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CASSIA DERIVATIVES

Technical Field

[0001] This invention generally relates to galactomannan derivatives. More specifically, the invention relates to cationically and hydrophobically modified galactomannan polymers obtained from the endosperm of seeds obtained from the plant genus Cassia and to their use in personal care, health care, household, institutional and industrial care compositions and the like. The cationically and hydrophobically modified Cassia galactomannan polymers of this invention are useful as deposition aids, stabilizers, emulsifiers, spreading aids and carriers for enhancing the efficacy, deposition and delivery of chemically and physiologically active ingredients. In addition, such polymers are useful as an active component in personal care compositions as film formers, hair fixatives, hair conditioners, deposition aids, and skin conditioners. These polymers are also useful for improving the psychosensory and aesthetic properties of personal care formulations in which they are included.

Background of the Invention

[0002] Galactomannans (used interchangeably with the term polygalactomannan herein) are a class of polysaccharides that are found in the endosperm material of seeds from leguminous plants such as Cyamopsis tetragonoloba (guar gum), Cesalpinia spinosa (tara gum), Ceratonia siliqua (locust bean gum), and other members of the Leguminosae family. A galactomannan is composed of backbone of 1→4-linked β-D-mannopyranosyl main chain units (also designated herein as a mannoside unit or residue) with recurring 1→6-linked α-D-galactosyl side groups (also designated herein as a galactoside unit or residue) branching from the number 6 carbon atom of a mannopyranose residue in the polymer backbone. The galactomannan polymers of the different Leguminosae species differ from one another in the frequency of the occurrence of the galactoside side units branching from the polymannoside backbone. The mannoside and galactoside units are generically referred to herein as glycoside units or residues. The average ratio of D-mannoside to D-galactoside units in the galactomannan contained in guar gum is approximately 1.5 or 2:1, approximately 3:1 for tara gum, and approximately 4:1 for

locust bean gum. Another important source of polygalactomannan is isolated from the endosperm of the seeds of Cassia tora and Cassia obtusifolia (collectively known as cassia gum). The average ratio of D-mannosyl to D-galactosyl units in the polygalactomannan contained in cassia gum (derived from Cassia tora and Cassia obtusifolia) is at least 5:1.

[0003] It is well understood by those skilled in the art that natural galactomannans, even when obtained from a single source, will contain varying ranges of mannose to galactose ratios. Accordingly, these mannose to galactose ratios are reported as average ratios. The monosaccharide content of Cassia gum can be determined using a method adapted from Englyst et al. ("Determination of Dietary Fibre as Non-Starch Polysaccharides by Gas-Liquid Chromatography." Analyst (117), November 1992, pp. 1707-1714).

[0004] For illustrative purposes galactomannans obtained from the endosperm of cassia seed can be schematically represented by the structure:

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array}\\ \end{array}\\ \end{array}\\ \end{array}\\ \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array}\\ \end{array}\\ \end{array}\\ \begin{array}{c} \end{array}\\ \end{array}\\ \begin{array}{c} \begin{array}{c} \\ \end{array}\\ \end{array}\\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \end{array}\\ \begin{array}{c} \begin{array}{c} \\ \end{array}\\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \begin{array}{c} \\ \end{array}\\ \end{array}$$

wherein n is an integer representing the number of repeat units in the polymer. The polygalactomannan used in the practice of this invention typically has a weight average molecular weight (Mw) which is within the range of 200,000 to 5,000,000 Daltons. In many cases, the polygalactomannan has a weight average molecular weight, which is within the range of 300,000 to 2,000,000 Daltons. It is common for the galactomannan used in the practice of this invention to have a weight average molecular weight, which is within the range of 400,000 to 1,500,000 Daltons. The molecular weight of the galactomannan can be varied through controlled degradation procedures known in the art.

[0005] The underivatized Cassia galactomannan used as a starting material in the practice of this invention typically has a number average molecular weight (Mn) which is

within the range of 100,000 to 1,500,000 Daltons. In many cases, the polygalactomannan has a number average molecular weight, which is within the range of 200,000 to 1,000,000 Daltons. It is common for the polygalactomannan used in the practice of this invention to have a number average molecular weight, which is within the range of 300,000 to 900,000 Daltons. The weight average molecular weights and number average molecular weights referenced herein can be determined by gel permeation chromatography (GPC) with refractive index and low angle light scattering detectors.

[0006] Galactomannans are hydrocolloids that have a high affinity for water. They have been widely used as, thickening, emulsifying, and gelling agents in applications as diverse as foodstuffs, coatings, personal care compositions and in oil well fracturing fluids. Although the use of these polymers has been met with great success, galactomannans used in their natural form have suffered some drawbacks from a water solubility standpoint. An unsubstituted polymannose backbone is completely insoluble in water. The attachment of galactose side units to the C-6 atom in the recurring mannose residues of the polymannose backbone increases the water solubility of the polymer, particularly in cold water (i.e., ambient temperature and below). The greater the galactose side unit substitution, the greater is the cold water solubility properties of the polygalactomannan. Consequently, lower ratios of D-mannosyl to D-galactosyl units in the polygalactomannan leads to better cold water solubility. For example, the polygalactomannan contained in guar gum (average D-mannosyl to D-galactosyl ratio 2:1) is mostly soluble in cold water, while the polygalactomannan obtained from cassia gum (average D-mannosyl to D-galactosyl ratio of at least 5:1) is only sparingly soluble in cold and hot water.

[0007] U.S. Patent 4,753,659 to Bayerlein et al. discloses inter alia that improved cold water solubility can be imparted to cassia gum by chemically modifying the polygalactomannan. The reaction of cassia gum polygalactomannan with selected reagents to yield derivatized Cassia is disclosed. Exemplary reaction products include substituted and unsubstituted alkyl ethers, substituted phosphate esters, and substituted quaternary ammonium derivatives. Disclosed uses for the chemically modified cassia

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gum polygalactomannans include textile printing applications, oil well drilling auxiliaries, mining and explosives applications.

[0008] U.S. Patent 7,262,157 to Utz et al. discloses a personal care composition comprising a Cassia galactomannan polymer having repeating units containing a D-mannosyl to D-galactosyl residue ratio of 5 to 1 wherein a portion of the hydrogen groups on the pendant hydroxy substituents on the mannosyl and galactosyl residues are substituted with a group represented by the formula: $-AR^1$ wherein A is a substituted or unsubstituted alkylene group containing 1 to 6 carbon atoms, and R^1 is a group independently selected from $-N^+(R^3)_3 X^-$, $-S^+(R^3)_2 X^-$, and $-P^+(R^3)_3 X^-$, wherein R^3 independently represents substituted and unsubstituted C_1 - C_{24} alkyl, substituted and unsubstituted benzyl and substituted and unsubstituted phenyl; and X is any suitable anion that balances the charge on the onium cation.

[0009] WO 2010/009071 discloses home and personal care compositions including a cationically and hydrophobically modified guar galactomannan and a silicone. The disclosed cationically and hydrophobically modified guar galactomannan contains specific ranges of cationic and hydrophobic degrees of substitution. In the broadest embodiment, the degree of cationic substitution ranges from 0.01 to 0.5, and the degree of hydrophobic substitution ranges from 0.0001 to less than 0.001.

[0010] In personal care, health care, household care, and institutional and industrial care applications the solubility characteristics of active ingredients and formulation aids in aqueous systems are of paramount importance. While the cationically derivatized Cassia galactomannans disclosed in U.S. Patent 7,262,157 are disclosed to be soluble in aqueous based formulations, a relatively high degree of cationic substitution is needed to achieve useful properties. There also is a need to provide cationically derivatized Cassia galactomannans that exhibit cationic substantivity across a wide range of substitution levels as well as possessing other properties significant for personal care, health care, household care, and institutional and industrial care formulations while retaining significant water solubility. Such properties include enhanced sensory characteristics combined with superior compatibility with typical personal care, health care, household care, and institutional and industrial care ingredients for a given formulation. Such

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galactomannans would have widespread utility to applications not heretofore obtained in the prior art.

Summary of the Invention

[0011] In one embodiment, the present invention concerns a cationically and hydrophobically modified galactomannan having an average mannose to galactose ratio embracing the M:G ratios set forth herein, wherein a portion or all of the hydrogen atoms of the hydroxyl groups present on the galactomannan are substituted with at least one cationic moiety represented by formula (I) and at least one hydrophobic moiety set forth in formula (II) below.

$$(II) \qquad \qquad --(A) - (O) - R^1$$

wherein A, independently, is selected from a divalent linear or branched, substituted or unsubstituted C_1 - C_6 alkylene radical; R, independently, is selected from -S⁺R³R⁴ X⁻, - N⁺R³R⁴R⁵ X⁻, and -P⁺R³R⁴R⁵ X⁻, wherein R³ and R⁴, and R⁵, independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X⁻ represents an anion; R¹, independently, is selected from a hydrocarbon group having from about 2 to about 35 carbon atoms; a is 0 or 1; and b is 0 or 1, subject to the proviso that when a is 0, b is 0, and when a and b are both 0, or when a is 1 and b is 0, R¹ can not represent a hydroxyalkyl group having 2 to 4 carbon atoms.

[0012] In another embodiment, the present invention concerns a cationically and hydrophobically modified galactomannan isolated from the endosperm of the seeds of Cassia tora, Cassia obtusifolia, and combinations thereof, wherein a portion or all of the hydrogen atoms of the hydroxyl groups present on the galactomannan are substituted with at least one cationic moiety represented by formula (I) and at least one hydrophobic moiety set forth in formula (II) below.

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$$(II) \qquad \qquad --(A) - (O) - R^1$$

wherein A, independently, is selected from a divalent linear or branched, substituted or unsubstituted C_1 - C_6 alkylene radical; R, independently, is selected from -S⁺R³R⁴ X⁻, - N⁺R³R⁴R⁵ X⁻, and -P⁺R³R⁴R⁵ X⁻, wherein R³ and R⁴, and R⁵, independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X⁻ represents an anion; R¹, independently, is selected from a hydrocarbon group having from about 2 to about 35 carbon atoms; a is 0 or 1; and b is 0 or 1, subject to the proviso that when a is 0, b is 0, and when a and b are both 0, or when a is 1 and b is 0, R¹ can not represent a hydroxyalkyl group having 2 to 4 carbon atoms.

[0013] Without wishing to be bound by theory, it is postulated that the hydrophobic modification of the polygalactomannan backbone with substituents conforming to formula (II) confers enhanced compatibility with formulation ingredients that contain hydrophobic moieties when compared to unmodified cationic polygalactomannan (e.g., Cassia gum) and other cationically modified polysaccharides. Surprisingly, the hydrophobic modification of cationically derivatized Cassia imparts a better sensory profile in terms of conditioning such as, for example, wet and dry sensory attributes (feel) and combing properties of the hair.

[0014] The invention also concerns a personal care composition comprising A) the cationically and hydrophobically modified galactomannan herein described and B) at least one ingredient selected from surfactants, emulsifiers, emollients, moisturizers, fatty acid derived soaps, auxiliary hair and skin conditioning agents, auxiliary hair fixatives, auxiliary film-formers, skin protectants (e.g., sunscreen agents), binders, chelating agents, disinfectants, insecticides, fungicides, deodorants, pest repellants, odoriferous materials, antimicrobial agents, antifungal agents, antibiotics, antidandruff agents, abrasives, adhesives, skin anti-aging and anti-wrinkle agents, absorbents, colorants, deodorants, antiperspirant agents, humectants, opacifying and pearlescing agents, antioxidants, preservatives, propellants, spreading agents, exfoliants, keratolytic agents,

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blood coagulants, vitamins, artificial tanning accelerators, pH adjusting agents, botanicals, hair colorants, oxidizing agents reducing agents, skin bleaching agents, pigments, anti-inflammatory agents, topical anesthetics, fragrance and fragrance solubilizers, particulates, microabrasives, abrasives, and combinations thereof.

Detailed Description of the Invention

[0015] Exemplary embodiments in accordance with the present invention will be described. Various modifications, adaptations or variations of such exemplary embodiments described herein may become apparent to those skilled in the art as such are disclosed. It will be understood that all such modifications, adaptations or variations that rely upon the teachings of the present invention, and through which these teachings have advanced the art, are considered to be within the scope and spirit of the present invention.

[0016] The polymers and compositions of the present invention may suitably comprise, consist of, or consist essentially of the components, elements, and process delineations described herein. The invention illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein.

[0017] Unless otherwise stated, all percentages, parts, and ratios expressed herein are based upon weight of the total compositions of the present invention.

[0018] In one embodiment of the invention, the average ratio of D-mannosyl to D-galactosyl units (M:G units) in the polygalactomannan contained in Cassia endosperm is at least 5:1. In another embodiment, the average ratio of M:G units ranges from about 5:1 to about 49:1 in one aspect, from about 5:1 to about 35:1 in another aspect, from about 5:1 to about 25:1 in still another aspect, from about 5:1 to about 10:1 in a further aspect, and about 5:1, about 6:1, about 7:1, or about 8:1 in other aspects of the invention. In another embodiment, the Cassia gum encompassing the M:G ratios set forth above is obtained from the endosperm of Cassia tora, Cassia obtusifolia, and mixtures thereof.

[0019] In another embodiment, the amount of galactose contained in the Cassia polygalactomannan is at least 2 wt.% based on the total amount of mannose and galactose present in the galactomannan. In one aspect, the amount of galactose ranges from about 2 wt.% to about 17 wt.%, in another aspect from about 3 wt.% to about 14

wt. %, in still another aspect from about 4 wt.% to about 13 wt.%, and in a further aspect from about 5 wt.% to about 11 wt.%, wherein all weights are based on the total amount of mannose and galactose present in the galactomannan. In another embodiment, the Cassia gum encompassing the galactose weight ranges set forth above is obtained from the endosperm of the seeds of Cassia tora, Cassia obtusifolia, and mixtures thereof.

[0020] In one aspect, the present invention concerns a cationically and hydrophobically modified galactomannan having a mannose to galactose ratio embracing the M:G ratios set forth in the embodiments described above, wherein a portion or all of the hydrogen atoms of the hydroxyl groups present on the galactomannan are substituted with a least one cationic moiety represented by formula (I) and at least one hydrophobic moiety represented by formula (II) as follows:

$$(II) \qquad \qquad --(A) - (O) - R^1$$

wherein A, independently, is selected from a divalent linear or branched, substituted or unsubstituted C_1 - C_6 alkylene radical; R, independently, is selected from - $S^+R^3R^4$ X^- , - $N^+R^3R^4R^5$ X^- , and - $P^+R^3R^4R^5$ X^- , wherein R^3 and R^4 , and R^5 , independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X^- represents an anion; R^1 , independently, is selected from a hydrocarbon group and/or a substituted hydrocarbon group having from about 2 to about 35 carbon atoms; a is 0 or 1; and b is 0 or 1; and when a is 0, b is 0, and when a and b are both 0, or when a is 1 and b is 0, R^1 can not represent a hydroxyalkyl group having 2 to 4 carbon atoms (e.g., hydroxymethyl, hydroxypropyl, hydroxybutyl).

[0021] In one aspect, embodiments of the present invention relate to galactomannan compositions that are hydrophobically modified (e.g., alkylation) and cationically derivatized (e.g., quaternization) to enhance the sensory and compatibility attributes of Cassia galactomannans. Theoretically, an average of 3 hydroxyl groups reside on each unsubstituted glycoside unit in the Cassia galactomannan polymer backbone. The hydroxyl groups on each glycoside unit can be hydrophobically and/or cationically

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derivatized with hydrophobic and cationic moieties that are co-reactive therewith. The degree of substitution (DS) (with cationic and/or hydrophobic groups) is 1.0 when one hydroxyl group on each glycoside unit is derivatized, and 3.0 when, on average, 3 hydroxyl groups of each glycoside unit are derivatized. Average DS values can be expressed as decimal fractions of these integer values, and mean that the galactomannan comprises glycoside units having whole number DS values embracing the average.

[0022] The extent of the water solubility of the cationically and hydrophobically modified Cassia galactomannan of this invention represents a balance between the hydrophobic portions of the galactomannan molecule, such as provided by the hydrophobic moieties defined by formula (II) above, and the cationic portions of the galactomannan molecule, such as provided by the substituents defined under formula (I) above. The water solubility of the Cassia galactomannan of the invention can be tailored by increasing or decreasing the degree of substitution of cationic substituents defined by formula (I) (DS_I) relative to the degree of substitution of the hydrophobic substituents described by formula (II) (DS_{II}) and vise-versa. In other words, the substitution levels of DS_I and DS_{II} can vary according to the desired solubility characteristics of the galactomannan. The total degree of substitution, defined as (DS_T), is the sum of the degree of substitution of the cationic substituents defined by formula (I) referred to as (DS_I) and the degree of substitution of the hydrophobic substituents defined by formula (II) referred to as (DS_{II}).

[0023] The degree of substitution level for the cationic substituents defined under formula (I) or DS_I ranges from about 0.25 to about 2.0 in one aspect, from about 0.3 to about 1.75 in another aspect, from about 0.5 to about 1.5 in still another aspect, from above 0.5 to about 1.75 in a further aspect, from 0.51 to about 1.0 in a still further aspect, and from 0.6 to about 0.75 in another aspect of the invention. Individual numerical values, or limits, can be combined to form additional non-disclosed and/or non-stated ranges.

[0024] The degree of substitution level for the hydrophobic substituents defined under formula (II) or DS_{II} ranges from about 0.00001 to about 1.25 in one aspect, from about 0.0001 to about 1.0 in another aspect, from about 0.001 to about 0.75 in still another aspect, from about 0.01 to about 0.5 in a further aspect, and from about 0.1 to

about 0.25 in a still further aspect of the invention. Individual numerical values, or limits, can be combined to form additional non-disclosed and/or non-stated ranges.

[0025] The total average degree of substitution DS_T for the combined substituents of formulas (I) and (II) can range from about 0.25001 to about 3.0 in one aspect of the invention, from about 0.5005 to about 2.0 in another aspect, from about 0.5015 to about 1.75 in still another aspect, from about 0.511 to about 1.5 in a further aspect, from about 0.52 to about 1.25 in a still further aspect, and from about 0.55 to about 1.0 in another aspect, per constituent glycoside residual unit in the galactomannan backbone. Here, as well as elsewhere in the specification and claims, individual numerical values, or limits, can be combined to form additional non-disclosed and/or non-stated ranges.

[0026] In one embodiment of the invention, the average DS_I ranges from 0.25 and above and the average DS_{II} ranges from 0.001 and above, subject to the proviso that the average DS_T does not exceed 3.0 in one aspect, 2.0 in another aspect, 1.0 in still another aspect, and 0.75 in a further aspect.

[0027] In another embodiment of the invention, the average DS_I is above 0.5 and the average DS_{II} ranges from 0.00001 and above, subject to the proviso that the average DS_T does not exceed 3.0 in one aspect, 2.0 in another aspect, 1.0 in still another aspect, and 0.75 in a further aspect.

[0028] In a further embodiment of the invention, the average DS_I is above 0.5 and the average DS_{II} ranges from 0.001 and above, subject to the proviso that the average DS_T does not exceed 3.0 in one aspect, 2.0 in another aspect, 1.0 in still another aspect, and 0.75 in a further aspect.

[0029] In one embodiment of the invention, a portion of or all of the hydrogen atoms situated on the hydroxyl groups present on the Cassia galactomannan are substituted with at least one substituent selected from a cationic substituent represented by formula (I) and at least one substituent selected from a hydrophobic substituent represented by formula (II). For illustrative purposes, and without limitation thereto, this embodiment can be schematically represented by formula (III) as follows:

(III) OH O-AR
$$O-(A) - (O) - R^{1}$$

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wherein the bracketed moiety, independently, represents a glycoside residual unit of the Cassia galactomannan polymer backbone, and –AR, A, R¹, a, and b are as previously defined.

The embodiment schematically depicted in formula (III) above is disclosed [0030] for illustrative purposes and is not to be construed as a limitation upon the scope of the invention. While only one glycoside (mannosyl) residual unit having 3 hydroxyl substitution sites is illustrated, as discussed previously, the galactomannan backbone contains recurring mannosyl residual units with some having galactosyl side units bonded thereto. These galactosyl units have a potential DS of about 4 (3 hydroxyl groups are bonded directly to the galactosyl ring and a fourth hydroxyl group is situated on the C-6 carbon atom). Although the foregoing schematic formula depicts a DS value of 2 (e.g., 2 hydroxyl group hydrogen atoms are replaced with a cationic and a hydrophobic substituent), it should be recognized that this is for illustrative purposes only, and as discussed previously the actual DS value is a value that encompasses the average degree of substitution for all of the hydroxyl group hydrogen atoms situated on each glycoside unit of the galactomannan backbone. Further, it is pointed out in the schematic formula depicted above that the glycosidic linkage between adjacent repeating units in the galactomannan backbone is not shown.

[0031] In one embodiment of the invention, alkylation entails reacting the pendant hydroxyl groups present on the backbone of the Cassia galactomannan or derivative thereof with an alkylation agent. As defined here and throughout the specification an "alkylating" or "alkylation" agent" is a reactive compound containing a hydrocarbon group that can be reacted with a pendant hydroxyl group on the Cassia galactomannan to form an ether linkage with the galactomannan the starting material. The hydrocarbon group can be a saturated or unsaturated alicyclic group, a saturated or unsaturated, aliphatic group, and an aromatic group. In one aspect, typical alkylation agents reactive with the pendant galactomannan hydroxyl groups include halides, epoxides, and glycidyl ethers that contain a hydrocarbon group. Hydrocarbon group containing carboxylic acids, isocyanates, and acid halides are also suitable as alkylating agents. In one aspect of the invention, a suitable alkylating agent is represented by formula (IV) below:

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(IV) $X-R^1$

wherein X is a halogen atom selected from bromine, chlorine, fluorine, and iodine; and R¹ is a hydrocarbon group containing from about 2 to about 35 carbon atoms in one feature, from about 3 to about 30 carbon atoms in another feature, from about 4 to about 24 carbon atoms in a further feature, and from about 12 to about 22 in a still further feature.

[0032] In another aspect, R^1 represents a hydrocarbon group selected from a saturated or unsaturated alicyclic group, a saturated or unsaturated, linear or branched aliphatic group, and an aromatic group, wherein the alicyclic and aromatic groups can be optionally substituted with a substituent selected from halogen (e.g., bromine, chlorine, fluorine, iodine), hydroxyl, saturated or unsaturated, linear or branched C_1 to C_{22} aliphatic group, a C_6 - C_{10} aromatic group, and combinations thereof. In this aspect of the invention, the hydrocarbon group contains from about 2 to about 35 carbon atoms in one feature, from about 3 to about 30 carbon atoms in another feature, from about 4 to about 24 carbon atoms in a further feature, and from about 12 to about 22 carbon atoms in a still further feature.

[0033] In a further aspect, R¹ represents a hydrocarbon group selected from cycloalkyl, linear or branched alkyl, cycloalkenyl, linear or branched alkenyl, aryl, alkylaryl, alkenylaryl, and combinations thereof, wherein the hydrocarbon group contains from about 2 to about 35 carbon atoms in one feature, from about 3 to about 30 carbon atoms in another feature, from about 4 to about 24 carbon atoms in a further feature, and from about 12 to about 22 carbon atoms in a still further feature.

[0034] In still a further aspect of the invention, R^1 represents a hydrocarbon group selected from substituted and unsubstituted C_4 - C_8 cycloalkyl, substituted and unsubstituted C_5 - C_8 cycloalkenyl, linear or branched C_2 - C_{35} alkenyl, substituted and unsubstituted C_6 - C_{14} aryl, $(C_1$ - C_{22})alkyl $(C_6$ - C_{10})aryl, wherein the aryl group is optionally substituted, $(C_3$ - C_{22})alkenyl $(C_6$ - C_{10})aryl, wherein the aryl group is optionally substituted, and combinations thereof. When the foregoing cycloaliphatic and aromatic moieties are substituted the substituents are selected from

C₁-C₂₂ alkyl, C₂-C₂₂ alkenyl, hydroxyl, halo (e.g., bromo, chloro, fluoro, iodo), and combinations thereof.

[0035] In one embodiment of the invention, the alkylating agent is an alkyl halide wherein the alkyl group is a linear or branched C_2 to C_{24} alkyl group in one aspect, a linear or branched C_4 to C_{22} alkyl group in another aspect, and a linear or branched C_{12} to C_{22} alkyl group in a further aspect. The halide is selected from chloride, bromide, fluoride, and iodide. Exemplary alkyl halide alkylating agents include but are not limited to ethyl, propyl, isopropyl, n-butyl, t-butyl, pentyl, neopentyl, hexyl, octyl, decyl, dodecyl, myristyl, hexadecyl, stearyl and behenyl bromides, chlorides, and iodides.

[0036] In another embodiment, the alkylating agent is selected from an unsubstituted or substituted arylalkyl bromide or chloride or chloride or an unsubstituted or substituted arylalkyl bromide or chloride, wherein the aryl group is optionally substituted, with at least one substituent selected from ethyl, propyl, isopropyl, n-butyl, t-butyl, pentyl, neopentyl, hexyl, octyl, decyl, nonyl, dodecyl, myristyl, hexadecyl, stearyl and behenyl groups. In one aspect, aryl containing alkylating agents are selected from substituted or unsubstituted phenyl and phenyl alkyl halides (e.g., bromo and chloro). When substituted, the substituents are selected from ethyl, propyl, isopropyl, n-butyl, t-butyl, pentyl, neopentyl, hexyl, octyl, decyl, nonyl, dodecyl, myristyl, hexadecyl, stearyl and behenyl groups Exemplary aryl containing alkylating agents include but are not limited to benzyl chloride, benzyl bromide, phenylethyl bromide, 1-chloro-9-phenylnonane, and 1-chloro-4-nonyl-benzene.

[0037] In another aspect of the invention, the alkylating agent is represented by formula (V) as follows:

(V)
$$CH_{2}$$
 CH_{2} CH_{2}

wherein m is an integer of 1 to 4; b is 0 or 1; and R¹ is as defined in formula (IV) above.

[0038] Representative epoxylated alkylation agents set forth under formula (V) include but are not limited to 1,2-epoxyethylbenzene, 1,2-epoxy-2-phenylpropane, 2-(1,1dimethylethyl)-2-(phenylmethyl)-oxirane, 2-[2-(4-chlorophenyl)ethyl]-2-(1,1-dimethylethyl)-oxirane, 1,2-epoxybutane, 1,2-epoxybutane, 1,2-epoxybentane, 1,2-epoxybentane, 1,2-epoxydecane, 1,2-epoxyd

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epoxytetradecane, 1,2-epoxy hexadecane, 1,2-epoxyoctadecane, 1,2-epoxyeicosane, 1,2-epoxyethylbenzene, 3,4-epoxy-1-butene, 1,2-epoxy-5-hexene, 1,2-epoxy-9-decene, glycidyl methyl ether, ethyl glycidyl ether, butyl glycidyl ether, t-butyl glycidyl ether, glycidyl ether, 2-ethylhexyl glycidyl ether, dodecyl glycidyl ether, tetradecyl glycidyl ether, hexadecyl glycidyl ether, behenyl glycidyl ether, glycidyl phenyl ether, benzyl glycidyl ether, glycidyl triphenylmethyl ether, nonylphenyl glycidyl ether, and allyl glycidyl ether.

[0039] Cationization of the galactomannan can be effected by reacting the pendant hydroxyl groups present on the backbone of the Cassia galactomannan with a cationization agent. The cationization agent contains a functional group that is reactive with the hydroxyl groups on a cassia galactomannan glycoside and/or a hydroxyl terminated hydrophilic group that has previously been appended to the galactomannan backbone. In one aspect of the invention, the hydroxyl reactive functional group can be selected from a halohydrin and/or an epoxy group that is reactive with a pendant hydroxyl group on the galactomannan backbone and/or a hydroxyl terminated hydrophilic group. A suitable cationization agent can be represented by formula (VI) as follows:

(VI) A'R

wherein A' represents an epoxy group or a epoxylated linear and branched moiety containing 3 to 6 carbon atoms which can be optionally substituted with one or more halogen groups (e.g. chloro, bromo) or a halogenated (e.g., chloro, bromo) linear and branched moiety containing 3 to 6 carbon atoms which can be optionally substituted with one or more hydroxyl groups. In one aspect, A' represents an epoxy containing group and in another aspect A' represents a 3-halogeno-2-hydroxypropyl radical. The R substituent, independently, is selected from -S⁺R³R⁴ X⁻, -N⁺R³R⁴R⁵ X⁻, and -P⁺R³R⁴R⁵ X⁻, wherein R³ and R⁴, and R⁵, independently, are selected from hydrogen and linear and branched C₁-C₂₄ alkyl; and X⁻ represents an anion selected from chloride, bromide, iodide, sulfate, methylsulfate, sulfonate, nitrate, phosphate, and acetate. In another aspect, R is a quaternium nitrogen radical represented by the formula -N⁺R³R⁴R⁵ X⁻, wherein R³, R⁴, and R⁵, independently, are selected from hydrogen and linear and

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branched C_1 - C_{24} alkyl groups, and X^- represents an anion selected from chloride, bromide, iodide, sulfate, methylsulfate, sulfonate, nitrate, phosphate, and acetate. Representative alkyl groups defined under R^3 , R^4 , and R^5 include but are not limited to methyl, ethyl, propyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, dococyl, and combinations thereof. In another aspect, R^3 is selected from C_1 - C_8 alkyl, and R^4 and R^5 , independently, are selected from C_8 - C_{24} alkyl. In a further aspect, R^3 and R^4 , independently, are selected from C_1 - C_8 alkyl and R^5 is selected from C_8 - C_{24} alkyl. In a still further embodiment, R^3 , R^4 and R^5 are, independently, selected from C_1 - C_{10} alkyl in one aspect, from C_1 - C_8 alkyl in another aspect, and from C_1 - C_5 alkyl in a further aspect. In another embodiment, R^3 , R^4 and R^5 are each methyl. In all of the foregoing aspects of the invention, X^- is as previously defined. In a further aspect of the invention, A^+ R is represented by formulae (VII) and (VIII) and (IX) set forth below:

$$(IX) \qquad \qquad \begin{array}{c} OH \\ I \\ -CH_2 \\ -CH_2$$

wherein Y is a halogen atom selected from bromine, chlorine, and iodine and R is as previously defined.

[0040] In one embodiment, suitable cationizing reagents include but are not limited to glycidyltrimethylammonium chloride, glycidyltriethylammonium chloride, glycidyltripropylammonium chloride, glycidylethyldimethylammonium chloride, glycidyldiethylmethylammonium chloride, and their corresponding bromides and iodides; 3-chloro-2-hydroxypropyltrimethylammonium chloride, 3-chloro-2-

hydroxypropyltriethylammonium chloride, 3-chloro-2-hydroxypropyltripropylammonium chloride, 3-chloro-2-

hydroxypropylethyldimethylammonium chloride, and their corresponding bromides and iodides. In another embodiment, the cationization reaction can be conducted with a hydroxyl group provided by the hydrophilic moiety, e.g., subsequent to hydrophilization via alkoxylation with alkylene oxide(s) or a preformed hydroxyl terminated polyalkoxylated compound.

[0041] In the preparation of the cationically and hydrophobically modified polygalactomannans of the present invention, a hydroxyl group(s) on the polygalactomannan backbone is reacted with a functionalization reagent(s) set forth, for example, under formulae (IV), (VI), (VII), (VIII), and (IX) described above, such that a hydrogen atom situated on said hydroxyl group(s) is replaced by a substituent or residue defined under formulae (I) and (II) set forth above. The reaction can be schematically represented as follows:

Functionalization Reagent(s)

wherein D is selected from hydrogen, a residue or moiety obtained from a functionalization reagent(s) described above, and combinations thereof. In another aspect of the invention, D represents hydrogen, a moiety selected from formulae (I), a

moiety selected from formula (II), and combinations thereof subject to the proviso that moieties selected from formulae (I) and (II) are both present on the backbone of the galactomannan

The hydrophobic derivation can be conducted by reacting an alkylation agent, [0042] or mixtures thereof, containing a hydrophobe and a functional group which is reactive with the hydroxyl groups on the galactomannan backbone. The cationic derivation (cationization) can be accomplished by reacting a cationization agent such as a quaternizing agent, or mixtures thereof, containing, for example, a quaternary ammonium moiety and a functional group which is reactive with a hydroxyl group present on the galactomannan backbone. Furthermore, one or more alkylation or cationization agents can be combined to reduce the number of synthesis steps or to achieve different balances of various hydrophobic and cationic substituents on the Cassia galactomannan backbone. The hydrophobically modified, cationic Cassia galactomannans of this invention can be prepared (1) by alkylation followed by cationization; (2) cationization followed by alkylation; (3) simultaneous alkylation and cationization; (4) a sequential series of alkylation steps followed by a sequential series of cationization steps; (5) a sequential series of cationization steps followed by a sequential series of alkylation steps; (6) alternating alkylation and cationization steps; and (7) or any variation of the foregoing procedures.

[0043] In synthesizing the hydrophobically modified, cationic Cassia polygalactomannan polymers of this invention the functionalizing reagent will be capable of reacting with hydroxyl groups present in the galactosyl side unit and/or the mannosyl main chain backbone units of the Cassia polymer. For instance, the functionalizing reagent will be capable of reacting with hydroxyl groups on the C-2, C-3, C-4, and/or C-6 carbon atoms of the galactosyl side unit and/or the C-2, C-3, or C-6 carbon atoms of the mannosyl main chain units of the polymer. The cationically and hydrophobically modified Cassia galactomannan of this invention can be produced from readily available materials. Such compositions are derived from naturally occurring Cassia endosperm splits as discussed above, or can be derived from commercially available cationically modified cassia such as disclosed in U.S. Patent 4,753,659 and

U.S. Patent 7,262,157, which are herein incorporated by reference for their disclosure of cationically derivatized Cassia.

[0044] According to an embodiment of the invention, the hydrophobic and cationic modification can be carried out starting from unmodified Cassia galactomannan as such or from a partially substituted Cassia galactomannan (e.g., partially substituted with cationic and/or hydrophilic substituents). The cationic and hydrophobic derivatization steps can be conducted in any order, or simultaneously, as well as repeated, to produce the desired cationically and hydrophobically modified Cassia galactomannan of the invention. The hydrophobic and cationic modification of the Cassia galactomannan can be carried out without isolating the intermediate product.

Underivatized Cassia gum or flour is commercially available from Lubrizol [0045] Advanced Materials, Inc. under the Diagum trademark. The derivatization of hydroxyl groups on Cassia polygalactomannan can be accomplished by methods well known to those skilled in the art. Generally speaking, the hydroxyl groups of the Cassia can be reacted with any functionalization reagent that is co-reactive therewith. For example, to functionalize the hydroxyl group of the Cassia with a cationic substituent of this invention, the hydroxyl group(s) on the Cassia gum polygalactomannan are reacted with a functionalization reagent that contains a cationic group and a functional moiety that is co-reactive with the hydroxyl groups, such as an epoxy group, a glycidyl group and a haloalkyl group. The functionalization reaction is conducted in an appropriate solvent and at an appropriate temperature. The amount of functional group substitution (degree of substitution) on the polygalactomannan hydroxyl atom(s) can be controlled by adjusting the stoichiometric amount of functionalization reagent added to the Cassia polygalactomannan. Functionalization methods for Cassia gum polygalactomannans are disclosed in U.S. Patent 4,753,659. Additional methods of derivatizing polygalactomannans are set forth in U.S. Patent 5,733,854. The teachings of U.S. Patent 4,753,659 and U.S. Patent 5,733,854 are incorporated herein by reference for the purpose of illustrating methods for functionalizing Cassia gum polygalactomannans.

[0046] In one embodiment of the invention, cationic functionalization (e.g., quaternization) of the Cassia polygalactomannan is effected in an inert solvent or solvent mixture at a temperature ranging from about 5°C to about 150°C in one aspect, from

about 40°C to 100°C in another aspect, and from 45°C to about 80°C in still a further aspect, for a period of time necessary to attained the desired degree of cationic substitution, typically from about 0.5 to about 8 hours. Alkaline catalysts such as sodium hydroxide, potassium hydroxide, lithium hydroxide, and ammonium hydroxide can be employed. The amount of catalyst utilized in the reaction will depend upon whether the cationization agent (e.g., quaternizing agent) is a halohydrin or epoxide, as well as the degree of cationization desired. The alkaline catalysts are used in conventional amounts known in the art and are generally employed in an amount ranging from about 0.1 weight percent to about 50 weight percent based on the weight of the galactomannan to be modified.

[0047] In one embodiment of the invention, the alkylation is conducted in an inert solvent or mixtures of inert solvents in the presence of a caustic catalyst such as an alkali metal hydroxide (e.g., sodium hydroxide, potassium hydroxide, calcium hydroxide) under the same general temperature and time conditions as set forth for the cationization reaction. An alternative method to effect alkylation is set forth in U.S. Patent No. 5,872,246 the disclosure of which is incorporated by reference.

[0048] The Cassia used as a starting material is typically in powder form and is normally treated with an alcohol or an alcohol/water solution. In practice, the alcohol used can be methanol, ethanol, isopropanol, n-propyl alcohol, n-butyl alcohol, isobutyl-alcohol, t-butyl alcohol, or the like, and mixtures thereof. The alcohol can be used in neat (100%) form or as a aqueous solution. In such cases it is, of course, critical for the alcohol to be miscible with water. This treatment step is typically done at ambient temperatures (about 20°C). However, it can optionally be done at any temperature which is within the range of about 0°C to about 70°C. In some cases, it is advantageous to conduct this treatment step at an elevated temperature which is within the range of about 30°C up to about 70°C.

[0049] As discussed above, the cationization and the alkylation reactions are typically conducted in an inert solvent or diluent such as a lower aliphatic alcohol or ketone, or an aliphatic or aromatic hydrocarbon, and mixtures thereof. Exemplary solvents or diluents include water; alkanols, such as isopropyl alcohol, t-butyl alcohol,

and the like; ketones such as acetone, and the like; ethers such as diethyl ether, and the like; hydrocarbons, such as hexane, benzene, toluene, and the like; and mixtures thereof [0050] In practice, it is generally desired to use mixtures of water and organic solvents in the Cassia treatment step. Particularly effective results occur when using between about 10 to about 90 percent water by weight and between about 90 to about 10 percent organic solvent by weight. In another aspect, the use of between about 30 to about 80% by weight isopropyl alcohol and between about 20 to about 70% by weight water is desirable. For example, excellent results have been obtained wherein the solution selected for use is an isopropanol/water mixture, wherein the respective amounts by weight are 44% isopropanol and 54% water. The amount of alcohol or alcohol water solution to be used in this step is that amount which is necessary to fully saturate the Cassia powder. In practice, this amount is usually at least about twice the amount by weight of the starting Cassia powder in one aspect, and at least about three times the amount by weight of the starting Cassia in another aspect.

[0051] After addition of the alcohol or alcohol/water solution and the subsequent neutralization, followed by agitation as needed, the functionalizing agent(s) is added to the Cassia solution. As previously explained the functionalizing agent is a compound that contains at least one functional group that is capable of reacting with hydroxyl groups on the Cassia. These functional groups can be epoxy groups and/or halogen containing groups (although carboxyl and isocyanate containing groups are also contemplated).

[0052] To facilitate the reaction kinetics of the functionalization reaction, an alkaline material can be added as a catalyst. The alkaline material is typically an aqueous solution of a base, such as sodium hydroxide (NaOH). In one aspect, the aqueous solution will contain at least 12% by wt. of NaOH, and in another aspect from 12% to 60% NaOH. In still another aspect, the aqueous solution contains from 20% to 50% by wt. of NaOH. In one embodiment, between about 0.1 and about 50 parts of NaOH (100%) are added for every 100 parts of Cassia starting material.

[0053] In one aspect of the invention, the temperature of the reaction mixture ranges from between about 40°C to about 75°C, and in another aspect in the range of about 60°C to about. The reaction mixture is typically stirred for a period of time sufficient to insure

complete reaction of the reactants. In practice, this reaction time is generally between about 1 hour to about 5 hours and in another aspect within a range of about 2 hours to about 4 hours.

[0054] After functionalization the Cassia is neutralized. The neutralization is normally adjusted to a pH which is within a range of about 6 to about 8 in one aspect, and about 7 in another aspect. Any acid may selected for use to neutralize the solution, including strong acids such as hydrochloric acid and sulfuric acid or weak acids such as acetic acid, citric acid, carbon dioxide (carbonic acid), trifluoroacetic acid, etc. In one embodiment either hydrochloric or acetic acid is used. The amount of acid used is the amount necessarily for neutralization.

[0055] After the neutralization, the functionalized Cassia is typically filtered and then washed with water, an organic solvent, or a mixture of both. When utilizing organic solvent water mixtures, the organic solvent(s) are water miscible solvents including alcohols, such as methanol, ethanol, isopropanol, n-propyl alcohol, n-butyl alcohol, isobutyl alcohol, t-butyl alcohol, and the like. Other commonly used purification solvents such as acetone, glycols and the like may alternatively be selected. Mixtures of these solvents with the above disclosed water miscible alcohols are also useful.

Cassia and can be performed in batch wise or multiple applications. In one aspect the volume of the wash liquid is at least twice the volume of the functionalized Cassia and in another aspect at least three times the volume of the Cassia. In one aspect, 1 to 4 independent wash cycles are completed. However, additional wash cycles can be used if needed. The concentration of the wash liquid for each cycle can be the same or different. For example washing of the Cassia powder may be accomplished by first washing with a dilute isopropyl alcohol solution, followed by washing with stronger solutions of isopropyl alcohol, and finally with acetone. After washing, the functionalized Cassia can be dried and recovered using methods known in the art. Examples of such techniques include air drying, filtering, evaporative drying, vacuum drying, centrifuging, flash grinding, addition of solvents, freeze drying, and the like. The use of fluidized bed drying can be advantageous.

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[0057] In one aspect of the invention, the hydrophobic functionalization of underivatized Cassia can be accomplished by reacting an epoxy group containing hydrophobic functionalizing reagent with a hydroxyl group(s) on the backbone units of the Cassia galactomannan. The reaction can be schematically depicted as follows:

(X) Cassia-(OH)_n +
$$H_2C - CH - (-CH_2)_m (-O)_b - R^1$$

OH

$$_{n-x}(HO)$$
-Cassia $\left\{O-CH_{\frac{1}{2}}CH-\left\{CH_{\frac{1}{2}}\right\}_{m}\left\{O-\right\}_{b}R^{1}\right\}_{x}$

wherein R¹, m, and b are as previously defined; n represents the number of hydroxyl groups on the cassia galactomannan backbone; x represents the average total substitution of the hydrophobic moiety on the galactomannan backbone, wherein x can not be greater than n; and the result of the difference of n-x represents the free hydroxyl groups remaining on the derivatized backbone.

[0058] In another aspect, the hydrophobic functionalization of underivatized Cassia can be accomplished by reacting an alkyl halide functionalizing reagent with a hydroxyl group(s) on the backbone units of the Cassia galactomannan. This reaction can be schematically depicted as follows:

(XI) Cassia-(OH)_n + X-R¹
$$\longrightarrow$$

$$_{n-x}$$
(HO)-Cassia $-\left[-O-R^{1}\right]_{x}$

wherein R¹ is as previously defined; n represents the number of hydroxyl groups on the cassia galactomannan backbone; x represents the average degree of total substitution of the hydrophobic moiety on the galactomannan backbone, wherein x can not be greater

than n; and the result of the difference of n-x represents the free hydroxyl groups remaining on the derivatized Cassia backbone.

[0059] The hydrophobically modified cassia galactomannan product obtained in the reactions schematically represented by (X) and (XI) above can be cationically derivatized to obtain the cationically and hydrophobically modified cassia galactomannans of the invention. In one embodiment, the reaction product obtained in reaction scheme (XII) is reacted with a cationic functionalization reagent as follows:

(XII)

OH OH CH2 CH
$$\left(CH_{2}\right)_{m}\left(-O\right)_{b}$$
 $\left(CH_{2}\right)_{m}\left(-O\right)_{b}$ $\left(CH_{2}\right)_{m}\left(-O\right)_{m$

$$\int_{y}^{Q} \left[X^{-} R^{5} R^{4} R^{3} N^{+} - C H_{2}^{-} C H - C H_{2}^{-} O \right] Cassia \left\{ O - C H_{2}^{-} C H + C H_{2}^{-} \right\}_{x} \left(O H_{0 - (x+y)}^{-} \right)$$

wherein R^1 is as previously defined; R^3 , R^4 , and R^5 , independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl groups; X^- represents an anion selected from chloride, bromide, iodide, sulfate, methylsulfate, sulfonate, nitrate, phosphate, and acetate; n represents the number of hydroxyl groups on the cassia galactomannan backbone; c is as previously defined; x represents the average total substitution of the hydrophobic moiety on the galactomannan backbone; y represents the average total cationic substitution on the hydrophobically derivatized cassia galactomannan backbone, wherein the sum of x and y can not be greater than n; and the result of the difference of n-x represents the free hydroxyl groups remaining on the derivatized backbone.

[0060] In one aspect of the invention as set forth in reaction schemes (X) and (XI) depicted above, underivatized Cassia is subjected to an alkylation reaction to obtain a hydrophobically modified product(s). The hydrophobically modified product(s) is subsequently derivatized with a cationic functionalization reagent as set forth in reaction scheme (XII) to obtain the cationically and hydrophobically modified cassia

galactomannan of the invention. As discussed above, will be readily apparent to the artisan of ordinary skill in the art that the cationically and hydrophobically modified cassia galactomannans of the invention can also be prepared by reacting an epoxy group and/or halohydrin containing cationic functionalizing reagent selected from formulae (VI), (VII), (VIII) and (IX) and mixtures thereof with a hydroxyl group(s) on the backbone units of underivatized Cassia galactomannan followed by subsequent alkylation with a hydrophobic functionalization reagent selected from an alkyl halide and/or an epoxy containing alkylation reagent conforming to formulae (IV) and (V). As set forth previously, any of the following reaction schemes can be utilized to synthesize the hydrophobically modified, cationic Cassia galactomannans of the invention (1) alkylation followed by cationization; (2) cationization followed by alkylation; (3) simultaneous alkylation and cationization; (4) a sequential series of alkylation steps followed by a sequential series of cationization steps; (5) a sequential series of cationization steps followed by a sequential series of alkylation steps; (6) alternating alkylation and cationization steps; and (7) any variation of the foregoing procedures. The cationically and hydrophobically modified Cassia galactomannans of this [0061]invention can be employed as deposition aids, film formers, conditioners, fixative agents, emulsifiers, stabilizers, moisturizers, spreading aids and carriers for enhancing the efficacy, deposition or delivery of chemically and physiologically active ingredients and cosmetic materials, and as vehicles for improving the psychosensory, and aesthetic properties of a formulation in which they are included. The cationic character of the cationically and hydrophobically modified Cassia polymers of this invention makes them useful as antistatic agents, and, under certain conditions, may also provide biocidal, bacteriostatic, preservative, and anti-microbial activity. These polymer compositions can be utilized in a variety of products for personal care, health care, household care, institutional and industrial (collectively "I&I") care, and in a variety of products for medical and industrial applications. The hydrophobically modified, cationic Cassia polymer compositions of this invention can be incorporated in compositions that are non-

[0062] Some embodiments of the invention relate to the use of cationically and hydrophobically modified Cassia derivatives as multi-functional polymer ingredients in

alkaline, i.e., acidic to substantially neutral in pH, but are not limited thereto.

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personal care, health care, household, institutional and industrial product applications and the like. The hydrophobically modified, cationic Cassia polymers can be employed as emulsifiers, spreading aids and carriers for enhancing the efficacy, deposition and delivery of chemically and physiologically active ingredients and cosmetic materials, and as a vehicle for improving the psychosensory and aesthetic properties of a formulation in which they are included. The term "personal care products" as used herein includes, without limitation, cosmetics, toiletries, cosmeceuticals, beauty aids, personal hygiene and cleansing products that are applied to the skin, hair, scalp, and nails of humans and animals. The term "health care products" as used herein includes, without limitation, pharmaceuticals, pharmacosmetics, oral care products (mouth, teeth), eye care products, ear care products and over-the-counter products and appliances, such as patches, plasters, dressings and the like. The term also includes medical devices that are externally applied to or into the body of humans and animals for ameliorating a health related or medical condition. The term "body" includes the keratinous (hair, nails) and non-keratinous skin areas of the entire body (face, trunk, limbs, hands and feet), the tissues of body openings and the eyes. The term "skin" includes the scalp and mucous membranes. The term "household care products" as used herein includes, without limitation, products being employed in a household for surface protection and/or cleaning including biocidal cleaning products for maintaining sanitary conditions in the kitchen and bathroom and laundry products for fabric cleaning and the like. The term "institutional and industrial products" as used herein includes, without limitation, products employed for protection and/or cleaning or maintaining sanitary conditions in industrial and institutional environments, including hospitals and health care facilities, and the like.

[0063] The amount of cationically and hydrophobically modified polymer that can be employed depends upon the purpose for which it is included in the formulation and can be readily determined by person skilled in the formulation arts. Thus, as long as the physicochemical and functional properties of the compositions containing the cationically and hydrophobically modified polymer composition are achieved, a useful amount of the polymer, active weight percent, on a total composition weight basis, typically can vary in the range of about 0.01% to about 50%, but is not limited thereto. In a given composition or application, therefore, the cationically and hydrophobically

modified polymer composition of this invention can, but need not, serve more than one function, such as thickener and conditioner, film-former and carrier, and the like, as described in more detail below.

[0064] Compositions containing the cationically and hydrophobically modified Cassia polymer composition of this invention can be packaged and dispensed from containers, such as jars, bottles, tubes, spray bottles, wipes, cans, roll-on containers, stick containers, and the like, without limitation. There is no limitation as to the form of product in which the cationically and hydrophobically modified polymer composition can be incorporated, so long as the purpose for which the product is used is achieved. For example, personal care and health care products containing the cationically and hydrophobically modified polymer composition can be applied to the skin, hair, scalp and nails in the form of, without being limited thereto, gels, sprays (liquid or foam), emulsions (creams, lotions, pastes), liquids (rinses, shampoos), bars, ointments, suppositories, impregnated wipes, patches, and the like.

The cationically and hydrophobically modified compositions of the invention [0065]are suitable for the preparation of personal care (cosmetics, toiletries, cosmeceuticals) and topical health care products, including without limitation, hair care products, such as shampoos (including combination shampoos, such as "two-in-one" conditioning shampoos, and antidandruff shampoos); post-shampoo rinses; setting and style maintenance agents including setting aids, such as gels and sprays, grooming aids, such as pomades, conditioners, perms, relaxers, hair smoothing products, and the like; skin care products (facial, body, hands, scalp and feet), such as creams, lotions, conditioners, and cleansing products; antiacne products; antiaging products (exfoliant, keratolytic, anticellulite, antiwrinkle, and the like); skin protectants such as sunscreens, sunblock, barrier creams, oils, silicones, and the like; skin color products (whiteners, lighteners, sunless tanning accelerators, and the like); hair colorants (hair dyes, hair color rinses, highlighters, bleaches and the like); pigmented skin colorants (face and body makeups, foundation creams, mascara, rouge, lip products, and the like); bath and shower products (body cleansers, body wash, shower gel, liquid soap, soap bars, syndet bars, conditioning liquid bath oil, bubble bath, bath powders, and the like); nail care products (polishes, polish removers, strengtheners, lengtheners, hardeners, cuticle removers, softeners, and

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the like); and any aqueous acidic to substantially neutral to basic composition to which an effective amount of the present polymers can be incorporated for achieving a beneficial or desirable, physical or chemical, effect therein during storage and/or usage.

Toiletries and health and beauty aids, commonly referred to as HBAs, [0066] containing the cationically and hydrophobically modified polymer composition of this invention, can include, without limitation, hair-removal products (shaving creams and lotions, depilatories, after-shave skin conditioners, and the like); deodorants and antiperspirants; oral care products (mouth, teeth and gums), such as mouthwash, dentifrice, such as toothpaste, tooth powder, tooth polishes, tooth whiteners, breath fresheners, denture adhesives, and the like; facial and body hair bleach; and the like. Other health and beauty aids that can contain the present cationically and hydrophobically modified polymers, include, without limitation, sunless tanning applications containing artificial tanning accelerators, such as dihydroxyacetone (DHA), tyrosine, tyrosine esters, and the like; skin depigmenting, whitening, and lightening formulations containing such active ingredients as kojic acid, hydroquinone, arbutin, fruital, vegetal or plant extracts, (lemon peel extract, chamomile, green tea, paper mulberry extract, and the like), ascorbyl acid derivatives (ascorbyl palmitate, ascorbyl stearate, magnesium ascorbyl phosphate, and the like); foot care products, such as keratolytic corn and callous removers, foot soaks, foot powders (medicated, such as antifungal athlete's foot powder, ointments, sprays, and the like, and antiperspirant powders, or non-medicated moisture absorbent powder), liquid foot sprays (nonmedicated, such as cooling, and deodorant sprays, and medicated antifungal sprays, antiperspirant sprays, and the like), and foot and toenail conditioners (lotions and creams, nail softeners, and the like).

[0067] Topical health and beauty aids that can include the cationically and hydrophobically modified polymer composition of this invention (e.g., as spreading aids and film formers) include, without being limited thereto, skin protective spray, cream, lotion, gel, stick and powder products, such as insect repellants, itch relief, antiseptics, disinfectants, sun blocks, sun screens, skin tightening and toning milks, and lotions, wart removal compositions, and the like.

[0068] In a given composition or application, the cationically and hydrophobically modified Cassia polymers of this invention can, but need not, serve more than one function, such as a fixative, thickener, skin and hair conditioner, film former and carrier or deposition aid. In a personal care composition the amount of hydrophobically modified, cationic Cassia polymer that can be employed depends upon the purpose for which they are included in the formulation and can be determined by person skilled in the formulation art. Thus, as long as the desired physicochemical and functional properties are achieved, a useful amount of cationically and hydrophobically modified Cassia polymer on a total composition weight basis, typically can vary in the range of from about 0.01% to about 50% in one aspect of the invention, from about 0.1 wt. % to about 35 wt. % in another aspect, from about 0.2 wt. % to about 25 wt. % in a further aspect, and from 1 to about 10 wt. % in a still further aspect of the invention, based on the total weight of the composition, but is not limited thereto.

[0069] The cationically and hydrophobically modified Cassia polymers of the invention can be employed as conditioners and/or deposition aids in hair fixative and styling shampoo compositions. The cationically and hydrophobically modified Cassia polymer can be used in shampoos and conditioners to facilitate combability. The positively charged nitrogen atom interacts with the negatively charged hair fibers to form films. They also make the hair feel softer and smoother to the touch without creating excessive residual build-up. The cationically and hydrophobically modified Cassia polymers can be used as part of a conditioner package in a conditioning detersive formulation that not only imparts cleansing, wet detangling, dry detangling and manageability attributes to the hair, but also is relatively non-irritating. This composition is thus suitable for use by young children and adults having sensitive skin and eyes. In addition, the cationically and hydrophobically modified Cassia polymer of the present invention has been found to be an excellent deposition aid in the deposition of conditioning and therapeutic agents to the hair.

[0070] As is discussed herein, the cationically and hydrophobically modified Cassia polymers of the present invention permit, facilitate and/or enhance the delivery, deposition and/or activity of one or more active ingredients utilized in a personal care, home care, health care, and institutional care formulations, and for improving the

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psychosensory and aesthetic properties of a topical formulation in which they are included. Examples of such active ingredients include, but are not limited to, caffeine, vitamin C, vitamin D, vitamin E, anti-stretch mark compounds, astringents (e.g., alum, oatmeal, varrow, witch hazel, bayberry, and isopropyl alcohol), draining compounds, hair growth promoting compounds (e.g., monoxidil), skin and hair nourishing compounds, skin and hair protecting compounds, self-tanning compounds (e.g., mono- or polycarbonyl compounds such as, for example, isatin, alloxan, ninhydrin, glyceraldehyde, mesotartaric aldehyde, glutaraldehyde, erythrulose, tyrosine, tyrosine esters, and dihydroxyacetone), sunscreens (e.g., ethylhexyl methoxy cinnamate, octinoxate, octisalate, oxybenzone), skin lighteners (e.g., kojic acid, hydroquinone, arbutin, fruital, vegetal or plant extracts, such as lemon peel extract, chamomile, green tea, paper mulberry extract, and the like, ascorbyl acid derivatives, such as ascorbyl palmitate, ascorbyl stearate, magnesium ascorbyl phosphate, and the like), lip plumping compounds, anti-aging, anti-cellulite, and anti-acne compounds (e.g., acidic agents such as alpha-hydroxy acids (AHAs), beta-hydroxy acids (BHAs), alpha amino-acids, alphaketo acids (AKAs), acetic acid, azelaic acid, and mixtures thereof), anti-dandruff compounds (e.g., zinc pyrithione, zinc omadine, miconazole nitrate, selenium sulfide, piroctone olamine) anti-inflammatory compounds (e.g., aspirin, ibuprofen, and naproxen), analgesics (e.g., acetaminophen), antioxidant compounds, antiperspirant compounds (e.g., aluminum halides, aluminum hydroxyhalides, aluminum sulfate, zirconium (zirconyl) oxyhalides, zirconium (zirconyl) hydroxyhalides, and mixtures or complexes thereof), deodorant compounds (e.g., 2-amino-2-methyl-1-propanol (AMP), ammonium phenolsulfonate; benzalkonium chloride; benzethonium chloride, bromochlorophene, cetyltrimethylammonium bromide, cetyl pyridinium chloride, chlorophyllin-copper complex, chlorothymol, chloroxylenol, cloflucarban, dequalinium chloride, dichlorophene, dichloro-m-xylenol, disodium dihydroxyethyl sulfosuccinylundecylenate, domiphen bromide, hexachlorophene, lauryl pyridinium chloride, methylbenzethonium chloride, phenol, sodium bicarbonate, sodium phenolsulfonate, triclocarban, triclosan, zinc phenolsulfonate, zinc ricinoleate, and mixtures thereof), hair fixative polymers, hair and skin conditioners (e.g., synthetic oils, natural oils, such as vegetable, plant and animal oils, mineral oils, natural and synthetic

waxes, cationic polymers, monomeric and polymeric quaternized ammonium salt compounds, silicones such as silicone oils, resins and gums, proteins, hydrolyzed proteins, fatty acids, fatty amines; and mixtures thereof); and suitable mixtures of two or more of the above.

[0071]The cationically and hydrophobically modified Cassia polymer compositions of this invention are particularly useful as deposition aids for particulates, such as mica, pearlizing agents, beads, and the like, making them suitable for dermal products containing particulates, microabrasives, and abrasives, such as shower gels, masks and skin cleansers containing exfoliating agents. Numerous cosmetically useful particulate exfoliating agents are known in the art, and the selection and amount is determined by the exfoliating effect desired from the use of the composition, as recognized by those skilled in the cosmetic arts. Useful exfoliating agents include, but are not limited to, biological abrasives, inorganic abrasives, synthetic polymers, and the like, and mixtures thereof. Biological abrasives include, without limitation, shell, seed, and kernel or stone granules or powders, obtained from nuts, such as from walnut (Juglans regia) shells, almonds, pecans, and the like; fruit sources, such as apricots, avocados, coconuts, olives, peaches, and the like; vegetal sources, such as corn cob, oat bran, rice, rose hip seed, jojoba (wax, seed powder), microcrystalline cellulose, ground loofa, ground seaweed, and the like; animal sources, such as oyster shell, silk, microcrystalline collagen, and the like. Inorganic abrasives include, without limitation, stannic oxide, talc, silica (hydrated, colloidal and the like), kaolin, precipitated chalk, salts (sodium chloride, dead sea salt, and the like), ground pumice, and the like. Synthetic polymers include, without limitation, microcrystalline polyamides (nylons), microcrystalline polyesters (polycarbonates), and the like.

[0072] The cationically and hydrophobically modified Cassia polymers of this invention are useful as thickeners and film-formers in a variety of dermatological, cosmeceutical compositions employed for topically ameliorating skin conditions caused by drying, photo-damage, aging, acne, and the like, containing conditioners, moisturizers, antioxidants, keratolytic agents, vitamins, and the like, typically containing an active acidic ingredient and having a pH in the range of about 0.5 to about 5.

[0073] In one cosmeceutical aspect, the cationically and hydrophobically modified Cassia polymers of this invention can be employed as a thickener or deposition aid for active skin treatment lotions and creams containing, as active ingredients, acidic antiaging, anti-cellulite, and anti-acne agents, hydroxy carboxylic acids, such as alphahydroxy acid (AHA), beta-hydroxy acid (BHA), alpha-amino acid, alpha-keto acids (AKAs), and mixtures thereof. In such cosmeceuticals, AHAs can include, but are not limited to, lactic acid, glycolic acid, fruit acids, such as malic acid, citric acid, tartaric acid, extracts of natural compounds containing AHA, such as apple extract, apricot extract, and the like, honey extract, 2-hydroxyoctanoic acid, glyceric acid (dihydroxypropionic acid), tartronic acid (hydroxypropanedioic acid), gluconic acid, mandelic acid, benzilic acid, azelaic acid, alpha-lipoic acid, salicylic acid, AHA salts and derivatives, such as arginine glycolate, ammonium glycolate, sodium glycolate, arginine lactate, ammonium lactate, sodium lactate, alpha-hydroxybutyric acid, alphahydroxyisobutyric acid, alpha-hydroxyisocaproic acid, alpha-hydroxyisovaleric acid, atrolactic acid, and the like. BHAs can include, but are not limited to, 3-hydroxy propanoic acid, beta-hydroxybutyric acid, beta-phenyl lactic acid, beta-phenylpyruvic acid, and the like. Alpha-amino acids include, without being limited thereto, alphaamino dicarboxylic acids, such as aspartic acid, glutamic acid, and mixtures thereof, sometimes employed in combination with fruit acid. AKAs include pyruvic acid. In some antiaging compositions, the acidic active agent may be retinoic acid, a halocarboxylic acid, such as trichloroacetic acid, an acidic antioxidant, such as ascorbic acid (vitamin C), a mineral acid, phytic acid, lysophosphatidic acid, and the like. Some acidic anti-acne actives, for example, can include salicylic acid, derivatives of salicylic acid, such as 5-octanoylsalicylic acid, retinoic acid, and its derivatives.

[0074] A discussion of the use and formulation of active skin treatment compositions is in Cosmetics & Toiletries®, C&T Ingredient Resource Series, "AHAs & Cellulite Products How They Work", published 1995, and "Cosmeceuticals", published 1998, both available from Allured Publishing Corporation, incorporated herein by reference. Compositions containing alpha-amino acids acidified with ascorbic acid are described in U.S. No. 6,197,317 B1, and a commercial cosmeceutical preparation utilizing these acids in an anti-aging, skin care regimen is sold under the tradename, AFAs, by exCel

Cosmeceuticals (Bloomfield Hills, MI). The term "AFA", as described in the supplier's trade literature, was coined by the developer to describe the amino acid/vitamin C combination as Amino Fruit Acids and as the acronym for "Amino acid Filaggrin based Antioxidants."

[0075] Other health care products in which the cationically and hydrophobically modified Cassia polymers can be included are medical products, such as topical and nontopical pharmaceuticals, and devices. In the formulation of pharmaceuticals, the cationically and hydrophobically modified polymer composition of this invention can be employed as a thickener and/or lubricant in such products as creams, pomades, gels, pastes, ointments, tablets, gel capsules, purgative fluids (enemas, emetics, colonics, and the like), suppositories, anti-fungal foams, eye products (ophthalmic products, such as eye drops, artificial tears, glaucoma drug delivery drops, contact lens cleaner, and the like), ear products (wax softeners, wax removers, otitis drug delivery drops, and the like), nasal products (drops, ointments, sprays, and the like), and wound care (liquid bandages, wound dressings, antibiotic creams, ointments, and the like), without limitation thereto.

[0076] The film-forming cationically and hydrophobically modified Cassia polymers of this invention make them particularly suitable as a vehicle for topical medical compositions for promoting and enhancing the transdermal delivery of active ingredients to or through the skin, for enhancing the efficacy of anti-acne agents formulations and topical analgesics, and for controlling release of drugs, such as antacids from tablets, or syrups, at low pH, such as in the stomach; controlling drug release from tablets, lozenges, chewables, and the like in the mildly acidic environment of the mouth; or from suppositories, ointments, creams, and the like in the mildly acidic environment of the vagina; to promote deposition of dandruff control agents from shampoos, salves, and the like; to enhance the deposition of colorants on skin from pigmented cosmetics (makeups, lipsticks, rouges, and the like) and on hair from hair dyes, and the like.

[0077] In addition to the foregoing, the cationic character of the Cassia polymers of the present invention and its cationic compatibility, makes the polymer useful as a thickener or deposition aid for antistatic, biocidal, antimicrobial, and other preservative compositions, in a variety of personal care, health care, I&I, and medical applications.

For example, the polymer can be employed as a thickener in over-the-counter (OTC) health care and pharmaceutical products where cationic biocides are typically employed, such as in oral care compositions for plaque and tartar control, and liquid vehicles containing therapeutic agents, such as syrups, gels, and the like. Under certain controlled pH conditions, the cationic character of the hydrophobically modified polymer composition of this invention, itself, may also provide antistatic activity or biocidal, antimicrobial, or like preservative activity.

[0078] The cationically and hydrophobically modified Cassia polymers of the present invention can be employed, without limitation, as a lubricant coating for medical devices, such as soft tissue implants, surgical gloves, catheters, cannulae, and the like, as removable protective film coatings for medical instruments, wound dressings, and the like, as a muco-adhesive, especially in the acid environment of the stomach, as a carrier and thickener in formulated products for medical applications, such as disinfectant hand creams, antiviral products (for anionic viruses), antibiotic ointments, sprays and creams, non-drip, sprayable disinfectant in hospitals, hard surface antimicrobial finish applied during routine maintenance, and the like.

The cationically and hydrophobically modified Cassia polymers of the [0079] present invention can be used in home care, and I&I applications, for example, as a rheology modifier, fabric conditioning agent, antistatic agent, especially to improve formulation efficiency through "cling-on-surface" or improving efficacy of disinfectants, and biocidal formulations, and to synergistically improve fabric softening efficacy in combination with traditional fabric softeners. Typical household and I&I products that may contain polymers of the invention, include, without being limited thereto, laundry and fabric care products, such as detergents, fabric softeners (liquids or sheets), ironing sprays, dry cleaning aids, anti-wrinkle sprays, spot removers and the like; hard surface cleansers for the kitchen and bathroom and utilities and appliances employed or located therein, such as toilet bowl gels, tub and shower cleaners, hard water deposit removers, floor and tile cleansers, wall cleansers, floor and chrome fixture polishes, alkalistrippable vinyl floor cleaners, marble and ceramic cleaners, air freshener gels, liquid cleansers for dishes, and the like; disinfectant cleaners, such as toilet bowl and bidet cleaners, disinfectant hand soaps, room deodorizers, and the like.

[0800] The cationically and hydrophobically modified Cassia polymers of the present invention can be utilized as rheology modifiers, dispersants, stabilizers, promoters, or antimicrobials, and the like, in industrial product applications, such as, without being limited thereto, textiles (processing, finishing, printing, and dyeing aids, protective washable surface coatings, manufacture of synthetic leather by saturation of non-woven fabrics, and the like, manufacturing of woven fabrics, non-woven fabrics, natural and synthetic fibers and the like); water treatments (waste water, cooling water, potable water purification, and the like); chemical spill containments (acid-spill absorbent, and the like); leather and hide processing (processing aids, finishing, coating, embossing, and the like); paper and papermaking (surface coatings, such as pigmented coatings, antistatic coatings, and the like, pulp binders, surface sizings, dry and wet strength enhancers, manufacture of wet-laid felts, and the like); printing (inks, antiwicking ink-jet printer inks, thickeners for ink formulations containing cationic dyes for printing acrylic fabrics, and the like); paints (pigment and grinding additive); industrial plant effluent treatment (flocculants for phenolics in paper mill effluent, and the like); metal working (acid etch cleaners, low pH metal coatings, pickling agents in cold rolled steel processing, and the like); adhesives (clear adhesives, adhesion promoters for metal, plastic, wood, and the like, non-woven floc adhesive tie coatings, bonding, and the like); wood preservation; and industrial construction products for buildings and roads (cement plasticizers, asphalt emulsion stabilizers at low pH, acid etch for cement, consistency modifiers of concrete, mortar, putty, and the like). The polymers of the present invention are particularly useful as thickeners for rust removers, acid truck cleaners, scale removers, and the like, and as dispersion stabilizers of products containing particulates, such as clay, pigments (titanium dioxide, calcium carbonate, and other minerals), abrasives, and the like, employed in a variety of the foregoing industrial applications, and in drilling muds.

[0081] Products comprising the cationically and hydrophobically modified Cassia polymers of the present invention can contain various conventional additives and adjuvants known in the art, some of which can serve more than one function. The amounts employed will vary with the purpose and character of the product and can be readily determined by one skilled in the formulation arts and from the literature. The

term "cosmetic adjuvant" includes cosmetically and pharmaceutically acceptable product stabilizing and product finishing agents that maintain the physical stability of the composition and its visible aesthetic appearance and market appeal during the useful shelf life of the composition.

[0082] The term "fixative" as applied to polymers encompasses the properties of film-formation, adhesion, or coating deposited on a surface on which the polymer is applied. The terms "hair styling, hair setting, and hair fixative" as commonly understood in the hair care arts, and as used herein, refer collectively to hair setting agents that are hair fixatives and film formers and which are topically applied to the hair to actively contribute to the ease of styling and/or holding of a hair set, and to maintain the restylability of the hair set. Hence, hair setting compositions include hair styling, hair fixative, and hair grooming products that conventionally are applied to the hair (wet or dry) in the form of gels, rinses, emulsions (oil-in-water, water-in-oil or multiphase), such as lotions and creams, pomades, sprays (pressurized or non-pressurized), spritzes, foams, such as mousses, shampoos, solids, such as sticks, semisolids and the like, or are applied from a hair setting aid having the hair setting composition impregnated therein or coated thereon, to leave the hair setting agent in contact on the hair for some period until removed, as by washing.

[0083] In one embodiment, hair setting compositions encompasses products comprising at least one cationically and hydrophobically modified polymer of the present invention as a hair setting agent, which are applied to the hair (wet or dry) before, during or after configuring the hair into the shape (curly or straight) desired, without limitation as to product form. The cationically and hydrophobically modified Cassia polymers of the present invention are surprisingly useful in hair setting and hair styling compositions as the sole film-forming, rheology modifying, conditioning fixative agent. The cationically and hydrophobically modified polymers of the present invention are also useful in combination with commercially available auxiliary hair fixative polymers, such as nonionic, cationic, and amphoteric hair setting polymers, cationic conditioning polymers, and combinations thereof.

[0084] Conventional hair fixative and hair styling polymers include natural gums and resins and polymers of synthetic origin. Listings of commercially available hair fixative

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and conditioning fixative polymers can be readily found in the INCI Dictionary, on supplier websites, and in the trade literature. See, for example, the Polymer Encyclopedia published in Cosmetics & Toiletries[®], 117(12), December 2002 (Allured Publishing Corporation, Carol Stream, IL), the relevant disclosures of which are incorporated herein by reference.

Suitable commercially available fixative polymers include, polyacrylates, [0085] polyvinyls, polyesters, polyurethanes, polyamides, polyquaterniums, modified cellulose, starches, and mixtures thereof. These polymers can be nonionic, anionic, cationic and amphoteric in nature and include without limitation one or more of polyoxythylenated vinyl acetate/crotonic acid copolymers, vinyl acetate crotonic acid copolymers, vinyl methacrylate copolymers, monoalkyl esters of poly(methyl vinyl ether (PVM)/maleic acid (MA)), such as, for example, ethyl, butyl and isopropyl esters of PVM/MA copolymer acrylic acid/ethyl acrylate/N-tert-butyl-acrylamide terpolymers, and poly (methacrylic acid/acrylamidomethyl propane sulfonic acid), acrylates copolymer, corn starch modified, sodium polystyrene sulfonate, polyquaterniums such as, for example, Polyquaternium-4, Polyquaternium-11, Polyquaternium-24, Polyquaternium-28, Polyquaternium-29, Polyquaternium-32, Polyquaternium-34, Polyquaternium-37, Polyquaternium-39, Polyquaternium-44, Polyquaternium-46, Polyquaternium-47, Polyquarternium-55, Polyquaternium-69, Polyquaternium-87, polyether-1, polyurethanes, VA/acrylates/lauryl methacrylate copolymer, adipic acid/dimethylaminohydroxypropyl diethylene AMP/acrylates copolymer, methacrylol ethyl betaine/acrylates copolymer, polyvinylpyrrolidone (PVP), vinyl pyrrolidone (VP)/dimethylaminoethylmethacrylate copolymer, VP/methacrylamide/vinyl imidazole copolymer, VP/dimethylaminopropylamine (DMAPA) acrylates copolymer, VP/vinylcaprolactam/DMAPA acrylates copolymer,

VP/dimethylaminoethylmethacrylate copolymer, VP/DMAPA acrylates copolymer, vinyl caprolactam/VP/dimethylaminoethyl methacrylate copolymer, VA/butyl maleate/isobornyl acrylate copolymer, VA/crotonates copolymer, acrylate/acrylamide copolymer, VA/crotonates/vinyl propionate copolymer, VP/vinyl acetate/vinyl propionate terpolymers, VA/crotonates, VP/vinyl acetate copolymer, VP/acrylates copolymer, VA/crotonic acid/vinyl propionate, acrylates/acrylamide,

acrylates/octylacrylamide, acrylates/hydroxyacrylates copolymer, acrylates/hydroxyesteracrylates copolymer, acrylates/stereth-20 methacrylate copolymer, tert-butyl acrylate/acrylic acid copolymer,

diglycol/cyclohexanedimethanol/isophthalates/sulfoisophthalates copolymer, VA/butyl maleate and isobornyl acrylate copolymer, vinylcaprolactam/VP/dimethylaminoethyl methacrylate, VA/alkylmaleate half ester/N-substituted acrylamide terpolymers, vinyl caprolactam/VP/ methacryloamidopropyl trimethylammonium chloride terpolymer, methacrylates/acrylates copolymer/amine salt, polyvinylcaprolactam, polyurethanes, hydroxypropyl guar, poly (methacrylic acid/acrylamidomethyl propane sulfonic acid (AMPSA), ethylenecarboxamide (EC)/AMPSA/methacrylic acid (MAA), poylurethane/acrylate copolymers and hydroxypropyl trimmonium chloride guar, acrylates copolymer, acrylates crosspolymer, AMP-acrylates/allyl methacrylate copolymer, polyacrylate-14, polyacrylate-2 crosspolymer, octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer, acrylates/octylacrylamide copolymer, VA/crotonates/vinyl neodeanoate copolymer, poly(N-vinyl acetamide), poly(N-vinyl formamide), polyurethane, acrylates/lauryl acrylate/stearyl acrylate/ethylamine oxide methacrylate copolymer, methacryloyl ethyl betaines/methacrylates copolymer, corn starch modified, sodium polystyrene sulfonate, polyurethane/acrylates copolymer, pyrrolidone carboxylic acid salt of chitosan, chitosan glycolate, cationic polygalactomannans, such as, for example, quaternized derivatives of guar, such as, for example, guar hydroxypropyl trimmonium chloride and hydroxypropyl guar hydroxypropyl trimmonium chloride. Other suitable auxiliary fixative polymers are disclosed in U.S. Patent No. 7,205,271, the disclosure of which is herein incorporated by reference.

[0086] A fixative polymer typically comprises about 0.01 wt. % to about 25 wt. % in one aspect, from about 0.1 wt. % to about 10 wt. % in another aspect, and about 0.2 wt. % to about 5 wt. % in a further aspect of the total weight of the fixative composition.

[0087] In one embodiment, an exemplary hair care composition comprises a cationically and hydrophobically modified Cassia polymer of the present invention in an amount effective to provide to the hair care composition a property, such as a hair fixative property, a hair conditioning property, a viscid property (thickening, rheology

modifying), or a combination thereof. Optionally, the hair care composition can include one or more of an auxiliary film-forming agent, auxiliary hair-fixative agent, auxiliary hair conditioning agent, auxiliary rheology modifying agent, propellants, and a combination thereof.

[0088] In one embodiment, an exemplary skin care composition comprises a cationically and hydrophobically modified Cassia polymer of the present invention in an amount effective to provide to the skin care composition a property, such as a skin conditioning property, a viscid property (thickening, rheology modifying), or a combination thereof. Optionally, the skin care composition can include one or more auxiliary skin conditioning agent, auxiliary rheology modifying agent, or a mixture thereof.

The term "conditioning agent", and grammatical variations thereof, as it [0089] relates to compositions for skin care and hair care includes cosmetically and pharmaceutically useful materials that can function as humectants, moisturizers, and emollients. It is recognized that some conditioning agents can serve more than one function in a composition, such as an emulsifying agent, a lubricant, and/or a solvent. Conditioning agents include any material which is used to give a particular conditioning benefit to hair and/or skin. In hair treatment compositions, suitable conditioning agents are those which deliver one or more benefits relating to shine, softness, combability, antistatic properties, wet-handling, damage repair, manageability, detangling, body, and lubricity. Suitable conditioning agents for use in personal cleansing compositions are those conditioning agents characterized generally as silicones (e.g. silicone fluids, silicone oils, cationic silicones, silicone gums, high refractive silicones, silicone resins, emulsified silicones, and dimethicone copolyols), organic conditioning oils (e.g. hydrocarbon oils, natural oils, polyolefins, and fatty esters), natural and synthetic waxes, fatty esters, cationic polymers (including polyquaternium polymers), monomeric quaternary ammonium compounds, cationically modified polygalactomannans (e.g., quaternized derivatives of guar and cassia, such as, guar hydroxypropyl trimmonium chloride, hydroxypropyl guar hydroxypropyl trimmonium chloride, and cassia hydroxypropyl trimmonium chloride)., and combinations thereof.

[0090] The cationically and hydrophobically modified Cassia polymers of the present invention are surprisingly compatible with cationic surfactants and other cationic compounds suitable as antistatic agents, such as those employed in hair care, skin care, and fabric care products. The term "antistatic agents" as used herein refers to ingredients that alter the electrical properties of cosmetic raw materials or of human body surfaces (skin, hair, etc.) and textiles, for example, by reducing their tendency to acquire an electrical charge and thus, can condition hair, skin and fabrics. The cationic compatibility of the instant hydrophobically modified polymers makes them suitable for incorporation into formulations containing antistatic agents typically employed in hair care compositions, such as shampoos, post-shampoo conditioning rinses, hair sprays, hair dressings and the like.

[0091]Product formulations comprising a cationically and hydrophobically modified Cassia polymer of this invention can contain various additives and cosmetic adjuvants, conventionally or popularly included in personal care, household care, institutional care, and industrial care products, and in industrial processes, including, without being limited thereto, acidifying or alkalizing pH adjusting agents (neutralizing agents) and buffering agents; auxiliary fixatives and film formers, such as nonionic, anionic, cationic, or amphoteric polymers of synthetic or natural origin, and the like; auxiliary rheology modifiers, such as viscosity-increasing polymeric, gum, or resin thickeners or gellants; additives, such as emulsifiers, emulsion stabilizers, waxes, dispersants, and the like, and viscosity control agents, such as solvents, electrolytes, and the like; auxiliary conditioning agents, such as antistatic agents, synthetic oils, vegetable or animal oils, silicone oils, monomeric or polymeric quaternized ammonium compounds and derivatives thereof, sheen enhancers, moisturizers, emollients, humectants, lubricants, sunscreen agents, and the like; oxidizing agents; reducing agents; surfactants, such as anionic, cationic, nonionic, amphoteric, zwitterionic surfactants, and silicone derivatives thereof; polymer film modifying agents, such as plasticizers, tackifiers, detackifiers, wetting agents, and the like; product stabilizing and finishing agents, such as chelating agents, opacifiers, pearlescing agents, proteinaceous materials and derivatives thereof, vitamins and derivatives thereof, preservatives, fragrances, solubilizers, colorants (temporary or permanent), such as pigments and dyes, UV absorbers, and the like;

propellants (water-miscible or water-immiscible), such as fluorinated hydrocarbons, liquid volatile hydrocarbons, compressed gases, and the like; and mixtures thereof. [0092] Additives and adjuvant ingredients, products, or materials, which may be employed with the inventive cationically and hydrophobically modified polymer composition discussed herein will, in some cases, be referred to by the international nomenclature commonly referred to as INCI name given them in the International Cosmetic Ingredient Dictionary, published by the Personal Care Products Council (formally the Cosmetic, Toiletry, and Fragrance Association), Washington D.C.(hereafter INCI Dictionary), such as can be found in any edition thereof, for example, Volumes 1 and 2, Sixth Edition, (1995) or Volumes 1-3, Seventh and Eighth Editions, (1997, 2000), or by their commonly used chemical names. Numerous commercial suppliers of materials listed by INCI name, trade name or both can be found in the INCI Dictionary and in numerous commercial trade publications, including but not limited to the 2001 McCutcheon's Directories, Volume 1: Emulsifiers & Detergents and Volume 2: Functional Materials, published by McCutcheon's Division, The Manufacturing Confectioner Publishing Co., Glen Rock, NJ (2001); and 2001 Cosmetic Bench Reference, edition of Cosmetics & Toiletries[®], 115 (13), published by Allured Publishing Corporation, Carol Stream, IL (2001); the relevant disclosures of each are incorporated herein by reference. Such components and the formulation of compositions are also described in detail in well known references, such as Cosmetics Science and Technology, First Edition (Sagarin (ed)), published 1957, and Second Edition (Balsam, et al. (eds)), published 1972-74; and The Chemistry and Manufacture of Cosmetics, Second Edition (deNavarre (ed)), published 1975, and Third Edition (Schlossman (ed)), published 2000, both available from Allured Publishing Corporation; Rieger (ed), Harry's Cosmeticology, 8th Edition, Chemical Publishing, Co., Inc., New York, NY (2000); and various formularies available to those skilled in the pharmaceutical arts, such as Remington's Pharmaceutical Sciences, Fourteenth Edition, Mack Publishing Company, Easton, PA (1970); the relevant disclosures of each are incorporated herein by reference.

[0093] It is known that formulated compositions for personal care and topical, dermatological, health care, which are applied to the skin and mucous membranes for

cleansing or soothing, are compounded with many of the same or similar physiologically tolerable ingredients and formulated in the same or similar product forms, differing primarily in the purity grade of ingredient selected, by the presence of medicaments or pharmaceutically accepted compounds, and by the controlled conditions under which products may be manufactured. Likewise, many of the ingredients employed in products for households, and I&I are the same or similar to the foregoing, differing primarily in the amounts and material grade employed. It is also known that the selection and permitted amount of ingredients also may be subject to governmental regulations, on a national, regional, local, and international level. Thus, discussion herein of various useful ingredients for personal care and health care products can apply to household and I&I products and industrial applications.

The choice and amount of ingredients in formulated compositions containing [0094] the cationically and hydrophobically modified Cassia polymers of this invention will vary depending on the product and its function, as is well known to those skilled in the formulation arts. Formulation ingredients for personal care and topical health care products typically can include, but are not limited to, solvents, surfactants (as cleansing agents, emulsifying agents, foam boosters, hydrotropes, solubilizing agents, and suspending agents), fatty acid derived soaps, non-surfactant suspending agents, emulsifiers, skin conditioning agents (emollients, humectants, moisturizers, and the like), hair conditioning agents, hair fixatives, film-formers, skin protectants, binders, chelating agents, antimicrobial agents, antifungal agents, antidandruff agents, abrasives, adhesives, absorbents, dyes, deodorant agents, antiperspirant agents, opacifying and pearlescing agents, antioxidants, preservatives, propellants, spreading aids, sunscreen agents, sunless skin tanning accelerators, ultraviolet light absorbers, pH adjusting agents, botanicals, hair colorants, oxidizing agents, reducing agents, hair and skin bleaching agents, pigments, physiologically active agents, anti-inflammatory agents, topical anesthetics, fragrance and fragrance solubilizers, and the like, in addition to ingredients previously discussed that may not appear herein. Oral care products, for example, can contain anticaries, antitartar and/or anti-plaque agents in addition to surfactants, abrasives, humectants, and flavorants. An extensive listing of substances and their conventional functions and

product categories appears in the INCI Dictionary, generally, and in Vol. 2, Sections 4 and 5 of the Seventh Edition, in particular, incorporated herein by reference.

[0095] The cationically and hydrophobically modified Cassia polymers of the present invention are particularly useful for water-based, solvent based, hydroalcoholic based, and mixed solvent formulations, and for formulations containing water-miscible auxiliary solvents, but are not limited thereto. Useful solvents commonly employed are typically liquids, such as water (deionized, distilled or purified), polyols, and the like, and mixtures thereof. Non-aqueous or hydrophobic auxiliary solvents are commonly employed in substantially water-free products, such as nail lacquers, aerosol propellant sprays, or for specific functions, such as removal of oily soils, sebum, make-up, or for dissolving dyes, fragrances, and the like, or are incorporated in the oily phase of an emulsion. Non-limiting examples of auxiliary solvents, other than water, include linear and branched C₁-C₆ alcohols, such as ethanol, propanol, isopropanol, butanol, hexanol, and mixtures thereof; aromatic alcohols, such as benzyl alcohol, cycloaliphatic alcohols, such as cyclohexanol, and the like; saturated C₁₂-C₃₀ fatty alcohol, such as lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol, and the like. Nonlimiting examples of polyols include polyhydroxy alcohols, such as glycerin, propylene glycol, butylene glycol, hexylene glycol, C2-C4 alkoxylated alcohols and C2-C4 alkoxylated polyols, such as ethoxylated, propoxylated, and butoxylated ethers of alcohols, diols, and polyols having about 2 to about 30 carbon atoms and 1 to about 40 alkoxy units, polypropylene glycol, polybutylene glycol, and the like. Non-limiting examples of non-aqueous auxiliary solvents include silicones, and silicone derivatives, such as cyclomethicone, and the like, aliphatic solvents such as cyclohexane and heptane, ketones such as acetone and methyl ethyl ketone, and mixtures thereof; ethers such as dimethyl ether, dimethoxymethane, and mixtures thereof, natural and synthetic oils and waxes, such as vegetable oils, plant oils, animal oils, essential oils, mineral oils, C₇-C₄₀ isoparaffins, alkyl carboxylic esters, such as ethyl acetate, amyl acetate, ethyl lactate, and the like, jojoba oil, shark liver oil, and the like. Mixtures of the foregoing solvents can also be utilized in combination with the cationically and hydrophobically modified Cassia polymers of the invention. Some of the foregoing non-aqueous auxiliary solvents may also function as conditioners and emulsifiers.

[0096] Surfactants are generally employed as cleansing agents, emulsifying agents, foam boosters, hydrotropes and suspending agents. The cationically and hydrophobically modified Cassia polymers of the present invention may be employed in formulations containing all classes of surfactants, i.e., anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants, and mixtures thereof. The term "amphoteric surfactant" as used herein includes zwitterionic surfactants. In addition to the foregoing references, discussions of the classes of surfactants are in Cosmetics & Toiletries® C&T Ingredient Resource Series, "Surfactant Encyclopedia", 2nd Edition, Rieger (ed), Allured Publishing Corporation (1996); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, published 1949; and Surface Active Agents and Detergents, Volume II, published 1958, Interscience Publishers; each incorporated herein by reference.

[0097] Surprisingly, the cationically and hydrophobically modified Cassia polymers of the present invention are useful as thickeners and deposition aids in compositions containing a relatively high concentration (about 10-40 weight percent) of anionic surfactant, such as shampoos and two-in-one type liquid conditioning/cleansers for hair and body (bath) products.

[0098] Anionic surfactants include substances having a negatively charged hydrophobe or that carry a negative charge when the pH is elevated to neutrality or above, such as acylamino acids, and salts thereof, for example, acylglutamates, acyl peptides, sarcosinates, and taurates; carboxylic acids, and salts thereof, for example, alkanolic acids and alkanoates, ester carboxylic acids, and ether carboxylic acids; phosphoric acid ester and salts thereof; sulfonic acids and salts thereof, for example, acyl isethionates, alkylaryl sulfonates, alkyl sulfonates, and sulfosuccinates; and sulfuric acid esters, such as alkyl ether sulfates and alkyl sulfates.

[0099] Non-limiting examples of anionic surfactants include mono-basic salts of acylglutamates that are slightly acidic in aqueous solution, such as sodium acylglutamate and sodium hydrogenated tallow glutamate; salts of acyl-hydrolyzed protein, such as potassium, palmitoyl hydrolyzed milk protein, sodium cocoyl hydrolyzed soy protein, and TEA-abietoyl hydrolyzed collagen; salts of acyl sarcosinates, such as ammonium myristoyl sarcosine, sodium cocoyl sarcosinate, and TEA-lauroyl sarcosinate; salts of

sodium methyl acyltaurates, such as sodium lauroyl taurate and sodium methyl cocoyl taurate; alkanoic acids and alkanoates, such as fatty acids derived from animal and vegetable glycerides that form water-soluble soaps and water-insoluble emulsifying soaps, including sodium stearate, aluminum stearate, and zinc undecylenate; ester carboxylic acids, such as dinonoxynol-9-citrate; salts of acyl lactylates such as calcium stearoyl lactylate and laureth-6 citrate; ethercarboxylic acids derived from ethyoxylated alcohols or phenols having varying lengths of polyoxyethylene chains, such as nonoxynol-8 carboxylic acid, and sodium trideceth-13 carboxylate; mono- and di-esters of phosphoric acid and their salts, such as phospholipids, dilaureth-4-phosphate, DEA-oleth-10 phosphate and triethanolamine lauryl phosphate; salts of acylisethionate, such as sodium cocoyl isethionate; alkylarylbenzene sulfonates, such as alpha-olefin sulfonate (AOS) and alkali metal, alkaline earth metal, and alkanolamine salts thereof, and sodium dodecylbenzene sulfonate; alkyl sulfonates, such as sodium C₁₂-C₁₄ olefin sulfonate, sodium cocomonoglyceride sulfonate, sodium C₁₂-C₁₅ pareth-15 sulfonate, and sodium lauryl sulfoacetate; sulfosuccinates, such as mono- and di-esters of sulfosuccinic acid, salts thereof and alkoxylated alkyl and alkylamido derivatives thereof, such as di-C₄-C₁₀ alkyl sodium sulfosuccinate, disodium laureth sulfosuccinate, disodium oleamido MEA-sulfosuccinate, and disodium C₁₂-C₁₅ pareth sulfosuccinate; alkyl ether sulfates, such as sodium and ammonium lauryl ether sulfate (having about 1 to about 12 moles ethylene oxide); alkyl sulfates, such as sodium, ammonium and triethanolamine salts of C₁₂-C₁₈ alkylsulfates, sodium C₁₂-C₁₄ olefin sulfates, sodium laureth-6 carboxylate, sodium C_{12} - C_{18} pareth sulfate, and the like.

[0100] Cationic surfactants can have a hydrophobe that carries a positive charge or that is uncharged at pH values close to neutral or lower, such as alkylamines, alkyl imidazolines, ethoxylated amines, and quaternary ammonium compounds. Cationic surfactants used in cosmetics are preferably N-derivatives and the neutralizing anion may be inorganic or organic. Among the quaternary ammonium compounds useful as surfactants correspond to the general formula: (R¹⁰R¹¹R¹²R¹³N⁺) E⁻, wherein each of R¹⁰, R¹¹, R¹², and R¹³ are independently selected from an aliphatic group having from 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having 1 to about 22 carbon atoms in the alkyl

chain; and E⁻ is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfate, and alkylsulfate. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, ester linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated.

[0101]Alkylamine surfactants can be salts of primary, secondary and tertiary fatty C₁₂-C₂₂ alkylamines, substituted or unsubstituted, and substances sometimes referred to as "amidoamines". Non-limiting examples of alkylamines and salts thereof include dimethyl cocamine, dimethyl palmitamine, dioctylamine, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated stearylamine, dihydroxy ethyl stearylamine, arachidylbehenylamine, dimethyl lauramine, stearylamine hydrochloride, soyamine chloride, stearylamine formate, N-tallowpropane diamine dichloride, and amodimethicone (INCI name for a silicone polymer and blocked with amino functional groups, such as aminoethylamino propylsiloxane). Non-limiting examples of amidoamines and salts thereof include stearamido propyl dimethyl amine, stearamidopropyl dimethylamine citrate, palmitamidopropyl diethylamine, and cocamidopropyl dimethylamine lactate. Other cationic surfactants include distearyldimonium chloride, dicetyldimonium chloride, guar hydroxypropyltrimonium chloride, and the like. At low pH, amine oxides may protonate and behave similarly to N-alkyl amines.

[0102] Non-limiting examples of alkyl imidazoline surfactants include alkyl hydroxyethyl imidazoline, such as stearyl hydroxyethyl imidazoline, coco hydroxyethyl imidazoline, ethyl hydroxymethyl oleyl oxazoline, and the like. Non-limiting examples of ethyoxylated amines include PEG-cocopolyamine, PEG-15 tallow amine, quaternium-52, and the like.

[0103] Nonionic surfactants are generally uncharged amphiphiles and usually are alkoxylated to varying degrees. Classes of nonionic surfactants include alcohols, alkanolamides, amine oxides, esters, and ethers. Nonionic alcohols are usually hydroxy derivatives of long-chain C_8 - C_{18} alkane hydrocarbons, such as cetearyl alcohol,

hydrogenated tallow alcohol, lanolin alcohols, alkanolamides, and the like.

Alkanolamides contain at least one alkoxyl or one polyoxyethylene grouping and include alkanol-derived amides, such as acylamide DEA, N-alkyl pyrrolidone, palmamide MEA, peanutamide MIPA, and the like and ethoxylated amides, such as PEG-50 tallow amide. Amine oxides include alkylamine oxides, such as lauramine oxide; and acylamidopropyl morpholine oxides, such as cocamidopropylamine oxide; and the like. Esters include ethoxylated carboxylic acids, such as PEG-8 dilaurate, PEG-8 laurate, and the like; ethoxylated glycerides, such as PEG-4 castor oil, PEG-120 glyceryl stearate, triolein PEG-6 esters, and the like; glycol esters and derivatives thereof, such as glycol stearate SE, propylene glycol ricinoleate, and the like; monoglycerides, such as glyceryl myristate, glyceryl palmitate lactate, and the like; polyglyceryl esters, such as polyglyceryl-6-distearate, polyglyceryl-4 oleyl ether, and the like, polyhydric alcohol esters and ethers, such as methyl gluceth-20 sesquistearate, sucrose distearate; and the like; sorbitan/sorbitol esters, such as polysorbate-60, sorbitan sequiisostearate, and the like; and triesters of phosphoric acid, such as trideceth-3 phosphate, trioleth-8 phosphate, and the like. Ethers include ethoxylated alcohols, such as ceteareth-10, nonoxynol-9, and the like; ethoxylated lanolin, such as PEG-20 lanolin, PPG-12-PEG-65 lanolin oil, and the like; ethoxylated polysiloxanes, such as dimethicone copolyol, and the like; propoxylated POE ethers, such as meroxapol 314, poloxamer 122, PPG-5-ceteth-20, and the like; and alkyl polyglycosides, such as lauryl glucose, and the like.

[0104] Nonionic surfactants can be used as emulsifiers, suspending agents, solubilizers, foam boosters, and in some cases, as hydrotropes. Non-limiting examples of suitable nonionic surfactants include linear or branched alcohol ethoxylates, C₈-C₁₂ alkylphenol alkoxylates, such as octylphenol ethoxylates, polyoxyethylene polyoxypropylene block copolymers, and the like; C₈-C₂₂ fatty acid esters of polyoxyethylene glycol mono- and di-glycerides; sorbitan esters and ethoxylated sorbitan esters; C₈-C₂₂ fatty acid glycol esters; block copolymers of ethylene oxide and propylene oxide; and the like. Non-limiting examples of surfactant foam boosters or hydrotropes include alkanolamides, such as acetamide MEA, monoethanolamide, diethanolamide, cocamide DEA, isopropanolamide, and the like; amine oxides, such as hydrogenated

tallowamine oxide; short chain alkyl aryl sulfonates, such as sodium toluene sulfonate; sulfosuccinates, such as disodium stearyl sulfosuccinate; and the like.

[0105] Amphoteric and zwitterionic surfactants are those compounds that have the capacity of behaving either as an acid or a base, by carrying a positive charge in strongly acidic media, carrying a negative charge in strongly basic media, and forming zwitterionic species at intermediate pH. The major classes of amphoteric surfactants are acyl/dialkyl ethylenediamines and derivatives thereof, such as disodium cocoamphocarboxymethylhydroxy-propyl sulfate, disodium cocamphodipropionate, sodium cocoamphoacetate, sodium lauroampho PG-acetatephosphate, sodium tallowamphopropionate, sodium undecylenoamphopropionate, and the like; and N-alkylamino acids, such as aminopropyl laurylglutamide, dihydroxyethyl soya glycinate, lauraminopropionic acid, and the like.

[0106] Some suitable zwitterionic surfactants for use in the present compositions include those broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, wherein which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains about 8 to about 18 carbon atoms and another substituent contains an anionic water-solubilizing group, such as carboxy, sulfonate, sulfate, phosphate, phosphonate, and the like. Classes of zwitterionics include alkylamino sulfonates, alkyl betaines and alkylamido betaines, such as stearamidopropyldimethylamine, diethylaminoethylstearamide, dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (5 moles ethylene oxide) stearylamine, dihydroxy ethyl stearylamine, arachidylbehenylamine, and the like. Some suitable betaine surfactants include but are not limited to alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines, alkyl glycinates, alkyl carboxyglycinates, alkyl amphopropionates, alkyl amidopropyl hydroxysultaines, acyl taurates, and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 18 carbon atoms. Nonlimiting examples of amphoteric surfactants include cocamidopropyl betaine, sodium cocoamphoacetate, cocamidopropyl hydroxysultaine, and sodium cocoamphopropionate, which are particularly suitable as mild-type cleansers for skin and hair.

[0107] Suitable fatty acid soaps include the sodium, potassium, ammonium, and triethanolamine salts of a saturated and unsaturated fatty acid containing from about 8 to about 22 carbon atoms. In another aspect of the invention the liquid soap composition contains at least one fatty acid soap containing from about 12 to about 18 carbon atoms. The fatty acids utilized in the soaps can be saturated and unsaturated and can be derived from synthetic sources, as well as from the hydrolysis of fats and natural oils. The fatty acid soaps are derived from a fatty acid that contains from about 8 to about 22 carbon atoms. Exemplary saturated fatty acids include but are not limited to octanoic, decanoic, lauric, myristic, pentadecanoic, palmitic, margaric, steric, isostearic, nonadecanoic, arachidic, behenic, and the like, and mixtures thereof. Exemplary unsaturated fatty acids include but are not limited to myristoleic, palmitoleic, oleic, linoleic, linolenic, and the like, and mixtures thereof. The fatty acids can be derived from animal fat such as tallow or from vegetable oil such as coconut oil, red oil, palm kernel oil, palm oil, cottonseed oil, olive oil, soybean oil, peanut oil, corn oil, and mixtures thereof.

[0108] The soap can be prepared by a variety of well known means such as by the direct neutralization of a fatty acid or mixtures thereof or by the saponification of suitable fats and natural oils or mixtures thereof with a suitable base. Exemplary bases included ammonium hydroxide, potassium hydroxide, potassium carbonate, sodium hydroxide and triethanolamine.

[0109] Exemplary emulsifiers include but are not limited to C₁₂-C₁₈ fatty alcohols; alkoxylated C₁₂-C₁₈ fatty alcohols; C₁₂-C₁₈ fatty acids; and alkoxylated C₁₂-C₁₈ fatty acids, the alkoxylates each having 10 to 30 units of ethylene oxide, propylene oxide, and combinations of ethylene oxide/propylene oxide; C₈-C₂₂ alkyl mono- and oligoglycosides; ethoxylated sterols; partial esters of polyglycerols; esters and partial esters of polyols having 2 to 6 carbon atoms and saturated and unsaturated fatty acids having 12 to 30 carbon atoms; partial esters of polyglycerols; and organosiloxanes; and combinations thereof.

[0110] The fatty alcohols, acids and alkoxylated fatty alcohols and fatty acids are as described in the emollient description above. In one aspect of the invention, the fatty alcohols and fatty acids each are ethoxylated with 10 to 30 units of ethylene oxide.

[0111] The C₈-C₂₂ alkyl mono- and oligoglycoside emulsifiers are prepared by reacting glucose or an oligosaccharide with primary fatty alcohols having 8 to 22 carbon atoms. Products which are obtainable under the trademark Plantacare[®] comprise a glucosidically bonded C₈-C₁₆ alkyl group on an oligoglucoside residue whose average degree of oligomerization is 1 to 2. Exemplary alkyl glucosides and oligoglycosides are selected from octyl glucoside, decyl glucoside, lauryl glucoside, palmityl glucoside, isostearyl glucoside, stearyl glucoside, arachidyl glucoside and behenyl glucoside, and mixtures thereof.

[0112] Exemplary ethoxylated sterols include ethoxylated vegetable oil sterols such as, for example, soya sterols. The degree of ethoxylation is greater than about 5 in one aspect, and at least about 10 in another aspect. Suitable ethoxylated sterols are PEG-10 Soy Sterol, PEG-16 Soy Sterol and PEG-25 Soy Sterol.

[0113] The partial esters of polyglycerols have 2 to 10 glycerol units and are esterified with 1 to 4 saturated or unsaturated, linear or branched, optionally hydroxylated C₈-C₃₀ fatty acid residues. Representative partial esters of polyglycerols include diglycerol monocaprylate, diglycerol monocaprate, diglycerol monolaurate, triglycerol monocaprylate, triglycerol monocaprate, triglycerol monolaurate, tetraglycerol monocaprylate, tetraglycerol monocaprate, tetraglycerol monolaurate, pentaglycerol monocaprylate, pentaglycerol monocaprate, pentaglycerol monolaurate, hexaglycerol monocaprylate, hexaglycerol monocaprate, hexaglycerol monolaurate, hexaglycerol monomyristate, hexaglycerol monostearate, decaglycerol monocaprylate, decaglycerol monocaprate, decaglycerol monolaurate, decaglycerol monomyristate, decaglycerol monoisostearate, decaglycerol monostearate, decaglycerol monooleate, decaglycerol monohydroxystearate, decaglycerol dicaprylate, decaglycerol dicaprate, decaglycerol dilaurate, decaglycerol dimyristate, decaglycerol diisostearate, decaglycerol distearate, decaglycerol dioleate, decaglycerol dihydroxystearate, decaglycerol tricaprylate, decaglycerol tricaprate, decaglycerol trilaurate, decaglycerol trimyristate, decaglycerol triisostearate, decaglycerol tristearate, decaglycerol trioleate, decaglycerol trihydroxystearate, and mixtures thereof.

[0114] The saturated C_{12} - C_{30} fatty alcohol emulsifiers are as described in the emollient description set forth above. In one aspect of the invention, the fatty alcohol

emulsifier is selected from but not limited to cetyl alcohol, stearyl alcohol, arachidyl alcohol, behenyl alcohol and lanolin alcohol or mixtures of these alcohols, and as are obtainable in the hydrogenation of unsaturated vegetable oil and animal fatty acids.

- [0115] Emulsifiers based on the esters and partial esters of polyols having 2 to 6 carbon atoms and linear saturated and unsaturated fatty acids having 12 to 30 carbon atoms are, for example, the monoesters and diesters of glycerol or ethylene glycol or the monoesters of propylene glycol with saturated and unsaturated C_{12} - C_{30} fatty acids.
- **[0116]** The partially esterified polyglycerol emulsifiers include 2 to about 10 glycerol units and esterified with 1 to 5 saturated or unsaturated, linear or branched, optionally hydroxylated C_8 - C_{30} fatty acid residues.
- [0117] In one aspect of the invention, the emulsifier can be present in an amount ranging from about 0.5 wt. % to about 12 wt. %, from about 1 wt. % to about 15 wt. % in another aspect, and from about 5 wt. % to about 10 wt. % in a further aspect, based on the total weight of the personal care, home care, health care, and institutional care composition in which they are included.
- [0118] Suitable emollients include but are not limited to an emollient selected from silicone fluids (e.g., volatile silicone oils and non-volatile silicone oils described below); mineral oils; petrolatums; vegetable oils; fish oils; fatty alcohols; fatty acids; fatty acid and fatty alcohol esters; alkoxylated fatty alcohols; alkoxylated fatty acid esters; benzoate esters; Guerbet esters; alkyl ether derivatives of polyethylene glycols, such as, for example methoxypolyethylene glycol (MPEG); and polyalkylene glycols; lanolin and lanolin derivatives; and the like.
- [0119] Mineral oils and petrolatums include cosmetic, USP and NF grades and are commercially available from Penreco under the Drakeol[®] and Penreco[®] trade names. Mineral oil includes hexadecane and paraffin oil.
- [0120] Suitable fatty alcohol emollients include but are not limited to fatty alcohols containing 8 to 30 carbon atoms. Exemplary fatty alcohols include capryl alcohol, pelargonic alcohol, capric alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, isocetyl alcohol, stearyl alcohol, isostearyl alcohol, cetearyl alcohol, oleyl alcohol, ricinoleyl alcohol, arachidyl alcohol, icocenyl alcohol, behenyl alcohol, and mixtures thereof.

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[0121] Suitable fatty acid emollients include but are not limited to fatty acids containing 10 to 30 carbon atoms. Exemplary fatty acids are selected from capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, arachidic acid, behenic acid, and mixtures thereof.

[0122] Exemplary of the fatty acid and fatty alcohol ester emollients include but are not limited to hexyl laurate, decyl oleate, isopropyl stearate, isopropyl isostearate, butyl stearate, octyl stearate, cetyl stearate, myristyl myristate, octyldodecyl stearoylstearate, octylhydroxystearate, diisopropyl adipate, isopropyl myristate, isopropyl palmitate, ethyl hexyl palmitate, isodecyl oleate, isodecyl neopentanoate, diisopropyl sebacate, isostearyl lactate, lauryl lactate, diethyl hexyl maleate, PPG-14 butyl ether and PPG-2 myristyl ether propionate, cetearyl octanoate, and mixtures thereof.

Alkoxylated fatty alcohol emollients are ethers formed from the reaction of a [0123]fatty alcohol with an alkylene oxide, generally ethylene oxide or propylene oxide. Suitable ethoxylated fatty alcohols are adducts of fatty alcohols and polyethylene oxide. In one aspect of the invention, the ethoxylated fatty alcohols can be represented by the formula R'-(OCH₂CH₂)_{n'}-OH, wherein R' represents the aliphatic residue of the parent fatty alcohol and n represents the number of molecules of ethylene oxide. In another aspect of the invention, R' is derived from a fatty alcohol containing 8 to 30 carbon atoms. In one aspect, n' is an integer ranging from 2 to 50, 3 to 25 in another aspect, and 3 to 10 in a further aspect. In a still further aspect, R' is derived from a fatty alcohol emollient set forth above. Exemplary ethoxylated fatty alcohols are but are not limited to capryl alcohol ethoxylate, lauryl alcohol ethoxylate, myristyl alcohol ethoxylate, cetyl alcohol ethoxylate, stearyl alcohol ethoxylate, cetearyl alcohol ethoxylate oleyl alcohol ethoxylate, and, behenyl alcohol ethoxylate, wherein the number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 150 in another aspect. It is to be recognized that the propoxylated adducts of the foregoing fatty alcohols and mixed ethoxylated/propoxylated adducts of the foregoing fatty alcohols are also contemplated within the scope of the invention. The ethylene oxide and propylene oxide units of the ethoxylated/propoxylated fatty alcohols can be arranged in random or in blocky order.

[0124] More specific examples of ethoxylated alcohols are but are not limited to Beheneth 5-30 (the 5-30 meaning the range of repeating ethylene oxide units), Ceteareth 2-100, Ceteth 1-45, Cetoleth 24-25, Choleth 10-24, Coceth 3-10, C9-11 pareth 3-8, C11-15 Pareth 5-40, C11-21 Pareth 3-10, C12-13 Pareth 3-15, Deceth 4-6, Dodoxynol 5-12, Glycereth 7-26, Isoceteth 10-30, Isodeceth 4-6, Isolaureth 3-6, isosteareth 3-50, Laneth 5-75, Laureth 1-40, Nonoxynol 1-120, Nonylnonoxynol 5-150, Octoxynol 3-70, Oleth 2-50, PEG 4-350, Steareth 2-100, and Trideceth 2-10.

[0125] Specific examples of propoxylated alcohols are but are not limited to PPG-10 Cetyl Ether, PPG-20 Cetyl Ether, PPG-28 Cetyl Ether, PPG-30 Cetyl Ether, PPG-50 Cetyl Ether, PPG-2 Lanolin Alcohol Ether, PPG-5 Lanolin Alcohol Ether, PPG-10 Lanolin Alcohol Ether, PPG-20 Lanolin Alcohol Ether, PPG-30 Lanolin Alcohol Ether, PPG-4 Lauryl Ether, PPG-7 Lauryl Ether, PPG-10 Oleyl Ether, PPG-20 Oleyl Ether, PPG-23 Oleyl Ether, PPG-30 Oleyl Ether, PPG-37 Oleyl Ether, PPG-50 Oleyl Ether, PPG-11 Stearyl Ether, PPG-15 Stearyl Ether, PPG-2 Lanolin Ether, PPG-5 Lanolin Ether, PPG-10 Lanolin Ether, PPG-20 Lanolin Ether, PPG-30 Lanolin Ether, and PPG-1 Myristyl Ether.

Specific examples of ethoxylated/propoxylated alcohols are but are not [0126]limited to PPG-1 Beheneth-15, PPG-12 Capryleth-18, PPG-2-Ceteareth-9, PPG-4-Ceteareth-12, PPG-10-Ceteareth-20, PPG-1-Ceteth-1, PPG-1-Ceteth-5, PPG-1-Ceteth-10, PPG-1-Ceteth-20, PPG-2-Ceteth-1, PPG-2-Ceteth-5, PPG-2-Ceteth-10, PPG-2-Ceteth-20, PPG-4-Ceteth-1, PPG-4-Ceteth-5, PPG-4-Ceteth-10, PPG-4-Ceteth-20, PPG-5-Ceteth-20, PPG-8-Ceteth-1, PPG-8-Ceteth-2, PPG-8-Ceteth-5, PPG-8-Ceteth-10, PPG-8-Ceteth-20, PPG-2 C12-13 Pareth-8, PPG-2 C12-15 Pareth-6, PPG-4 C13-15 Pareth-15, PPG-5 C9-15 Pareth-6, PPG-6 C9-11 Pareth-5, PPG-6 C12-15 Pareth-12, PPG-6 C12-18 Pareth-11, PPG-3 C12-14 Sec-Pareth-7, PPG-4 C12-14 Sec-Pareth-5, PPG-5 C12-14 Sec-Pareth-7, PPG-5 C12-14 Sec-Pareth-9, PPG-1-Deceth-6, PPG-2-Deceth-3, PPG-2-Deceth-5, PPG-2-Deceth-7, PPG-2-Deceth-10, PPG-2-Deceth-12, PPG-2-Deceth-15, PPG-2-Deceth-20, PPG-2-Deceth-30, PPG-2-Deceth-40, PPG-2-Deceth-50, PPG-2-Deceth-60, PPG-4-Deceth-4, PPG-4-Deceth-6, PPG-6-Deceth-4, PPG-6-Deceth-9, PPG-8-Deceth-6, PPG-14-Deceth-6, PPG-6-Decyltetradeceth-12, PPG-6-Decyltetradeceth-20, PPG-6-Decyltetradeceth-30, PPG-13-Decyltetradeceth-24, PPG-20-Decyltetradeceth-10,

PPG-2-Isodeceth-4, PPG-2-Isodeceth-6, PPG-2-Isodeceth-8, PPG-2-Isodeceth-9, PPG-2-Isodeceth-10, PPG-2-Isodeceth-12, PPG-2-Isodeceth-18, PPG-2-Isodeceth-25, PPG-4-Isodeceth-10, PPG-12-Laneth-50, PPG-2-Laureth-5, PPG-2-Laureth-8, PPG-2-Laureth-12, PPG-3-Laureth-8, PPG-3-Laureth-10, PPG-3-Laureth-12, PPG-4-Laureth-12, PPG-4-Laureth-15, PPG-4-Laureth-15, PPG-4-Laureth-15, PPG-5-Laureth-5, PPG-6-Laureth-3, PPG-25-Laureth-25, PPG-7-Lauryl Ether, PPG-3-Myreth-3, PPG-3-Myreth-11, PPG-20-PEG-20 Hydrogenated Lanolin, PPG-2-PEG-11 Hydrogenated Lauryl Alcohol Ether, PPG-12-PEG-50 Lanolin, PPG-12-PEG-65 Lanolin Oil, PPG-40-PEG-60 Lanolin Oil, PPG-1-PEG-9 Lauryl Glycol Ether, PPG-3-PEG-6 Oleyl Ether, PPG-23-Steareth-34, PPG-30 Steareth-4, PPG-34-Steareth-3, PPG-38 Steareth-6, PPG-1 Trideceth-6, PPG-4 Trideceth-6, and PPG-6 Trideceth-8.

Alkoxylated fatty acid emollients are formed when a fatty acid is reacted with [0127]an alkylene oxide or with a pre-formed polymeric ether. The resulting product may be a monoester, diester, or mixture thereof. Suitable ethoxylated fatty acid ester emollients suitable for use in the present invention are products of the addition of ethylene oxide to fatty acids. The product is a polyethylene oxide ester of a fatty acid. In one aspect of the invention, the ethoxylated fatty acid esters can be represented by the formula R"-C(O)O(CH₂CH₂O)_n"-H, wherein R" represents the aliphatic residue of a fatty acid and n represents the number of molecules of ethylene oxide. In another aspect, n" is an integer ranging from 2 to 50, 3 to 25 in another aspect, and 3 to 10 in a further aspect. In still another aspect of the invention, R" is derived from a fatty acid containing 8 to 24 carbon atoms. In a still further aspect, R" is derived from a fatty acid emollient set forth above. It is to be recognized that propoxylated and ethoxylated/propoxylated products of the foregoing fatty acids are also contemplated within the scope of the invention. Exemplary alkoxylated fatty acid esters include but are not limited to capric acid ethoxylate, lauric acid ethoxylate, myristic acid ethoxylate, stearic acid ethoxylate, oleic acid ethoxylate, coconut fatty acid ethoxylate, and polyethylene glycol 400 propoxylated monolaurate, wherein the number of ethylene oxide units in each of the foregoing ethoxylates can range from 2 and above in one aspect, and from 2 to about 50 in another aspect. More specific examples of ethoxylated fatty acids are PEG-8 distearate (the 8 meaning the number of repeating ethylene oxide units), PEG-8 behenate, PEG-8 caprate, PEG-8

caprylate, PEG-8 caprylate/caprate, PEG cocoates (PEG without a number designation meaning that the number of ethylene oxide units ranges from 2 to 50), PEG-15 dicocoate, PEG-2 diisononanoate, PEG-8 diisostearate, PEG-dilaurates, PEG-dioleates PEG-distearates, PEG-ditallates, PEG-isostearates, PEG-jojoba acids, PEG-laurates, PEG-linolenates, PEG-myristates, PEG-oleates, PEG-palmitates, PEG-ricinoleates, PEG-stearates, PEG-tallates, and the like.

[0128] Guerbet ester emollients are formed from the esterification reaction of a Guerbet alcohol with a carboxylic acid. Guerbet ester emollients are commercially available from the Noveon Consumer Specialties Division of Lubrizol Advanced Materials, Inc. under product designations G-20, G-36, G-38, and G-66.

[0129] Lanolin and lanolin derivatives are selected from lanolin, lanolin wax, lanolin oil, lanolin alcohols, lanolin fatty acids, alkoxylated lanolin, isopropyl lanolate, acetylated lanolin alcohols, and combinations thereof. Lanolin and lanolin derivatives are commercially available from the Noveon Consumer Specialties Division of Lubrizol Advanced Materials, Inc. under the trade names Lanolin LP 108 USP, Lanolin USP AAA, AcetulanTM, CeralanTM, LanocerinTM, LanogelTM (product designations 21 and 41), LanogeneTM, ModulanTM, OhlanTM, SolulanTM (product designations 16, 75, L-575, 98, and C-24), VilvanolinTM (product designations C, CAB, L-101, and P).

[0130] The emollient(s) can be utilized in an amount ranging from about 0.5 wt. % to about 30 wt. % by weight of the total personal care composition in one aspect 0.1 wt. % to 25 wt. % in another aspect, and 5 wt. % to 20 wt. % in a further aspect. While emollients are generally employed in personal care compositions, they can be employed in home care, health care, and institutional care compositions in the same wt. ratios as set forth for personal care compositions so long as they effect a desired physical attribute (e.g., humectant properties) in such compositions.

[0131] Suitable humectants include allantoin, pyrrolidonecarboxylic acid and its salts, hyaluronic acid and its salts, sorbic acid and its salts, urea, lysine, arginine, cystine, guanidine, and other amino acids, polyhydroxy alcohols such as glycerin, propylene glycol, hexylene glycol, hexanetriol, ethoxydiglycol, dimethicone copolyol, and sorbitol, and the esters thereof, polyethylene glycol, glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium), lactic acid and lactate salts (e.g.

ammonium and quaternary alkyl ammonium), sugars and starches, sugar and starch derivatives (e.g. alkoxylated glucose), panthenols such as dl-panthenol, lactamide monoethanolamine, acetamide monoethanolamine, and the like, and mixtures thereof. In one embodiment, the humectants include the C₃-C₆ diols and triols, such as glycerin, propylene glycol, hexylene glycol, hexanetriol, and the like, and mixtures thereof. Such suitable humectants typically comprise about 1 wt. % to about 10 wt. % in one aspect, from about 2 wt. % to about 8 wt. % in another aspect, and from about 3 wt. % to about 5 wt. % in a further aspect, based on the total weight of the personal care compositions of the present invention.

[0132] Antistatic agents include, but are not limited to proteins and protein derivatives, quaternary ammonium compounds (monomeric and polymeric), amines, protonated amine oxides, betaines, and the like. While various quaternary ammonium compounds are listed for a specific purpose, one of ordinary skill will recognize that the quaternary ammonium compounds described here and throughout the specification can serve more than one function and can be used as surfactants, conditioners, and antimicrobial agents in addition to the antistatic utilities discussed herein.

Protein derivatives include cocodimonium hydroxypropyl hydrolyzed casein, [0133]cocodimonium hydroxypropyl hydrolyzed collagen, cocodimonium hydroxypropyl hydrolyzed hair keratin, cocodimonium hydroxypropyl hydrolyzed rice protein, cocodimonium hydroxypropyl hydrolyzed silk, cocodimonium hydroxypropyl hydrolyzed soy protein, cocodimonium hydroxypropyl hydrolyzed wheat protein, cocodimonium hydroxypropyl hydrolyzed silk amino acids, hydroxypropyl trimonium hydrolyzed collagen, hydroxypropyl trimonium hydrolyzed keratin, hydroxypropyl trimonium hydrolyzed silk, hydroxypropyl trimonium hydrolyzed rice bran, hydroxypropyl trimonium hydrolyzed soy protein, hydroxypropyl trimonium hydrolyzed vegetable protein, hydroxypropyl trimonium hydrolyzed wheat protein, hydrolyzed wheat protein, hydrolyzed sweet almond protein, hydrolyzed rice protein, hydrolyzed soy protein, hydrolyzed milk protein, hydrolyzed vegetable protein, hydrolyzed keratin, hydrolyzed collagen, hydrolyzed wheat gluten, potassium cocoyl hydrolyzed collagen, hydroxypropyl trimonium hydrolyzed collagen, cocodimonium hydroxypropyl hydrolyzed milk protein, lauryldimonium hydroxypropyl hydrolyzed wheat protein,

lauryldimonium hydroxypropyl hydrolyzed collagen, keratin amino acids, collagen amino acids, soyethyldimonium ethosulfate, soyethyl morpholinium ethosulfate, and the like.

- [0134] The monomeric quaternary ammonium compounds include, for example, alkylbenzyldimethyl ammonium salts, alkyl betaines, heterocyclic ammonium salts, and tetraalkylammonium salts. Long-chain (fatty) alkylbenzyldimethyl ammonium salts are utilized as conditioners, as antistatic agents, and as fabric softeners, discussed in more detail below.
- [0135] Non-limiting examples of alkylbenzyldimethylammonium salts include stearalkonium chloride, benzalkonium chloride, quaternium-63, olealkonium chloride, didecyldimonium chloride, and the like. Alkyl betaine compounds include alkylamidopropyl betaine, alkylamidopropyl hydroxysultaine, and sodium alkylamido propyl hydroxyphostaine.
- [0136] Non-limiting examples of alkyl betaine compounds include oleyl betaine, coco-betaine, cocoamidopropyl betaine, coco-hydroxy sultaine, coco/oleamidopropyl betaine, coco-sultaine, cocoamidopropylhydroxy sultaine, and sodium lauramidopropyl hydroxyphostaine. Heterocyclic ammonium salts include alkylethyl morpholinium ethosulfate, isostearyl ethylimidonium ethosulfate, and alkylpyridinium chlorides, and are generally used as emulsifying agents.
- [0137] Non-limiting examples of heterocyclic ammonium salts include cetylpyridinium chloride, isostearylethylimidonium ethosulfate, and the like. Non-limiting examples of tetraalkylammonium salts include cocamidopropyl ethyldimonium ethosulfate, hydroxyethyl cetyldimonium chloride, quaternium-18, and cocodimonium hyroxypropyl hydrolyzed protein, such as hair keratin, and the like.
- [0138] Non-limiting examples of monomeric quaternary ammonium compounds are acetamidopropyl trimonium chloride, behenamidopropyl dimethylamine, behenamidopropyl ethyldimonium ethosulfate, behentrimonium chloride, cetethyl morpholinium ethosulfate, cetrimonium chloride, cocoamidopropyl ethyldimonium ethosulfate, dicetyldimonium chloride, dimethicone hydroxypropyl trimonium chloride, hydroxyethyl behenamidopropyl dimonium chloride, quaternium-26, quaternium-27, quaternium-52, quaternium-53, quaternium-63, quaternium-70, quaternium-72,

quaternium-76 hydrolyzed collagen, PEG-2-cocomonium chloride, PPG-9 diethylmonium chloride, PPG-25 diethylmonium chloride, PPG-40 diethylmonium chloride, stearalkonium chloride, stearamidopropyl ethyl dimonium ethosulfate, steardimonium hydroxypropyl hydrolyzed wheat protein, steardimonium hydroxypropyl hydrolyzed collagen, wheat germamidopropalkonium chloride, wheat germamidopropyl ethyldimonium ethosulfate, and the like. The antistatic agent can be employed in amounts up to about 5 to 30 weight percent of the final composition, but is not limited thereto.

[0139] Non-limiting examples of quaternary ammonium polymers include polymers and copolymers of dimethyl diallyl ammonium chloride, such as polyquaternium-4, polyquaternium-6, polyquaternium-7, polyquaternium-10, polyquaternium-11 polyquaternium-15, polyquaternium-16, polyquaternium-22, polyquaternium-24, polyquaternium-28, polyquaternium-32, polyquaternium-33, polyquaternium-35, polyquaternium-37, polyquaternium-39, and polyquaternium-44. Other quaternary ammonium compounds include quaternary ammonium silicones and quaternized derivatives of natural gums, e.g., guar hydroxypropyltrimonium chloride and cassia hydroxypropyltrimonium chloride. Other polymeric quaternary ammonium compounds include quaternary ammonium silicones.

[0140] A number of quaternary ammonium compounds are used as antistatic agents for fabric conditioning and fabric care (generally referred to as fabric softening agents), and are typically employed in amounts of up to about 20 weight percent of the total weight of the formulation, but are not limited thereto.

[0141] Fabric softening agents useful in combination with the cationically and hydrophobically modified polymers of the present invention generally include long-chain alkylated quaternary ammonium compounds such as dialkyldimethyl quaternary ammonium compounds, imidazoline quaternary compounds, amidoamine quaternary compounds, dialkyl ester quat derivatives of dihydroxypropyl ammonium compounds; dialkyl ester quat derivatives of methyltriethanol ammonium compounds, ester amide amine compounds, and diester quat derivatives of dimethyldiethanol ammonium chloride, as described in the review article by Whalley, "Fabric Conditioning Agents", HAPPI, pp. 55-58 (February 1995), incorporated herein by reference.

[0142] Non-limiting examples of dialkyldimethyl quaternary ammonium compounds, include N,N-dioleyl-N,N-dimethylammonium chloride, N,N-ditallowyl-N,N-dimethylammonium ethosulfate, N,N-di(hydrogenated-tallowyl)-N,N-dimethylammonium chloride, and the like. Non-limiting examples of imidazoline quaternary compounds include 1-N-methyl-3-N-tallowamidoethylimidazolium chloride, 3-methyl-1-tallowylamidoethyl-2-tallowylimidazolinium methylsulfate, available from Witco Chemical Company under the tradename VARISOFT® 475, and the like. Non-limiting examples of amidoamine quaternary compounds include N-alkyl-N-methyl-N,N-bis(2-tallowamidoethyl)ammonium salts where the alkyl group can be methyl, ethyl, hydroxyethyl, and the like. Non-limiting examples of dialkyl ester quat derivatives of dihydroxypropyl ammonium compounds include 1,2-ditallowoyloxy-3-N,N,N-trimethylammoniopropane chloride, 1,2-dicanoloyloxy-3-N,N,N-trimethylammoniopropane chloride, and the like.

In addition, other types of long chain (e.g. natural oil and fatty acid-derived) [0143] alkylated quaternary ammonium compounds are suitable fabric softening agents, including, but not limited, to N,N-di(alkyloxyethyl)-N,N-dimethylammonium salts such as N,N-di(tallowyloxyethyl)-N,N-dimethylammonium chloride, N,N-di(canolyloxyethyl)-N,N-dimethylammonium chloride, and the like; N,N-di(alkyloxyethyl)-N-methyl-N-(2-hydroxyethyl)ammonium salts such as N,N-di(tallowyloxyethyl)-N-methyl-N-(2-hydroxyethyl)ammonium chloride, N,N-di(canolyloxyethyl)-N-methyl-N-(2-hydroxyethyl)ammonium chloride, and the like; N,N-di(2-alkyloxy-2-oxoethyl)-N,N-dimethylammonium salts, such as N,N-di(2tallowyloxy-2-oxoethyl)-N,N-dimethylammonium chloride, N,N-di(2-canolyloxy-2oxoethyl)-N,N-dimethylammonium chloride, and the like; N,N-di(2alkyloxyethylcarbonyloxyethyl)-N,N-dimethylammonium salts, such as N,N-di(2tallowyloxyethylcarbonyloxyethyl)-N,N-dimethylammonium chloride, N,N-di(2canolyloxyethylcarbonyloxyethyl)-N,N-dimethylammonium chloride, and the like; N-(2-alkanoyloxy-2-ethyl)-N-(2-alkyloxy-2-oxoethyl)-N,N-dimethyl ammonium salts, such as N-(2-tallowoyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxoethyl)-N,N-dimethyl ammonium chloride, N-(2-canoloyloxy-2-ethyl)-N-(2-canolyloxy-2-oxoethyl)-N,Ndimethyl ammonium chloride, and the like; N,N,N-tri(alkyloxyethyl)-N-methyl

ammonium salts, such as N,N,N-tri(tallowyloxyethyl)-N-methylammonium chloride, N,N,N-tri(canolyloxyethyl)-N-methylammonium chloride, and the like; N-(2-alkyloxy-2-oxoethyl)-N-alkyl-N,N-dimethyl ammonium salts, such as N-(2-tallowyloxy-2-oxoethyl)-N-tallowyl-N,N-dimethyl ammonium chloride, N-(2-canolyloxy-2-oxoethyl)-N-canolyl-N,N-dimethyl ammonium chloride, and the like.

[0144] In one aspect, the long-chain alkyl groups are derived from tallow, canola oil, or from palm oil, however, other alkyl groups derived from soybean oil and coconut oil, for example, are also suitable, as are lauryl, oleyl, ricinoleyl, stearyl, palmityl, and like fatty alkyl groups. The quaternary ammonium salt compounds can have any anionic group as a counter-ion, for example, chloride, bromide, methosulfate (i.e. methylsulfate), acetate, formate, sulfate, nitrate, and the like.

[0145] In one aspect, quaternary ammonium fabric softening compounds include N-methyl-N,N-bis(tallowamidoethyl)-N-(2-hydroxyethyl)ammonium methylsulfate and N-methyl-N,N-bis(hydrogenated-tallowamidoethyl)-N-(2-hydroxyethyl) ammonium methylsulfate, each of which materials are available from Witco Chemical Company under the trade names VARISOFT® 222 and VARISOFT® 110, respectively; dialkyl esterquat derivatives of methyltriethanol ammonium salts such as the DEHYQUART® AU series of bis(acyloxyethyl)hydroxyethylmethylammonium methosulfate esterquats available from Cognis, such as DEHYQUART® AU35, AU46, AU56, and the like; and N,N-di(tallowoyloxyethyl)-N,N-dimethylammonium chloride, where the tallow chains are at least partially unsaturated.

[0146] In another aspect, fabric softening agents include the well-known dialkyldimethyl ammonium salts such as N,N-ditallowyl-N,N-dimethyl ammonium methylsulfate, N,N-di(hydrogenated-tallowyl)-N,N-dimethyl ammonium chloride, N,N-distearyl-N,N-dimethyl ammonium chloride, N,N-dibehenyl-N,N-dimethyl ammonium chloride, N,N-di(hydrogenated tallow)-N,N-dimethyl ammonium chloride (trade name ADOGEN® 442), N,N-ditallowyl-N,N-dimethyl ammonium chloride (trade name ADOGEN® 470, PRAEPAGEN® 3445), N,N-distearyl-N,N-dimethyl ammonium chloride (trade name AROSURF® TA-100), all available from Witco Chemical Company; N,N-dibehenyl-N,N-dimethyl ammonium chloride, sold under the trade name KEMAMINE® Q-2802C by Humko Chemical Division of Witco

Chemical Corporation; and N,N-dimethyl-N-stearyl-N-benzylammonium chloride sold under the trade names VARISOFT® SDC by Witco Chemical Company and AMMONYX® 490 by Onyx Chemical Company.

[0147] Any of the foregoing fabric softening agents, and mixtures thereof, can be utilized in combination with the cationically and hydrophobically modified polymers of the present invention, particularly in laundry and fabric care products. For estercontaining fabric softening agents, the pH of the compositions can influence the stability of the fabric softening agents, especially in prolonged storage conditions. The pH, as defined in the present context, is measured in the neat compositions at about 20°C. In one aspect, the pH of the composition is less than about 6. In another aspect, the pH is in the range of from about 2 to about 5, and from about 2.5 to about 3.5 in a further aspect.

[0148]A pH adjusting agent or neutralizer can be added to a formulation containing the cationically and hydrophobically modified Cassia polymers of the invention. Thus, the pH adjusting agent can be utilized in any amount necessary to obtain a desired pH value in the final composition. Non-limiting examples of alkaline pH adjusting agents include alkali metal hydroxides, such as sodium hydroxide, and potassium hydroxide; ammonium hydroxide; organic bases, such as triethanolamine, diisopropylamine, dodecylamine, diisopropanolamine, aminomethyl propanol, cocamine, oleamine, morpholine, triamylamine, triethylamine, trimethamine (2-amino-2-hydroxymethyl)-1,3propanediol), and tetrakis(hydroxypropyl)ethylenediamine; and alkali metal salts of inorganic acids, such as sodium borate (borax), sodium phosphate, sodium pyrophosphate, and the like, and mixtures thereof. Acidic pH adjusting agents can be organic acids, including amino acids, and inorganic mineral acids. Non-limiting examples of acidic pH adjusting agents include acetic acid, citric acid, fumaric acid, glutamic acid, glycolic acid, hydrochloric acid, lactic acid, nitric acid, phosphoric acid, sodium bisulfate, sulfuric acid, tartaric acid, and the like, and mixtures thereof.

[0149] Suitable buffering agents include but are not limited to alkali or alkali earth carbonates, phosphates, bicarbonates, citrates, borates, acetates, acid anhydrides, succinates and the like, such as sodium phosphate, citrate, borate, acetate, bicarbonate, and carbonate.

[0150] The pH adjusting agent and/or buffering agent is utilized in any amount necessary to obtain and/or maintain a desired pH value in the composition. In one aspect, the composition of the invention can contain at least one alkalizing (alkaline pH adjusting agent) or acidifying agent (acidic pH adjusting agent) in amounts from 0.01 to 30 wt. % of the total weight of the composition.

The cationically and hydrophobically modified Cassia polymers of the [0151] present invention can be used as a thickener, film former, and deposition aid for promoting the deposition of colorants on hair and skin. Colorants for hair can be temporary, semipermanent or permanent hair dyes or color restorers that pigment the hair gradually. Temporary and semipermanent hair dyes typically are rinses, gels, sprays, shampoos, sticks, and the like, and hair color restorers are typically in the form of hair dressings or emulsions. Permanent hair dyes, and longer-lasting semipermanent hair dyes, are generally two-part products, one part containing the oxidative dye intermediates and dye couplers, and the other part containing stabilized oxidizing agent, usually hydrogen peroxide at about pH 3-4, and are mixed together immediately before use. It is known that such two-part hair dyeing products are formulated with combinations of surfactant ingredients, usually nonionic surfactants or anionic surfactants, to thicken when the dye mixture is prepared. In addition to the foregoing literature, a general discussion of hair dyeing chemistry and compositions is in Brown et al., SCC Monograph, "Permanent Hair Dyes", Society of Cosmetic Chemists (1996), incorporated herein by reference. The polymers of the present invention may be incorporated in one or both of the two-parts of such hair dyeing systems, either as the thickener for the acidic stabilized oxidizing portion or in the non-oxidizing portion to be thickened upon mixing with the acidic portion.

[0152] In addition to ingredients discussed above, other ingredients commonly used for antiacne products, facial and body hair bleaches, and antiseptic products include oxidizing agents, such as hydrogen peroxide, benzoyl peroxide, and water-soluble inorganic persulfate compounds such as ammonium persulfate, potassium persulfate, and sodium persulfate.

[0153] The cationically and hydrophobically modified Cassia polymers of the present invention are surprisingly useful stabilizers and/or deposition aids for silicone

conditioning agents which are commonly used in rinse off hair conditioner products and in shampoo products, such as the so-called "two-in-one" combination cleansing/conditioning shampoos. In one aspect, the conditioning agent is an insoluble silicone conditioning agent. Typically, the conditioning agent will be mixed in the shampoo composition to form a separate, discontinuous phase of dispersed, insoluble particles (also referred to as droplets). The silicone hair conditioning agent phase can be a silicone fluid and can also comprise other ingredients, such as a silicone resin, to improve silicone fluid deposition efficiency or enhance the glossiness of the hair especially when high refractive index (e.g. above about 1.46) silicone conditioning agents are used. The optional silicone hair conditioning agent phase may comprise volatile silicone, nonvolatile silicone, or combinations thereof. The silicone droplets are typically suspended with an optional suspending agent. The silicone conditioning agent particles may comprise volatile silicone, non-volatile silicone, or combinations thereof. In one aspect, non-volatile silicone conditioning agents are utilized. If volatile silicones are present, they will typically be incidental to their use as a solvent or carrier for commercially available forms of non-volatile silicone materials ingredients, such as silicone gums and resins. The silicone hair conditioning agents for use in the present invention have a viscosity of from about 20 to about 2,000,000 centistokes (1 centistokes equals 1 x 10⁻⁶ m²/s) in one aspect, from about 1,000 to about 1,800,000 centistokes in another aspect, from about 50,000 to about 1,500,000 in a further aspect, and from about 100,000 to about 1,500,000 centistokes in a still further aspect, as measured at 25°C. The concentration of the silicone conditioning agent can range from about 0.01% to about 10%, by weight of the composition in which it is included. In another

10.01% to about 10%, by weight of the composition in which it is included. In another aspect the amount of silicone conditioning agent ranges from about 0.1% to about 8%, from about 0.1% to about 5% in still another aspect, and from about 0.2% to about 3% by wt. in a further aspect, all based on the total weight of the composition.

[0155] In one embodiment, the dispersed silicone conditioning agent particles can have a volume average particle diameter ranging from about 5 μ m to about 125 μ m. For small particle application to hair, the volume average particle diameters range from about 0.01 μ m to about 4 μ min one aspect, from about 0.01 μ m to about 2 μ m in another aspect, and from about 0.01 μ m to about 0.5 μ min still another aspect. For larger particle

application to hair, the volume average particle diameters typically range from about 5 μm to about 125 μm in one aspect, from about 10 μm to about 90 μm in another aspect, from about 15 μm to about 70 μm in still another aspect, and from about 20 μm to about 50 μm in a further aspect.

[0156] Background 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 fluids are generally described as alkylsiloxane polymers. 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.

[0157] Silicone fluids include silicone oils, which are flowable silicone materials having a viscosity, as measured at 25°C of less than 1,000,000 cSt, and typically range from about 5 cSt to about 1,000,000 cSt. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, non-volatile silicone fluids having hair conditioning properties may also be used.

[0158] Silicone oils include polyalkyl, polyaryl siloxanes, or polyalkylaryl siloxanes which conform to the following formula:

$$R = \begin{cases} R^{20} & R^{20} & R^{20} \\ Si - O - \begin{bmatrix} Si - O - Si - \frac{1}{3} \\ R^{20} & R^{20} \end{bmatrix} w \end{cases} R^{20}$$

wherein R²⁰ is aliphatic, independently selected from alkyl, alkenyl, and aryl, R²⁰ can be substituted or unsubstituted, and w is an integer from 1 to about 8,000. Suitable unsubstituted R²⁰ groups for use in the personal cleansing compositions of the present invention include, but are not limited to: alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkamino, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic

and aryl groups. Suitable R^{20} groups also include cationic amines and quaternary ammonium groups.

[0159] In one aspect of the invention, exemplary R^{20} alkyl and alkenyl substituents range from C_1 - C_5 alkyl and alkenyl, from C_1 - C_4 in another aspect, from C_1 - C_2 in a further aspect. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains, and range from C_1 - C_5 in one aspect, from C_1 - C_4 in another aspect, and from C_1 - C_2 in a further aspect. As discussed above, the R^{20} substituents can also contain amino functionalities (e.g. alkamino groups), which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri-alkylamino and alkoxyamino groups, wherein the aliphatic portion chain length is as described above.

[0160] Exemplary siloxanes are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. These siloxanes are available, for example, from the General Electric Company in their Viscasil R and SF 96 series, and from Dow Corning marketed under the Dow Corning 200 series. Exemplary polyalkylaryl siloxane fluids that may be used, include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

[0161] Cationic silicone fluids are also suitable for use with the cationically and hydrophobically modified Cassia polymers of the invention. The cationic silicone fluids can be represented, but are not limited, to the general formula):

$$(R^{21})_eG_{3-f}$$
— Si — $(OSiG_2)_g$ — $(OSiG_f(R_1)_{(2-f)h}$ — O — $SiG_{3-e}(R^{21})_f$

wherein G is hydrogen, phenyl, hydroxy, or C_1 - C_8 alkyl (e.g.,methyl or phenyl); e is 0 or an integer having of from 1 to 3; f is 0 or 1; g is a number from 0 to 1,999; h is an integer from 1 to 2,000 in one aspect, and from 1 to 10 in another aspect; the sum of g and h is a number from 1 to 2,000 in one aspect, and from 50 to 500 in another aspect of the invention; R^{21} is a monovalent radical conforming to the general formula $C_qH_{2q}L$, wherein q is an integer having a value from 2 to 8 and L is selected from the following groups:

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- a) $-N(R^{22})CH_2CH_2N(R^{22})_2$
- b) $-N(R^{22})$
- c) $-N(R^{22})_3 CA^-$
- d) $-N(R^{22})CH_2CH_2N(R^{22})_2H_2CA^{-1}$

wherein R^{22} is independently selected from hydrogen, C_1 - C_{20} alkyl, phenyl, benzyl; and A^- is a halide ion selected from chloride, bromide, fluoride, and iodide. An exemplary cationic silicone corresponding to the previous formula defined immediately above is the polymer known as "trimethylsilylamodimethicone" of formula:

$$(CH_3)_3$$
-Si- $[O-Si(CH_3)_2)]_g$ - $[O-(CH_3)Si((CH_2)_3$ -NH- $(CH_2)_2$ -NH₂)]_h-O-Si(CH₃)₃

[0162] Another cationic silicone useful in combination with the cationically and hydrophobically modified Cassia polymers of the invention can be represented by the formula:

$$\begin{array}{c} OH & + & - \\ CH_{2}-CH-CH_{2}-N-(R)_{3}^{22} Q \\ \\ R^{22} & R^{23} & R^{22} & R^{22} \\ R^{22}-Si-O & Si-O & Si-O & Si-R^{22} \\ R^{22} & R^{22} & R^{22} & R^{22} \end{array}$$

wherein where R^{22} represents a radical selected from a C_1 - C_{18} alkyl and C_1 - C_{18} alkenyl radical; R^{23} independently represents a radical selected from a C_1 - C_{18} alkylene radical or a C_1 - C_{18} alkyleneoxy radical; Q is a halide ion; r denotes an average statistical value from 2 to 20 in one aspect, and from 2 to 8 in another aspect; r denotes an average statistical value from 20 to 200 in one aspect, and from 20 to 50 in another aspect. In one aspect, r is methyl. In another aspect, r is chloride.

[0163] Other optional silicone fluids are the insoluble silicone gums. These gums are polysiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described in U.S. Pat. No. 4,152,416; Noll and Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968; and

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in General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76, all of which are incorporated herein by reference. The silicone gums will typically have a mass molecule weight in excess of about 200,000 Daltons, generally between about 200,000 to about 1,000,000 Daltons, specific examples of which include polydimethylsiloxane, polydimethylsiloxane/methylvinylsiloxane copolymer, polydimethylsiloxane/diphenyl siloxane/methylvinylsiloxane) copolymer, and mixtures thereof.

[0164] Another category of nonvolatile, insoluble silicone fluid conditioning agents are the high refractive index polysiloxanes, having a refractive index of at least about 1.46 in one aspect, at least about 1.48 in another aspect, at least about 1.52 in a further aspect, and at least about 1.55 in a still further aspect. The refractive index of the polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60. In this context, polysiloxane "fluid" includes oils as well as gums.

[0165] The high refractive index polysiloxane fluid includes those represented by the general formula set forth for the polyalkyl, polyaryl, and polyalkylaryl siloxanes described above, as well as cyclic polysiloxanes (cyclomethicones) represented by the formula:

$$\begin{bmatrix} R^{20} \\ Si \\ C^{20} \end{bmatrix}$$

wherein the substituent R²⁰ is as defined above, and the number of repeat units, k, ranges from about 3 to about 7 in one aspect, and from 3 to 5 in another aspect. The high refractive index polysiloxane fluids can contain an amount of aryl containing R²⁰ substituents sufficient to increase the refractive index to the desired level, which is described above. Additionally, R²⁰ and k must be selected so that the material is non-volatile. Aryl containing substituents include those which contain alicyclic and heterocyclic five and six member aryl rings and those which contain fused five or six member rings. The aryl rings can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents,

ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with C₁-C₅ alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl C₂-C₄ alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine. The high refractive index polysiloxane fluids will have a degree of aryl containing substituents of at least about 15% by wt. in one aspect, at least about 20% by wt. in another aspect, at least about 25% by wt. in a further aspect, at least about 35% by wt. in still further aspect, and at least about 50% by wt. in an additional aspect, based on the wt. of the polysiloxane fluid. Typically, the degree of aryl substitution will be less than about 90% by wt., more typically less than about 85% by wt., and can generally ranges from about 55% to about 80% by wt. of the polysiloxane fluid.

[0166] In another aspect, the high refractive index polysiloxane fluids have a combination of phenyl or substituted phenyl derivatives. The substituents can be selected from C_1 - C_4 alkyl (e.g., methyl), hydroxy, and C_1 - C_4 alkylamino (e.g., $-R^{24}NHR^{25}NH_2$ wherein each R^{24} and R^{25} group independently is a C_1 - C_3 alkyl, alkenyl, and/or alkoxy.

[0167] When high refractive index silicones are used in the compositions of the present invention, they optionally can be used in solution with a spreading agent, such as a silicone resin or a surfactant, to reduce the surface tension by a sufficient amount to enhance spreading and thereby enhance the glossiness (subsequent to drying) of hair treated with such compositions. Silicone fluids suitable for use in the compositions of the present invention are disclosed in U.S. Pat. No. 2,826,551, U.S. Pat. No. 3,964,500, U.S. Pat. No. 4,364,837, British Pat. No. 849,433, and Silicon Compounds, Petrarch Systems, Inc. (1984), all of which are incorporated herein by reference. High refractive index polysiloxanes are available from Dow Corning Corporation (Midland, Mich.) Huls America (Piscataway, N.J.), and General Electric Silicones (Waterford, N.Y.).

[0168] Silicone resins can be included in the silicone conditioning agent suitable for use in combination with the cationically and hydrophobically modified Cassia polymers of the present invention. These resins are crosslinked polysiloxanes. The crosslinking is

introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional (or both) silanes during manufacture of the silicone resin.

[0169] As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. In one aspect, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and terachlorosilane, with the methyl-substituted silanes being most commonly utilized. Silicone resins are offered by General Electric as GE SS4230 and SS4267.

Silicone materials and silicone resins in particular, are identified according to [0170] a shorthand nomenclature system known to those of ordinary skill in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit (CH₃)₃SiO_{0.5}; D denotes the difunctional unit (CH₃)₂SiO; T denotes the trifunctional unit (CH₃)SiO_{1.5}; and Q denotes the quadra- or tetra-functional unit SiO₂. Primes of the unit symbols (e.g. M', D', T', and Q') denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbol indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

[0171] Exemplary silicone resins for use in the compositions of the present invention include, but are not limited to MQ, MT, MTQ, MDT and MDTQ resins. In one aspect, methyl is the silicone resin substituent. In another aspect, the silicone resin is selected from a MQ resins, wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the silicone resin is from about 1000 to about 10,000 Daltons.

[0172] When employed with non-volatile silicone fluids having a refractive index below 1.46, the weight ratio of the non-volatile silicone fluid to the silicone resin component, ranges from about 4:1 to about 400:1 in one aspect, from about 9:1 to about 200:1 in another aspect, from about 19:1 to about 100:1 in a further aspect, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above. Insofar as the silicone resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e., the conditioning active, the sum of the fluid and resin should be included in determining the level of silicone conditioning agent in the composition.

[0173] The volatile silicones described above include cyclic and linear polydimethylsiloxanes, and the like. Cyclic volatile silicones (cyclomethicones) typically contain about 3 to about 7 silicon atoms, alternating with oxygen atoms, in a cyclic ring structure such as described above for the non-volatile cyclic silicones. However, each R²⁰ substituent and repeating unit, k, in the formula must be selected so that the material is non-volatile. Typically, R²⁰ is substituted with two alkyl groups (e.g., methyl groups). The linear volatile silicones are silicone fluids, as described above, having viscosities of not more than about 25 mPa·s. "Volatile" means that the silicone has a measurable vapor pressure, or a vapor pressure of at least 2 mm of Hg at 20°C. Non-volatile silicones have a vapor pressure of less than 2 mm Hg at 20°C. A description of cyclic and linear volatile silicones is found in Todd and Byers, "Volatile Silicone Fluids for Cosmetics", Cosmetics and Toiletries, Vol. 91(1), pp. 27-32 (1976), and in Kasprzak, "Volatile Silicones", Soap/Cosmetics/Chemical Specialities, pp. 40-43 (December 1986), each incorporated herein by reference.

[0174] Exemplary volatile cyclomethicones are D4 cyclomethicone (octamethylcyclotetrasiloxane), D5 cyclomethicone (decamethylcyclopentasiloxane), D6

cyclomethicone, and blends thereof (e.g., D4/D5 and D5/D6). Volatile cyclomethicones and cyclomethicone blends are commercially available from G.E. Silicones as SF1173, SF1202, SF1256, and SF1258, Dow Corning Corporation as Dow Corning[®] 244, 245, 246, 345, and 1401 Fluids. Blends of volatile cyclomethicones and volatile linear dimethicones are also contemplated.

[0175] Exemplary volatile linear dimethicones include hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane and blends thereof. Volatile linear dimethicones and dimethicone blends are commercially available from Dow Corning Corporation as Dow Corning 200[®] Fluid (e.g., product designations 0.65 CST, 1 CST, 1.5 CST, and 2 CST) and Dow Corning[®] 2-1184 Fluid.

[0176] Emulsified silicones are also suitable for combination with the cationically and hydrophobically modified Cassia polymers of the invention. Typically, silicone emulsions have an average silicone particle size in the composition of less than 30 µm in one aspect, less than 20 µm in another aspect, and less than 10 µm in a further aspect. In one embodiment of the invention, the average silicone particle size of the emulsified silicone in the composition is less than 2 µm, and ideally it ranges from 0.01 to 1 µm. Silicone emulsions having an average silicone particle size of <0.15 micrometers are generally termed micro-emulsions. Particle size may be measured by means of a laser light scattering technique, using a 2600D Particle Sizer from Malvern Instruments. Suitable silicone emulsions for use in the invention are also commercially available in a pre-emulsified form. Examples of suitable pre-formed emulsions include emulsions DC2-1766, DC2-1784, and micro-emulsions DC2-1865 and DC2-1870, all available from Dow Corning. These are all emulsions/micro-emulsions of dimethiconol. Crosslinked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation. An exemplary material is available from Dow Corning as DC X2-1787, which is an emulsion of crosslinked dimethiconol gum. Another exemplary material is available from Dow Corning as DC X2-1391, which is a micro-emulsion of crosslinked dimethiconol gum. Preformed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Particularly suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant. Specific examples include DC929

Cationic Emulsion, DC939 Cationic Emulsion, DC949 Cationic emulsion, and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all available from Dow Corning). Mixtures of any of the above types of silicone may also be used. Specific examples of amino functional silicones suitable are the aminosilicone oils DC2-8220, DC2-8166, DC2-8466, and DC2-8950-114 (all available from Dow Corning), and GE 1149-75, (ex General Electric Silicones). An example of a quaternary silicone polymer useful in the present invention is the material K3474, available from Goldschmidt, Germany.

[0177] Other suitable silicone oils include the dimethicone copolyols, which are linear or branched copolymers of dimethylsiloxane (dimethicone) modified with alkylene oxide units. The alkylene oxide units can be arranged as random or block copolymers. A generally useful class of dimethicone polyols are block copolymers having terminal and/or pendent blocks of polydimethylsiloxane and blocks of polyalkylene oxide, such as blocks of polyethylene oxide, polypropylene oxide, or both. Dimethicone copolyols can be water soluble or insoluble depending on the amount of polyalkylene oxide present in the dimethicone polymer and can be anionic, cationic, or nonionic in character.

[0178] The water soluble or water dispersible silicones can also be used in combination with the cationically and hydrophobically modified Cassia polymers of the invention. Such water soluble silicones contain suitable anionic functionality, cationic functionality, and/or nonionic functionality to render the silicone water soluble or water dispersible. In one embodiment, the water soluble silicones contain a polysiloxane main chain to which is grafted at least one anionic moiety. The anionic moiety can be grafted to a terminal end of the polysiloxane backbone, or be grafted as a pendant side group, or both. By anionic group is meant any hydrocarbon moiety that contains at least one anionic group or at least one group that can be ionized to an anionic group following neutralization by a base. As discussed previously, the quantity of the hydrocarbon groups of anionic character which are grafted onto the silicone chain are chosen so that the corresponding silicone derivative is water-soluble or water-dispersible after neutralization of the ionizable groups with a base. The anionic silicone derivatives can be selected from existing commercial products or can be synthesized by any means

known in the art. The nonionic silicones contain alkylene oxide terminal and/or pendant side chain units (e.g., dimethicone copolyols).

[0179] Silicones with anionic groups can be synthesized by reaction between (i) a polysiloxane containing a silinic hydrogen and (ii) a compound containing olefinic unsaturation that also contains an anionic functional group. Exemplary of such a reaction is the hydrosilylation reaction between poly(dimethylsiloxanes) containing a Si-H group(s) and an olefin, CH₂=CHR²⁶, wherein R²⁶ represents a moiety containing an anionic group. The olefin can be monomeric, oligomeric or polymeric. Polysiloxane compounds that contain a pendant reactive thio (-SH) group(s) are also suitable for grafting an unsaturated anionic group containing compound to the poly(siloxane) backbone.

[0180] According to one aspect of the present invention, the anionic monomers containing ethylenic unsaturation are used alone or in combination and are selected from linear or branched, unsaturated carboxylic acids. Exemplary unsaturated carboxylic acids are acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid and crotonic acid. The monomers can optionally be partially or completely neutralized by base to form an alkali, alkaline earth metal, and ammonium salt. Suitable bases include but are not limited to the alkali, alkaline earth (e.g., sodium, potassium, lithium, calcium) and ammonium hydroxides. It will be noted that, similarly, the oligomeric and polymeric graft segments formed from the forgoing monomers can be post-neutralized with a base (sodium hydroxide, aqueous ammonia, etc) to form a salt. Examples of silicone derivatives which are suitable for use in the present invention are described in patent applications numbers EP-A-0 582,152 and WO 93/23009. An exemplary class of silicone polymers are the polysiloxanes containing repeat units represented by the following structure:

wherein G^1 represents hydrogen, C_1 - C_{10} alkyl and phenyl radical; G^2 represents C_1 - C_{10} alkylene; G^3 represents an anionic polymeric residue obtained from the polymerization of at least one anionic monomer containing ethylenic unsaturation; j is 0 or 1; t is an integer ranging from 1 to 50; and u is an integer from 10 to 350. In one embodiment of the invention, G^1 is methyl; j is 1; and G_2 is propylene radical; G^3 represents a polymeric radical obtained from the polymerization of at least one unsaturated monomer containing a carboxylic acid group (e.g., acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, maleic acid, or aconitic acid, and the like).

[0181]In one aspect, the carboxylate group content in the final polymer ranges from 1 mole of carboxylate per 200 g of polymer to 1 mole of carboxylate per 5000 g of polymer. In one aspect, the number molecular mass of the silicone polymer ranges from about 10,000 to about 1,000,000, and from 10,000 to 100,000 in another aspect. Exemplary unsaturated monomers containing carboxylic acid groups are acrylic acid and methacrylic acid. In addition, to the carboxylic acid group containing monomers, C₁-C₂₀ alkyl esters of acrylic acid and methacrylic acid can be copolymerized into the polymeric backbone. Exemplary esters include but are not limited to the ethyl and butyl esters of acrylic and methacrylic acid. A commercially available silicone-acrylate polymer is marketed by the 3M Company under the trademark Silicones "Plus" Polymer 9857C (VS80 Dry). These polymers contain a polydimethylsiloxanes (PDMS) backbone onto which is grafted (through a thiopropylene group) random repeating units of poly(meth)acrylic acid and the butyl ester of poly(meth)acrylate. These products can be obtained conventionally by radical copolymerization between thiopropyl functionalized polydimethylsiloxane and a mixture of monomers comprising (meth)acrylic acid and of butyl(meth)acrylate.

[0182] In another embodiment, the water soluble silicone copolyol useful in the practice of the present invention can be represented silicone copolyol carboxylates represented by the formula:

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where R^{27} and R^{28} are independently selected from C_1 - C_{30} alkyl, C_6 - C_{14} aryl, C_7 - C_{15} aralkyl, C_1 - C_{15} alkaryl, or an alkenyl group of 1 to 40 carbons, hydroxyl, $-R^{31}$ -G' or $-(CH_2)_3O(EO)_a(PO)_b(EO)_c$ -G', with the proviso that both R^{27} and R^{28} are not methyl; R^{29} is selected from C_1 - C_5 alkyl or phenyl; in this formula a, b, and c are integers independently ranging from 0 to 100; EO is ethylene oxide, $-(CH_2CH_2O)$ -; PO is propylene oxide, $-(CH_2CH(CH_3)O)$ -; in this formula o is an integer ranging from 1 to 200, p is an integer ranging from 0 to 200, and q is an integer ranging from 0 to 1000; R^{30} is hydrogen, C_1 - C_{30} alkyl, aryl, C_7 - C_{15} aralkyl, C_7 - C_{15} alkaryl, or alkenyl group of 1 to 40 carbons or -C(O)-X wherein X is C_1 - C_{30} alkyl, C_6 - C_{14} aryl, C_7 - C_{15} aralkyl, C_1 - C_{15} alkaryl, or an alkenyl group of 1 to 40 carbons, or a mixture thereof; R^{31} is a divalent group selected from alkylene radical of 1 to 40 carbon atoms which may be interrupted with arylene group of 6 to 18 carbons or an alkylene group containing unsaturation of 2 to 8 carbons; and G' is independently are selected from:

$$\begin{array}{ccc} O & & & O \\ II & -S - O M \\ II & & O \end{array}; \quad \begin{array}{ccc} O & - M \\ II & -S - O M \\ O & & O \end{array}$$

where R^{32} is a divalent group selected from alkylene of 1 to 40 carbons, an unsaturated group containing 2 to 5 carbon atoms, or an arylene group of 6 to 12 carbon atoms; where M is a cation selected from Na, K, Li, NH₄, or an amine containing C_1 - C_{10} alkyl, C_6 - C_{14} aryl (e.g., phenyl, naphthyl), C_2 - C_{10} alkenyl, C_1 - C_{10} hydroxyalkyl, C_7 - C_{24} arylalkyl or

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 C_7 - C_{24} alkaryl groups. Representative R^{32} radicals are: -CH₂CH₂-, -CH=CH-, -CH=CHCH₂-, and phenylene.

[0183] In another embodiment, the water soluble silicones useful in the practice of the present invention can be represented an anionic silicone copolyol represented by the formula:

where is R^{33} is methyl or hydroxyl; R^{34} is selected from C_1 - C_8 alkyl or phenyl; R^{35} represents the radical - $(CH_2)_3O(EO)_x(PO)_y(EO)_z$ - SO_3 -M+; where M is a cation selected from Na, K, Li, or NH₄; in this formula x, y and z are integers independently ranging from 0 to 100; R^{36} represents the radical - $(CH_2)_3O(EO)_x(PO)_y(EO)_z$ -H; in this formula a and c are independently integers ranging from 0 to 50, and b is an integer ranging from 1 to 50; EO is ethylene oxide, e.g., - (CH_2CH_2O) -; PO is propylene oxide, e.g., - $(CH_2CH(CH_3)O)$ -. In still another embodiment, the water soluble silicones useful in the practice of the present invention can be represented an anionic silicone copolyol represented by the formula:

wherein R^{37} and R^{38} independently are -CH₃ or a radical represented by: -(CH₂)₃O(EO)_a(PO) _b(EO)_c-C(O)-R⁴⁰-C(O)OH, subject to the proviso that both R^{37} and R^{38} are not -CH₃ at the same time; R^{40} is selected from the divalent radical -CH₂CH₂, -CH=CH-, and phenylene; R^{39} is selected from C₁-C₅ alkyl or phenyl; in this formula a, b and c are integers independently ranging from 0 to 20; EO is an ethylene oxide residue, e.g., -(CH₂CH₂O)-; PO is a propylene oxide residue, e.g.,

-(CH₂CH(CH₃)O)-; in this formula o is an integer ranging from 1 to 200 and q is an integer ranging from 0 to 500.

[0184] Other water soluble silicones useful in the invention are quaternized silicone copolyol polymers. These polymers have a pendant quaternary nitrogen functional group present and are represented by the formula:

where R^{41} represents a quaternary substituent $-N^+R^3R^4R^5$ X^- , wherein R^3 and R^4 , and R^5 , independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X^- represents an anion suitable to balance the cationic charge on the nitrogen atom; R^{42} is selected from C_1 - C_{10} alkyl and phenyl; R^{43} is - $(CH_2)_3O(EO)_x(PO)_y(EO)_z$ -H, where EO is an ethylene oxide residue, e.g., - (CH_2CH_2O) -; PO is a propylene oxide residue, e.g., - $(CH_2CH(CH_3)O)$ -; in this formula a is an integer from 0 to 200, b is an integer from 0 to 200, and c is an integer from 1 to 200; in this formula x, y and z are integers and are independently selected from 0 to 20. In one aspect, the anion X^- represents an anion selected from chloride, bromide, iodide, sulfate, methylsulfate, sulfonate, nitrate, phosphate, and acetate.

[0185] Other suitable water soluble silicones are amine substituted silicone copolyols represented by the formula:

$$(CH_{2})_{3}O(EO)_{x}(PO)_{y}(EO)_{z}-H_{2}(PO)_{y}-H_{2}(PO)_{y}$$

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where R^{44} is selected from $-NH(CH_2)_nNH_2$ or $-(CH_2)_nNH_2$, where in this formula n is an integer from 2 to 6; and x, is n integer from 0 to 20; where EO is an ethylene oxide residue, e.g., $-(CH_2CH_2O)$ -; PO is a propylene oxide residue, e.g., $-(CH_2CH(CH_3)O)$ -; in this formula a is an integer from 0 to 200, b is an integer from 0 to 200, and c is an integer from 1 to 200; in this formula x, y and z are integers and are independently selected from 0 to 20.

[0186] Still other water soluble silicones can be selected from nonionic silicone copolyols (dimethicone copolyols) represented by the formula:

$$\begin{array}{c} \mathsf{R}^{46} \\ | \\ (\mathsf{R}^{45})_3 \mathsf{Si}(\mathsf{OSiR}^{46} \mathsf{R}^{47})_{\mathsf{x}} (\mathsf{OSi})_{\mathsf{y}} \mathsf{OSi}(\mathsf{R}^{45})_3 \\ | \\ \mathsf{CH}_2 \\ \mathsf{CH}_2 \\ \mathsf{CH}_2 \\ \mathsf{CH}_2 \\ \mathsf{CH}_2 \\ \mathsf{O}\text{-}(\mathsf{EO})_{\mathsf{a}} (\mathsf{PO})_{\mathsf{b}} (\mathsf{EO})_{\mathsf{c}}\text{-}\mathsf{H} \end{array}$$

where R^{45} , independently, represents a radical selected from C_1 - C_{30} alkyl, C_6 - C_{14} aryl, and C_2 - C_{20} alkenyl; R^{46} represents a radical selected from C_1 - C_{30} alkyl, C_6 - C_{14} aryl, and C_2 - C_{20} alkenyl; EO is an ethylene oxide residue, e.g., -(CH₂CH₂O)-; PO is a propylene oxide residue, e.g., -(CH₂CH(CH₃)O)-; in this formula a, b, and c are, independently, 0 to 100; in this formula x is 0 to 200; and y is 1 to 200.

[0187] In another embodiment, water soluble silicones can be selected from nonionic silicone copolyols represented by the formula:

wherein R^{48} and R^{49} , independently, represent a radical selected from C_1 - C_{30} alkyl, C_6 - C_{14} aryl, and C_2 - C_{20} alkenyl; EO is an ethylene oxide residue, e.g., -(CH₂CH₂O)-; PO is a propylene oxide residue, e.g., -(CH₂CH(CH₃)O)-; in this formula a, b, and c are independently 0 to 100; and in this formula n is 0 to 200.

[0188] In the copolyol embodiments set forth above, the EO and PO residues can be arranged in random, non-random, or blocky sequences.

[0189] Dimethicone copolyols are disclosed in U.S. Patent Nos. 5,136,063 and 5,180,843, the disclosures of which are incorporated herein by reference. In addition, dimethicone copolyols are commercially available under the Silsoft® and Silwet® brand names from the General Electric Company (GE-OSi). Specific product designations include but are not limited to Silsoft 305, 430, 475, 810, 895, Silwet L 7604 (GE-OSi); Dow Corning® 5103 and 5329 from Dow Corning Corporation; and Abil® dimethicone copolyols, such as, for example WE 09, WS 08, EM 90 and EM 97 from Evonik Goldschmidt Corporation; and SilsenseTM dimethicone copolyols, such as Silsense Copolyol-1 and Silsense Copolyol-7, available from Lubrizol Advanced Materials, Inc. The conditioning component of the conditioner and shampoo compositions of the present invention can also comprise from about 0.05% to about 3%, by weight of the composition in one aspect, from about 0.08% to about 1.5% in another aspect, and from about 0.1% to about 1% in a further aspect, of at least one conditioning oil as the conditioning agent, either alone or in combination with other conditioning agents, such as the silicones (described above) and the other conditioning agents described below.

[0190] Suitable conditioning oils for use as conditioning agents in the compositions of the present invention include, but are not limited to, hydrocarbon oils having at least about 10 carbon atoms, such as cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated), including polymers and mixtures thereof. Straight chain hydrocarbon oils typically contain about 12 to 19 carbon atoms. Branched chain hydrocarbon oils, including hydrocarbon polymers, typically will contain more than 19 carbon atoms.

[0191] Specific non-limiting examples of these hydrocarbon oils include paraffin oil, mineral oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane,

saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, polybutene, polydecene, and mixtures thereof. Branchedchain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used, examples of which include highly branched, saturated or unsaturated, alkanes such as the permethyl-substituted isomers, e.g., the permethyl-substituted isomers of hexadecane and eicosane, such as 2,2,4,4,6,6,8,8-dimethyl-10-methylundecane and 2,2,4,4,6,6-dimethyl-8-methylnonane, available from Permethyl Corporation. Hydrocarbon polymers such as polybutene and polydecene. In one aspect a hydrocarbon polymer is a polybutene, such as the copolymer of isobutylene and butene. A commercially available material of this type is L-14 polybutene from BP Chemical Company.

[0192] Natural oil conditioners are also useful in the practice of this invention and include but are not limited to peanut, sesame, avocado, coconut, cocoa butter, almond, safflower, corn, cotton seed, sesame seed, walnut oil, castor, olive, jojoba, palm, palm kernel, soybean, wheat germ, linseed, sunflower seed; eucalyptus, lavender, vetiver, litsea, cubeba, lemon, sandalwood, rosemary, chamomile, savory, nutmeg, cinnamon, hyssop, caraway, orange, geranium, cade, and bergamot oils, fish oils, glycerol tricaprocaprylate; and mixtures thereof. The natural oils can also be utilized as emollients.

[0193] Natural and synthetic wax conditioning agents can be employed in the compositions of the invention, including but are not limited to carnauba wax, candelila wax, alfa wax, paraffin wax, ozokerite wax, olive wax, rice wax, hydrogenated jojoba wax, bees wax, modified bees wax, e.g., cerabellina wax, marine waxes, polyolefin waxes, e.g., polyethylene wax; and mixtures thereof.

[0194] Liquid polyolefin conditioning oils can be used in the compositions of the present invention. The liquid polyolefin conditioning agents are typically poly- α -olefins that have been hydrogenated. Polyolefins for use herein can be prepared by the polymerization of C_4 to about C_{14} olefinic monomers. Non-limiting examples of olefinic monomers for use in preparing the polyolefin liquids herein include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, branched chain isomers such as 4-methyl-1-pentene, and mixtures thereof. In one aspect of the

invention hydrogenated α -olefin monomers include, but are not limited to: 1-hexene to 1-hexadecenes, 1-octene to 1-tetradecene, and mixtures thereof.

[0195] Fluorinated or perfluorinated oils are also contemplated within the scope of the present invention. Fluorinated oils include perfluoropolyethers described in European Patent 0 486 135 and the fluorohydrocarbon compounds described in WO 93/11103. The fluoridated oils may also be fluorocarbons such as fluoramines, e.g., perfluorotributylamine, fluoridated hydrocarbons, such as perfluorodecahydronaphthalene, fluoroesters, and fluoroethers.

[0196] Other suitable organic conditioners for use as the conditioning agent in the compositions of the present invention include, but are not limited to, fatty esters having at least 10 carbon atoms. These fatty esters include esters derived from fatty acids or alcohols (e.g., mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters). The fatty esters hereof may include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

[0197] Exemplary fatty esters include, but are not limited to isopropyl isostearate, hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, dihexyldecyl adipate, lauryl lactate, myristyl lactate, cetyl lactate, oleyl stearate, oleyl oleate, oleyl myristate, lauryl acetate, cetyl propionate, and oleyl adipate.

[0198] Other fatty esters suitable for use in the compositions of the present invention are mono-carboxylic acid esters of the general formula $R^{50}C(O)OR^{51}$, wherein R^{50} and R^{51} are alkyl or alkenyl radicals, and the sum of carbon atoms in R^{50} and R^{51} is at least 10 in one aspect, and at least 22 in another aspect of the invention.

[0199] Still other fatty esters suitable for use in the compositions of the present invention are di- and tri-alkyl and alkenyl esters of carboxylic acids, such as esters of C_4 - C_8 dicarboxylic acids (e.g., C_1 - C_{22} esters or, C_1 - C_6 esters, of succinic acid, glutaric acid, adipic acid). Specific non-limiting examples of di- and tri-alkyl and alkenyl esters of carboxylic acids include isocetyl stearyol stearate, diisopropyl adipate, and tristearyl citrate.

[0200] Other fatty esters suitable for use in the compositions of the present invention are those known as polyhydric alcohol esters. Such polyhydric alcohol esters include alkylene glycol esters, such as ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol mono- and di-fatty acid esters, polypropylene glycol monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty acid esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters.

[0201] Specific non-limiting examples of suitable synthetic fatty esters for use in the personal cleansing compositions of the present invention include: P-43 (C₈-C₁₀ triester of trimethylolpropane), MCP-684 (tetraester of 3,3 diethanol-1,5 pentadiol), MCP 121 (C₈-C₁₀ diester of adipic acid), all of which are available from ExxonMobil Chemical Company.

[0202] Other oily material conditioning agents that are useful in combination with the polymers of the present invention include, for example, acetylated lanolin alcohols; lanolin alcohol concentrates; esters of lanolin fatty acids such as the isopropyl esters of lanolin fatty acid; polyol fatty acids; ethoxylated alcohols, such as ethoxylate and castor oils; sterols; sterol esters; sterol ethoxylates; and like materials.

[0203] Cationic polymers are also useful as conditioning agents alone or in combination with the other conditioning agents described herein. Suitable cationic polymers can be synthetically derived or modified natural polymers such as the cationically modified polysaccharides. While several of the cationic polymers listed herein as suitable conditioning agents are duplicative of those described above for uses in other applications, those of skill in the art will recognize that many polymers serve multiple functions.

[0204] Representative cationic polymer conditioners include but are not limited to homopolymers and copolymers derived from free radically polymerizable acrylic or methacrylic ester or amide monomers. The copolymers can contain one or more units derived from acrylamides, methacrylamides, diacetone acrylamides, acrylic or

methacrylic acids or their esters, vinyllactams such as vinyl pyrrolidone or vinyl caprolactam, and vinyl esters. Exemplary polymers include copolymers of acrylamide and dimethyl amino ethyl methacrylate quaternized with dimethyl sulfate or with an alkyl halide; copolymers of acrylamide and methacryloyl oxyethyl trimethyl ammonium chloride; the copolymer of acrylamide and methacryloyl oxyethyl trimethyl ammonium methosulfate; copolymers of vinyl pyrrolidone/dialkylaminoalkyl acrylate or methacrylate, optionally quaternized, such as the products sold under the name GAFQUATTM by International Specialty Products; the dimethyl amino ethyl methacrylate/vinyl caprolactam/vinyl pyrrolidone terpolymers, such as the product sold under the name GAFFIXTM VC 713 by International Specialty Products; the vinyl pyrrolidone/methacrylamidopropyl dimethylamine copolymer, marketed under the name STYLEZETM CC 10 available from International Specialty Products; and the vinyl pyrrolidone/quaternized dimethyl amino propyl methacrylamide copolymers such as the product sold under the name GAFQUATTM HS 100 by International Specialty Products.

[0205] Cationic conditioning agents can also be selected from the quaternary polymers of vinyl pyrrolidone and vinyl imidazole such as the products sold under the trade name Luviquat® (product designation FC 905, FC 550, and FC 370) by BASF. Other cationic polymer conditioners that can be used in the compositions of the invention include polyalkyleneimines such as polyethyleneimines, polymers containing vinyl pyridine or vinyl pyridinium units, condensates of polyamines and epichlorhydrins, quaternary polysaccharides, quaternary polyurethanes, and quaternary derivatives of chitin.

[0206] Other non-limiting examples of quaternary ammonium compounds (monomeric and polymeric) useful as cationic conditioners in the present invention (in addition to and which may overlap with those discussed hereinabove) include acetamidopropyl trimonium chloride, behenamidopropyl dimethylamine, behenamidopropyl ethyldimonium ethosulfate, behentrimonium chloride, cetethyl morpholinium ethosulfate, cetrimonium chloride, cocoamidopropyl ethyldimonium ethosulfate, dicetyldimonium chloride, dimethicone hydroxypropyl trimonium chloride, hydroxyethyl behenamidopropyl dimonium chloride, quaternium-26, quaternium-27, quaternium-53, quaternium-63, quaternium-70, quaternium-72, quaternium-76

hydrolyzed collagen, PPG-9 diethylmonium chloride, PPG-25 diethylmonium chloride, PPG-40 diethylmonium chloride, stearalkonium chloride, stearamidopropyl ethyl dimonium ethosulfate, steardimonium hydroxypropyl hydrolyzed wheat protein, steardimonium hydroxypropyl hydrolyzed collagen, wheat germamidopropalkonium chloride, wheat germamidopropyl ethyldimonium ethosulfate, polymers and copolymers of dimethyl diallyl ammonium chloride, such as Polyguaternium-4, Polyguaternium-6, Polyquaternium-7, Polyquaternium-10, Polyquaternium-11, Polyquarternium-16, Polyquaternium-22, Polyquaternium-24, Polyquaternium-28, Polyquaternium-29, Polyquaternium-32, Polyquaternium-33, Polyquaternium-35, Polyquaternium-37, Polyquaternium-39, Polyquaternium-44, Polyquaternium-46, Polyquaternium-47, Polyquaternium-52, Polyquaternium-53, Polyquaternium-59, Polyquaternium-61, Polyquaternium-64, Polyquaternium-65, Polyquaternium-67, Polyquaternium-69, Polyquaternium-70, Polyquaternium-71, Polyquaternium-72, Polyquaternium-73, Polyquaternium-74, Polyquaternium-76, Polyquaternium-77, Polyquaternium-78, Polyquaternium-79, Polyquaternium-80, Polyquaternium-81, Polyquaternium-82, Polyquaternium-84, Polyquaternium-85, Polyquaternium-87, PEG-2-cocomonium chloride.

[0207] Other useful cationic polymers useful as conditioning agents include the cationic polygalactomannans (e.g., quaternized derivatives of guar and cassia, such as, guar hydroxypropyl trimmonium chloride, hydroxypropyl guar hydroxypropyl trimmonium chloride, and cassia hydroxypropyl trimmonium chloride).

[0208] As discussed above, numerous ingredients are known in the art as conditioning agents for hair or skin. In addition to those discussed, other non-limiting examples include PCA (DL-pyrrolidone carboxylic acid) and its salts, such as lysine PCA, aluminum PCA, copper PCA, chitosan PCA, and the like, allantoin; urea; hyaluronic acid and its salts; ceramides; sorbic acid and its salts; sugars and starches and derivatives thereof; lactamide MEA; and the like.

[0209] In another embodiment of the invention, the hydrophobically modified, cationic Cassia polymers of the invention can be formulated in combination with one or more auxiliary rheology modifiers and thickeners. Suitable rheology modifiers and thickeners include synthetic and semi-synthetic rheology modifiers. Exemplary

synthetic rheology modifiers include acrylic based polymers and copolymers. One class of acrylic based rheology modifiers are the carboxyl functional alkali-swellable and alkali-soluble thickeners (ASTs) produced by the free-radical polymerization of acrylic acid alone or in combination with other ethylenically unsaturated monomers. The polymers can be synthesized by solvent/precipitation as well as emulsion polymerization techniques. Exemplary synthetic rheology modifiers of this class include homopolymers of acrylic acid or methacrylic acid and copolymers polymerized from one or more monomers of acrylic acid, substituted acrylic acid, and salts and C₁-C₃₀ alkyl esters of acrylic acid and substituted acrylic acid. As defined herein, the substituted acrylic acid contains a substituent positioned on the alpha and/or beta carbon atom of the molecule, wherein in one aspect the substituent is p independently selected from C_{1-4} alkyl, -CN, and -COOH. Optionally, other ethylenically unsaturated monomers such as, for example, styrene, vinyl acetate, ethylene, butadiene, acrylonitrile, as well as mixtures thereof can be copolymerized into the backbone. The foregoing polymers are optionally crosslinked by a monomer that contains two or more moieties that contain ethylenic unsaturation. In one aspect, the crosslinker is selected from a polyalkenyl polyether of a polyhydric alcohol containing at least two alkenyl ether groups per molecule. Other Exemplary crosslinkers are selected from allyl ethers of sucrose and allyl ethers of pentaerythritol, and mixtures thereof. These polymers are more fully described in U.S. Patent No. 5,087,445; U.S. Patent No. 4,509,949; and U.S. Pat. No. 2,798,053 herein incorporated by reference.

[0210] In one embodiment, the AST rheology modifier or thickener is a crosslinked homopolymer polymerized from acrylic acid or methacrylic acid and is generally referred to under the INCI name of Carbomer. Commercially available Carbomers include Carbopol® polymers 934, 940, 941, 956, 980 and 996 available from Lubrizol Advanced Materials, Inc. In a further aspect, the rheology modifier is selected from a crosslinked copolymer polymerized from a first monomer selected from one or more monomers of acrylic acid, substituted acrylic acid, salts of acrylic acid and salts of substituted acrylic acid and a second monomer selected from one or more C₁₀-C₃₀ alkyl acrylate esters of acrylic acid or methacrylic acid. In one aspect, the monomers can be polymerized in the presence of a steric stabilizer such as disclosed in U.S. Patent No.

5,288,814 which is herein incorporated by reference. Some of the forgoing polymers are designated under INCI nomenclature as Acrylates/C10-30 Alkyl Acrylate Crosspolymer and are commercially available under the trade names Carbopol[®] 1342 and 1382, Carbopol[®] Ultrez 20 and 21, Carbopol[®] ETD 2020 and Pemulen[®] TR-1 and TR-2 from Lubrizol Advanced Materials. Inc.

Another class of synthetic rheology modifiers and thickeners suitable for use [0211] in the present invention includes hydrophobically modified ASTs commonly referred to as hydrophobically modified alkali-swellable and alkali-soluble emulsion (HASE) polymers. Typical HASE polymers are free radical addition polymers polymerized from pH sensitive or hydrophilic monomers (e.g., acrylic acid and/or methacrylic acid), hydrophobic monomers (e.g., C₁-C₃₀ alkyl esters of acrylic acid and/or methacrylic acid, acrylonitrile, styrene), an "associative monomer", and an optional crosslinking monomer. The associative monomer comprises an ethylenically unsaturated polymerizable end group, a non-ionic hydrophilic midsection that is terminated by a hydrophobic end group. The non-ionic hydrophilic midsection comprises a polyoxyalkylene group, e.g., polyethylene oxide, polypropylene oxide, or mixtures of polyethylene oxide/polypropylene oxide segments. The terminal hydrophobic end group is typically a C₈-C₄₀ aliphatic moiety. Exemplary aliphatic moieties are selected from linear and branched alkyl substituents, linear and branched alkenyl substituents, carbocyclic substituents, aryl substituents, aralkyl substituents, arylalkyl substituents, and alkylaryl substituents. In one aspect, associative monomers can be prepared by the condensation (e.g., esterification or etherification) of a polyethoxylated and/or polypropoxylated aliphatic alcohol (typically containing a branched or unbranched C₈-C₄₀ aliphatic moiety) with an ethylenically unsaturated monomer containing a carboxylic acid group (e.g., acrylic acid, methacrylic acid), an unsaturated cyclic anhydride monomer (e.g., maleic anhydride, itaconic anhydride, citraconic anhydride), a monoethylenically unsaturated monoisocyanate (e.g., α,α -dimethyl-m-isopropenyl benzyl isocyanate) or an ethylenically unsaturated monomer containing a hydroxyl group (e.g., vinyl alcohol, allyl alcohol). Polyethoxylated and/or polypropoxylated aliphatic alcohols are ethylene oxide and/or propylene oxide adducts of a monoalcohol containing the C₈-C₄₀ aliphatic moiety. Nonlimiting examples of alcohols containing a C₈-C₄₀ aliphatic moiety are capryl alcohol,

iso-octyl alcohol (2-ethyl hexanol), pelargonic alcohol (1-nonanol), decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, cetyl alcohol, cetearyl alcohol (mixture of C_{16} - C_{18} monoalcohols), stearyl alcohol, isostearyl alcohol, elaidyl alcohol, oleyl alcohol, arachidyl alcohol, behenyl alcohol, lignoceryl alcohol, ceryl alcohol, montanyl alcohol, melissyl, lacceryl alcohol, geddyl alcohol, and C_2 - C_{20} alkyl substituted phenols (e.g., nonyl phenol), and the like.

[0212] Exemplary HASE polymers are disclosed in U.S. Patent Nos. 3,657,175; 4,384,096; 4,464,524; 4,801,671; and 5,292,843 which are herein incorporated by reference. In addition, an extensive review of HASE polymers is found in Gregory D. Shay, Chapter 25, "Alkali-Swellable and Alkali-Soluble Thickener Technology A Review", Polymers in Aqueous Media - Performance Through Association, Advances in Chemistry Series 223, J. Edward Glass (ed.), ACS, pp. 457-494, Division Polymeric Materials, Washington, DC (1989), the relevant disclosures of which are incorporated herein by reference. The HASE polymers are commercially available from Rohm & Haas under the trade designations Aculyn® 22 (INCI Name: Acrylates/Steareth-20 Methacrylate Copolymer), Aculyn® 44 (INCI Name: PEG-150/Decyl Alcohol/SMDI Copolymer), Aculyn 46[®] (INCI Name: PEG-150/Stearyl Alcohol/SMDI Copolymer), and Aculvn® 88 (INCI Name: Acrylates/Steareth-20 Methacrylate Crosspolymer). Another class of synthetic and semi-synthetic rheology modifiers and [0213] thickeners suitable for use in the present invention includes cationically modified acrylic polymers and copolymers and cationically modified cellulose ethers. The acrylic polymers and copolymers and cellulose ethers are cationically modified via quaternization. For the acrylic polymers and copolymers, quaternization can occur by polymerizing a quaternized monomer into the acrylic polymer backbone or by post functionalizing the acrylic polymer with a quaternizing agent. An exemplary quaternary acrylic polymer is designated under INCI nomenclature as Polyquaternium-37 and is commercially available under the trade names Synthalen CR21 and Synthalen CN, from 3V Inc. The quaternized celluloses are prepared by post functionalizing the desired cellulosic backbone (e.g., hydroxyethyl cellulose) with a quaternizing agent such as a quaternary ammonium salt (e.g., diallyldimethyl ammonium chloride, trimethyl ammonium chloride substituted epoxide). Exemplary quaternary cellulosic polymers are

designated under the INCI names Polyquaternium-4, Polyquaternium-10, and Polyquaternium-67.

[0214]In another embodiment, acid swellable associative polymers can be used with the hydrophobically modified, cationic polymers of the present invention. Such polymers generally have cationic and associative characteristics. These polymers are free radical addition polymers polymerized from a monomer mixture comprising an acid sensitive amino substituted hydrophilic monomer (e.g., dialkylamino alkyl (meth)acrylates or (meth)acrylamides), an associative monomer (defined hereinabove), a lower alkyl (meth)acrylate or other free radically polymerizable comonomers selected from hydroxyalkyl esters of (meth)acrylic acid, vinyl and/or allyl ethers of polyethylene glycol, vinyl and/or allyl ethers of polypropylene glycol, vinyl and/or allyl ethers of polyethylene glycol/polypropylene glycol, polyethylene glycol esters of (meth)acrylic acid, polypropylene glycol esters of (meth)acrylic acid, polyethylene glycol/polypropylene glycol esters of (meth)acrylic acid), and combinations thereof. These polymers can optionally be crosslinked. By acid sensitive is meant that the amino substituent becomes cationic at low pH values, typically ranging from about 0.5 to about 6.5. Exemplary acid swellable associative polymers are commercially available under the trade name Structure® Plus (INCI Name: Acrylates/Aminoacrylates/C10-C30 Alkyl PEG-20 Itaconate) from Akzo Nobel, and Carbopol® Aqua CC (INCI Name: Polyacrylates-1 Crosspolymer) from Lubrizol Advanced Materials, Inc. In one aspect, the acid swellable polymer is a copolymer of one or more C₁-C₅ alkyl esters of (meth)acrylic acid, C₁-C₄ dialkylamino C₁-C₆ alkyl methacrylate, PEG/PPG-30/5 allyl ether, PEG 20-25 C₁₀-C₃₀ alkyl ether methacrylate, hydroxy C₂-C₆ alkyl methacrylate crosslinked with ethylene glycol dimethacrylate. Other useful acid swellable associative polymers are disclosed in U.S. Patent No. 7,378,479, the disclosure of which is herein incorporated by reference.

[0215] Hydrophobically modified alkoxylated methyl glucoside, such as, for example, PEG-120 Methyl Glucose Dioleate, PEG-120 Methyl Glucose Trioleate, and PEG-20 Methyl Glucose Sesquistearate, available from Lubrizol Advanced Materials, Inc., under the trade names, Glucamate® DOE-120, Glucamate™ LT, and Glucamate™ SSE-20, respectively, are also suitable rheology modifiers.

[0216] Polysaccharides obtained from tree and shrub exudates, such as gum Arabic, gum gahatti, and gum tragacanth, as well as pectin; seaweed extracts, such as alginates and carrageenans; algae extracts, such as agar; microbial polysaccharides, such as xanthan, gellan, and wellan; cellulose ethers, such as ethylhexylethylcellulose, hydroxybutylmethylcellulose, hydroxyethylmethylcellulose, hydroxyethylmethylcellulose, hydroxyethylcellulose, carboxymethylcellulose, hydroxyethylcellulose, methylcellulose; polygalactomannans, such as fenugreek gum, cassia gum, locust bean gum, tara gum, and guar gum; starches, such as corn starch, tapioca starch, rice starch, wheat starch, potato starch and sorghum starch can also be employed in the compositions herein as suitable thickeners and rheology modifiers.

[0217] Other rheology modifiers suitable for use in the personal care compositions of the invention are disclosed in U.S. Patent No. 7,205,271 the disclosure of which is herein incorporated by reference.

[0218] The rheology modifiers set forth above, when employed, can be used alone or in combination and typically are used in an amount ranging from about 0.1 wt. % to about 5 wt. % in one aspect, from about 0.3 wt. % to about 3 wt. % in another aspect, and from about 0.5 wt. % to about 2 wt. % in further aspect, based on the total weight of the personal care compositions of the present invention.

[0219] Where applicable, any known aerosol propellant can be utilized to deliver the personal care, home care, health care and institutional care compositions containing the cationically and hydrophobically modified Cassia polymers of the present invention in combination with one or more of the foregoing active ingredients and/or with the one or more additives and/or adjuvants, conventionally or popularly included in personal care, health care, home care, and institutional care products discussed above. Exemplary propellants include, but are not limited to, lower boiling hydrocarbons such as C₃-C₆ straight and branched chain hydrocarbons. Exemplary hydrocarbon propellants include propane, butane, isobutene, and mixtures thereof. Other suitable propellants include ethers, such as, dimethyl ether, hydrofluorocarbons, such as, 1,1-difluoroethane, and compressed gasses, such as air and carbon dioxide. These compositions can contain from about 0.5 to about 60 wt. % of the propellant in one embodiment and from about

0.5 to about 35 wt. % in another embodiment, based on the total weight of the composition.

[0220] While overlapping weight ranges for the various components and ingredients that can be contained in the compositions of the invention have been expressed for selected embodiments and aspects of the invention, it should be readily apparent that the specific amount of each component in the disclosed personal care, home care, health care, and institutional care compositions will be selected from its disclosed range such that the amount of each component is adjusted such that the sum of all components in the composition will total 100 wt. %. The amounts employed will vary with the purpose and character of the desired product and can be readily determined by one skilled in the formulation arts and from the literature.

[0221] It is also to be recognized that the choice and amount of ingredients in personal care, home care, health care and institutional care compositions that include the hydrophobically modified, cationically derived Cassia polymers of the invention can vary depending on the intended product and its function, as is well known to those skilled in the formulation arts. An extensive listing of ingredients and their conventional functions and product categories have been disclosed and can be readily ascertained from the literature, some of which can serve more than one function.

[0222] This invention is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

Methods

Monosaccharide Content

[0223] The monosaccharide content of Cassia gum can be determined using a method adapted from Englyst et al. ("Determination of Dietary Fibre as Non-Starch Polysaccharides by Gas-Liquid Chromatography." Analyst (117), November 1992, pp. 1707-1714. In this method, Cassia seed endosperm (300 mg), sand (300 mg), and acetone (40 mL) are stirred together for 30 minutes. The acetone (containing the fat fraction) is decanted and the remaining sample is dried in an 80°C bath. Polysaccharide

hydrolysis is performed using sulfuric acid (12 M, 5 mL) in a 35°C bath with magnetic stirring for 1 hr. Then, water (25 mL) is added, and hydrolysis is allowed to continue for another hour with stirring at a temperature of 100°C bath. The sample vial is cooled to room temperature in tap water. The hydrolysate solution (3 mL) is transferred to a new vial, and an ammonia solution (12.5 M, 1 mL) is added and mixed briefly (If the pH of the hydrolysate solution is not greater than 7, a little more ammonia solution is added). For the reduction of the monosaccharides in the hydrolysate, octan-2-ol (5 µL) and an ammonia-sodium tetrahydroborate solution (200 µL of a solution of 1.2 g sodium tetrahydroborate in 6 mL of 12.5M aqueous ammonia) are stirred together in a 40°C bath 30 minutes, after which glacial acetic acid (400 µL) is mixed in to neutralize the solution. The reduction solution (500 µL) is transferred to new glass vial and acetylated by adding 1-methyl imidazole (500 µL) and acetic anhydride (5 mL) and mixing for 10 minutes. Ethanol (900 µL) is added and mixing is continued for another 5 minutes, followed by adding deionized water (10 mL) and continued mixing for another 5 minutes. Bromophenol blue (500 µL) is added to the mixture. The vial is placed in an ice bath and aqueous potassium hydroxide (5 mL of a 7.5 M solution in water) is mixed into the vial. After 2 minutes, another 5 mL of the potassium hydroxide solution is placed into the vial and mixed. After 15 minutes, or when liquid separation occurs, the clear upper phase (ethyl acetate) is collected, leaving behind a lower blue aqueous phase. The ethyl acetate phase is diluted in methanol (4X by volume) and injected

into a Hewlett Packard 6890 gas chromatograph equipped with a flame ionization detector. The components of the sample are separated by a 30 m by 0.32 mm fused silica column coated with 0.5 µm RTX-50 stationary phase. The GC oven is maintained at 225°C isothermally throughout the run. Inlet and detector temperatures are maintained at 275°C. Mannitol-hexaacetate is detected at 12.1-12.2 minutes, sorbitol-hexaacetate is detected at 12.4-12.5 minutes, and galactitol-hexaacetate is detected at 12.9-13.0 minutes. Utilizing this procedure the mannose:galactose ratios of tested galactomannans is as follows:

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Galactomannan	Mannose:Galactose Ratio	Galactose (wt.%)
Cassia Gum	8.5	11
Guar Gum	1.5	40
Tara Gum	3.0	25
Locust Bean Gum	3.2	24

Molecular Weight

[0225]For dissolution of each gum sample, 250mg of gum is weighed and dispersed into 50ml of DI water. This slurry/solution is then de-gassed by bubbling nitrogen gas through the mixture for 30 minutes followed by refluxing at 115°C for 2 hours. The sample is then cooled to 0°C at which time 1.5g of NaOH and 1.0g urea are added with stirring. Once all of the components are dissolved, the sample is placed in a freezer at -12°C and frozen solid overnight. The following day the sample is warmed to room temperature in a water bath and is fully thawed. It is then placed back into the freezer and frozen solid overnight. Each sample is subjected to a total of 3 freeze/thaw cycles before being neutralized to pH 7 with approx. 2.2mL of glacial acetic acid. This process renders fully soluble viscous solutions. The weight average molecular weights and number average molecular weights referenced herein are measured by refractive index and low angle light scattering detectors at room temperature using a 2x PLaquagel OH-Mixed-H 8 µm 300 x 7.5 mm column at a concentration of approximately 0.9 mg/mL in a buffer solution of 0.2M NaNO₃, 0.01M NaH₂PO₄ at pH-7 as the eluent at a flow rate of 1 mL/min. (Each sample was pre-filtered through a 0.5 μm syringe filter.) The detectors employed are a PL-GPC 50 Plus Refractive Index Detector with a PD 2020 Light Scattering Detector. PL-Cirrus software is used to analyze the results and to calculate M_n and M_w of the polygalactomannan. The M_w of the starting (unmodified) Cassia gum used herein is determined to be 900,000 Daltons, and the M_w of the starting (unmodified) guar gum used herein is determined to be 2,000,000 Daltons.

Degree Of Substitution

[0226] The degree of cationic substitution, DS_I is determined from the wt.% nitrogen determined in the first step— $DS_I = \%N_{\text{step}1} \text{ X } (MW_{\text{anhydrous saccharide}}) / (MW_N \text{ X } a - \%N_{\text{step}1} \text{ X } MW_{\text{cat}})$, where a is the number of nitrogen equivalents contained in the cationic

substituent, $MW_{anhydrous\ saccharide} = 162\ g/mol$, $MW_N = 14\ g/mol$, and MW_{cat} is the molecular weight of the cationic substituent. The degree of hydrophobic substitution (DS_{II}) can be determined using 1H -NMR. First, the hydrophobic and cationic galactomannan is dispersed into water. Then, the dispersion is diluted with an equal volume of isopropanol. To remove any residual hydrophobic reagent, the resulting solution is filtered using tangential flow filtration (10,000 Dalton molecular weight cutoff membrane), and the solution is concentrated followed by diluting with an equal volume of water (repeated ten times). After concentrating a final time, the solution is frozen and then freeze-dried. A 1H -NMR spectrum is acquired in d₆-DMSO/D₂O (1:1 (v/v)) at a temperature of 363° Kelvin. DS_{II} is derived from the ratio of the integrals of the methyl and methylene peaks of the hydrophobe and the anomeric proton of the saccharide residues.

Fixative Properties

High Humidity Spiral Curl Retention (HHSCR) Test

[0227] The resistance of a polymer fixative composition to high humidity (about 90% Relative Humidity (RH)) is an important property for fixative applications and is measured by its ability to hold a curl set on hair after absorption of water from the applied composition and from the surrounding atmosphere employing the well known technique commonly referred to as high humidity spiral curl retention (HHSCR). Descriptions of the HHSCR methodology are readily found in the cosmetic literature (see, for example, Ch. 30, Harry's Cosmeticology, 8th Ed., M. J. Rieger, Ph.D. (ed.), pp. 666-667, Chemical Publishing Co., Inc., New York, N.Y., 2000, and Diaz et al., J. Soc. Cosmet. Chem., 34, pp. 205-212, July 1983, the relevant disclosures of each are incorporated herein by reference.

[0228] Tresses of commercially blended untreated (virgin) human hair are prepared employing natural brown or black color European hair supplied by International Hair Importers and Products Inc., New York. The tresses used for this test are comprised of European brown hair, weighing 0.5g, 7 inches long and 0.5 inches wide with a sewn/glued flat binding and are individually wrapped (from root to tip) around a spiral perm rod (Cyber Sprials™ large spiral curling rods, 8 mm inner diameter, 13.5 mm outer

diameter, 162 mm length, American Discount Beauty Supply, 269 South Beverly Drive #250, Beverly Hills, Calif.). Prior to use, each tress is washed with a dilute aqueous solution of sodium lauryl sulfate (10% SLS) followed by thorough rinsing with deionized water at ambient room temperature. The tresses are dried by towel blotting. The initial extended length of the hair tress (L_e) is measured and recorded. 0.1g of the polymer fixative compositions to be evaluated is applied to each hair tress. The polymer fixative composition to be evaluated is applied to the hair tress and distributed uniformly from the root portion of the hair to tip portion. The treated hair tress is wrapped around a spiral hair curler and dried for 12 hours at ambient room temperature of about 21 to 23°C and controlled relative humidity (50%). After drying, the curler is carefully removed, leaving the hair tress styled into a spiral curl, the initial length of the hair curl (L_i) is measured and recorded. The curled hair tress is vertically hung in a humidity chamber set at a temperature of about 23°C and a relative humidity level of 90%.

[0229] High humidity spiral curl retention is determined by measuring the length of the hair curl as the curl relaxes (L_t). The change in curl length (droop) is periodically measured at selected intervals and is monitored over a period of 24 hours. An initial measurement is taken at time zero, followed by measurements at 0.25 hour intervals for the first hour of exposure, followed by measurements taken at 0.5 hour intervals for the second hour of exposure, followed by measurements taken at 1.0 hour intervals for the remaining 22 hours of exposure. The following equation is used to calculate percent curl retention, relative to the initial curl length (L_i) and length of the fully extended hair, before curling (L_e):

[0230] A curl retention of about 70% or more for a minimum period of about 0.75 hours at about 90% RH is a conventional benchmark for good high humidity resistance, and an HHSCR greater than 70% after a period of at least about 3 hours is deemed very good to excellent.

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Mechanical Stiffness Test Method

[0231] A TA XTPlus Texture Analyser (Stable Micro Systems, Surrey, UK) fitted with a rectangular loading nose (3 mm thick x 70 mm wide x 99 mm high) and a 3-point bending rig is employed to evaluate the mechanical stiffness of a fixative treated hair tress. The Texture Analyser is interfaced with a personal computer loaded with Texture Exponent 32 data acquisition software that collects and analysis the data inputted from the instrument. The bending rig consists of two parallel support legs that are spaced apart by approximately 25.4 mm. The treated hair swatch test sample is centered across the span of the support legs and the loading nose which is centered above and between the support legs is pressed through the sample at a rate of 40 mm/s for a distance of 20 mm. Data acquisition starts when the loading nose contacts the sample. The data acquisition software calculates and records the amount of force (Newtons) it takes to deflect the sample through a distance of 20 mm. The results are reported as Peak Force (N) and Work (N·mm).

[0232] Hair swatches (6.5" long, 2.5 g in weight) consisting of virgin natural human hair are bound with a flat (sewn and waxed) binding so that the tress has a uniform rectangular cross section along its whole length. The tresses are washed with a stripping shampoo containing 10 wt. % ammonium lauryl sulfate and rinsed with deionized water. A designated amount of experimental fixative is evenly applied to the damp hair swatches. A first set of swatches are laid flat on Teflon® foil to dry at 23°C and 50 % relative humidity in a controlled laboratory environment for 16 hours and tested. A second set of swatches is similarly prepped and subsequently placed in a humidity chamber (Espec LHU-113) set at 23°C and 90 % relative humidity for 16 hours and subsequently tested for mechanical stiffness.

Sensory Panel Testing of Conditioning Attributes

[0233] Two-in-one shampoo formulations are compared by a trained panel (at least 3 panelists) for conditioning attributes using a forced choice test design between two treated hair tresses. Hair tresses treated with a base 2-in-1 shampoo formulation that includes a cationically and hydrophobically modified Cassia polymer of the invention (Formulation 1) are compared to hair tresses treated with an identical base shampoo

formulation containing a commercially available cationic polymer (Formulation 2). Each panelist is asked to indicate which tress performs better for each of 4 sensory attributes evaluated in comparing the two test formulations on the treated hair tresses. The sensory attributes evaluated by the panel include (1) ease of wet combing, (2) wet feel (slippery feel or wet conditioned feel), (3) ease of dry combing, and (4) dry feel (soft feel or dry conditioned feel). The test protocol utilizes a matrix design of 6 treated tresses (3 replicates for each of test Formulations 1 and 2). The test matrix allows for the direct blind comparison of the 3 replicate treated tresses of Formulation 1 versus the 3 replicate treated tresses of Formulation 2. By permutation of the 3 replicate treatments for each of Formulations 1 and 2, nine comparisons of paired tresses (Formulation 1 versus Formulation 2) are possible. The matrix is designed such that duplicate evaluations are included from the panel members. A total of 36 comparisons are carried out with the matrix design. A statistical analysis (Z-value calculation of preference of Formulation 1 versus Formulation 2) is used to determine the level of confidence that Formulation 1 is statistically different (better or worse for the selected sensory attribute) from Formulation 2.

Hair Tress Preparation Procedure for Sensory Panel Testing

[0234] Hair tresses (Caucasian brown hair or Caucasian bleached hair) weighing 2.5 g (dry wt.) are prewashed with a stripping shampoo (surfactant iso-propanol mixture containing 10 wt. % sodium lauryl sulfate and 10 wt. % iso-propanol) and thoroughly rinsed under warm tap water to remove the shampoo. Excess water is removed by pinching each tress between the index finger and the middle finger and gently pulling the tress through the gap of the fingers. The damp tress is placed on top of the weighing dish and 0.5 g of the test shampoo formulation is applied evenly down the length of the hair tress. The shampoo is massaged into the tress from the root to the tip of the hair tress. The tress is then rinsed under warm tap water for approximately 60 seconds. While rinsing, the tress is combed through its length at least 20 to 25 times to ensure that all residual shampoo is removed. The treatment step is repeated a second time for a total of two washes/rinses.

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Dispersion Viscosity Measurements

Dispersions of the galactommanan (cassia or guar) at 1 wt.% can be prepared [0235] by adding 4.0 g of the guar or cassia sample to 396 g of distilled water at room temperature and stirring at about 700 rpm. In the case of a cold water-soluble galactomannan such as guar gum, derivatives of guar gum, or derivatives of cassia gum; the dispersion is stirred for 30 minutes at room temperature (20°C) and kept for an additional hour at a temperature of 20°C. In the case of galactomannans that are not cold water-soluble such as cassia gum, the dispersion is stirred for 30 minutes at room temperature and heated in a hot water bath to 85°C for an additional 30 minutes. After cooling to between 60 to 70°C, the loss of water is compensated and the solution is kept at a temperature of 20°C for another hour. The Brookfield viscosity (BV) of each polymer containing composition is measured as mPa·s, employing a Brookfield rotating spindle viscometer, Model RVT (Brookfield Engineering Laboratories, Inc.), at about 20 revolutions per minute (rpm), at ambient room temperature of about 20 to 25°C (hereafter referred to as viscosity). Spindle sizes are selected in accordance with the standard operating recommendations from the manufacturer.

Shampoo Formulation

[0236] The shampoo compostions set forth in the examples are formulated as follows:

- 1. Slowly add the modified cationic test polymer to water and agitate until homogeneous.
- 2. Add cocamidopropylbetaine to and agitate until homogenous.
- 3. Add sodium laureth sulfate and agitate until homogenous.
- 4. Add conditioner(s) component one at a time, mixing well after the addition of each component before proceeding.
- 5. Add sodium chloride.
- 6. Adjust pH.

Example A

[0237] To a reaction vessel 160 g of Cassia gum (containing about 10% moisture by weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm

of Cassia tora and Cassia obtusifolia is added to a solution of 921 g of 44% isopropanol and slurried. To this slurry, 4.5 g of potassium hydroxide is added and the mixture is heated at 40°C for 30 minutes under a nitrogen blanket. 92.8 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is diluted with 380 g of 99% isopropanol and neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 380 g of 99% isopropanol, air dried overnight and oven dried at 100°C for 4 hours to produce 179.3 of cationically derived Cassia. The final product contains 2.18 wt % nitrogen on a dry weight basis, or a degree of cationic substitution DS_I of 0.33, and has a BV of 364 mPa·s (1 wt.% in water).

Example 1

[0238] To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1400 g of 60% isopropanol, and filtered again. To a reaction vessel 650 g of filter cake is added to a solution of 1160 g of 62% isopropanol and slurried. To this slurry, 6.4 g of sodium hydroxide is added under a nitrogen blanket. 340 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70° C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 2300 g of 80% isopropanol, and filtered again. The product contains 3.3 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.59, as measured by elemental analysis. To a reaction vessel 330 g of the filter cake of the cationically derived Cassia is added to a solution of 840 g of 70% isopropanol and

slurried. To this slurry, $4.7 \, \mathrm{g}$ of sodium hydroxide is added under a nitrogen blanket. 14 g of 2,3-epoxypropyl hexadecyl ether (SaChem) is then added to the slurry. The reaction slurry is heated to $70^{\circ}\mathrm{C}$ and the reaction allowed to proceed at this temperature for 3 hours. After cooling to $50^{\circ}\mathrm{C}$, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 335 g of 80% isopropanol, air dried overnight and oven dried at $100^{\circ}\mathrm{C}$ for 4 hours to produce 160 g of cationically and hydrophobically modified Cassia. The final product contains a degree of hydrophobic substitution DS_{II} of 0.01 hexadecyl (C16) functionality as determined by $^{1}\mathrm{H}$ -NMR and has a BV of 500 mPa·s (1 wt.% in water).

Example 2

[0239] To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1400 g of 60% isopropanol, and filtered again. To a reaction vessel 650 g of filter cake is added to a solution of 1160 g of 62% isopropanol and slurried. To this slurry, 6.4 g of sodium hydroxide is added under a nitrogen blanket. 340 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 2300 g of 80% isopropanol, and filtered again. The product contains 3.3 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.59, as measured by elemental analysis. To a reaction vessel 330 g of filter cake of cationically derived Cassia is added to a solution of 840 g of 70% isopropanol and slurried. To this slurry, 4.7 g of sodium hydroxide is added under a nitrogen blanket. 42 g of 2,3epoxypropyl hexadecyl ether (SaChem) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After

cooling to 50° C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 340 g of 80% isopropanol, air dried overnight and oven dried at 100°C for 4 hours to produce 160 g of cationically and hydrophobically modified Cassia. The final product contains a degree of hydrophobic substitution DS_{II} of 0.02 hexadecyl (C16) functionality as determined by ¹H-NMR, and has a BV of 400 mPa·s (1 wt.% in water).

Example 3

To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by [0240] weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1400 g of 60% isopropanol, and filtered again. To a reaction vessel 640 g of filter cake is added to a solution of 1270 g of 62% isopropanol and slurried. To this slurry, 6.3 g of sodium hydroxide is added under a nitrogen blanket. 340 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70° C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 2360 g of 80% isopropanol, and filtered again. The product contains 2.9 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.49, as measured by elemental analysis. To a reaction vessel 140 g of filter cake of cationically derived Cassia is added to a solution of 370 g of 70% isopropanol and slurried. To this slurry, 2.0 g of sodium hydroxide is added under a nitrogen blanket. 18 g of 2,3epoxypropyl hexadecyl ether (SaChem) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 240 g of 80% isopropanol, air dried overnight and oven dried at 100°C for 4 hours to produce 93 g of cationically and hydrophobically

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modified Cassia. The final product contains a degree of hydrophobic substitution DS_{II} of 0.01 hexadecyl (C16) functionality as determined by $^{1}\text{H-NMR}$, and has a 1 wt.% (in water) BV of 250 mPa·s.

Example 4

To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by [0241] weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1350 g of 60% isopropanol, and filtered again. To a reaction vessel 640 g of filter cake is added to a solution of 1150 g of 62% isopropanol and slurried. To this slurry, 6.3 g of sodium hydroxide is added under a nitrogen blanket. 270 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 1980 g of 80% isopropanol, and filtered again. The product contains 3.5 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.65, as measured by elemental analysis. To a reaction vessel 150 g of filter cake of cationically derived Cassia is added to a solution of 420 g of 68% isopropanol and slurried. To this slurry, 2.0 g of sodium hydroxide is added under a nitrogen blanket. 6.7 g of 2,3epoxypropyl behenyl ether (SaChem) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 250 g of 80% isopropanol, air dried overnight and oven dried at 100°C for 4 hours to produce 98 g of cationically and hydrophobically modified Cassia. The final product contains a degree of hydrophobic substitution DS_{II} of 0.01 behenyl (C22) functionality as determined by ¹H-NMR, and has a BV of 540 mPa·s (1 wt.% in water).

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Example 5

To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by [0242] weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1350 g of 60% isopropanol, and filtered again. To a reaction vessel 640 g of filter cake is added to a solution of 1150 g of 62% isopropanol and slurried. To this slurry, 6.3 g of sodium hydroxide is added under a nitrogen blanket. 270 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70° C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50° C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 1980 g of 80% isopropanol, and filtered again. The product contains 3.5 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.65, as measured by elemental analysis. To a reaction vessel 150 g of filter cake of cationically derived Cassia is added to a solution of 420 g of 68% isopropanol and slurried. To this slurry, 2.3 g of sodium hydroxide is added under a nitrogen blanket. 20.2 g of n-butyl glycidyl ether (SaChem) is then added to the slurry. The reaction slurry is heated to 70° C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 250 g of 80% isopropanol, air dried overnight and oven dried at 100°C for 4 hours to produce 100 g of cationically and hydrophobically modified Cassia. The final product contains a degree of hydrophobic substitution DS_{II} of 0.31 butyl functionality as determined by ¹H-NMR, and has a BV of 472 mPa·s (1 wt.% in water).

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Example 6

To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by [0243] weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1300 g of 59% isopropanol, and filtered again. To a reaction vessel 650 g of filter cake is added to a solution of 1300 g of 61% isopropanol and slurried. To this slurry, 5.1 g of sodium hydroxide is added under a nitrogen blanket. 270 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 1970 g of 80% isopropanol, and filtered again. The product contains 2.7 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.44, as measured by elemental analysis. To a reaction vessel 140 g of filter cake of cationically derived Cassia is added to a solution of 370 g of 68% isopropanol and slurried. To this slurry, 2.0 g of sodium hydroxide is added under a nitrogen blanket. 18.2 g of n-butyl glycidyl ether (SaChem) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 230 g of 80% isopropanol, air dried overnight and oven dried at 100°C for 4 hours to produce 94 g of cationically and hydrophobically modified Cassia. The final product contains a degree of hydrophobic substitution DS_{II} of 0.13 butyl functionality as determined by ¹H-NMR and has a BV of 160 mPa·s (1 wt.% in water).

Example 7

[0244] To a reaction vessel 200 g of Cassia gum (containing about 10% moisture by weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm

of Cassia tora and Cassia obtusifolia is added to a solution of 1450 g of 24% isopropanol and slurried. To this slurry, 4.1 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 620 g of 66% isopropanol, and filtered again. To a reaction vessel 580 g of filter cake is added to a solution of 720 g of 55% isopropanol and slurried. To this slurry, 3.0 g of sodium hydroxide is added under a nitrogen blanket. 110 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 810 g of 80% isopropanol, and filtered again. To a reaction vessel 260 g of filter cake of cationically derived Cassia is added to a solution consisting of 150 g of water, 820 grams of tert-butanol, and 90 g of acetone and slurried. To this slurry, 5.0 g of sodium hydroxide is added under a nitrogen blanket. 9.4 g of hexadecyl bromide (Aldrich) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with a solution consisting of 30 g of water, 170 grams of tertbutanol, and 20 g of acetone, air dried overnight and oven dried at 100°C for 4 hours to produce 130 g of cationically and hydrophobically modified Cassia. The final product has a BV of 550 mPa·s (1 wt.% in water).

Example 8

[0245] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 1 (Formulation A) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 3.5 wt.% nitrogen (DS_I of 0.65) and devoid of hydrophobic modification (Formulation B) are formulated with the components set forth in Table 1.

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Table 1

Component	Formulation A Active (wt.%)	Formulation B Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced	14	14
Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 1)	0.25	
Cationic Cassia (Example A)		0.25
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0246] A sensory panel test is conducted to compare the conditioning performance of Formulation A versus Formulation B on Caucasian brown hair tresses in accordance with the methodology in the Sensory Panel Testing of Conditioning Attributes methodology described above. Formulation A containing the cationically and hydrophobically modified Cassia polymer of Example 1 displays statistically significant better wet and dry conditioning properties in comparison to Formulation B containing the cationically modified cassia (3.5%N or DS_I of 0.65) that is devoid of hydrophobic modification on Caucasian brown hair. The results of the panel test indicate that hair tresses treated with Formulation A have better wet combing attributes (99% confidence level), and better wet feel attributes (95% confidence level), better dry combing attributes (99% confidence level) and better dry feel attributes (99% confidence level) than formulation B on Caucasian brown hair.

Example 9

[0247] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 1 (Formulation C) and a cationically derivatized Cassia polymer synthesized in accordance with Example A

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containing 3.5 wt.% nitrogen (DS_I of 0.65) and devoid of hydrophobic modification (Formulation D) are formulated with the components set forth in Table 2.

Table 2

Component	Formulation C Active (wt.%)	Formulation D Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 1)	0.25	
Cationic Cassia (Example A)		0.25
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH= 6.0	q.s. to pH= 6.0

[0248] A sensory panel test is conducted to compare the conditioning performance of Formulation C versus Formulation D on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol described above. Formulation C containing the cationically and hydrophobically modified Cassia polymer of Example 1 displays statistically significant better wet and dry conditioning properties in comparison to Formulation D containing the cationically modified cassia (3.5%N or DS₁ of 0.65) that is devoid of hydrophobic modification on Chinese hair. The results of the panel test indicate that hair tresses treated with Formulation C have better wet combing attributes (99% confidence level), and better wet feel attributes (99% confidence level), better dry combing attributes (99% confidence level) and better dry feel attributes (99% confidence level) than formulation D on Chinese hair.

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Example 10

[0249] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 2 (Formulation E) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 3.5 wt.% nitrogen (DS_I of 0.65) and devoid of hydrophobic modification (Formulation F) are formulated with the components set forth in Table 3.

Table 3

Component	Formulation E Active (wt.%)	Formulation F Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine [™] (Lubrizol Advanced Materials, Inc.)	3	3
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 2)	0.25	
Cationic Cassia (Example A)		0.25
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH= 6.0	q.s. to pH= 6.0

[0250] A sensory panel test is conducted to compare the conditioning performance of Formulation E versus Formulation F on Caucasian brown hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes methodology above. Formulation E containing the cationically and hydrophobically modified Cassia polymer of Example 2 displays statistically significant better wet and dry conditioning properties in comparison to Formulation F containing the cationically modified cassia (3.5%N or DS_I of 0.65) that is devoid of hydrophobic modification on Caucasian brown hair. The results of the panel test indicate that hair tresses treated with Formulation E have better wet combing attributes (99% confidence level), better dry combing attributes (99% confidence level) than formulation F on Caucasian Brown hair. No significant statistical

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differences in the wet feel attributes are observed between tresses treated with the two formulations.

Example 11

[0251] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 2 (Formulation G) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 3.5 wt.% nitrogen (DS_I of 0.65) and devoid of hydrophobic modification (Formulation H) are formulated with the components set forth in Table 4.

Table 4

Component	Formulation G Active (wt.%)	Formulation H Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 2)	0.25	
Cationic Cassia (Example A)		0.25
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0252] A sensory panel test is conducted to compare the conditioning performance of Formulation G versus Formulation H on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol above. Formulation G containing the cationically and hydrophobically modified polymer of Example 2 displays statistically significant better wet and dry conditioning properties in comparison to Formulation H containing the cationically modified cassia (3.5%N or DS_I of 0.65) that is devoid of hydrophobic modification on Chinese hair. The results of the panel test indicate that hair tresses treated with Formulation G have better

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wet combing attributes (99% confidence level), better wet feel attributes (99% confidence level), better dry combing attributes (99% confidence level) and better dry feel attributes (99% confidence level) than formulation H on Chinese hair.

Example 12

[0253] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified derivatized Cassia polymer of Example 3 (Formulation I) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 2.9 wt.% nitrogen (DS_I of 0.49) and devoid of hydrophobic modification (Formulation J) are formulated with the components set forth in Table 5.

Table 5

Component	Formulation I Active (wt.%)	Formulation J Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 3)	0.25	
Cationic Cassia (Example A)		0.25
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0254] A sensory panel test is conducted to compare the conditioning performance of Formulation I versus Formulation J on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol above. Formulation I containing the cationically and hydrophobically modified Cassia polymer of Example 3 displays statistically significant better wet and dry conditioning properties in comparison to Formulation J containing the cationically modified Cassia (2.9%N or DS_I of 0.49) that is devoid of hydrophobic modification on Chinese hair. The

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results of the panel test indicate that hair tresses treated with Formulation I have better wet combing attributes (99% confidence level), and better dry combing attributes (99% confidence level) than formulation J on Chinese hair. No statistically significant difference in wet feel is observed between the two formulations on Chinese hair. Better dry feel (99% confidence level) is observed for formulation J on Chinese hair.

Example 13

[0255] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 4 (Formulation K) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 3.5 wt.% nitrogen (DS_I of 0.65) and devoid of hydrophobic modification (Formulation L) are formulated with the components set forth in Table 6.

Table 6

Component	Formulation K Active (wt.%)	Formulation L Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 4)	0.25	
Cationic Cassia (Example A)		0.25
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0256] A sensory panel test is conducted to compare the conditioning performance of Formulation K versus Formulation L on Caucasian brown hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol described above. Formulation K containing the cationically and hydrophobically modified Cassia polymer of Example 4 displays statistically significant

better wet and dry conditioning properties in comparison to Formulation L containing the cationically modified cassia (3.5%N DS_I of 0.65) that is devoid of hydrophobic modification on Caucasian brown hair. The results of the panel test indicate that hair tresses treated with Formulation K have better wet combing attributes (95% confidence level), better dry combing attributes (95% confidence level), and better dry feel attributes (95% confidence level) than formulation L on Caucasian brown hair. No significant statistical differences in the wet feel attributes are observed between tresses treated with the two formulations.

Example 14

[0257] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 1 (Formulation M) and a commercially available cationic guar polymer (Formulation N) are formulated with the components set forth in Table 7.

Table 7

Component	Formulation M Active (wt.%)	Formulation N Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 1)	0.25	
Guar Hydroxypropyltrimonium Chloride Jaguar C-13S (Rhodia)		0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0258] A sensory panel test is conducted to compare the conditioning performance of Formulation M versus Formulation N on Caucasian brown hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes

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protocol above. Formulation M containing the cationically and hydrophobically modified Cassia polymer of Example 1 displays statistically significant better wet and dry conditioning properties in comparison to Formulation N containing the cationic guar on Caucasian brown hair. The results of the panel test indicate that hair tresses treated with Formulation M have better wet combing attributes (99% confidence level), better wet feel attributes (99% confidence level), better dry combing attributes (99% confidence level) and better dry feel attributes (99% confidence level) than formulation N on Caucasian brown hair.

Example 15

[0259] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified derivatized Cassia polymer of Example 1 (Formulation O) and a commercially available cationic guar polymer (Formulation P) are formulated with the components set forth in Table 8.

Table 8

Component	Formulation O Active (wt.%)	Formulation P Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 1)	0.25	
Guar Hydroxypropyltrimonium Chloride Jaguar C-13s (Rhodia)		0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0260] A sensory panel test is conducted to compare the conditioning performance of Formulation O versus Formulation P on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol

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above. Formulation O containing the cationically and hydrophobically modified Cassia polymer of Example 1 displays statistically significantly better wet and dry conditioning properties in comparison to Formulation P containing the cationic guar on Chinese hair. The results of the panel test indicate that hair tresses treated with Formulation O have better wet combing attributes (99% confidence level), better wet feel attributes (99% confidence level) and better dry combing attributes (99% confidence level) than formulation P on Chinese hair. No statistically significant differences in dry feel attributes are observed between the formulations.

Example 16

[0261] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 1 (Formulation Q) and a commercially available cationic polyquaternium 10 polymer (Formulation R) are formulated with the components set forth in Table 9.

Table 9

Component	Formulation Q Active (wt.%)	Formulation R Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 1)	0.25	
Polyquaternium-10 Ucare JR400 (Dow Chemical – Amerchol Corporation)		0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH= 6.0	q.s. to pH= 6.0

[0262] A sensory panel test is conducted to compare the conditioning performance of Formulation Q versus Formulation R on Caucasian brown hair tresses in accordance with

the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol above. Formulation Q containing the cationically and hydrophobically modified Cassia polymer of Example 1 displays statistically significant better wet and dry conditioning properties in comparison to Formulation R containing the PQ 10 polymer on Caucasian brown hair. The results of the panel test indicate that hair tresses treated with Formulation Q have better wet combing attributes (99% confidence level), better wet feel attributes (99% confidence level), better dry combing attributes (99% confidence level) and better dry feel attributes (99% confidence level) than formulation R on Caucasian brown hair.

Example 17

[0263] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 1 (Formulation S) and a commercially available cationic polyquaternium 10 polymer (Formulation T) are formulated with the components set forth in Table 10.

Table 10

Component	Formulation S Active (wt.%)	Formulation T Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 1)	0.25	
Polyquaternium-10 Ucare JR400 (Dow Chemical – Amerchol Corporation)		0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0264] A sensory panel test is conducted to compare the conditioning performance of Formulation S versus Formulation T on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol above. Formulation S containing the cationically and hydrophobically modified Cassia polymer of Example 1 displays statistically significant better wet and dry conditioning properties in comparison to Formulation T containing the Polyquaternium 10 polymer on Chinese hair. The results of the panel test indicate that hair tresses treated with Formulation S have better wet combing attributes (99% confidence level), better wet feel attributes (99% confidence level) and better dry combing attributes (99% confidence level) than formulation T on Chinese hair.

Example 18

[0265] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 1 (Formulation U) and a commercially available cationic polyquaternium 10 polymer (Formulation V) are formulated with the components set forth in Table 11.

Table 11

Component	Formulation U Active (wt.%)	Formulation V Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 1)	0.25	
Polyquaternium-10 Ucare JR400 (Dow Chemical – Amerchol Corporation)		0.25
Silicone Emulsion (DC 1491) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

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[0266] A sensory panel test is conducted to compare the conditioning performance of Formulation U versus Formulation V on Caucasian brown hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol above. Formulation U containing the cationically and hydrophobically modified Cassia polymer of Example 1 displays statistically significant better wet and dry conditioning properties in comparison to Formulation V containing the PQ 10 polymer on Caucasian brown hair. The results of the panel test indicate that hair tresses treated with Formulation U have better wet feel attributes (99% confidence level), and better dry feel attributes (99% confidence level) than formulation V on Caucasian brown hair. No significant differences in dry combing attributes and wet combing attributes are observed in the two formulations on Caucasian brown hair.

Example 19

To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by [0267] weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 2000 g of 60% isopropanol, and filtered again. To a reaction vessel 630 g of filter cake is added to a solution of 1100 g of 62% isopropanol and slurried. To this slurry, 6.2 g of sodium hydroxide is added under a nitrogen blanket. 330 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 2300 g of 80% isopropanol, and filtered again. The product contains 3.5 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.65, as measured by elemental analysis. To a reaction vessel 240 g of filter cake of the cationically derivatized Cassia is added to a solution of 590 g of 70% isopropanol and slurried. To this slurry, 3.34 g of sodium hydroxide is added under a nitrogen blanket.

An alkylation reagent, 19.8 g of 2,3-epoxypropyl dodecyl ether (SaChem), is then added to the slurry. The alkylation agent is employed in a significantly greater stoichiometric amount relative to the glycoside content of the Cassia galactomannan utilized in Example 1 above to obtain a degree of hydrophobic substitution that is higher than the degree of hydrophobic substitution obtained therein. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 370 g of 80% isopropanol, air dried overnight and oven dried at 100°C for 4 hours to produce 95 g of hydrophobically-modified cationic Cassia. The final product has a BV of 510 mPa·s (1 wt.% in water).

Example 20

[0268] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 19 (Formulation W) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 3.5 wt.% nitrogen (DS₁ of 0.65) and devoid of hydrophobic modification (Formulation X) are formulated with the components set forth in Table 12.

Table 12

Component	Formulation W Active (wt.%)	Formulation X Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 19)	0.25	
Cationic Cassia (Example A)		0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

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[0269] A sensory panel test is conducted to compare the conditioning performance of Formulation W versus Formulation X on Caucasian brown hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes methodology described above. Formulation W containing the cationically and hydrophobically modified Cassia polymer of Example 19 displays statistically significant better wet conditioning properties in comparison to Formulation X containing the cationically modified cassia polymer that is devoid of hydrophobic modification on Caucasian brown hair. The results of the panel test indicate that hair tresses treated with Formulation W have statistically better wet feel attributes (99% confidence level), and better wet combing attributes (99% confidence level) than formulation X on Caucasian brown hair. No significant differences in dry combing attributes and dry feel attributes are observed in the two formulations on Caucasian brown hair.

Example 21

This comparative example illustrates the synthesis of a cationically and [0270] hydrophobically modified Cassia gum having a similar degree of cationic and hydrophobic substitution as the cationically and hydrophobically modified guar gum exemplified in Example 1 of WO 2010/009071. To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by weight and having a BV of 200 mPa·s (1 wt.%) in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1400 g of 50% isopropanol, and filtered again. To a reaction vessel 285 g of filter cake is added to a solution of 530 g of 62% isopropanol and slurried. To this slurry, 0.7 g of sodium hydroxide is added under a nitrogen blanket. 38 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 620 g of 80% isopropanol, and filtered

again. The product contains 1.1 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_T of 0.14, as measured by elemental analysis. To a reaction vessel, 210 g of filter cake of the cationically derivatized Cassia is added to a solution of 580 g of 70% isopropanol and slurried. To this slurry, 3.2 g of sodium hydroxide is added under a nitrogen blanket. An alkylation agent, 0.43 g of 2,3-epoxypropyl hexadecyl ether (SaChem), is then added to the slurry. The alkylation agent is employed in the same stoichiometric amount relative to the glycoside residue content of the polygalactomannan utilized in Example 1 of WO 2010/009071. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 530 g of 80% isopropanol, air-dried overnight and oven dried at 100°C for 4 hours to produce 92 g of cationically and hydrophobically modified Cassia having a similar degree of cationic and hydrophobic substitution as the cationically and hydrophobically modified guar polymer exemplified in Example 1 of WO 2010/009071. The final product has a BV of 450 mPa·s (1 wt.% in water).

Example 22

[0271] Two-in-one conditioning shampoo compositions including the comparative cationically and hydrophobically modified Cassia polymer of Example 21 (Formulation Y) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 1.2 wt.% nitrogen (DS_I of 0.16) and devoid of hydrophobic modification (Formulation Z) are formulated with the components set forth in Table 13.

Table 13

Component	Formulation Y Active (wt.%)	Formulation Z Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3	3
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Cassia (Example 21)	0.25	

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Component	Formulation Y Active (wt.%)	Formulation Z Active (wt.%)
Cationic Cassia (Example A)		0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0272] A sensory panel test is conducted to compare the conditioning performance of Formulation Y versus Formulation Z on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol set forth above. Formulation Z containing the cationic cassia polymer of 1.2% N (DS $_{\rm I}$ = 0.16) with no hydrophobe substitution displays statistically significant better wet conditioning properties in comparison to Formulation Y containing the cationically and hydrophobically modified Cassia polymer of comparative Example 21 on Chinese hair. The results of the panel test indicate that hair tresses treated with Formulation Z have statistically better wet feel attributes (99% confidence level), and better wet combing attributes (99% confidence level) than formulation Y on Chinese hair. No significant differences in dry combing attributes and dry feel attributes are observed between the two formulations on Chinese hair. These results show that a cassia polymer containing the degree of cationic and hydrophobic substitution as taught in WO2010009071A2 application does not lead to improved conditioning properties in cassia galactomannans.

Example 23

[0273] To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1400 g of 50% isopropanol, and filtered again. To a reaction vessel 285 g of filter cake is added to a solution of 530 g of 62% isopropanol and slurried. To this slurry, 0.7 g of sodium hydroxide is added under a nitrogen blanket.

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38 g of 2,3-epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%) is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 630 g of 80% isopropanol, and filtered again. The product contains 1.1 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.14, as measured by elemental analysis. To a reaction vessel, 210 g of the filter cake of the cationically derivatized Cassia is added to a solution of 575 g of 70% isopropanol and slurried. To this slurry, 3.2 g of sodium hydroxide is added under a nitrogen blanket. 14 g of 2,3-epoxypropyl hexadecyl ether (SaChem) is then added to the slurry. The reaction slurry is heated to 70° C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50° C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 720 g of 80% isopropanol, airdried overnight and oven dried at 100°C for 4 hours to produce 91 g of cationically and hydrophobically modified Cassia. The final product has a degree of hydrophobic substitution DS_{II} similar to or slightly higher than the modified Cassia of Example 1 based on the stoichiometry of the synthesis reaction. The final product has a BV of 460 mPa·s (1 wt.% in water).

Example 24

[0274] Two-in-one conditioning shampoo compositions including the cationically and hydrophobically modified Cassia polymer of Example 23 (Formulation AA) and a cationically derivatized Cassia polymer synthesized in accordance with Example A containing 1.2 wt.% nitrogen (DS_I of 0.16) and devoid of hydrophobic modification (Formulation BB) are formulated with the components set forth in Table 14.

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Table 14

	Formulation	Formulation
Component	AA	BB
	Active (wt.%)	Active (wt.%)
Sodium Laureth-2 sulfate		
Sulfochem [™] ES-2 (Lubrizol Advanced	14	14
Materials, Inc.)		
Cocamidopropylbetaine		
Chembetaine [™] (Lubrizol Advanced	3	3
Materials, Inc.)		
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified	0.25	
Cassia (Example 23)	0.25	
Cationic Cassia (Example A)		0.25
Silicone Emulsion (DC 1352)	2	2
(Dow Corning)	2	<u> </u>
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

A sensory panel test is conducted to compare the conditioning performance of [0275]Formulation AA versus Formulation BB on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol above. Formulation AA containing the cationically and hydrophobically modified Cassia polymer of Example 23 displays statistically significant better wet and dry combing properties in comparison to Formulation BB containing the cationic cassia polymer of 1.2%N (DS_I= 0.16) which has not been hydrophobically modified on Chinese hair. The results of the panel test indicate that hair tresses treated with Formulation AA have statistically better wet combing attributes (99% confidence level), and better dry combing attributes (99% confidence level) than formulation BB on Chinese hair. No significant difference in wet feel combing attributes is observed between the two formulations on Chinese hair. Better dry feel (95% confidence level) is observed for formulation BB compared formulation AA. Overall these results show that for a Cassia polymer containing a low degree of cationic substitution and a higher degree of hydrophobic substitution, as taught in this patent application, is needed to improve conditioning properties of Cassia galactomannan.

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Example 25

[0276] This example illustrates the synthesis of a cationically and hydrophobically modified Cassia gum having a greater degree of cationic substitution and a comparable degree of hydrophobic substitution than the cationically and hydrophobically modified guar polymer exemplified in Example 1 of WO 2010/009071. To a reaction vessel 335 g of Cassia gum (containing about 10% moisture by weight and having a BV of 200 mPa·s (1 wt.% in water)) obtained from the endosperm of Cassia tora and Cassia obtusifolia is added to a solution of 2,400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The Cassia is filtered, washed once with 1800 g of 50% isopropanol, and filtered again. To a reaction vessel 270 g of filter cake is added to a solution of 427 g of 62% isopropanol and slurried. To this slurry, 2.5 g of sodium hydroxide is added under a nitrogen blanket. A cationization agent, 130 g of 2,3epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc, 70%), is then added to the slurry. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride Cassia product is filtered, washed once with 922 g of 80% isopropanol, and filtered again. The product contains 3.4 wt % nitrogen on a dry weight basis or a degree of cationic substitution DS_I of 0.62, as measured by elemental analysis. To a reaction vessel, 240 g of filter cake of the cationically derivatized Cassia is added to a solution of 605 g of 70% isopropanol and slurried. To this slurry, 3.4 g of sodium hydroxide is added under a nitrogen blanket. An alkylation agent, 0.31 g of 2,3epoxypropyl hexadecyl ether (SaChem), is added to the slurry. The alkylation agent is employed in the same stoichiometric amount relative to the glycoside residue content of the polygalactomannan utilized in Example 1 of WO 2010/009071. The reaction slurry is heated to 70°C and the reaction proceeds at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 370 g of 80% isopropanol, air-dried overnight and

oven dried at 100°C for 4 hours to produce 91 g of cationically and hydrophobically modified Cassia. The final product has a BV of 520 mPa·s (1 wt.% in water).

Example 26

[0277] A two-in-one conditioning shampoo formulation including the cationically and hydrophobically modified Cassia polymer of Example 25 is prepared from the components set forth in Table 15.

Table 15

Component	Formulation CC Active (wt.%)
Sodium Laureth-2 sulfate Sulfochem [™] ES-2 (Lubrizol Advanced Materials, Inc.)	14
Cocamidopropylbetaine Chembetaine (Lubrizol Advanced Materials, Inc.)	3
Sodium Chloride	0.5
Cationically and Hydrophobically Modified Cassia (Example 25)	0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2
D.I. Water	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0

Example 27

[0278] This comparative example illustrates the synthesis of cationically and hydrophobically modified guar having a similar degree of cationic and hydrophobic substitution as the cationically and hydrophobically modified guar gum exemplified in Example 1 of WO 2010/009071. To a reaction vessel 335 g of guar gum (containing about 10% moisture by weight and having a BV of 2,700 mPa·s (1 wt.% in water)) is added to a solution of 2,400 g of 24% isopropanol and slurried. To this slurry, 22 g of sodium hydroxide is added under a nitrogen blanket. The slurry is heated to 60°C and this temperature is maintained for 3 hours. The guar gum is filtered, washed once with 1,500 g of 50% isopropanol, and filtered again. To a reaction vessel 260 g of filter cake is added to a solution of 475 g of 62% isopropanol and slurried. To this slurry, 0.64 g of sodium hydroxide is added under a nitrogen blanket. A cationization agent, 34 g of 2,3-

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epoxypropyltrimethyl ammonium chloride (Quab 151 from SKW Quab Chemicals Inc. 70%), is then added to the slurry. The cationization agent is employed in the same stoichiometric amount relative to the glycoside residue content of the polygalactomannan utilized in Example 1 of WO 2010/009071. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The hydroxypropyltrimethyl ammonium chloride guar product is filtered, washed once with 580 g of 80% isopropanol, and filtered again. To a reaction vessel, 220 g of filter cake of the cationically derivatized guar is added to a solution of 570 g of 70% isopropanol and slurried. To this slurry, 3.2 g of sodium hydroxide is added under a nitrogen blanket. An alkylation agent, 0.45 g of 2,3-epoxypropyl hexadecyl ether (SaChem), then added to the slurry. The alkylation agent is employed in the same stoichiometric amount relative to the glycoside residue content of the polygalactomannan utilized in Example 1 of WO 2010/009071. The reaction slurry is heated to 70°C and the reaction allowed to proceed at this temperature for 3 hours. After cooling to 50°C, the mixture is neutralized to a pH of about 7.0 with glacial acetic acid. The product is filtered, washed once with 390 g of 80% isopropanol, air-dried overnight and oven dried at 100°C for 4 hours to produce 93 g of hydrophobically-modified cationic guar. The product has a BV of 2,900 mPa·s (1 wt.% in water).

Example 28

[0279] Two-in-one conditioning shampoo formulations including the cationically and hydrophobically modified guar polymer of Example 27 (Formulation CC DD) and a commercially available cationically derivatized guar polymer devoid of hydrophobic modification (JaguarTM C13S with 1.5 wt.% nitrogen or a DS_I of 0.18) (Formulation EE) are prepared with the components set forth in Table 15.

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Table 15

Component	Formulation DD	Formulation EE
Sodium Laureth-2 sulfate	Active (wt.%)	Active (wt.%)
Sulfochem [™] ES-2 (Lubrizol Advanced	14	14
Materials, Inc.)	11	
Cocamidopropylbetaine		
Chembetaine (Lubrizol Advanced	3	3
Materials, Inc.)		
Sodium Chloride	0.5	0.5
Cationically and Hydrophobically Modified Guar (Example 27)	0.25	
Guar Hydroxypropyltrimonium Chloride Jaguar [™] C13S (Rhodia)		0.25
Silicone Emulsion (DC 1352) (Dow Corning)	2	2
D.I. Water	q.s. to 100	q.s. to 100
Citric Acid (20 % aqueous wt./wt.)	q.s. to pH 6.0	q.s. to pH 6.0

[0280] A sensory panel test is conducted to compare the conditioning performance of Formulation DD versus Formulation EE on Chinese hair tresses in accordance with the methodology set forth in the Sensory Panel Testing of Conditioning Attributes protocol above. Formulation EE containing the non-hydrophobically modified cationic guar polymer JaguarTM C13S displays statistically significant better wet and dry conditioning properties in comparison to Formulation DD containing the cationically and hydrophobically modified guar polymer of Example 27 on Chinese hair. The results of the panel test indicate that hair tresses treated with Formulation EE have statistically better wet combing attributes (99% confidence level), better wet feel (99% confidence level) hetter dry combing attributes (99% confidence level) and better dry feel (99% confidence level) than formulation DD on Chinese hair. These results show that a guar polymer containing the degrees of cationic and hydrophobic substitution disclosed in WO2010009071 do not lead to improved conditioning properties of a modified guar galactomannan.

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Example 29

[0281] Fixative compositions are tested for high humidity spiral curl retention as described in the Test Methodolgy above with 2.0 wt.% (in deionized water) modified polymer dispersions of the following compositions: hydrophobically and cationically modified cassia of Example 1 and cationic cassia devoid of hydrophobic modification synthesized as in Example A but containing 3.5% nitrogen (DS_I= 0.65).

[0282] 0.1g of the polymer fixative composition to be evaluated is applied to European brown hair tress. The treated hair tress is wrapped around a spiral hair curler and dried for 12 hours at ambient room temperature of about 21 to 23°C and controlled relative humidity (50%). After drying, the curler is carefully removed, leaving the hair tress styled into a spiral curl. The curled hair tress is vertically hung in a humidity chamber set at a temperature of about 23°C and a relative humidity level of 90%. The average of the high humidity spiral curl retention of 5 tresses is reported in Table 16.

Spiral curl Spiral curl Spiral curl Spiral curl 90%RH-23°C retention at 1 retention at 4 retention at 8 retention at 24 hour (%) hours (%) hours (%) hours (%) Hydrophocially and Cationically 84.7 ± 3.0 88.2 ± 0 88.2 ± 0 84.7 ± 3.0 Modified Cassia of Example 1 Cationic Cassia (3.5% Nitrogen - 84.1 ± 0.6 84.1 ± 0.6 81.8 ± 3.0 81.8 ± 3.0 $DS_{I} = 0.65$)

Table 16

[0283] The results show that the hydrophobically and cationically modified cassia polymer of Example 1 displays excellent high humidity spiral curl retention after 1, 4, 8 and 24 hrs. after exposure to 90% relative humidity at 23°C and is superior to the cationically modified cassia of comparable cationic charge density but without hydrophobic modification.

Example 30

[0284] Aqueous dispersions in deionized water containing 1 wt% of the hydrophobically and cationically modified cassia of Example 1 and cationic cassia

devoid of hydrophobic modification having 3.5% nitrogen content (DS_I= 0.65) are evaluated for mechanical stiffness properties as described in the Mechanical Stiffness Test Method above. European brown hair swatches are prepared and treated (0.8g of fixative composition/swatch) and evaluated for mechanical stiffness at 50 % relative humidity. Five replicates of each test sample are prepared and tested. The average peak force for the 5 replicates are calculated and recorded in Table 17.

Table 17

Sample	Work (N·mm)	Peak Force (N)
Hydrophocially and cationically modified cassia of Example 1	34.1 ± 3.3	6.7 ± 0.7
Cationic Cassia (3.5% Nitrogen or DS _I = 0.65)	27.7 ± 3.8	4.6 ± 0.6

[0285] The hydrophobically and cationically modified polymer of Example 1 demonstrates higher stiffness (higher peak force and Work) than the cationically modified cassia polymer of comparable cationic charge density with no hydrophobic substitution on European brown hair.

[0286] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention.

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WHAT IS CLAIMED IS:

1. A cationically and hydrophobically modified galactomannan having a mannose to galactose ratio of at least 5:1 wherein a portion of the hydrogen atoms of the hydroxyl groups present on the galactomannan are substituted with a least one cationic moiety represented by formula (I) and at least one hydrophobic moiety represented by formula (II) as follows:

$$(II) \qquad -(A) - (O) - R^1$$

wherein A, independently, is selected from a divalent linear or branched, substituted or unsubstituted C_1 - C_6 alkylene radical; R, independently, is selected from -S⁺R³R⁴ X⁻, - N⁺R³R⁴R⁵ X⁻, and -P⁺R³R⁴R⁵ X⁻, wherein R³ and R⁴, and R⁵, independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X⁻ represents an anion; R¹, independently, is selected from a hydrocarbon group having from about 2 to about 35 carbon atoms; a is 0 or 1; and b is 0 or 1; wherein the average cationic degree of substitution is from about 0.25 and above; and the average degree of hydrophobic substitution ranges from about 0.001 and above; subject to the provisos that when a is 0, b is 0, and when a and b are both 0, or when a is 1 and b is 0, R¹ can not represent a hydroxyalkyl group having 2 to 4 carbon atoms, and the total average degree of cationic and hydrophobic substitution can not exceed 3.0.

2. A cationically and hydrophobically modified galactomannan having a mannose to galactose ratio of at least 5:1 wherein a portion of the hydrogen atoms of the hydroxyl groups present on the galactomannan are substituted with a least one cationic moiety represented by formula (I) and at least one hydrophobic moiety represented by formula (II) as follows:



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(II)
$$---(A) ---(O) ----R^1$$

wherein A, independently, is selected from a divalent linear or branched, substituted or unsubstituted C_1 - C_6 alkylene radical; R, independently, is selected from -S⁺R³R⁴ X⁻, - N⁺R³R⁴R⁵ X⁻, and -P⁺R³R⁴R⁵ X⁻, wherein R³ and R⁴, and R⁵, independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X⁻ represents an anion; R¹, independently, is selected from a hydrocarbon group having from about 2 to about 35 carbon atoms; a is 0 or 1; and b is 0 or 1; wherein the average cationic degree of substitution is above 0.5; and the average degree of hydrophobic substitution is at least 0.00001 and above, subject to the provisos that when a is 0, b is 0, and when a and b are both 0, or when a is 1 and b is 0, R¹ can not represent a hydroxyalkyl group having 2 to 4 carbon atoms, and the total average degree of cationic and hydrophobic substitution can not exceed 3.0.

3. A cationically and hydrophobically modified galactomannan isolated from the endosperm of the seeds of Cassia tora, Cassia obtusifolia, and combinations thereof wherein a portion of the hydrogen atoms of the hydroxyl groups present on the galactomannan are substituted with a least one cationic moiety represented by formula (I) and at least one hydrophobic moiety represented by formula (II) as follows:

$$(II) \qquad \qquad -(A) - (O) - R^1$$

wherein A, independently, is selected from a divalent linear or branched, substituted or unsubstituted C_1 - C_6 alkylene radical; R, independently, is selected from - $S^+R^3R^4$ X^- , - $N^+R^3R^4R^5$ X^- , and - $P^+R^3R^4R^5$ X^- , wherein R^3 and R^4 , and R^5 , independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X^- represents an anion; R^1 ,

independently, is selected from a hydrocarbon group having from about 2 to about 35 carbon atoms; a is 0 or 1; and b is 0 or 1; wherein the average cationic degree of substitution is from about 0.25 and above; and the average degree of hydrophobic substitution ranges from about 0.001 and above; subject to the provisos that when a is 0, b is 0, and when a and b are both 0, or when a is 1 and b is 0, R¹ can not represent a hydroxyalkyl group having 2 to 4 carbon atoms, and the total average degree of cationic and hydrophobic substitution can not exceed 3.0.

4. A cationically and hydrophobically modified galactomannan isolated from the endosperm of the seeds of Cassia tora, Cassia obtusifolia, and combinations thereof wherein a portion of the hydrogen atoms of the hydroxyl groups present on the galactomannan are substituted with a least one cationic moiety represented by formula (I) and at least one hydrophobic moiety represented by formula (II) as follows:

$$(II) \qquad -(A) - (O) - R^1$$

wherein A, independently, is selected from a divalent linear or branched, substituted or unsubstituted C_1 - C_6 alkylene radical; R, independently, is selected from -S⁺R³R⁴ X⁻, - N⁺R³R⁴R⁵ X⁻, and -P⁺R³R⁴R⁵ X⁻, wherein R³ and R⁴, and R⁵, independently, are selected from hydrogen and linear and branched C_1 - C_{24} alkyl, and X⁻ represents an anion; R¹, independently, is selected from a hydrocarbon group having from about 2 to about 35 carbon atoms; a is 0 or 1; and b is 0 or 1; wherein the average cationic degree of substitution is above 0.5; and the average degree of hydrophobic substitution is at least 0.00001 and above, subject to the provisos that when a is 0, b is 0, and when a and b are both 0, or when a is 1 and b is 0, R¹ can not represent a hydroxyalkyl group having 2 to 4 carbon atoms, and the total average degree of cationic and hydrophobic substitution can not exceed 3.0.

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- 5. A cationically and hydrophobically modified galactomannan of claim 1 or 3, wherein the average cationic degree of substitution ranges from about 0.25 to about 1.75.
- 6. A cationically and hydrophobically modified galactomannan of claim 5, wherein the average cationic degree of substitution ranges from above 0.5 to about 1.75
- 7. A cationically and hydrophobically modified galactomannan of claim 6, wherein the average cationic degree of substitution ranges from 0.55 to about 1.75.
- 8. A cationically and hydrophobically modified galactomannan of claim 7, wherein the average cationic degree of substitution ranges from 0.6 to about 1.
- 9. A cationically and hydrophobically modified galactomannan of claim 1, 3, 5, 6, 7, or 8, wherein the average hydrophobic degree of substitution ranges from about 0.001 to about 1.25.
- 10. A cationically and hydrophobically modified galactomannan of claim 9, wherein the average hydrophobic degree of substitution ranges from 0.005 to about 0.75.
- 11. A cationically and hydrophobically modified galactomannan of claim 10, wherein the average hydrophobic degree of substitution ranges from 0.01 to about 0.5.
- 12. A cationically and hydrophobically modified galactomannan of claim 2 or 4, wherein the average cationic degree of substitution ranges from above 0.5 to about 1.75.
- 13. A cationically and hydrophobically modified galactomannan of claim 12, wherein the average cationic degree of substitution ranges from 0.55 to about 1.75.
- 14. A cationically and hydrophobically modified galactomannan of claim 13, wherein the average cationic degree of substitution ranges from 0.6 to about 1.

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- 15. A cationically and hydrophobically modified galactomannan of claim 2, 4, 12, 13, or 14 wherein the average hydrophobic degree of substitution ranges from about 0.001 to about 1.25.
- 16. A cationically and hydrophobically modified galactomannan of claim 15, wherein the average hydrophobic degree of substitution ranges from 0.005 to about 0.75.
- 17. A cationically and hydrophobically modified galactomannan of claim 16, wherein the average hydrophobic degree of substitution ranges from 0.01 to about 0.5.
- 18. A cationically and hydrophobically modified galactomannan of any of claims 1 to 17, wherein said divalent alkylene radical A is represented by the formulae:

- 19. A cationically and hydrophobically modified galactomannan of any of claims 1 to 18, wherein R¹ is selected from a cyclic or saturated or unsaturated, linear or branched hydrocarbon group having from about 12 to about 30 carbon atoms.
- 20. A cationically and hydrophobically modified galactomannan of any of claims 1 to 19, wherein said hydrocarbon group is selected from cycloalkyl, linear or branched alkyl, cycloalkenyl, linear or branched alkenyl, aryl, alkylaryl, alkenylaryl, and combinations thereof.
- 21. A cationically and hydrophobically modified galactomannan of any of claims 1 to 20, wherein said hydrocarbon group is selected from C_4 - C_8 cycloalkyl, C_5 - C_8 cycloalkenyl, linear or branched C_2 - C_{35} alkyl, linear or branched C_2 - C_{35} alkenyl, C_6 - C_{14} aryl, $(C_1$ - $C_{22})$ alkyl $(C_6$ - $C_{10})$ aryl, $(C_3$ - $C_{22})$ alkenyl $(C_6$ - $C_{10})$ aryl, and combinations thereof.

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- 22. A cationically and hydrophobically modified galactomannan of claim 21, wherein said aryl moiety is substituted with a substituent selected from C_1 - C_{22} alkyl, C_2 - C_{22} alkenyl, hydroxyl, chloro, bromo, and combinations thereof.
- 23. A cationically and hydrophobically modified galactomannan of any of claims 1 to 22, wherein –AR is represented by the structure:

$$\begin{array}{cccc} & \text{OH} & + & - \\ - & \text{CH}_{2}^{-}\text{CH} - \text{CH}_{2}^{-}\text{N} \; \text{R}^{3}\text{R}^{4}\text{R}^{5} \; \text{X} \end{array}$$

wherein R³ and R⁴, and R⁵, and X are as previously defined.

- 24. A cationically and hydrophobically modified galactomannan of claim 23, wherein X is selected from a chloride, bromide, iodide, sulfate, methylsulfate, sulfonate, nitrate, phosphate, and acetate anion.
- 25. A composition comprising:
- a) A cationically and hydrophobically modified galactomannan of any of claims 1 to 24; and
- b) at least one component selected from surfactants, fatty acid soap, hair and skin conditioning agents, suspending aids, emollients, emulsifiers, rheology modifiers, thickening agents, vitamins, hair growth promoters, self-tanning agents, sunscreens, skin lighteners, anti-aging compounds, anti-wrinkle compounds, anti-cellulite compounds, anti-acne compounds, anti-dandruff agents, anti-inflammatory compounds, analgesics, antiperspirant agents, deodorant agents, hair fixatives, particulates, abrasives, moisturizers, antioxidants, keratolytic agents, anti-static agents, foam boosters, hydrotropes, solublizing agents, chelating agents, antimicrobial agents, antifungal agents, pH adjusting agents, chelating agents, buffering agents, botanicals, hair colorants, oxidizing agents, reducing agents, hair and skin bleaching agents, pigments, anticaries, anti-tartar agents, anti-plaque agents, solvents; and combinations thereof.

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- 26. A composition of claim 25, wherein said surfactant is selected from an anionic surfactant, a cationic surfactant, an amphoteric surfactant, a nonionic surfactant and combinations thereof.
- 27. A composition of claim 25, wherein said conditioning agent is selected from silicones, organic conditioning oils, natural and synthetic waxes, cationic polymers, and combinations thereof.
- 28. A composition of claim 27, wherein said silicone is selected from silicone fluids, silicone oils, cationic silicones, silicone gums, high refractive silicones, silicone resins, emulsified silicones, dimethicone copolyols; and combinations thereof.
- 29. A composition of claim 27, wherein said cationic modified polymer is selected from a polyquaternium, a cationically modified polygalactomannan, and combinations thereof.
- 30. A detersive composition comprising:
- a) A cationically and hydrophobically modified galactomannan of any of claims 1 to 24;
- b) a surfactant selected from an anionic surfactant, a cationic surfactant, an amphoteric surfactant, a nonionic surfactant and combinations thereof; and
 - c) an optional rheology modifier.
- 31. A detersive composition of claim 30, wherein said said rheology modifier is present and is selected from an acrylic based polymer, an acrylic based copolymer, and combinations thereof.
- 32. A detersive composition of claim 30, wherein said acrylic based polymer is polymerized from acrylic acid or methacrylic acid.

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- 33. A detersive composition of claim 30, wherein said acrylic based copolymer is polymerized from acrylic acid and/or methacrylic acid in combination with at least one C_1 - C_{30} alkyl ester of acrylic acid or methacrylic acid.
- 34. A detersive composition of claim 31, wherein said acrylic based polymer and copolymer are crosslinked.
- 35. A detersive composition of claim 30, wherein said said rheology modifier is present and is selected from a HASE polymer.
- 36. A detersive composition of any of claims 30 to 35, further comprising a conditioning agent.
- 37. A detersive composition of claim 36, wherein said conditioning agent is selected from silicones, organic conditioning oils, natural and synthetic waxes, cationic polymers, and combinations thereof.
- 38. A detersive composition of claim 37, wherein said silicone is selected from silicone fluids, silicone oils, cationic silicones, silicone gums, high refractive silicones, silicone resins, emulsified silicones, dimethicone copolyols; and combinations thereof.
- 39. A detersive composition of claim 37, wherein said cationic polymer is selected from a quaternium ammonium compound, a cationically modified polygalactomannan, and combinations thereof.
- 40. A hair fixative composition comprising:
- a) a cationically and hydrophobically modified galactomannan of any of claims 1 to 24; and
- b) a component selected from a rheology modifier, a surfactant, an auxiliary fixative, a solvent, water, a conditioner, a propellant, neutralizing agent, fragrance,

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fragrance solubilizer, thickener, preservative, emulsifier, emollient, humectant, colorant, wax, and mixtures thereof.

- 41. A hair fixative composition of claim 40, wherein said conditioner is selected from silicones, organic conditioning oils, natural and synthetic waxes, cationic polymers, and combinations thereof.
- 42. A hair fixative composition of claim 41, wherein said cationic polymer is selected from a polyquaternium compound, a cationically modified polygalactomannan, and combinations thereof.
- 43. A hair fixative composition of any of claims 40 to 42, wherein said propellant is selected from propane, butane, isobutene, dimethyl ether, 1,1-difluoroethane, carbon dioxide, and mixtures thereof.
- 44. A skin care composition comprising:
- a) a cationically and hydrophobically modified galactomannan of any of claims 1 to 24; and
- b) a component selected from a rheology modifier, a surfactant, a solvent, water, a conditioner, a propellant, neutralizing agent, fragrance, fragrance solubilizer, thickener, preservative, emulsifier, emollient, humectant, a sunscreen agent, UV blocking agent, colorant, wax, and mixtures thereof.
- 45. A skin care composition of claim 44, wherein said conditioner is selected from a silicone, a cationic polymer, and combinations thereof.
- 46. A skin care composition of claim 44, wherein said solvent is selected from a C_1 - C_6 alcohol, a ketone, an ether, and combinations thereof.

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- 47. A skin care composition of claim 45, wherein said cationic polymer is selected from a polyquaternium compound, a cationically modified polygalactomannan, and combinations thereof.
- 48. A composition of any of claims 1 to 47, wherein the average mannose to galactose ratio of said cationically and hydrophobically modified galactomannan ranges from about 5:1 to about 49:1.
- 49. A composition of any of claims 1 to 47, wherein the average mannose to galactose ratio of said cationically and hydrophobically modified galactomannan ranges from about 5:1 to about 25:1.
- 50. A composition of any of claims 1 to 46, wherein the average mannose to galactose ratio of said cationically and hydrophobically modified galactomannan ranges from about 5:1 to about 10:1.
- 51. A composition of any of claims 1 to 47, wherein the average mannose to galactose ratio of said cationically and hydrophically modified galactomannan is about from about 5:1, 6:1, 7:1, 8:1, 9:1, and mixtures thereof.
- 52. A composition of any of claims 1 to 47, wherein the weight of galactose in said cationically and hydrophobically modified galactomannan ranges from about 2 wt.% to about 17 wt.% based on the weight of the galactomannan.

INTERNATIONAL SEARCH REPORT

International application No PCT/US2011/034274

A. CLASSIFICATION OF SUBJECT MATTER INV. C08B37/00 C08L5/00 A61K8/73 A61Q5/02 A61Q5/06 A61Q19/00 C11D3/22 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) CO8B CO8L A61K A61Q C11D 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 practical, search terms used) EPO-Internal, BIOSIS, COMPENDEX, INSPEC, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category* Citation of document, with indication, where appropriate, of the relevant passages WO 2010/009071 A2 (DOW CORNING [US]; 1,2,5-52 Χ BOUZELOC SYLVIE [BE]; POSTIAUX STEPHANIE [BE]; SCHIR) 21 January 2010 (2010-01-21) cited in the application Υ claims; examples 3,4 US 2009/010855 A1 (LEPILLEUR CAROLE A [US] 3.4 ET AL) 8 January 2009 (2009-01-08) claims; examples WO 2011/081907 A1 (LUBRIZOL ADVANCED MAT Ε 1-52 INC [US]; LEPILLEUR CAROLE A [US]; MALABA DENNIS) 7 July 2011 (2011-07-07) claims; examples Х Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but "A" document defining the general state of the art which is not considered to be of particular relevance cited to understand the principle or theory underlying the invention "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention citation or other special reason (as specified) cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled in the art. "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 4 August 2011 16/08/2011 Authorized officer 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 Vaccaro, Eleonora

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/034274

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010009071	21-01-2010	CN 102088952 A EP 2313075 A2	08-06-2011 27-04-2011
US 2009010855	08-01-2009	AR 073097 A1 CA 2735958 A1 EP 2340263 A1 US 2010284955 A1 WO 2010033302 A1	13-10-2010 25-03-2010 06-07-2011 11-11-2010 25-03-2010
WO 2011081907	1 07-07-2011	NONE	