - b) from 0.1% to 10% of one or more surfactant soluble antidandruff agents;
 wherein when the hair care composition is diluted to 1.3% surfactant concentration has a ratio of surfactant diffusion coefficient to soluble agent diffusion coefficient less than 0.8 or greater than 1.2, preferably a ratio of surfactant diffusion coefficient to soluble agent diffusion coefficient less than or equal to 0.6 and greater than or equal to 1.4.
  
2. A hair care composition according to any preceding claims wherein the surfactant is an anionic surfactant or combinations of anionic surfactants, preferably wherein the surfactant is an anionic surfactant selected from the group consisting of anionic alkyl sulfates and alkyl ether sulfates having straight or branched alkyl chains and mixtures thereof.
  
3. A hair care composition according to any preceding claims wherein the surfactant is an anionic surfactant selected from 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 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 1 when y is not zero (0), and M is a monovalent or divalent, positively-charged cation.
  
4. A hair care composition according to any preceding claims wherein the surfactant is a surfactant or combination of surfactants selected from the group consisting of sodium lauryl sulfate, sodium laureth-n sulfate where n is between 0.5 to 3.5, sodium C10-15 alkyl sulfate where the alkyl chain can be linear or branched, sodium C10-15 pareth-n

sulfate where n is between 0.5 to 3.5 and the alkyl chain can be linear or branched, sodium decyl sulfate, sodium deceth-n sulfate where n is between 0.5 to 3.5, sodium undecyl sulfate, sodium undeceth-n sulfate where n is between 0.5 to 3.5, sodium tridecyl sulfate, sodium trideceth-n sulfate where n is between 0.5 to 3.5, an anionic surfactant selected from 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 R1 represents  $CH_3 (CH_2)_{10}$ , R2 represents H or a hydrocarbon radical comprising 1 to 4 carbon atoms such that the sum of the carbon atoms in z and R2 is 8, R3 is H or  $CH_3$ , y is 0 to 7, the average value of y is 1 when y is not zero (0), and M is a monovalent or divalent, positively-charged cation.

5. A hair care composition according to any preceding claims further comprising from 0.25% to 15% of one or more amphoteric, nonionic or zwitterionic co-surfactants.
6. A hair care composition according to any preceding claims wherein the surfactant soluble agent is a hydroxyl pyridine, preferably wherein the hydroxyl pyridone is piroctone olamine.
7. A hair care composition according to any preceding claims wherein the surfactant soluble agent is an azole, preferably wherein the azole is climbazole.
8. A hair care composition according to any preceding claims wherein the composition further comprising a cationic polymer.
9. A hair care composition according to any preceding claims wherein the composition further comprising a conditioning agent, preferably wherein the conditioning agent is a silicone.
10. A hair care composition according to any preceding claims further comprising one or more scalp health agent, preferably wherein the scalp health agent is zinc pyrithione,

preferably wherein the scalp health agent is salicylic acid, preferably wherein the scalp health agent is menthol and/or menthyl lactate.

11. A hair care composition according to any preceding claims further comprising from 1% to 7% of a perfume.
12. A hair care composition according to any preceding claims wherein the hair care composition is dispensed as a foam.
13. A hair care composition according to any preceding claims wherein the hair care composition is dispensed as an aerosol foam, preferably wherein a propellant or a blowing agent to dispense the composition as an aerosol foam is a chemically inert hydrocarbon, a halogenated hydrocarbon, and mixtures thereof.
14. A hair care composition according to any preceding claims wherein the hair care composition is dispensed as a pumped foam.
15. A hair care composition according to any preceding claims wherein the hair care composition is applied using an applicator.

1/1

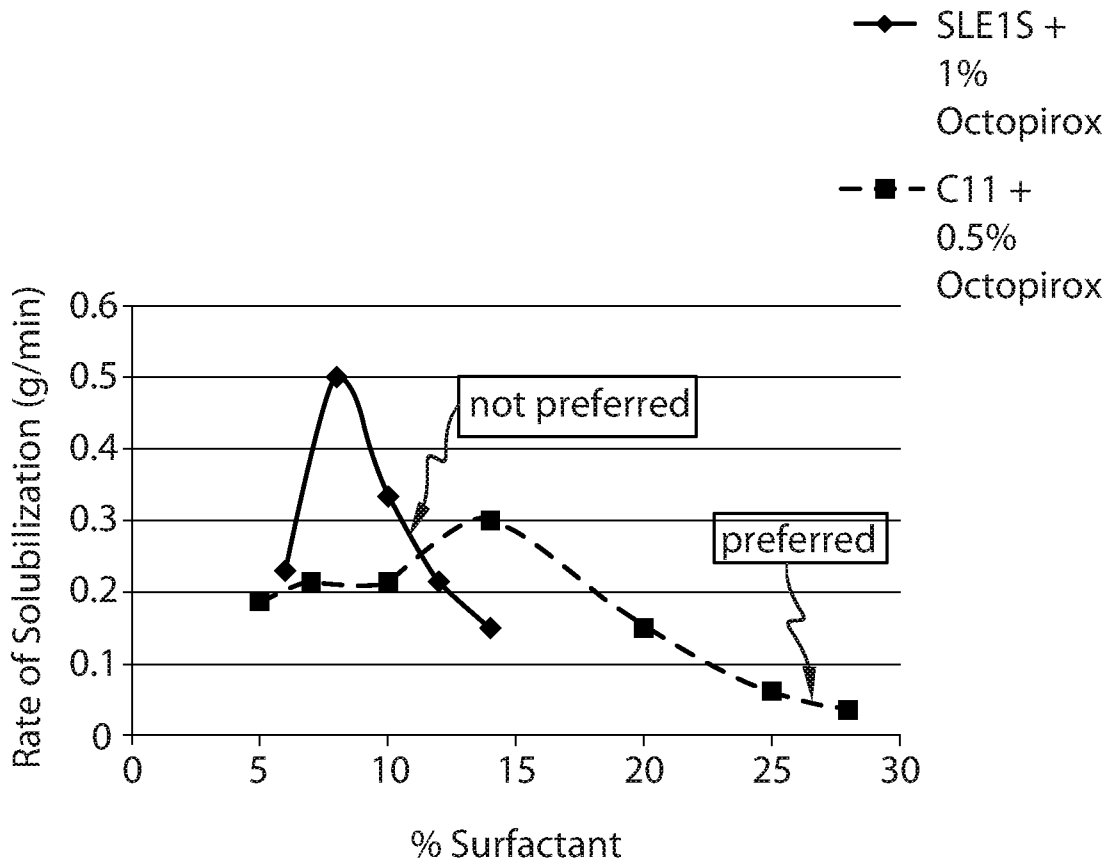


Figure 1

INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2016/028742

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. A61K8/49 A61Q5/00 A61Q5/02 A61K8/04  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
 Minimum documentation searched (classification system followed by classification symbols)  
 A61K A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

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Date of the actual completion of the international search <b>6 July 2016</b>	Date of mailing of the international search report <b>18/07/2016</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <b>Donovan-Beermann, T</b>
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