

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

(19) World Intellectual Property
Organization

International Bureau

(43) International Publication Date

22 February 2018 (22.02.2018)



(10) International Publication Number

WO 2018/034878 A1

(51) International Patent Classification:

A61Q 5/02 (2006.01) A61K8/92 (2006.01)

A61Q 5/12 (2006.01)

(21) International Application Number:

PCT/US2017/045677

(22) International Filing Date:

07 August 2017 (07.08.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/376,603 18 August 2016 (18.08.2016) US

(71) Applicant: THE PROCTER & GAMBLE COMPANY

[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

(72) Inventors: STELLA, Qing; One Procter & Gamble Plaza,

Cincinnati, Ohio 45202 (US). SCHUBERT, Beth, Ann;

One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

MAILE, Michael, Stephen; One Procter & Gamble Plaza,

Cincinnati, Ohio 45202 (US).

(74) Agent: KREBS, Jay A.; c/o The Procter & Gamble Com-

pany, Global IP Services, One Procter & Gamble Plaza, C9,

Cincinnati, Ohio 45202 (US).

(81) Designated States (unless otherwise indicated, for every

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

(84) Designated States (unless otherwise indicated, for every

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

Published:

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

(54) Title: HAIR CARE COMPOSITIONS COMPRISING METATHESIZED UNSATURATED POLYOL ESTERS

(57) Abstract: Disclosed are hair care compositions, such as shampoos, containing an anionic surfactant, an aqueous carrier, and one or more oligomers derived from metathesis of unsaturated polyol esters. The oligomers provide beneficial hair conditioning benefits. Also disclosed are methods of using the hair care compositions.



WO 2018/034878 A1

HAIR CARE COMPOSITIONS COMPRISING METATHESIZED UNSATURATED POLYOL ESTERS

FIELD OF THE INVENTION

The present invention relates to a hair care composition containing an anionic surfactant,
5 an aqueous carrier, and an oligomer derived from metathesis of unsaturated polyol esters, and
methods of using the same.

BACKGROUND OF THE INVENTION

Human hair becomes soiled due to its contact with the surrounding environment and from
the sebum secreted by the scalp. The soiling of hair causes it to have a dirty feel and an unattractive
10 appearance.

Shampooing cleans the hair by removing excess soil and sebum. However, shampooing
can leave the hair in a wet, tangled, and generally unmanageable state. Once the hair dries, it is
often left in a dry, rough, lusterless, or frizzy condition due to removal of the hair's natural oils.

A variety of approaches have been developed to alleviate these after-shampoo problems.
15 One approach is the application of hair shampoos which attempt to both cleanse and condition the
hair from a single product.

In order to provide hair conditioning benefits in a cleansing shampoo base, a wide variety
of conditioning actives have been proposed. However, including active levels of conditioning
agents in shampoos may result in rheology and stability issues, creating consumer trade-offs in
20 cleaning, lather profiles, and weigh-down effects. Additionally, the rising costs of silicone and the
petroleum based nature of silicone have minimized silicone's desirability as a conditioning active.

Based on the foregoing, there is a need for a conditioning active which can provide
conditioning benefits to hair and can replace, or be used in combination with silicone, or other
conditioning actives, to maximize the conditioning activity of hair care compositions.
25 Additionally, there is a desire to find a conditioning active which can be derived from a natural
source, thereby providing a conditioning active derived from a renewable resource. There is also
a desire to find a conditioning active that is both derived from a natural source and leads to a stable
product comprising a micellar surfactant system.

SUMMARY OF THE INVENTION

In one aspect, the present invention is directed to hair care composition comprising: a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having one or more of the following properties: (i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%; (ii) a weight average molecular weight of from about 5,000 Daltons to about 50,000 Daltons; (iii) an iodine value of from about 30 to about 200; b) from about 5% to about 50% of one or more anionic surfactants, by weight of said hair care composition; and c) at least about 20% of an aqueous carrier, by weight of said hair care composition.

In another aspect, the present invention is directed to hair care composition comprising: a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having a weight average molecular weight of from about 2,000 Daltons to about 50,000 Daltons; and one or more of the following properties: (i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%; or (ii) an iodine value of from about 8 to about 200; b) from about 5% to about 50% of one or more anionic surfactants, by weight of said hair care composition; and c) at least about 20% of an aqueous carrier, by weight of said hair care composition.

The present invention also is directed to a method for cleansing hair with an effective amount of the hair care composition described above.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

5 The terms "natural oils," "natural feedstocks," or "natural oil feedstocks" may refer to oils derived from plants or animal sources. The term "natural oil" includes natural oil derivatives, unless otherwise indicated. The terms also include modified plant or animal sources (e.g., genetically modified plant or animal sources), unless indicated otherwise. Examples of natural oils include, but are not limited to, vegetable oils, algae oils, fish oils, animal fats, tall oils, derivatives
10 of these oils, combinations of any of these oils, and the like. Representative non-limiting examples of vegetable oils include canola oil, rapeseed oil, coconut oil, corn oil, cottonseed oil, olive oil, palm oil, peanut oil, safflower oil, sesame oil, soybean oil, sunflower oil, linseed oil, palm kernel oil, tung oil, jatropha oil, mustard oil, pennycress oil, camelina oil, and castor oil. Representative non-limiting examples of animal fats include lard, tallow, poultry fat, yellow grease, and fish oil.
15 Tall oils are by-products of wood pulp manufacture.

The term "natural oil derivatives" refers to derivatives thereof derived from natural oil. The methods used to form these natural oil derivatives may include one or more of addition, neutralization, overbasing, saponification, transesterification, esterification, amidification, hydrogenation, isomerization, oxidation, alkylation, acylation, sulfurization, sulfonation, rearrangement, reduction, fermentation, pyrolysis, hydrolysis, liquefaction, anaerobic digestion, hydrothermal processing, gasification or a combination of two or more thereof. Examples of natural derivatives thereof may include carboxylic acids, gums, phospholipids, soapstock, acidulated soapstock, distillate or distillate sludge, fatty acids, fatty acid esters, as well as hydroxy substituted variations thereof, including unsaturated polyol esters. In some embodiments, the natural oil derivative may comprise an unsaturated carboxylic acid having from about 5 to about 30 carbon atoms, having one or more carbon-carbon double bonds in the hydrocarbon (alkene) chain. The natural oil derivative may also comprise an unsaturated fatty acid alkyl (e.g., methyl) ester derived from a glyceride of natural oil. For example, the natural oil derivative may be a fatty acid methyl ester ("FAME") derived from the glyceride of the natural oil. In some embodiments, a feedstock includes canola or soybean oil, as a non-limiting example, refined, bleached, and deodorized soybean oil (i.e., RBD soybean oil).

The term "free hydrocarbon" refers to any one or combination of unsaturated or saturated straight, branched, or cyclic hydrocarbons in the C₂ to C₂₄ range.

The term "metathesis monomer" refers to a single entity that is the product of a metathesis reaction which comprises a molecule of a compound with one or more carbon-carbon double bonds which has undergone an alkylidene unit interchange via one or more of the carbon-carbon double bonds either within the same molecule (intramolecular metathesis) and/or with a molecule of another compound containing one or more carbon-carbon double bonds such as an olefin (intermolecular metathesis).

The term "metathesis dimer" refers to the product of a metathesis reaction wherein two reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the metathesis reaction.

The term "metathesis trimer" refers to the product of one or more metathesis reactions wherein three molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the trimer containing three bonded groups derived from the reactant compounds.

The term "metathesis tetramer" refers to the product of one or more metathesis reactions wherein four molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the tetramer containing four bonded groups derived from the reactant compounds.

The term "metathesis pentamer" refers to the product of one or more metathesis reactions wherein five molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the pentamer containing five bonded groups derived from the reactant compounds.

The term "metathesis hexamer" refers to the product of one or more metathesis reactions wherein six molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the hexamer containing six bonded groups derived from the reactant compounds.

The term "metathesis heptamer" refers to the product of one or more metathesis reactions wherein seven molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the heptamer containing seven bonded groups derived from the reactant compounds.

The term "metathesis octamer" refers to the product of one or more metathesis reactions wherein eight molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the octamer containing eight bonded groups derived from the reactant compounds.

The term "metathesis nonamer" refers to the product of one or more metathesis reactions wherein nine molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more

metathesis reactions, the nonamer containing nine bonded groups derived from the reactant compounds.

The term "metathesis decamer" refers to the product of one or more metathesis reactions wherein ten molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the decamer containing ten bonded groups derived from the reactant compounds.

The term "metathesis oligomer" refers to the product of one or more metathesis reactions wherein two or more molecules (e.g., 2 to about 10, or 2 to about 4) of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the oligomer containing a few (e.g., 2 to about 10, or 2 to about 4) bonded groups derived from the reactant compounds. In some embodiments, the term "metathesis oligomer" may include metathesis reactions wherein greater than ten molecules of two or more reactant compounds, which can be the same or different and each with one or more carbon-carbon double bonds, are bonded together via one or more of the carbon-carbon double bonds in each of the reactant compounds as a result of the one or more metathesis reactions, the oligomer containing greater than ten bonded groups derived from the reactant compounds.

As used herein, the terms "metathesize" and "metathesizing" may refer to the reacting of an unsaturated polyol ester feedstock in the presence of a metathesis catalyst to form a metathesized unsaturated polyol ester product comprising a new olefinic compound and/or esters. Metathesizing may refer to cross-metathesis (a.k.a. co-metathesis), self-metathesis, ring-opening metathesis, ring-opening metathesis polymerizations ("ROMP"), ring-closing metathesis ("RCM"), and acyclic diene metathesis ("ADMET"). As a non-limiting example, metathesizing may refer to reacting two triglycerides present in a natural feedstock (self-metathesis) in the presence of a metathesis catalyst, wherein each triglyceride has an unsaturated carbon-carbon double bond, thereby forming an oligomer having a new mixture of olefins and esters that may comprise one or more of: metathesis monomers, metathesis dimers, metathesis trimers, metathesis tetramers, metathesis pentamers, and higher order metathesis oligomers (e.g., metathesis hexamers, metathesis heptamers, metathesis octamers, metathesis nonamers, metathesis decamers, and higher than metathesis decamers and above).

The term "Oligomer Index" is defined in Section B of the Test Methods section below.

As used herein, the term "polyol" means an organic material comprising at least two hydroxy moieties.

As used herein, the term "cleaning and/or treatment composition" is a subset of consumer products that includes beauty care products. Such products include, but are not limited to, products for treating hair (human, dog, and/or cat), including, bleaching, coloring, dyeing, conditioning, shampooing, styling; deodorants and antiperspirants; personal cleansing; cosmetics; skin care including application of creams, lotions, and other topically applied products for consumer use.

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

As used herein, the terms "include", "includes" and "including" are meant to be non-limiting.

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

All percentages and ratios are calculated by weight unless otherwise indicated. All percentages and ratios are calculated based on the total composition unless otherwise indicated.

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

Compositions and Methods of Use

Table 1 Compositions

Comp. No.	Composition
1	A composition comprising, a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having one or more of the following properties:

	<p>(i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%;</p> <p>(ii) a weight average molecular weight of from about 5,000 Daltons to about 50,000 Daltons, from about 5,500 Daltons to about 50,000 Daltons, from about 5,500 Daltons to about 40,000 Daltons, or from about 6,000 Daltons to about 30,000 Daltons;</p> <p>(iii) an iodine value of from about 30 to about 200, from about 30 to about 150, from about 30 to about 120, or from about 50 to about 110;</p> <p>b) from about 5% to about 50% of one or more anionic surfactants, by weight of said hair care composition; and</p> <p>c) at least about 20% of an aqueous carrier, by weight of said hair care composition.</p>
2	In one aspect of said composition 1 of Table 1, said metathesized unsaturated polyol ester has the free hydrocarbon content property from a)(i) above.
3	In one aspect of said composition 1 of Table 1, said metathesized unsaturated polyol ester has the weight average molecular weight property from a)(ii) above.
4	In one aspect of said composition 1 of Table 1, said metathesized unsaturated polyol ester has the iodine value property from a)(iii) above.
5	In one aspect of said composition 1 of Table 1, said metathesized unsaturated polyol ester has the property from a)(i) and from a)(ii) above.
6	In one aspect of said composition 1 of Table 1, said metathesized unsaturated polyol ester has the properties from a)(i) and from a)(iii) above.
7	In one aspect of said composition 1 of Table 1, said metathesized unsaturated polyol ester has the properties from a)(ii) and from a)(iii) above.
8	In one aspect of said composition 1 of Table 1, said metathesized unsaturated polyol ester has the properties from a)(i), a)(ii) and from a)(iii) above.
9	In one aspect of compositions 1, 2, 3, 4, 5, 6, 7, and 8 of Table 1, said metathesized unsaturated polyol ester has a free hydrocarbon content, based

	on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%, from about 0.1% to about 5%, from about 0.1% to about 4%, or from about 0.1 to about 3%.
10	In one aspect of Table 1 Compositions 1, 2, 3, 4, 5, 6, 7, 8, and 9 the metathesized unsaturated polyol ester is metathesized at least once.
11	In one aspect of said composition 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 of Table 1, said metathesized unsaturated polyol ester has an oligomer index from greater than 0 to 1, from 0.001 to 1, 0.01 to 1, or from 0.05 to 1.
12	In one aspect, of compositions 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 of Table 1, said composition comprises, based on total composition weight, from about 0.05% to about 30%, from about 0.1% to about 15%, from about 0.25% to about 10%, or from about 0.5% to about 5% of said metathesized unsaturated polyol ester.

Table 2 Compositions

Comp. No.	Composition
1	<p>A composition comprising:</p> <p>a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having a weight average molecular weight of from about 2,000 Daltons to about 50,000 Daltons, from about 2,500 Daltons to about 50,000 Daltons, from about 3,000 Daltons to about 40,000 Daltons, from about 4,000 Daltons to about 30,000 Daltons, from about 5,000 Daltons to about 30,000 Daltons; and one or more of the following properties:</p> <p>(i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%, from about 0.1% to about 5%, from about 0.1% to about 4%, or from about 0.1 to about 3%;</p> <p>(ii) an iodine value of from about 8 to about 200, from about 10 to about 200, from about 20 to about 150, from about 30 to about 120; and</p>

	<p>b) from about 5% to about 50% of one or more anionic surfactants, by weight of said hair care composition; and</p> <p>c) at least about 20% of an aqueous carrier, by weight of said hair care composition.</p>
2	In one aspect of said composition 1 of Table 2, said metathesized unsaturated polyol ester has the free hydrocarbon content property from a)(i) above.
3	In one aspect of said composition 1 of Table 2, said metathesized unsaturated polyol ester has the iodine value property from a)(ii) above.
4	In one aspect of said composition 1 of Table 2, said metathesized unsaturated polyol ester has the property from a)(i) and from a)(ii) above.
5	In one aspect of Table 2, compositions 1, 2, 3 and 4, said metathesized unsaturated polyol ester has an oligomer index from greater than 0 to 1, from 0.001 to 1, 0.01 to 1, or from 0.05 to 1.
6	In one aspect of Table 2, for compositions 1, 2, 3, 4, and 5, said metathesized unsaturated polyol ester is metathesized at least once.
7	In one aspect of Table 2, for compositions 1, 2, 3, 4, 5, and 6, said composition comprises, based on total composition weight, from about 0.05% to about 30%, from about 0.1% to about 15%, from about 0.25% to about 10%, or from about 0.5% to about 5% of said metathesized unsaturated polyol ester.

In one aspect, Table 1 Compositions 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12; and Table 2 Compositions 1, 2, 3, 4, 5, 6, and 7 comprise one or more of the following:

- 5 a) anionic surfactants for use in the hair care composition include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl
- 10 sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate,

triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium cocoyl isethionate and combinations thereof;

- b) from about 0.5% to about 20%, or from about 1% to about 10% of an amphoteric or zwitterionic surfactants;
- c) from about 20% to about 95%, or from about 60% to about 85% aqueous carrier;
- d) from about 0.01% to about 10%, from about 0.1% to about 8%, or from about 0.2% to about 4% of one or more conditioning agents;
- e) a benefit agent comprising a material selected from the group consisting of anti-dandruff agents, vitamins, lipid soluble vitamins, chelants, perfumes, brighteners, enzymes, sensates, attractants, anti-bacterial agents, dyes, pigments, bleaches, and mixtures thereof; and
- f) mixtures thereof.

In one aspect, for Table 1 Compositions 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12; and Table 2 Compositions 1, 2, 3, 4, 5, 6, and 7, the metathesized unsaturated polyol ester is derived from a natural polyol ester and/or a synthetic polyol ester, in one aspect, said natural polyol ester is selected from the group consisting of a vegetable oil, an animal fat, an algae oil and mixtures thereof; and said synthetic polyol ester is derived from a material selected from the group consisting of ethylene glycol, propylene glycol, glycerol, polyglycerol, polyethylene glycol, polypropylene glycol, poly(tetramethylene ether) glycol, pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolpropane, neopentyl glycol, a sugar, in one aspect, sucrose, and mixtures thereof.

In one aspect, for Table 1 Compositions 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12; and Table 2 Compositions 1, 2, 3, 4, 5, 6, and 7, the metathesized unsaturated polyol ester is selected from the group consisting of metathesized Abyssinian oil, metathesized Almond oil, metathesized Apricot oil, metathesized Apricot Kernel oil, metathesized Argan oil, metathesized Avocado oil, metathesized Babassu oil, metathesized Baobab oil, metathesized Black Cumin oil, metathesized Black Currant oil, metathesized Borage oil, metathesized Camelina oil, metathesized Carinata oil, metathesized Canola oil, metathesized Castor oil, metathesized Cherry Kernel oil, metathesized Coconut oil, metathesized Corn oil, metathesized Cottonseed oil, metathesized Echium oil, metathesized Evening Primrose oil, metathesized Flax Seed oil, metathesized Grape Seed oil, metathesized Grapefruit Seed oil, metathesized Hazelnut oil, metathesized Hemp Seed oil, metathesized Jatropha oil, metathesized Jojoba oil, metathesized Kukui Nut oil, metathesized

Linseed oil, metathesized Macadamia Nut oil, metathesized Meadowfoam Seed oil, metathesized Moringa oil, metathesized Neem oil, metathesized Olive oil, metathesized Palm oil, metathesized Palm Kernel oil, metathesized Peach Kernel oil, metathesized Peanut oil, metathesized Pecan oil, metathesized Pennycress oil, metathesized Perilla Seed oil, metathesized Pistachio oil, metathesized Pomegranate Seed oil, metathesized Pongamia oil, metathesized Pumpkin Seed oil, metathesized Raspberry oil, metathesized Red Palm Olein, metathesized Rice Bran oil, metathesized Rosehip oil, metathesized Safflower oil, metathesized Seabuckthorn Fruit oil, metathesized Sesame Seed oil, metathesized Shea Olein, metathesized Sunflower oil, metathesized Soybean oil, metathesized Tonka Bean oil, metathesized Tung oil, metathesized Walnut oil, metathesized Wheat Germ oil, metathesized High Oleoyl Soybean oil, metathesized High Oleoyl Sunflower oil, metathesized High Oleoyl Safflower oil, metathesized High Erucic Acid Rapeseed oil, metathesized lard, metathesized tallow, metathesized poultry fat, metathesized yellow grease, metathesized fish oil and mixtures thereof.

In one aspect, for Table 1 Compositions 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12; and Table 2 Compositions 1, 2, 3, 4, 5, 6, and 7, said compositions comprise:

- a) as the deterative surfactant, an anionic surfactant selected from ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium cocoyl isethionate and combinations thereof;
- b) as an amphoteric surfactant, derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate; or as a zwitterionic surfactant, derivatives of aliphatic quaternaryammonium, phosphonium, and sulfonium compounds, in which the

aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate;

- 5 c) as the aqueous carrier, water, a miscible mixture of water and organic solvent, and in one aspect water with minimal or no significant concentrations of organic solvent, except as otherwise incidentally incorporated into the composition as minor ingredients of other components;
- 10 d) optionally one or more additional components selected from conditioning agents (e.g., silicones, hydrocarbon oils, fatty esters), natural cationic deposition polymers, synthetic cationic deposition polymers, anti-dandruff agents, particles, suspending agents, paraffinic hydrocarbons, propellants, viscosity modifiers, dyes, non-volatile solvents or diluents (water-soluble and water-insoluble), pearlescent aids, foam boosters, additional surfactants or nonionic cosurfactants, pediculocides, pH adjusting agents, perfumes, preservatives, proteins, skin active agents, sunscreens, UV absorbers, and vitamins;
- 15 e) when a conditioning agent is included, the conditioning agent is selected from silicones (e.g., silicone oils, cationic silicones, silicone gums, high refractive silicones, and silicone resins), organic conditioning oils (e.g., hydrocarbon oils, polyolefins, and fatty esters) or combinations thereof; and
- 20 f) mixtures thereof.

Methods of Making Compositions

The compositions of the present invention can be formulated into any suitable form and prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. 5,879,584 which is incorporated herein by reference. For example, the metathesized unsaturated polyol esters can be combined directly with the composition's other ingredients without pre-emulsification and/or pre-mixing to form the finished products. Alternatively, the metathesized unsaturated polyol esters can be combined with surfactants or emulsifiers, solvents, suitable adjuncts, and/or any other suitable ingredients to prepare emulsions prior to compounding the finished products.

25

30

Suitable equipment for use in the processes disclosed herein may include continuous stirred tank reactors, homogenizers, turbine agitators, recirculating pumps, paddle mixers, plough shear mixers, ribbon blenders, vertical axis granulators and drum mixers, both in batch and, where available, in continuous process configurations, spray dryers, and extruders. Such equipment can

be obtained from Lodige GmbH (Paderborn, Germany), Littleford Day, Inc. (Florence, Kentucky, U.S.A.), Forberg AS (Larvik, Norway), Glatt Ingenieurtechnik GmbH (Weimar, Germany), Niro (Soeborg, Denmark), Hosokawa Bepex Corp. (Minneapolis, Minnesota, U.S.A.), Arde Barinco (New Jersey, U.S.A.).

5

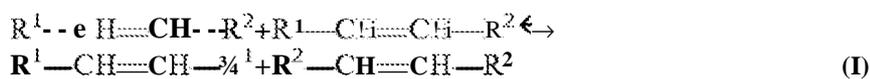
Metathesized Unsaturated Polvol Ester

The hair care composition comprises, based on total composition weight, from about 0.05% to about 30%, from about 0.1% to about 15%, from about 0.25% to about 10%, or from about 0.5% to about 5%, of the metathesized unsaturated polyol ester.

10

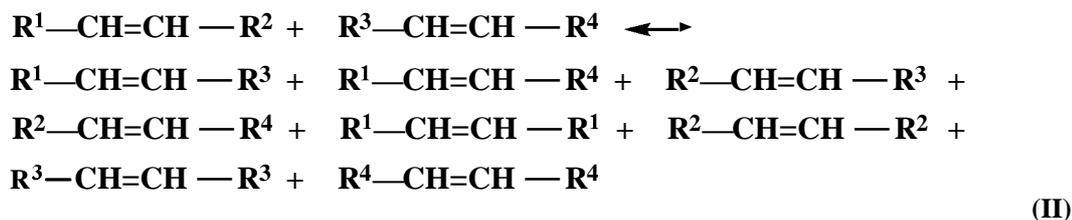
Exemplary metathesized unsaturated polyol esters and their starting materials are set forth in U.S. Patent Applications U.S. 2009/0220443 A1, U.S. 2013/0344012 A1 and US 2014/0357714 A1, which are incorporated herein by reference. A metathesized unsaturated polyol ester refers to the product obtained when one or more unsaturated polyol ester ingredient(s) are subjected to a metathesis reaction. Metathesis is a catalytic reaction that involves the interchange of alkyldiene units among compounds containing one or more double bonds (i.e., olefinic compounds) via the formation and cleavage of the carbon-carbon double bonds. Metathesis may occur between two of the same molecules (often referred to as self-metathesis) and/or it may occur between two different molecules (often referred to as cross-metathesis). Self-metathesis may be represented schematically as shown in Equation I.

15



20

where R¹ and R² are organic groups.



Cross-metathesis may be represented schematically as shown in Equation II,

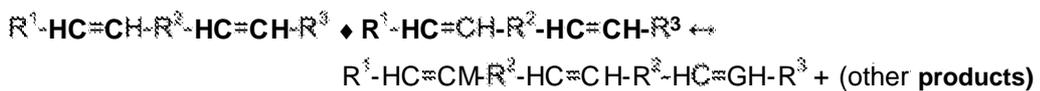
where R¹, R², R³, and R⁴ are organic groups.

25

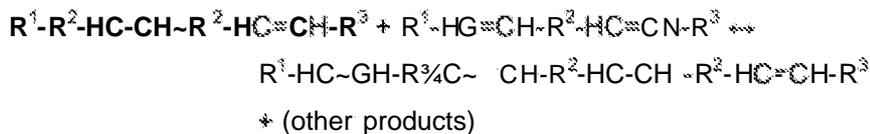
When a polyol ester comprises molecules having more than one carbon-carbon double bond, self-metathesis may result in oligomerization or polymerization of the unsaturates in the starting material. For example, Equation C depicts metathesis oligomerization of a representative species (e.g., a polyol ester) having more than one carbon-carbon double bond. In Equation C, the self-metathesis reaction results in the formation of metathesis dimers, metathesis trimers, and

metathesis tetramers. Although not shown, higher order oligomers such as metathesis pentamers, hexamers, heptamers, octamers, nonamers, decamers, and higher than decamers, and mixtures of two or more thereof, may also be formed. The number of metathesis repeating units or groups in the metathesized natural oil may range from 1 to about 100, or from 2 to about 50, or from 2 to about 30, or from 2 to about 10, or from 2 to about 4. The molecular weight of the metathesis dimer may be greater than the molecular weight of the unsaturated polyol ester from which the dimer is formed. Each of the bonded polyol ester molecules may be referred to as a "repeating unit or group." Typically, a metathesis trimer may be formed by the cross-metathesis of a metathesis dimer with an unsaturated polyol ester. Typically, a metathesis tetramer may be formed by the cross-metathesis of a metathesis trimer with an unsaturated polyol ester or formed by the cross-metathesis of two metathesis dimers.

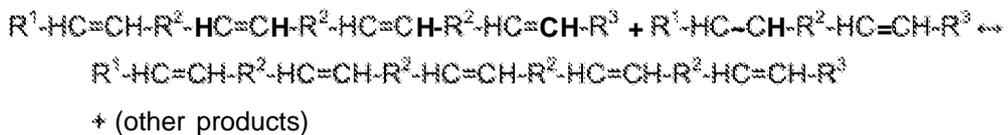
Equation C



(metathesis dimer)



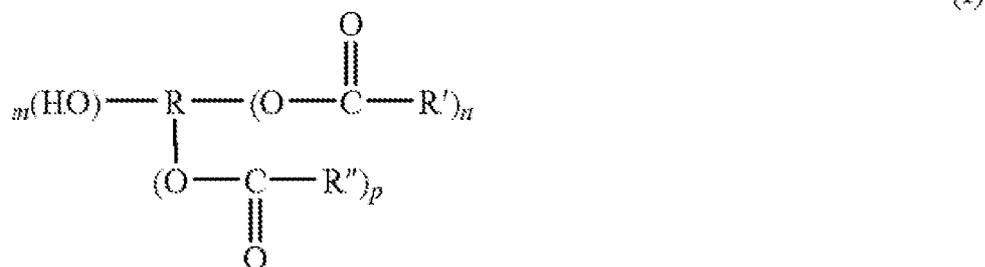
(metathesis trimer)



(metathesis tetramer)

where R¹, R², and R³ are organic groups.

As a starting material, metathesized unsaturated polyol esters are prepared from one or more unsaturated polyol esters. As used herein, the term "unsaturated polyol ester" refers to a compound having two or more hydroxyl groups wherein at least one of the hydroxyl groups is in the form of an ester and wherein the ester has an organic group including at least one carbon-carbon double bond. In many embodiments, the unsaturated polyol ester can be represented by the general structure (I):

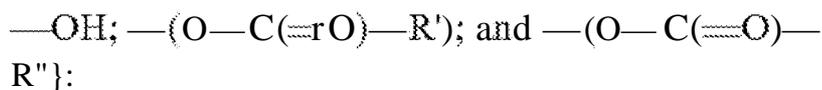


where $n > 1$; $m > 0$; $p > 0$; $(n+m+p) > 2$; R is an organic group; R' is an organic group having at least one carbon-carbon double bond; and R'' is a saturated organic group.

In many embodiments of the invention, the unsaturated polyol ester is an unsaturated polyol ester of glycerol. Unsaturated polyol esters of glycerol have the general structure (II):



where -X, -Y, and -Z are independently selected from the group consisting of:

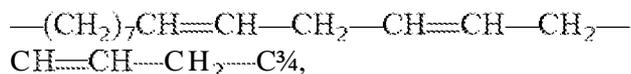
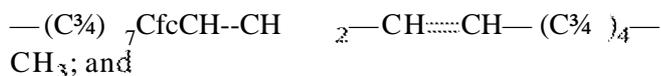
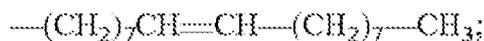


where -R' is an organic group having at least one carbon-carbon double bond and -R'' is a saturated organic group.

In structure (II), at least one of -X, -Y, and -Z is -(O-C(=O)-R').

In some embodiments, R' is a straight or branched chain hydrocarbon having about 50 or less carbon atoms (e.g., about 36 or less carbon atoms or about 26 or less carbon atoms) and at least one carbon-carbon double bond in its chain. In some embodiments, R' is a straight or branched chain hydrocarbon having about 6 carbon atoms or greater (e.g., about 10 carbon atoms or greater or about 12 carbon atoms or greater) and at least one carbon-carbon double bond in its chain. In some embodiments, R' may have two or more carbon-carbon double bonds in its chain. In other embodiments, R' may have three or more double bonds in its chain. In exemplary embodiments, R' has 17 carbon atoms and 1 to 3 carbon-carbon double bonds in its chain.

Representative examples of R' include:



In some embodiments, R" is a saturated straight or branched chain hydrocarbon having about 50 or less carbon atoms (e.g., about 36 or less carbon atoms or about 26 or less carbon atoms). In some embodiments, R" is a saturated straight or branched chain hydrocarbon having about 6 carbon atoms or greater (e.g., about 10 carbon atoms or greater or about 12 carbon atoms or greater. In exemplary embodiments, R" has 15 carbon atoms or 17 carbon atoms.

Sources of unsaturated polyol esters of glycerol include synthesized oils, natural oils (e.g., vegetable oils, algae oils, bacterial derived oils, and animal fats), combinations of these, and the like. Recycled used vegetable oils may also be used. Representative non-limiting examples of vegetable oils include Abyssinian oil, Almond oil, Apricot oil, Apricot Kernel oil, Argan oil, Avocado oil, Babassu oil, Baobab oil, Black Cumin oil, Black Currant oil, Borage oil, Camelina oil, Carinata oil, Canola oil, Castor oil, Cherry Kernel oil, Coconut oil, Corn oil, Cottonseed oil, Echium oil, Evening Primrose oil, Flax Seed oil, Grape Seed oil, Grapefruit Seed oil, Hazelnut oil, Hemp Seed oil, Jatropha oil, Jojoba oil, Kukui Nut oil, Linseed oil, Macadamia Nut oil, Meadowfoam Seed oil, Moringa oil, Neem oil, Olive oil, Palm oil, Palm Kernel oil, Peach Kernel oil, Peanut oil, Pecan oil, Pennycress oil, Perilla Seed oil, Pistachio oil, Pomegranate Seed oil, Pongamia oil, Pumpkin Seed oil, Raspberry oil, Red Palm Olein, Rice Bran oil, Rosehip oil, Safflower oil, Seabuckthorn Fruit oil, Sesame Seed oil, Shea Olein, Sunflower oil, Soybean oil, Tonka Bean oil, Tung oil, Walnut oil, Wheat Germ oil, High Oleoyl Soybean oil, High Oleoyl Sunflower oil, High Oleoyl Safflower oil, High Erucic Acid Rapeseed oil, combinations of these, and the like. Representative non-limiting examples of animal fats include lard, tallow, chicken fat, yellow grease, fish oil, emu oil, combinations of these, and the like. A representative non-limiting example of a synthesized oil includes tall oil, which is a byproduct of wood pulp manufacture. In some embodiments, the natural oil is refined, bleached, and/or deodorized.

Other examples of unsaturated polyol esters include esters such as those derived from ethylene glycol or propylene glycol, polyethylene glycol, polypropylene glycol, or poly(tetramethylene ether) glycol, esters such as those derived from pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolpropane, or neopentyl glycol, or sugar esters such as SEFOSE®. Sugar esters such as SEFOSE® include one or more types of sucrose polyesters,

with up to eight ester groups that could undergo a metathesis exchange reaction. Sucrose polyesters are derived from a natural resource and therefore, the use of sucrose polyesters can result in a positive environmental impact. Sucrose polyesters are polyester materials, having multiple substitution positions around the sucrose backbone coupled with the chain length, saturation, and derivation variables of the fatty chains. Such sucrose polyesters can have an esterification ("IBAR") of greater than about 5. In one embodiment the sucrose polyester may have an IBAR of from about 5 to about 8. In another embodiment the sucrose polyester has an IBAR of about 5-7, and in another embodiment the sucrose polyester has an IBAR of about 6. In yet another embodiment the sucrose polyester has an IBAR of about 8. As sucrose polyesters are derived from a natural resource, a distribution in the IBAR and chain length may exist. For example a sucrose polyester having an IBAR of 6, may contain a mixture of mostly IBAR of about 6, with some IBAR of about 5 and some IBAR of about 7. Additionally, such sucrose polyesters may have a saturation or iodine value ("IV") of about 3 to about 140. In another embodiment the sucrose polyester may have an IV of about 10 to about 120. In yet another embodiment the sucrose polyester may have an IV of about 20 to 100. Further, such sucrose polyesters have a chain length of about C₁₂ to C₂₀ but are not limited to these chain lengths.

Non-limiting examples of sucrose polyesters suitable for use include SEFOSE® 1618S, SEFOSE® 1618U, SEFOSE® 1618H, Sefa Soyate IMF 40, Sefa Soyate LP426, SEFOSE® 2275, SEFOSE® C1695, SEFOSE® C18:0 95, SEFOSE® C1495, SEFOSE® 1618H B6, SEFOSE® 1618S B6, SEFOSE® 1618U B6, Sefa Cottonate, SEFOSE® C1295, Sefa C895, Sefa C1095, SEFOSE® 1618S B4.5, all available from The Procter and Gamble Co. of Cincinnati, Ohio.

Other examples of suitable polyol esters may include but not be limited to sorbitol esters, maltitol esters, sorbitan esters, maltodextrin derived esters, xylitol esters, polyglycerol esters, and other sugar derived esters.

Natural oils of the type described herein typically are composed of triglycerides of fatty acids. These fatty acids may be either saturated, monounsaturated or polyunsaturated and contain varying chain lengths ranging from C₈ to C₃₀. The most common fatty acids include saturated fatty acids such as lauric acid (dodecanoic acid), myristic acid (tetradecanoic acid), palmitic acid (hexadecanoic acid), stearic acid (octadecanoic acid), arachidic acid (eicosanoic acid), and lignoceric acid (tetracosanoic acid); unsaturated acids include such fatty acids as palmitoleic (a C₁₆ acid), and oleic acid (a C₁₈ acid); polyunsaturated acids include such fatty acids as linoleic acid (a di-unsaturated C₁₈ acid), linolenic acid (a tri-unsaturated C₁₈ acid), and arachidonic acid (a tetra-unsaturated C₂₀ acid). The natural oils are further comprised of esters of these fatty acids in random placement onto the three sites of the trifunctional glycerine molecule. Different natural oils will

have different ratios of these fatty acids, and within a given natural oil there is a range of these acids as well depending on such factors as where a vegetable or crop is grown, maturity of the vegetable or crop, the weather during the growing season, etc. Thus, it is difficult to have a specific or unique structure for any given natural oil, but rather a structure is typically based on some statistical average. For example soybean oil contains a mixture of stearic acid, oleic acid, linoleic acid, and linolenic acid in the ratio of 15:24:50: 11, and an average number of double bonds of 4.4-4.7 per triglyceride. One method of quantifying the number of double bonds is the iodine value (IV) which is defined as the number of grams of iodine that will react with 100 grams of oil. Therefore for soybean oil, the average iodine value range is from 120-140. Soybean oil may comprises about 95% by weight or greater (e.g., 99% weight or greater) triglycerides of fatty acids. Major fatty acids in the polyol esters of soybean oil include saturated fatty acids, as a non-limiting example, palmitic acid (hexadecanoic acid) and stearic acid (octadecanoic acid), and unsaturated fatty acids, as a non-limiting example, oleic acid (9-octadecenoic acid), linoleic acid (9,12-octadecadienoic acid), and linolenic acid (9,12,15-octadecatrienoic acid).

In an exemplary embodiment, the vegetable oil is canola oil, for example, refined, bleached, and deodorized canola oil (i.e., RBD canola oil). Canola oil is an unsaturated polyol ester of glycerol that typically comprises about 95% weight or greater (e.g., 99% weight or greater) triglycerides of fatty acids. Major fatty acids in the polyol esters of canola oil include saturated fatty acids, for example, palmitic acid (hexadecanoic acid) and stearic acid (octadecanoic acid), and unsaturated fatty acids, for example, oleic acid (9-octadecenoic acid), linoleic acid (9,12-octadecadienoic acid), and linolenic acid (9,12,15-octadecatrienoic acid). Canola oil is a highly unsaturated vegetable oil with many of the triglyceride molecules having at least two unsaturated fatty acids (i.e., a polyunsaturated triglyceride).

In exemplary embodiments, an unsaturated polyol ester is self-metathesized in the presence of a metathesis catalyst to form a metathesized composition. Typically, after metathesis has occurred, the metathesis catalyst is removed from the resulting product. One method of removing the catalyst is treatment of the metathesized product with clay. In many embodiments, the metathesized composition comprises one or more of: metathesis monomers, metathesis dimers, metathesis trimers, metathesis tetramers, metathesis pentamers, and higher order metathesis oligomers (e.g., metathesis hexamers). A metathesis dimer refers to a compound formed when two unsaturated polyol ester molecules are covalently bonded to one another by a self-metathesis reaction. In many embodiments, the molecular weight of the metathesis dimer is greater than the molecular weight of the individual unsaturated polyol ester molecules from which the dimer is formed. A metathesis trimer refers to a compound formed when three unsaturated polyol ester

molecules are covalently bonded together by metathesis reactions. In many embodiments, a metathesis trimer is formed by the cross-metathesis of a metathesis dimer with an unsaturated polyol ester. A metathesis tetramer refers to a compound formed when four unsaturated polyol ester molecules are covalently bonded together by metathesis reactions. In many embodiments, a metathesis tetramer is formed by the cross-metathesis of a metathesis trimer with an unsaturated polyol ester. Metathesis tetramers may also be formed, for example, by the cross-metathesis of two metathesis dimers. Higher order metathesis products may also be formed. For example, metathesis pentamers and metathesis hexamers may also be formed. The self-metathesis reaction also results in the formation of internal olefin compounds that may be linear or cyclic. If the metathesized polyol ester is fully or partially hydrogenated, the linear and cyclic olefins would typically be fully or partially converted to the corresponding saturated linear and cyclic hydrocarbons. The linear/cyclic olefins and saturated linear/cyclic hydrocarbons may remain in the metathesized polyol ester or they may be removed or partially removed from the metathesized polyol ester using one or more known stripping techniques, including but not limited to wipe film evaporation, falling film evaporation, rotary evaporation, steam stripping, vacuum distillation, etc.

In some embodiments, the unsaturated polyol ester is partially hydrogenated before being metathesized. For example, in some embodiments, the unsaturated polyol ester is partially hydrogenated to achieve an iodine value (IV) of about 120 or less before subjecting the partially hydrogenated polyol ester to metathesis.

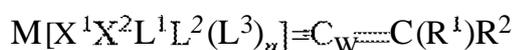
In some embodiments, the unsaturated polyol ester may be hydrogenated (e.g., fully or partially hydrogenated) in order to improve the stability of the oil or to modify its viscosity or other properties. Representative techniques for hydrogenating unsaturated polyol esters are known in the art and are discussed herein.

In some embodiments, the natural oil is winterized. Winterization refers to the process of: (1) removing waxes and other non-triglyceride constituents, (2) removing naturally occurring high-melting triglycerides, and (3) removing high-melting triglycerides formed during partial hydrogenation. Winterization may be accomplished by known methods including, for example, cooling the oil at a controlled rate in order to cause crystallization of the higher melting components that are to be removed from the oil. The crystallized high melting components are then removed from the oil by filtration resulting in winterized oil. Winterized soybean oil is commercially available from Cargill, Incorporated (Minneapolis, Minn.).

In other embodiments, the metathesized unsaturated polyol esters can be used as a blend with one or more fabric care benefit agents and/or fabric softening actives.

Method of Making Metathesized Unsaturated Polyol Ester

The self-metathesis of unsaturated polyol esters is typically conducted in the presence of a catalytically effective amount of a metathesis catalyst. The term "metathesis catalyst" includes any catalyst or catalyst system that catalyzes a metathesis reaction. Any known or future-developed metathesis catalyst may be used, alone or in combination with one or more additional catalysts. Suitable homogeneous metathesis catalysts include combinations of a transition metal halide or oxo-halide (e.g., WOCl_4 or WCl_6) with an alkylating cocatalyst (e.g., Me_4Sn), or alkylidene (or carbene) complexes of transition metals, particularly Ru or W. These include first and second-generation Grubbs catalysts, Grubbs-Hoveyda catalysts, and the like. Suitable alkylidene catalysts have the general structure:



where M is a Group 8 transition metal, L^1 , L^2 , and L^3 are neutral electron donor ligands, n is 0 (such that L^3 may not be present) or 1, m is 0,1, or 2, X^1 and X^2 are anionic ligands, and R^1 and R^2 are independently selected from H, hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, and functional groups. Any two or more of X^1 , X^2 , L^1 , L^2 , L^3 , R^1 and R^2 can form a cyclic group and any one of those groups can be attached to a support.

First-generation Grubbs catalysts fall into this category where $m=n=0$ and particular selections are made for n, X^1 , X^2 , L^1 , L^2 , L^3 , R^1 and R^2 as described in U.S. Pat. Appl. Publ. No. 2010/0145086, the teachings of which related to all metathesis catalysts are incorporated herein by reference.

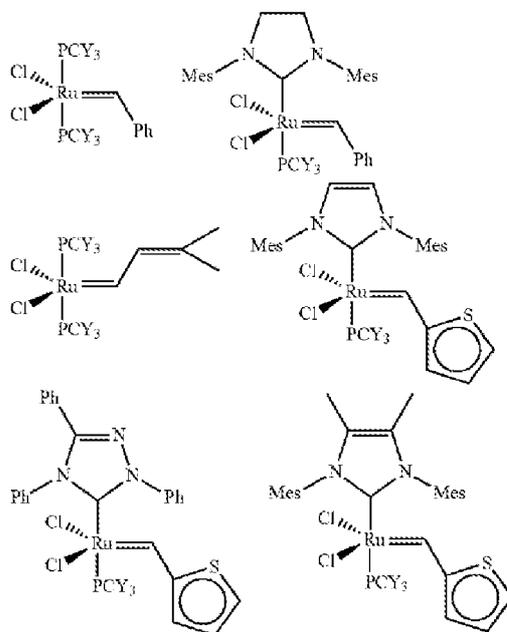
Second-generation Grubbs catalysts also have the general formula described above, but L^1 is a carbene ligand where the carbene carbon is flanked by N, O, S, or P atoms, preferably by two N atoms. Usually, the carbene ligand is part of a cyclic group. Examples of suitable second-generation Grubbs catalysts also appear in the '086 publication.

In another class of suitable alkylidene catalysts, L^1 is a strongly coordinating neutral electron donor as in first- and second-generation Grubbs catalysts, and L^2 and L^3 are weakly coordinating neutral electron donor ligands in the form of optionally substituted heterocyclic groups. Thus, L^2 and L^3 are pyridine, pyrimidine, pyrrole, quinoline, thiophene, or the like.

In yet another class of suitable alkylidene catalysts, a pair of substituents is used to form a bi- or tridentate ligand, such as a biphosphine, dialkoxide, or alkyldiketonate. Grubbs-Hoveyda catalysts are a subset of this type of catalyst in which L^2 and R^2 are linked. Typically, a neutral oxygen or nitrogen coordinates to the metal while also being bonded to a carbon that is α -, β -, or

γ - with respect to the carbene carbon to provide the bidentate ligand. Examples of suitable Grubbs-Hoveyda catalysts appear in the '086 publication.

The structures below provide just a few illustrations of suitable catalysts that may be used:



5 An immobilized catalyst can be used for the metathesis process. An immobilized catalyst is a system comprising a catalyst and a support, the catalyst associated with the support. Exemplary associations between the catalyst and the support may occur by way of chemical bonds or weak interactions (e.g. hydrogen bonds, donor acceptor interactions) between the catalyst, or any portions thereof, and the support or any portions thereof. Support is intended to include any material suitable to support the catalyst. Typically, immobilized catalysts are solid phase catalysts that act on liquid or gas phase reactants and products. Exemplary supports are polymers, silica or alumina. Such an immobilized catalyst may be used in a flow process. An immobilized catalyst can simplify purification of products and recovery of the catalyst so that recycling the catalyst may be more convenient.

15 In certain embodiments, prior to the metathesis reaction, the unsaturated polyol ester feedstock may be treated to render the natural oil more suitable for the subsequent metathesis reaction. In one embodiment, the treatment of the unsaturated polyol ester involves the removal of catalyst poisons, such as peroxides, which may potentially diminish the activity of the metathesis catalyst. Non-limiting examples of unsaturated polyol ester feedstock treatment methods to diminish catalyst poisons include those described in PCT/US2008/09604, PCT/US2008/09635, and U.S. patent application Ser. Nos. 12/672,651 and 12/672,652, herein incorporated by reference

in their entireties. In certain embodiments, the unsaturated polyol ester feedstock is thermally treated by heating the feedstock to a temperature greater than 100°C in the absence of oxygen and held at the temperature for a time sufficient to diminish catalyst poisons in the feedstock. In other embodiments, the temperature is between approximately 100°C and 300°C, between approximately 120°C and 250°C, between approximately 150°C and 210°C, or approximately between 190 and 200°C. In one embodiment, the absence of oxygen is achieved by sparging the unsaturated polyol ester feedstock with nitrogen, wherein the nitrogen gas is pumped into the feedstock treatment vessel at a pressure of approximately 10 atm (150 psig).

In certain embodiments, the unsaturated polyol ester feedstock is chemically treated under conditions sufficient to diminish the catalyst poisons in the feedstock through a chemical reaction of the catalyst poisons. In certain embodiments, the feedstock is treated with a reducing agent or a cation-inorganic base composition. Non-limiting examples of reducing agents include bisulfate, borohydride, phosphine, thiosulfate, and combinations thereof.

In certain embodiments, the unsaturated polyol ester feedstock is treated with an adsorbent to remove catalyst poisons. In one embodiment, the feedstock is treated with a combination of thermal and adsorbent methods. In another embodiment, the feedstock is treated with a combination of chemical and adsorbent methods. In another embodiment, the treatment involves a partial hydrogenation treatment to modify the unsaturated polyol ester feedstock's reactivity with the metathesis catalyst. Additional non-limiting examples of feedstock treatment are also described below when discussing the various metathesis catalysts.

In certain embodiments, a ligand may be added to the metathesis reaction mixture. In many embodiments using a ligand, the ligand is selected to be a molecule that stabilizes the catalyst, and may thus provide an increased turnover number for the catalyst. In some cases the ligand can alter reaction selectivity and product distribution. Examples of ligands that can be used include Lewis base ligands, such as, without limitation, trialkylphosphines, for example tricyclohexylphosphine and tributyl phosphine; triarylphosphines, such as triphenylphosphine; diarylalkylphosphines, such as, diphenylcyclohexylphosphine; pyridines, such as 2,6-dimethylpyridine, 2,4,6-trimethylpyridine; as well as other Lewis basic ligands, such as phosphine oxides and phosphinites. Additives may also be present during metathesis that increase catalyst lifetime.

Any useful amount of the selected metathesis catalyst can be used in the process. For example, the molar ratio of the unsaturated polyol ester to catalyst may range from about 5:1 to about 10,000,000:1 or from about 50:1 to 500,000:1. In some embodiments, an amount of about 1 to about 10 ppm, or about 2 ppm to about 5 ppm, of the metathesis catalyst per double bond of the starting composition (i.e., on a mole/mole basis) is used.

In some embodiments, the metathesis reaction is catalyzed by a system containing both a transition and a non-transition metal component. The most active and largest number of catalyst systems are derived from Group VI A transition metals, for example, tungsten and molybdenum.

Multiple, sequential metathesis reaction steps may be employed. For example, the metathesized unsaturated polyol ester product may be made by reacting an unsaturated polyol ester in the presence of a metathesis catalyst to form a first metathesized unsaturated polyol ester product. The first metathesized unsaturated polyol ester product may then be reacted in a self-metathesis reaction to form another metathesized unsaturated polyol ester product. Alternatively, the first metathesized unsaturated polyol ester product may be reacted in a cross-metathesis reaction with an unsaturated polyol ester to form another metathesized unsaturated polyol ester product. Also in the alternative, the transesterified products, the olefins and/or esters may be further metathesized in the presence of a metathesis catalyst. Such multiple and/or sequential metathesis reactions can be performed as many times as needed, and at least one or more times, depending on the processing/compositional requirements as understood by a person skilled in the art. As used herein, a "metathesized unsaturated polyol ester product" may include products that have been once metathesized and/or multiply metathesized. These procedures may be used to form metathesis dimers, metathesis trimers, metathesis tetramers, metathesis pentamers, and higher order metathesis oligomers (e.g., metathesis hexamers, metathesis heptamers, metathesis octamers, metathesis nonamers, metathesis decamers, and higher than metathesis decamers). These procedures can be repeated as many times as desired (for example, from 2 to about 50 times, or from 2 to about 30 times, or from 2 to about 10 times, or from 2 to about 5 times, or from 2 to about 4 times, or 2 or 3 times) to provide the desired metathesis oligomer or polymer which may comprise, for example, from 2 to about 100 bonded groups, or from 2 to about 50, or from 2 to about 30, or from 2 to about 10, or from 2 to about 8, or from 2 to about 6 bonded groups, or from 2 to about 4 bonded groups, or from 2 to about 3 bonded groups. In certain embodiments, it may be desirable to use the metathesized unsaturated polyol ester products produced by cross metathesis of an unsaturated polyol ester, or blend of unsaturated polyol esters, with a C2-C100 olefin, as the reactant in a self-metathesis reaction to produce another metathesized unsaturated polyol ester product. Alternatively, metathesized products produced by cross metathesis of an unsaturated polyol ester, or blend of unsaturated polyol esters, with a C2-C100 olefin can be combined with an unsaturated polyol ester, or blend of unsaturated polyol esters, and further metathesized to produce another metathesized unsaturated polyol ester product.

The metathesis process can be conducted under any conditions adequate to produce the desired metathesis products. For example, stoichiometry, atmosphere, solvent, temperature, and

pressure can be selected by one skilled in the art to produce a desired product and to minimize undesirable byproducts. The metathesis process may be conducted under an inert atmosphere. Similarly, if a reagent is supplied as a gas, an inert gaseous diluent can be used. The inert atmosphere or inert gaseous diluent typically is an inert gas, meaning that the gas does not interact with the metathesis catalyst to substantially impede catalysis. For example, particular inert gases are selected from the group consisting of helium, neon, argon, nitrogen, individually or in combinations thereof.

In certain embodiments, the metathesis catalyst is dissolved in a solvent prior to conducting the metathesis reaction. In certain embodiments, the solvent chosen may be selected to be substantially inert with respect to the metathesis catalyst. For example, substantially inert solvents include, without limitation, aromatic hydrocarbons, such as benzene, toluene, xylenes, etc.; halogenated aromatic hydrocarbons, such as chlorobenzene and dichlorobenzene; aliphatic solvents, including pentane, hexane, heptane, cyclohexane, etc.; and chlorinated alkanes, such as dichloromethane, chloroform, dichloroethane, etc. In one particular embodiment, the solvent comprises toluene. The metathesis reaction temperature may be a rate-controlling variable where the temperature is selected to provide a desired product at an acceptable rate. In certain embodiments, the metathesis reaction temperature is greater than about -40°C , greater than about -20°C , greater than about 0°C , or greater than about 10°C . In certain embodiments, the metathesis reaction temperature is less than about 150°C , or less than about 120°C . In one embodiment, the metathesis reaction temperature is between about 10°C and about 120°C .

The metathesis reaction can be run under any desired pressure. Typically, it will be desirable to maintain a total pressure that is high enough to keep the cross-metathesis reagent in solution. Therefore, as the molecular weight of the cross-metathesis reagent increases, the lower pressure range typically decreases since the boiling point of the cross-metathesis reagent increases. The total pressure may be selected to be greater than about 0.1 atm (10 kPa), in some embodiments greater than about 0.3 atm (30 kPa), or greater than about 1 atm (100 kPa). Typically, the reaction pressure is no more than about 70 atm (7000 kPa), in some embodiments no more than about 30 atm (3000 kPa). A non-limiting exemplary pressure range for the metathesis reaction is from about 1 atm (100 kPa) to about 30 atm (3000 kPa). In certain embodiments it may be desirable to run the metathesis reactions under an atmosphere of reduced pressure. Conditions of reduced pressure or vacuum may be used to remove olefins as they are generated in a metathesis reaction, thereby driving the metathesis equilibrium towards the formation of less volatile products. In the case of a self-metathesis of a natural oil, reduced pressure can be used to remove C_{12} or lighter olefins including, but not limited to, hexene, nonene, and dodecene, as well as byproducts including, but

not limited to cyclohexa-diene and benzene as the metathesis reaction proceeds. The removal of these species can be used as a means to drive the reaction towards the formation of diester groups and cross linked triglycerides.

Hydrogenation:

5 In some embodiments, the unsaturated polyol ester is partially hydrogenated before it is subjected to the metathesis reaction. Partial hydrogenation of the unsaturated polyol ester reduces the number of double bonds that are available for in the subsequent metathesis reaction. In some embodiments, the unsaturated polyol ester is metathesized to form a metathesized unsaturated polyol ester, and the metathesized unsaturated polyol ester is then hydrogenated (e.g., partially or
10 fully hydrogenated) to form a hydrogenated metathesized unsaturated polyol ester.

Hydrogenation may be conducted according to any known method for hydrogenating double bond-containing compounds such as vegetable oils. In some embodiments, the unsaturated polyol ester or metathesized unsaturated polyol ester is hydrogenated in the presence of a nickel catalyst that has been chemically reduced with hydrogen to an active state. Commercial examples
15 of supported nickel hydrogenation catalysts include those available under the trade designations "NYSOFACT", "NYSOSEL", and "NI 5248 D" (from Englehard Corporation, Iselin, N.H.). Additional supported nickel hydrogenation catalysts include those commercially available under the trade designations "PRICAT 9910", "PRICAT 9920", "PRICAT 9908", "PRICAT 9936" (from Johnson Matthey Catalysts, Ward Hill, Mass.).

20 In some embodiments, the hydrogenation catalyst comprising, for example, nickel, copper, palladium, platinum, molybdenum, iron, ruthenium, osmium, rhodium, or iridium. Combinations of metals may also be used. Useful catalyst may be heterogeneous or homogeneous. In some embodiments, the catalysts are supported nickel or sponge nickel type catalysts.

In some embodiments, the hydrogenation catalyst comprises nickel that has been
25 chemically reduced with hydrogen to an active state (i.e., reduced nickel) provided on a support. In some embodiments, the support comprises porous silica (e.g., kieselguhr, infusorial, diatomaceous, or siliceous earth) or alumina. The catalysts are characterized by a high nickel surface area per gram of nickel.

In some embodiments, the particles of supported nickel catalyst are dispersed in a
30 protective medium comprising hardened triacylglyceride, edible oil, or tallow. In an exemplary embodiment, the supported nickel catalyst is dispersed in the protective medium at a level of about 22 wt. % nickel.

Hydrogenation may be carried out in a batch or in a continuous process and may be partial

hydrogenation or complete hydrogenation. In a representative batch process, a vacuum is pulled on the headspace of a stirred reaction vessel and the reaction vessel is charged with the material to be hydrogenated (e.g., RBD soybean oil or metathesized RBD soybean oil). The material is then heated to a desired temperature. Typically, the temperature ranges from about 50 deg. C. to 350 deg. C, for example, about 100 deg. C. to 300 deg. C. or about 150 deg. C. to 250 deg. C. The desired temperature may vary, for example, with hydrogen gas pressure. Typically, a higher gas pressure will require a lower temperature. In a separate container, the hydrogenation catalyst is weighed into a mixing vessel and is slurried in a small amount of the material to be hydrogenated (e.g., RBD soybean oil or metathesized RBD soybean oil). When the material to be hydrogenated reaches the desired temperature, the slurry of hydrogenation catalyst is added to the reaction vessel. Hydrogen gas is then pumped into the reaction vessel to achieve a desired pressure of H₂ gas. Typically, the H₂ gas pressure ranges from about 15 to 3000 psig, for example, about 15 psig to 90 psig. As the gas pressure increases, more specialized high-pressure processing equipment may be required. Under these conditions the hydrogenation reaction begins and the temperature is allowed to increase to the desired hydrogenation temperature (e.g., about 120 deg. C. to 200 deg. C.) where it is maintained by cooling the reaction mass, for example, with cooling coils. When the desired degree of hydrogenation is reached, the reaction mass is cooled to the desired filtration temperature.

The amount of hydrogenation catalysts is typically selected in view of a number of factors including, for example, the type of hydrogenation catalyst used, the amount of hydrogenation catalyst used, the degree of unsaturation in the material to be hydrogenated, the desired rate of hydrogenation, the desired degree of hydrogenation (e.g., as measure by iodine value (IV)), the purity of the reagent, and the H₂ gas pressure. In some embodiments, the hydrogenation catalyst is used in an amount of about 10 wt. % or less, for example, about 5 wt. % or less or about 1 wt. % or less.

After hydrogenation, the hydrogenation catalyst may be removed from the hydrogenated product using known techniques, for example, by filtration. In some embodiments, the hydrogenation catalyst is removed using a plate and frame filter such as those commercially available from Sparkler Filters, Inc., Conroe Tex. In some embodiments, the filtration is performed with the assistance of pressure or a vacuum. In order to improve filtering performance, a filter aid may be used. A filter aid may be added to the metathesized product directly or it may be applied to the filter. Representative examples of filtering aids include diatomaceous earth, silica, alumina, and carbon. Typically, the filtering aid is used in an amount of about 10 wt. % or less, for example, about 5 wt. % or less or about 1 wt. % or less. Other filtering techniques and filtering aids may

also be employed to remove the used hydrogenation catalyst. In other embodiments the hydrogenation catalyst is removed using centrifugation followed by decantation of the product.

Surfactant

The hair care composition may comprise a deterative surfactant, which provides cleaning performance to the composition. The deterative surfactant in turn comprises an anionic surfactant, amphoteric or zwitterionic surfactants, or mixtures thereof. Various examples and descriptions of deterative surfactants are set forth in U.S. Patent No. 6,649,155; U.S. Patent Application Publication No. 2008/0317698; and U.S. Patent Application Publication No. 2008/0206355, which are incorporated herein by reference in their entirety.

The concentration of the deterative surfactant component in the hair care composition should be sufficient to provide the desired cleaning and lather performance, and generally ranges from about 2 wt% to about 50 wt%, from about 5 wt% to about 30 wt%, from about 8 wt% to about 25 wt%, or from about 10 wt% to about 20 wt%. Accordingly, the hair care composition may comprise a deterative surfactant in an amount of about 5 wt%, about 10 wt%, about 12 wt%, about 15 wt%, about 17 wt%, about 18 wt%, or about 20 wt%, for example.

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

Exemplary anionic surfactants for use in the hair care composition include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, sodium cocoyl isethionate and combinations thereof. In a further embodiment, the anionic surfactant is sodium lauryl sulfate or sodium laureth sulfate.

Suitable amphoteric or zwitterionic surfactants for use in the hair care composition herein include those which are known for use in hair care or other personal care cleansing. Concentrations of such amphoteric surfactants range from about 0.5 wt% to about 20 wt%, and from about 1 wt% to about 10 wt%. Non limiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Patent Nos. 5,104,646 and 5,106,609, which are incorporated herein by reference in their entirety.

Amphoteric deterative surfactants suitable for use in the hair care composition include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate. Exemplary amphoteric deterative surfactants for use in the present hair care composition include cocoamphoacetate, cocoamphodiacetate, lauroamphoacetate, lauroamphodiacetate, and mixtures thereof.

Zwitterionic deterative surfactants suitable for use in the hair care composition include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. In another embodiment, zwitterionics such as betaines are selected.

Non limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Patent Nos. 3,929,678, 2,658,072; 2,438,091; 2,528,378, which are incorporated herein by reference in their entirety.

25 Aqueous Carrier

The hair care compositions can be in the form of pourable liquids (under ambient conditions). Such compositions will therefore typically comprise a carrier, which is present at a level of from about 20 wt% to about 95 wt%, or even from about 60 wt% to about 85 wt%. The carrier may comprise water, or a miscible mixture of water and organic solvent, and in one aspect may comprise water with minimal or no significant concentrations of organic solvent, except as otherwise incidentally incorporated into the composition as minor ingredients of other components.

The carrier useful in embodiments of the hair care composition includes water and water

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

5 **Additional Optional Components**

The hair care composition may further comprise one or more additional components known for use in hair care or personal care products, provided that the additional components do not otherwise unduly impair product stability, aesthetics, or performance. Such optional ingredients are most typically those described in reference books such as the CTFA Cosmetic Ingredient Handbook, Second Edition, The Cosmetic, Toiletries, and Fragrance Association, Inc. 1988, 1992. Individual concentrations of such additional components may range from about 0.001 wt% to about 10 wt% by weight of the personal care compositions.

Non-limiting examples of additional components for use in the hair care composition include conditioning agents (e.g., silicones, hydrocarbon oils, fatty esters), natural cationic deposition polymers, synthetic cationic deposition polymers, anti-dandruff agents, particles, suspending agents, paraffinic hydrocarbons, propellants, viscosity modifiers, dyes, non-volatile solvents or diluents (water-soluble and water-insoluble), pearlescent aids, foam boosters, additional surfactants or nonionic cosurfactants, pediculocides, pH adjusting agents, perfumes, preservatives, proteins, skin active agents, sunscreens, UV absorbers, and vitamins.

20 1. Conditioning Agent

In one embodiment, the hair care compositions comprise one or more conditioning agents. Conditioning agents include materials that are used to give a particular conditioning benefit to hair and/or skin. The conditioning agents useful in the hair care compositions typically comprise a water-insoluble, water-dispersible, non-volatile, liquid that forms emulsified, liquid particles. Suitable conditioning agents for use in the hair care composition are those conditioning agents characterized generally as silicones (e.g., silicone oils, cationic silicones, silicone gums, high refractive silicones, and silicone resins), organic conditioning oils (e.g., hydrocarbon oils, polyolefins, and fatty esters) or combinations thereof, or those conditioning agents which otherwise form liquid, dispersed particles in the aqueous surfactant matrix.

30 One or more conditioning agents are present from about 0.01 wt% to about 10 wt%, alternatively from about 0.1 wt% to about 8 wt%, and alternatively from about 0.2 wt% to about 4 wt%, by weight of the composition.

a. Silicones

The conditioning agent of the hair care composition may be an insoluble silicone conditioning agent. The silicone conditioning agent particles may comprise volatile silicone, non-volatile silicone, or combinations thereof. If volatile silicones are present, it 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 conditioning agent particles may comprise a silicone fluid conditioning agent and may also comprise other ingredients, such as a silicone resin to improve silicone fluid deposition efficiency or enhance glossiness of the hair.

The concentration of the silicone conditioning agent typically ranges from about 0.01% to about 10%, by weight of the composition, alternatively from about 0.1% to about 8%, alternatively from about 0.1% to about 5%, and alternatively from about 0.2% to about 3%. Non-limiting examples of suitable silicone conditioning agents, and optional suspending agents for the silicone, are described in U.S. Reissue Pat. No. 34,584, U.S. Pat. No. 5,104,646, and U.S. Pat. No. 5,106,609, which descriptions are incorporated herein by reference. The silicone conditioning agents for use in the hair care composition may have a viscosity, as measured at 25°C, from about 20 to about 2,000,000 centistokes ("cSt"), alternatively from about 1,000 to about 1,800,000 cSt, alternatively from about 50,000 to about 1,500,000 cSt, and alternatively from about 100,000 to about 1,500,000 cSt.

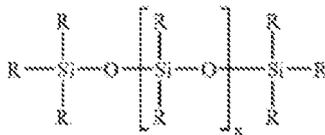
The dispersed silicone conditioning agent particles typically have a volume average particle diameter ranging from about 0.01 micrometer to about 50 micrometer. For small particle application to hair, the volume average particle diameters typically range from about 0.01 micrometer to about 4 micrometer, alternatively from about 0.01 micrometer to about 2 micrometer, and alternatively from about 0.01 micrometer to about 0.5 micrometer. For larger particle application to hair, the volume average particle diameters typically range from about 5 micrometer to about 125 micrometer, alternatively from about 10 micrometer to about 90 micrometer, alternatively from about 15 micrometer to about 70 micrometer, and alternatively from about 20 micrometer to about 50 micrometer.

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.

i. Silicone Oils

Silicone fluids include silicone oils, which are flowable silicone materials having a viscosity, as measured at 25°C, less than 1,000,000 cSt, alternatively from about 5 cSt to about 1,000,000 cSt, and alternatively from about 100 cSt to about 600,000 cSt. Suitable silicone oils for use in the hair care composition 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.

Silicone oils include polyalkyl or polyaryl siloxanes which conform to the following Formula (I):



wherein R is aliphatic, in some embodiments alkyl, alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable R groups for use in the compositions 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 groups also include cationic amines and quaternary ammonium groups.

Possible alkyl and alkenyl substituents include C₁ to C₅ alkyls and alkenyls, alternatively from C₁ to C₄, and alternatively from C₁ to C₂. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains, and may be from C₁ to C₅, alternatively from C₁ to C₄, alternatively from C₁ to C₃, and alternatively from C₁ to C₂. As discussed above, the R 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 may be as described herein.

ii. Amino and Cationic Silicones

Cationic silicone fluids suitable for use in the compositions include, but are not limited to, those which conform to the general formula (II):



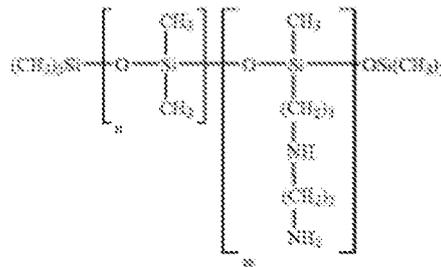
wherein G is hydrogen, phenyl, hydroxy, or C₁-C_s alkyl, in some embodiments, methyl; a is 0 or an integer having a value from 1 to 3; b is 0 or 1; n is a number from 0 to 1,999, alternatively from

49 to 499; m is an integer from 1 to 2,000, alternatively from 1 to 10; the sum of n and m is a number from 1 to 2,000, alternatively from 50 to 500; R¹ is a monovalent radical conforming to the general formula C_qH_{2_q}L, wherein q is an integer having a value from 2 to 8 and L is selected from the following groups:

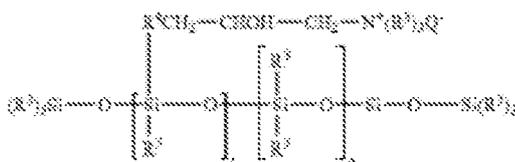
- 5 --N(R²)CH₂--CH₂--N(R²)₂
- N(R²)₂
- N(R²)₃ A⁻
- N(R²)CH₂-CH₂-NR²H₂ A⁻

wherein R² is hydrogen, phenyl, benzyl, or a saturated hydrocarbon radical, in some embodiments an alkyl radical from about C₁ to about C₂₀, and A⁻ is a halide ion.

In one embodiment, the cationic silicone corresponding to formula (II) is the polymer known as "trimethylsilylamodimethicone", which is shown below in formula (III):



Other silicone cationic polymers which may be used in the hair care composition are represented by the general formula (IV):



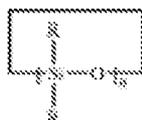
wherein R³ is a monovalent hydrocarbon radical from C₁ to C₁₅, in some embodiments an alkyl or alkenyl radical, such as methyl; R₄ is a hydrocarbon radical, in some embodiments a C₁ to C₁₈ alkylene radical or a C₁₀ to C₁₈ alkyleneoxy radical, alternatively a C₁ to C₈ alkyleneoxy radical; Q⁻ is a halide ion, in some embodiments chloride; r is an average statistical value from 2 to 20, in some embodiments from 2 to 8; s is an average statistical value from 20 to 200, in some embodiments from 20 to 50. One polymer of this class is known as UCARE SILICONE ALE 56®, available from Union Carbide.

iii. Silicone Gums

Other silicone fluids suitable for use in the hair care composition are the insoluble silicone gums. These gums are polyorganosiloxane materials having a viscosity, as measured at 25°C, of greater than or equal to 1,000,000 cSt. 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
 5 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. Specific non-limiting examples of silicone gums for use in the hair care include polydimethylsiloxane, (polydimethylsiloxane)(methylvinylsiloxane)copolymer, poly(dimethylsiloxane)(diphenylsiloxane)(methylvinylsiloxane)copolymer and mixtures thereof.

10 iv. High Refractive Index Silicones

Other non-volatile, insoluble silicone fluid conditioning agents that are suitable for use in the hair care composition are those known as "high refractive index silicones," having a refractive index of at least about 1.46, alternatively at least about 1.48, alternatively at least about 1.52, and alternatively at least about 1.55. The refractive index of the polysiloxane fluid will generally be
 15 less than about 1.70, typically less than about 1.60. In this context, polysiloxane "fluid" includes oils as well as gums. The high refractive index polysiloxane fluid includes those represented by general Formula (I) above, as well as cyclic polysiloxanes such as those represented by Formula (V) below:



20 wherein R is as defined above, and n is a number from about 3 to about 7, alternatively from about 3 to about 5.

The high refractive index polysiloxane fluids contain an amount of aryl-containing R substituents sufficient to increase the refractive index to the desired level, which is described herein. Additionally, R and n may be selected so that the material is non-volatile.

25 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 themselves can be substituted or unsubstituted.

Generally, the high refractive index polysiloxane fluids will have a degree of aryl-containing substituents of at least about 15%, alternatively at least about 20%, alternatively at least
 30 about 25%, alternatively at least about 35%, and alternatively at least about 50%. Typically, the degree of aryl substitution will be less than about 90%, more generally less than about 85%,

alternatively from about 55% to about 80%. In some embodiments, the high refractive index polysiloxane fluids have a combination of phenyl or phenyl derivative substituents, with alkyl substituents, in some embodiments C1-C4 alkyl, hydroxy, or C1-C4 alkylamino (especially— $R^4NHR^5NH_2$ wherein each R^4 and R^5 independently is a C1-C3 alkyl, alkenyl, and/or alkoxy).

5 When high refractive index silicones are used in the hair care composition, they may 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 the compositions.

Silicone fluids suitable for use in the hair care composition are disclosed in U.S. Pat. No. 10 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.

v. Silicone Resins

Silicone resins may be included in the silicone conditioning agent of the hair care composition. These resins are highly cross-linked polymeric siloxane systems. The cross-linking 15 is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin.

Silicone materials and silicone resins in particular, can conveniently be identified according to 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 presence of 20 various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit $(CH_3)_3SiO_{0.5}$; D denotes the difunctional unit $(CH_3)_2SiO$; T denotes the trifunctional unit $(CH_3)_SiO_{1.5}$; and Q denotes the quadra- or tetra-functional unit SiO_2 . 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.

25 Silicone resins for use in the hair care composition may include, but are not limited to MQ, MT, MTQ, MDT and MDTQ resins. Methyl is a possible silicone substituent. In some embodiments, silicone resins are 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.

The weight ratio of the non-volatile silicone fluid, having refractive index below 1.46, to 30 the silicone resin component, when used, may be from about 4:1 to about 400:1, alternatively from about 9:1 to about 200:1, and alternatively from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described herein. 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.

b. Organic Conditioning Oils

5 The conditioning agent of the hair care hair care composition may also comprise at least one organic conditioning oil, either alone or in combination with other conditioning agents, such as the silicones described above.

i. Hydrocarbon Oils

10 Suitable organic conditioning oils for use as conditioning agents in the hair care composition 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 may be from about C_{12} to about C_{19} . Branched chain hydrocarbon oils, including hydrocarbon polymers, typically will contain more than 19
15 carbon atoms.

ii. Polyolefins

Organic conditioning oils for use in the hair care composition can also include liquid polyolefins, alternatively liquid poly- α -olefins, alternatively hydrogenated liquid poly- α -olefins. Polyolefins for use herein are prepared by polymerization of C_4 to about C_{14} olefinic monomers,
20 in some embodiments from about C_6 to about C_{12} .

iii. Fatty Esters

Other suitable organic conditioning oils for use as the conditioning agent in the hair care hair care composition include fatty esters having at least 10 carbon atoms. These fatty esters include esters with hydrocarbyl chains derived from fatty acids or alcohols. The hydrocarbyl
25 radicals of 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.).

iv. Fluorinated Conditioning Compounds

Fluorinated compounds suitable for delivering conditioning to hair or skin as organic conditioning oils include perfluoropolyethers, perfluorinated olefins, fluorine based specialty
30 polymers that may be in a fluid or elastomer form similar to the silicone fluids previously described, and perfluorinated dimethicones.

v. Fatty Alcohols

Other suitable organic conditioning oils for use in the personal care hair care composition include, but are not limited to, fatty alcohols having at least about 10 carbon atoms, alternatively from about 10 to about 22 carbon atoms, and alternatively from about 12 to about 16 carbon atoms.

5 vi. Alkyl Glucosides and Alkyl Glucoside Derivatives

Suitable organic conditioning oils for use in the personal care hair care composition include, but are not limited to, alkyl glucosides and alkyl glucoside derivatives. Specific non-limiting examples of suitable alkyl glucosides and alkyl glucoside derivatives include Glucam E-10, Glucam E-20, Glucam P-10, and Glucquat 125 commercially available from Amerchol.

10 c. Other Conditioning Agents

i. Quaternary Ammonium Compounds

Suitable quaternary ammonium compounds for use as conditioning agents in the personal care hair care composition include, but are not limited to, hydrophilic quaternary ammonium compounds with a long chain substituent having a carbonyl moiety, like an amide moiety, or a phosphate ester moiety or a similar hydrophilic moiety.

15 Examples of useful hydrophilic quaternary ammonium compounds include, but are not limited to, compounds designated in the CTFA Cosmetic Dictionary as ricinoleamidopropyl trimonium chloride, ricinoleamido trimonium ethylsulfate, hydroxy stearamidopropyl trimoniummethylsulfate and hydroxy stearamidopropyl trimonium chloride, or combinations
20 thereof.

ii. Polyethylene Glycols

Additional compounds useful herein as conditioning agents include polyethylene glycols and polypropylene glycols having a molecular weight of up to about 2,000,000 such as those with CTFA names PEG-200, PEG-400, PEG-600, PEG-1000, PEG-2M, PEG-7M, PEG-14M, PEG-
25 45M and mixtures thereof.

iii. Cationic deposition polymers

The personal care composition may further comprise a cationic deposition polymer. Any known natural or synthetic cationic deposition polymer can be used herein. Examples include those polymers disclosed in U.S. Patent No. 6,649,155; U.S. Patent Application Publication Nos.
30 2008/03 17698; 2008/0206355; and 2006/0099167, which are incorporated herein by reference in their entirety.

The cationic deposition polymer is included in the composition at a level from about 0.01 wt% to about 1 wt%, in one embodiment from about 0.05 wt% to about 0.75 wt%, in another

embodiment from about 0.25 wt% to about 0.50 wt%, in view of providing the benefits of the hair care composition.

The cationic deposition polymer is a water soluble polymer with a charge density from about 0.5 milliequivalents per gram to about 12 milliequivalents per gram. The cationic deposition polymer used in the composition has a molecular weight of about 100,000 Daltons to about 5,000,000 Daltons. The cationic deposition polymer is a low, medium or high charge density cationic polymer.

These cationic deposition polymers can include at least one of (a) a cationic guar polymer, (b) a cationic non-guar polymer, (c) a cationic tapioca polymer, (d) a cationic copolymer of acrylamide monomers and cationic monomers, and/or (e) a synthetic, non-crosslinked, cationic polymer, which forms lyotropic liquid crystals upon combination with the deterative surfactant. Additionally, the cationic deposition polymer can be a mixture of deposition polymers.

(1) Cationic Guar Polymers

According to one embodiment, the cationic guar polymer has a weight average M.Wt. of less than about 1million g/mol, and has a charge density of from about 0.1 meq/g to about 2.5 meq/g. In an embodiment, the cationic guar polymer has a weight average M.Wt. of less than 900 thousand g/mol, or from about 150 thousand to about 800 thousand g/mol, or from about 200 thousand to about 700 thousand g/mol, or from about 300 thousand to about 700 thousand g/mol, or from about 400 thousand to about 600 thousand g/mol. from about 150 thousand to about 800 thousand g/mol, or from about 200 thousand to about 700 thousand g/mol, or from about 300 thousand to about 700 thousand g/mol, or from about 400 thousand to about 600 thousand g/mol. In one embodiment, the cationic guar polymer has a charge density of from about 0.2 to about 2.2 meq/g, or from about 0.3 to about 2.0 meq/g, or from about 0.4 to about 1.8 meq/g; or from about 0.5 meq/g to about 1.5 meq/g.

In an embodiment, the composition comprises from about 0.01% to less than about 0.6%, or from about 0.04% to about 0.55%, or from about 0.08% to about 0.5%, or from about 0.16% to about 0.5%, or from about 0.2% to about 0.5%, or from about 0.3% to about 0.5%, or from about 0.4% to about 0.5%, of cationic guar polymer (a), by total weight of the composition.

Suitable cationic guar polymers include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride. In an embodiment, the cationic guar polymer is a guar hydroxypropyltrimonium chloride. Specific examples of guar hydroxypropyltrimonium chlorides include the Jaguar® series commercially available from Rhone-Poulenc Incorporated, for example Jaguar® C-500, commercially available from Rhodia. Jaguar® C-500 has a charge density of 0.8

meq/g and a M.Wt. of 500,000 g/mole. Another guar hydroxypropyltrimonium chloride with a charge density of about 1.1 meq/g and a M.Wt. of about 500,000 g/mole is available from Ashland. A further guar hydroxypropyltrimonium chloride with a charge density of about 1.5 meq/g and a M.Wt. of about 500,000 g/mole is available from Ashland.

5 Other suitable polymers include: Hi-Care 1000, which has a charge density of about 0.7 meq/g and a M.Wt. of about 600,000 g/mole and is available from Rhodia; N-Hance 3269 and N-Hance 3270, which have a charge density of about 0.7 meq/g and a M.Wt. of about 425,000 g/mole and is available from Ashland; AquaCat CG518 has a charge density of about 0.9 meq/g and a M.Wt. of about 50,000 g/mole and is available from Ashland. A further non-limiting example is
10 N-Hance 3196 from Ashland.

(2) Cationic Non-Guar Polymers

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

20 The galactomannan polymer derivatives for use in the shampoo compositions of the present invention have a molecular weight from about 1,000 to about 10,000,000. In one embodiment of the present invention, the galactomannan polymer derivatives have a molecular weight from about 5,000 to about 3,000,000. As used herein, the term "molecular weight" refers to the weight average molecular weight. The weight average molecular weight may be measured by gel permeation
25 chromatography.

The shampoo compositions of the present invention include galactomannan polymer derivatives which have a cationic charge density from about 0.9 meq/g to about 7 meq/g. In one embodiment of the present invention, the galactomannan polymer derivatives have a cationic charge density from about 1 meq/g to about 5 meq/g. The degree of substitution of the cationic
30 groups onto the galactomannan structure should be sufficient to provide the requisite cationic charge density.

(3) Cationically Modified Starch Polymer

The shampoo compositions of the present invention comprise water-soluble cationically modified starch polymers. As used herein, the term "cationically modified starch" refers to a starch to which a cationic group is added prior to degradation of the starch to a smaller molecular weight, or wherein a cationic group is added after modification of the starch to achieve a desired molecular weight. The definition of the term "cationically modified starch" also includes amphoterically modified starch. The term "amphoterically modified starch" refers to a starch hydrolysate to which a cationic group and an anionic group are added.

The shampoo compositions of the present invention comprise cationically modified starch polymers at a range of about 0.01% to about 10%, and more preferably from about 0.05% to about 5%, by weight of the composition.

Non-limiting examples of these ammonium groups may include substituents such as hydroxypropyl trimmonium chloride, trimethylhydroxypropyl ammonium chloride, dimethylstearylhydroxypropyl ammonium chloride, and dimethyldodecylhydroxypropyl ammonium chloride. See Solarek, D. B., *Cationic Starches in Modified Starches: Properties and Uses*, Wurzburg, O. B., Ed., CRC Press, Inc., Boca Raton, Fla. 1986, pp 113-125. The cationic groups may be added to the starch prior to degradation to a smaller molecular weight or the cationic groups may be added after such modification.

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

In one embodiment of the present invention, cationically modified starch polymers are selected from degraded cationic maize starch, cationic tapioca, cationic potato starch, and mixtures thereof. In another embodiment, cationically modified starch polymers are cationic corn starch and cationic tapioca. Cationic tapioca starch is preferred.

In another embodiment, the cationic deposition polymer is a naturally derived cationic polymer. The term, "naturally derived cationic polymer" as used herein, refers to cationic deposition polymers which are obtained from natural sources. The natural sources may be polysaccharide polymers. Therefore, the naturally derived cationic polymer may be selected from the group comprising starch, guar, cellulose, cassia, locust bean, konjac, tara, galactomannan, and tapioca. In a further embodiment, cationic deposition polymers are selected from Jaguar® C17, cationic tapioca starch (Akzo), and mixtures thereof.

(4) Cationic copolymer of an Acrylamide Monomer and a Cationic Monomer

According to an embodiment of the present invention, the shampoo composition comprises a cationic copolymer of an acrylamide monomer and a cationic monomer, wherein the copolymer has a charge density of from about 1.0 meq/g to about 3.0 meq/g. In an embodiment, the cationic copolymer is a synthetic cationic copolymer of acrylamide monomers and cationic monomers.

In an embodiment, the cationic copolymer (b) is AM:TRIQUAT which is a copolymer of acrylamide and 1,3-Propanediaminium,N-[2-[[[dimethyl[3-[(2-methyl-1-oxo-2-propenyl)amino]propyl]arrmionio]acetyl]amino]ethyl]2-hydroxy-N,N,N',N',N'-pentamethyl-, trichloride. AM:TRIQUAT is also known as polyquaternium 76 (PQ76). AM:TRIQUAT may have a charge density of 1.6 meq/g and a M.Wt. of 1.1 million g/mol.

In an embodiment, the cationic copolymer is a trimethylammoniopropylmethacrylamide chloride-N-Acrylamide copolymer, which is also known as AM:MAPTAC. AM:MAPTAC may have a charge density of about 1.3 meq/g and a M.Wt. of about 1.1 million g/mol. In an embodiment, the cationic copolymer is AM:ATPAC. AM:ATPAC may have a charge density of about 1.8 meq/g and a M.Wt. of about 1.1 million g/mol.

(5) Cationic Synthetic Polymer

The cationic polymer described herein aids in providing damaged hair, particularly chemically treated hair, with a surrogate hydrophobic F-layer. Lyotropic liquid crystals are formed by combining the synthetic cationic polymers described herein with the aforementioned anionic 20
detergent surfactant component of the shampoo composition. The synthetic cationic polymer has a relatively high charge density. It should be noted that some synthetic polymers having a relatively high cationic charge density do not form lyotropic liquid crystals, primarily due to their abnormal linear charge densities. Such synthetic cationic polymers are described in WO 94/06403 to Reich et al.

The concentration of the cationic polymers ranges about 0.025% to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 1%, by weight of the shampoo composition.

The cationic polymers have a cationic charge density of from about 2 meq/gm to about 7 meq/gm, preferably from about 3 meq/gm to about 7 meq/gm, more preferably from about 4 meq/gm to about 7 meq/gm. In some embodiments, the cationic charge density is about 6.2 meq/gm. The polymers also have a molecular weight of from about 1,000 to about 5,000,000, more preferably from about 10,000 to about 2,000,000, most preferably 100,000 to about 2,000,000.

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

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

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

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

2. Anionic emulsifiers

30 A variety of anionic emulsifiers can be used in the hair care composition as described below. The anionic emulsifiers include, by way of illustrating and not limitation, water-soluble salts of alkyl sulfates, alkyl ether sulfates, alkyl isothionates, alkyl carboxylates, alkyl sulfosuccinates, alkyl succinamates, alkyl sulfate salts such as sodium dodecyl sulfate, alkyl

sarcosinates, alkyl derivatives of protein hydrolyzates, acyl aspartates, alkyl or alkyl ether or alkylaryl ether phosphate esters, sodium dodecyl sulphate, phospholipids or lecithin, or soaps, sodium, potassium or ammonium stearate, oleate or palmitate, alkylarylsulfonic acid salts such as sodium dodecylbenzenesulfonate, sodium dialkylsulfosuccinates, dioctyl sulfosuccinate, sodium
5 dilaurylsulfosuccinate, poly(styrene sulfonate) sodium salt, isobutylene-maleic anhydride copolymer, gum arabic, sodium alginate, carboxymethylcellulose, cellulose sulfate and pectin, poly(styrene sulfonate), isobutylene-maleic anhydride copolymer, gum arabic, carrageenan, sodium alginate, pectic acid, tragacanth gum, almond gum and agar; semi-synthetic polymers such as carboxymethyl cellulose, sulfated cellulose, sulfated methylcellulose, carboxymethyl starch, phosphated starch, lignin sulfonic acid; and synthetic polymers such as maleic anhydride
10 copolymers (including hydrolyzates thereof), polyacrylic acid, polymethacrylic acid, acrylic acid butyl acrylate copolymer or crotonic acid homopolymers and copolymers, vinylbenzenesulfonic acid or 2-acrylamido-2-methylpropanesulfonic acid homopolymers and copolymers, and partial amide or partial ester of such polymers and copolymers, carboxymodified polyvinyl alcohol,
15 sulfonic acid-modified polyvinyl alcohol and phosphoric acid-modified polyvinyl alcohol, phosphated or sulfated tristyrylphenol ethoxylates.

In addition, anionic emulsifiers that have acrylate functionality may also be used in the instant shampoo compositions. Anionic emulsifiers useful herein include, but aren't limited to: poly(meth)acrylic acid; copolymers of (meth)acrylic acids and its (meth)acrylates with C1-22
20 alkyl, C1-C8 alkyl, butyl; copolymers of (meth)acrylic acids and (meth)acrylamide; Carboxyvinylpolymer; acrylate copolymers such as Acrylate/C 10-30 alkyl acrylate crosspolymer, Acrylic acid/vinyl ester copolymer/Acrylates/Vinyl Isodecanoate crosspolymer, Acrylates/Palmeth-25 Acrylate copolymer, Acrylate/Steareth-20 Itaconate copolymer, and Acrylate/Celeth-20 Itaconate copolymer; Polystyrene sulphonate, copolymers of methacrylic acid
25 and acrylamidomethylpropane sulfonic acid, and copolymers of acrylic acid and acrylamidomethylpropane sulfonic acid; carboxymethylcellulose; carboxy guar; copolymers of ethylene and maleic acid; and acrylate silicone polymer. Neutralizing agents may be included to neutralize the anionic emulsifiers herein. Non-limiting examples of such neutralizing agents include sodium hydroxide, potassium hydroxide, ammonium hydroxide, monoethanolamine,
30 diethanolamine, triethanolamine, diisopropanolamine, aminomethylpropanol, tromethamine, tetrahydroxypropyl ethylenediamine, and mixtures thereof. Commercially available anionic emulsifiers include, for example, Carbomer supplied from Noveon under the tradename Carbopol 981 and Carbopol 980; Acrylates/CIO-30 Alkyl Acrylate Crosspolymer having tradenames Pemulen TR-1, Pemulen TR-2, Carbopol 1342, Carbopol 1382, and Carbopol ETD 2020, all

available from Noveon; sodium carboxymethylcellulose supplied from Hercules as CMC series; and Acrylate copolymer having a tradename Capigel supplied from Seppic. In another embodiment, anionic emulsifiers are carboxymethylcelluloses.

3. Benefit Agents

5 In an embodiment, the hair care composition further comprises one or more additional benefit agents. The benefit agents comprise a material selected from the group consisting of anti-dandruff agents, vitamins, lipid soluble vitamins, chelants, perfumes, brighteners, enzymes, sensates, attractants, anti-bacterial agents, dyes, pigments, bleaches, and mixtures thereof.

10 In one aspect said benefit agent may comprise an anti-dandruff agent. Such anti-dandruff particulate should be physically and chemically compatible with the components of the composition, and should not otherwise unduly impair product stability, aesthetics or performance.

According to an embodiment, the hair care composition comprises an anti-dandruff active, which may be an anti-dandruff active particulate. In an embodiment, the anti-dandruff active is selected from the group consisting of: pyridinethione salts; azoles, such as ketoconazole, econazole, and elubiol; selenium sulphide; particulate sulfur; keratolytic agents such as salicylic acid; and mixtures thereof. In an embodiment, the anti-dandruff particulate is a pyridinethione salt.

Pyridinethione particulates are suitable particulate anti-dandruff actives. In an embodiment, the anti-dandruff active is a 1-hydroxy-2-pyridinethione salt and is in particulate form. In an embodiment, the concentration of pyridinethione anti-dandruff particulate ranges from about 0.01 wt% to about 5 wt%, or from about 0.1 wt% to about 3 wt%, or from about 0.1 wt% to about 2 wt%. In an embodiment, the pyridinethione salts are those formed from heavy metals such as zinc, tin, cadmium, magnesium, aluminium and zirconium, generally zinc, typically the zinc salt of 1-hydroxy-2-pyridinethione (known as "zinc pyridinethione" or "ZPT"), commonly 1-hydroxy-2-pyridinethione salts in platelet particle form. In an embodiment, the 1-hydroxy-2-pyridinethione salts in platelet particle form have an average particle size of up to about 20 microns, or up to about 5 microns, or up to about 2.5 microns. Salts formed from other cations, such as sodium, may also be suitable. Pyridinethione anti-dandruff actives are described, for example, in U.S. Pat. No. 2,809,971; U.S. Pat. No. 3,236,733; U.S. Pat. No. 3,753,196; U.S. Pat. No. 3,761,418; U.S. Pat. No. 4,345,080; U.S. Pat. No. 4,323,683; U.S. Pat. No. 4,379,753; and U.S. Pat. No. 4,470,982.

In an embodiment, in addition to the anti-dandruff active selected from polyvalent metal salts of pyrrithione, the composition further comprises one or more anti-fungal and/or anti-

microbial actives. In an embodiment, the anti-microbial active is selected from the group consisting of: coal tar, sulfur, charcoal, whitfield's ointment, castellani's paint, aluminum chloride, gentian violet, octopirox (picrotone olamine), ciclopirox olamine, undecylenic acid and its metal salts, potassium permanganate, selenium sulphide, sodium thiosulfate, propylene glycol, oil of bitter orange, urea preparations, griseofulvin, 8-hydroxyquinoline ciloquinol, thiobendazole, thiocarbamates, haloprogin, polyenes, hydroxypyridone, morpholine, benzylamine, allylamines (such as terbinafine), tea tree oil, clove leaf oil, coriander, palmarosa, berberine, thyme red, cinnamon oil, cinnamic aldehyde, citronellic acid, hinokitol, ichthyol pale, Sensiva SC-50, Elestab HP-100, azelaic acid, lyticase, iodopropynyl butylcarbamate (IPBC), isothiazalinones such as octyl isothiazalinone, and azoles, and mixtures thereof. In an embodiment, the anti-microbial is selected from the group consisting of: itraconazole, ketoconazole, selenium sulphide, coal tar, and mixtures thereof.

In an embodiment, the azole anti-microbials is an imidazole selected from the group consisting of: benzimidazole, benzothiazole, bifonazole, butaconazole nitrate, climbazole, clotrimazole, croconazole, eberconazole, econazole, elubiol, fenticonazole, fluconazole, flutimazole, isoconazole, ketoconazole, lanoconazole, metronidazole, miconazole, neticonazole, omoconazole, oxiconazole nitrate, sertaconazole, sulconazole nitrate, tioconazole, thiazole, and mixtures thereof, or the azole anti-microbials is a triazole selected from the group consisting of: terconazole, itraconazole, and mixtures thereof. When present in the hair care composition, the azole anti-microbial active is included in an amount of from about 0.01 wt% to about 5 wt%, or from about 0.1 wt% to about 3 wt%, or from about 0.3 wt% to about 2 wt%. In an embodiment, the azole anti-microbial active is ketoconazole. In an embodiment, the sole anti-microbial active is ketoconazole.

Embodiments of the hair care composition may also comprise a combination of anti-microbial actives. In an embodiment, the combination of anti-microbial active is selected from the group of combinations consisting of: octopirox and zinc pyrithione, pine tar and sulfur, salicylic acid and zinc pyrithione, salicylic acid and elubiol, zinc pyrithione and elubiol, zinc pyrithione and climbasole, octopirox and climbasole, salicylic acid and octopirox, and mixtures thereof.

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

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

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

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

Yet another class of ZLMs can be prepared called hydroxy double salts (Morioka, H., Tagaya, H., Karasu, M, Kadokawa, J, Chiba, K *Inorg. Chem.* 1999, 38, 421 1-6). In an embodiment, the ZLM is a hydroxy double salt conforming to the formula $[M^{2+i-x}M^{2+i+x}(OH)_3(i-y)]^+ A^{n-(i=3y)/n} \cdot nH_2O$ where the two metal ions (M^{2+}) may be the same or different. If they are the same and represented by zinc, the formula simplifies to $[Zn_{i+x}(OH)_2]^{2x+} 2x A^{x/n} \cdot nH_2O$. This latter formula represents (where $x=0.4$) materials such as zinc hydroxychloride and zinc hydroxynitrate. In an embodiment, the ZLM is zinc hydroxychloride and/or zinc hydroxynitrate. These are related to hydrozincite as well wherein a divalent anion replace the monovalent anion. These materials can also be formed *in situ* in a composition or in or during a production process.

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

The on-scalp deposition of the anti-dandruff active is at least about 1 microgram/cm². The on-scalp deposition of the anti-dandruff active is important in view of ensuring that the anti-

dandruff active reaches the scalp where it is able to perform its function. In an embodiment, the deposition of the anti-dandruff active on the scalp is at least about 1.5 microgram/cm², or at least about 2.5 microgram/cm², or at least about 3 microgram/cm², or at least about 4 microgram/cm², or at least about 6 microgram/cm², or at least about 7 microgram/cm², or at least about 8 microgram/cm², or at least about 8 microgram/cm², or at least about 10 microgram/cm². The on-scalp deposition of the anti-dandruff active is measured by having the hair of individuals washed with a composition comprising an anti-dandruff active, for example a composition pursuant to the present invention, by trained a cosmetician according to a conventional washing protocol. The hair is then parted on an area of the scalp to allow an open-ended glass cylinder to be held on the surface while an aliquot of an extraction solution is added and agitated prior to recovery and analytical determination of anti-dandruff active content by conventional methodology, such as HPLC.

Embodiments of the hair care composition may also comprise fatty alcohol gel networks, which have been used for years in cosmetic creams and hair conditioners. These gel networks are formed by combining fatty alcohols and surfactants in the ratio of about 1:1 to about 40:1 (alternatively from about 2:1 to about 20:1, and alternatively from about 3:1 to about 10:1). The formation of a gel network involves heating a dispersion of the fatty alcohol in water with the surfactant to a temperature above the melting point of the fatty alcohol. During the mixing process, the fatty alcohol melts, allowing the surfactant to partition into the fatty alcohol droplets. The surfactant brings water along with it into the fatty alcohol. This changes the isotropic fatty alcohol drops into liquid crystalline phase drops. When the mixture is cooled below the chain melt temperature, the liquid crystal phase is converted into a solid crystalline gel network. The gel network contributes a stabilizing benefit to cosmetic creams and hair conditioners. In addition, they deliver conditioned feel benefits for hair conditioners.

Thus according to an embodiment, the fatty alcohol is included in the fatty alcohol gel network at a level by weight of from about 0.05 wt% to about 14 wt%. For example, the fatty alcohol may be present in an amount ranging from about 1 wt% to about 10 wt%, and alternatively from about 6 wt% to about 8 wt%.

The fatty alcohols useful herein are those having from about 10 to about 40 carbon atoms, from about 12 to about 22 carbon atoms, from about 16 to about 22 carbon atoms, or about 16 to about 18 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof. Mixtures of cetyl and stearyl alcohol in a ratio of from about 20:80 to about 80:20, are suitable.

Gel network preparation: A vessel is charged with water and the water is heated to about 74°C. Cetyl alcohol, stearyl alcohol, and SLES surfactant are added to the heated water. After incorporation, the resulting mixture is passed through a heat exchanger where the mixture is cooled to about 35°C. Upon cooling, the fatty alcohols and surfactant crystallized to form a crystalline gel network. Table 3 provides the components and their respective amounts for the gel network composition.

Table 3

Gel network components

Ingredient	Wt. %
Water	77%
Cetyl Alcohol	4.29%
Stearyl Alcohol	7.71%
Sodium laureth-1 sulfate (28% Active)	11.00%

10

TEST METHODS

A. Molecular Weight Distribution

The weight average molecular weight (Mw) of the metathesized unsaturated polyol ester is measured using gel permeation chromatography (GPC) and multi-angle laser light scattering (MALLS). The GPC/MALLS system used for the analysis is comprised of a Waters Alliance e2695 Separations Module, a Waters 2414 interferometric refractometer, and a Wyatt Heleos II 18 angle laser light scattering detector. The column set used for separation is purchased from TOSOH Biosciences LLC, King of Prussia, PA and included: Guard Column TSKgel G1000Hxl-GMHxl-L (Cat # 07113), TSKgel G3000Hxl (Cat # 0016136), TSKgel G2500Hxl (Cat # 0016135), and TSKgel G2000Hxl (Cat # 0016134). Wyatt ASTRA 6 software was used for instrument operation and data analysis. The 90 degree light scattering detection angle is calibrated using filtered, anhydrous toluene. The remaining detection angles are normalized using an isotropic scatterer in THF. To verify instrument performance of the MALLS and RI (refractive index) detectors, a poly(styrene) standard with a known Mw and known dn/dc (in the mobile phase) is run. Acceptable performance of the MALLS and RI detectors gives a calculated Mw within 5% of the reported Mw of the poly(styrene) standard and a mass recovery between 95 and 105%.

To complete the GPC/MALLS analysis, a value of dn/dc is needed. The value of dn/dc is measured as follows. The RI detector is thermostated to 35 degrees Celsius. A series of five concentration standards of the metathesized unsaturated polyol ester in THF is prepared in the

range 0.5 mg/ml to 5.5 mg/ml. A THF blank is injected directly into the refractive index detector, followed by each of the metathesized unsaturated polyol ester concentration standards, and ending with another THF blank. The volume of each sample injected is large enough to obtain a flat plateau region of constant differential refractive index versus time; a value of 1.0 ml is typically used. In the ASTRA software, a baseline is constructed from the initial and final THF injections. For each sample, peak limits are defined and the concentrations entered to calculate dn/dc in the ASTRA software. For the metathesized canola oil of Example 2 in THF, a dn/dc value of 0.072 ml/g is obtained.

For the GPC/MALLS analysis of a metathesized unsaturated polyol ester, a total of three samples are evaluated: the metathesized unsaturated polyol ester, a non-metathesized unsaturated polyol ester (glycerol trioleate [122-32-7], Sigma-Aldrich, Milwaukee, WI), and a representative olefin (1-octadecene, [112-88-9], Sigma-Aldrich, Milwaukee, WI). The GPC samples are dissolved in tetrahydrofuran (THF). Concentrations for the metathesized unsaturated polyol ester are approximately 20 mg/ml, and concentrations for the non-metathesized unsaturated polyol ester and olefin are approximately 5 mg/ml. After all the material is dissolved, each solution is filtered by a 0.45 micron nylon filter disk into a GPC autosampler vial for analysis. The GPC column temperature is at room temperature, approximately 25 degrees Celsius. HPLC grade THF is used as the mobile phase and is delivered at a constant flow rate of 1.0 ml/min. The injection volume is 100 microliters and the run time is 40 minutes. Baselines are constructed for all signals. Peak elution limits include metathesized unsaturated polyol ester and non-metathesized unsaturated polyol ester, but exclude later eluting residual olefin. The retention times of the non-metathesized unsaturated polyol ester and olefin were determined from the separate injection runs of both the non-metathesized unsaturated polyol ester and olefin. Baselines and scattering detectors are reviewed.

B. Oligomer Index

The oligomer index of the metathesized unsaturated polyol ester is calculated from data that is determined by Supercritical Fluid Chromatography-Fourier Transform Orbital Trapping Mass Spectrometry (SFC-Orbitrap MS). The sample to be analyzed is typically dissolved in methylene chloride or a methylene chloride - hexane mixture at a concentration of 1000 ppm (1 mg/mL). A further 25x-100x dilution is typically made into hexane (for a final concentration of 10-40 ppm). A volume of 2-7.5 μ L is typically injected on to a SFC column (for example, a commercially available 3 mm i.d. x 150 mm Ethylpyridine column, 3 μ m particle size).

During the chromatography run, the mobile phase is typically programmed from 100% carbon dioxide with a gradient of one percent per minute methanol. The effluent from the column is directed to a mixing tee where an ionization solution is added. The ionization medium is typically 20 mM ammonium formate in methanol at a flow of 0.7 mL/min while the SFC flow is typically 1.6 mL/min into the tee. The effluent from the mixing tee enters the ionization source of the Orbitrap Mass Spectrometer, which is operated in the heated electrospray ionization mode at 320°C.

In one aspect, a hybrid linear ion trap - Orbitrap mass spectrometer (i.e., the Orbitrap Elite from Thermoelectron Corp.) is calibrated and tuned according to the manufacturer's guidelines. A mass resolution ($m/\Delta m$ peak width at half height) from 100,000 to 250,000 is typically used. C,H,O compositions of eluting species (typically associated with various cations, e.g., NH_4^+ , H^+ , Na^+) are obtained by accurate mass measurement (0.1-2 ppm) and are correlated to metathesis products. Also, sub-structures may be probed by linear ion trap "MSⁿ" experiments with subsequent accurate-mass analysis in the Orbitrap, as practiced typically in the art.

The metathesis monomers, dimers, trimers, tetramers, pentamers, and higher order oligomers are fully separated by SFC. The chromatogram based on ion current from the Orbitrap MS may be integrated, as typically practiced in the art, for each of the particular oligomer groups including metathesis monomers, metathesis dimers, metathesis trimers, metathesis pentamers, and each of the higher order oligomers. These raw areas may then be formulated into various relative expressions, based on normalization to 100%. The sum of the areas of metathesis trimers through the highest oligomer detected is divided by the sum of all metathesis species detected (metathesis monomers to the highest oligomer detected). This ratio is called the "Oligomer Index". As used herein, the Oligomer Index" is a relative measure of the fraction of the metathesized unsaturated polyol ester which is comprised of trimers, tetramers, pentamers, and higher order oligomers.

C. Iodine Value

Another aspect of the invention provides a method to measure the iodine value of the metathesized unsaturated polyol ester. The iodine value is determined using AOCS Official Method Cd 1-25 with the following modifications: carbon tetrachloride solvent is replaced with chloroform (25ml), an accuracy check sample (oleic acid 99%, Sigma-Aldrich; IV = 89.86 ± 2.00 cg/g) is added to the sample set, and the reported IV is corrected for minor contribution from olefins identified when determining the free hydrocarbon content of the metathesized unsaturated polyol ester.

D. Free Hydrocarbon Content

Another aspect of this invention provides a method to determine the free hydrocarbon content of the metathesized unsaturated polyol ester. The method combines gas chromatography / mass spectroscopy (GC/MS) to confirm identity of the free hydrocarbon homologs and gas chromatography with flame ionization detection (GC/FID) to quantify the free hydrocarbon present.

5 Sample Prep: The sample to be analyzed was typically trans-esterified by diluting (e.g. 400:1) in methanolic KOH (e.g. 0.1N) and heating in a closed container until the reaction was complete (i.e. 90°C for 30 min.) then cooled to room temperature. The sample solution could then be treated with 15% boron tri-fluoride in methanol and again heated in a closed vessel until the reaction was complete (i.e. at 60°C for 30 min.) both to acidify (methyl orange - red) and to methylate any free acid present in the sample. After allowing to cool to room temperature, the reaction was quenched by addition of saturated NaCl in water. An organic extraction solvent such as cyclohexane containing a known level internal standard (e.g. 150ppm dimethyl adipate) was then added to the vial and mixed well. After the layers separated, a portion of the organic phase was transferred to a vial suitable for injection to the gas chromatograph. This sample extraction solution was analyzed by GC/MS to confirm identification of peaks matching hydrocarbon retention times by comparing to reference spectra and then by GC/FID to calculate concentration of hydrocarbons by comparison to standard FID response factors.

10 A hydrocarbon standard of known concentrations, such as 50ppm each, of typically observed hydrocarbon compounds (i.e. 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane and octadecane) was prepared by dilution in the same solvent containing internal standard as was used to extract the sample reaction mixture. This hydrocarbon standard was analyzed by GC/MS to generate retention times and reference spectra and then by GC/FID to generate retention times and response factors.

25 GC/MS: An Agilent 7890 GC equipped with a split/splitless injection port coupled with a Waters QuattroMicroGC mass spectrometer set up in EI+ ionization mode was used to carry out qualitative identification of peaks observed. A non-polar DB1-HT column (15m x 0.25mm x 0.1um df) was installed with 1.4mL/min helium carrier gas. In separate runs, 1uL of the hydrocarbon standard and sample extract solution were injected to a 300° injection port with a split ratio of 25:1. The oven was held at 40°C for 1 minute then ramped 15C/minute to a final temperature of 325°C which was held for 10 minutes resulting in a total run time of 30 minutes. The transfer line was kept at 330°C and the temperature of the EI source was 230°C. The ionization energy was set at 70eV and the scan range was 35-550m/z.

GC/FID: An Agilent 7890 GC equipped with a split/splitless injection port and a flame ionization detector was used for quantitative analyses. A non-polar DB1-HT column (5m x 0.25mm x 0.1um df) was installed with 1.4mL/min helium carrier gas. In separate runs, 1uL of the hydrocarbon standard and sample extract solution was injected to a 330° injection port with a split ratio of 100:1. The oven was held at 40°C for 0.5 minutes then ramped at 40C/minute to a final temperature of 380°C which was held for 3 minutes resulting in a total run time of 12 minutes. The FID was kept at 380°C with 40mL/minute hydrogen gas flow and 450mL/min air flow. Make up gas was helium at 25mL/min. The hydrocarbon standard was used to create a calibration table in the Chemstation Data Analysis software including known concentrations to generate response factors. These response factors were applied to the corresponding peaks in the sample chromatogram to calculate total amount of free hydrocarbon found in each sample.

EXAMPLES

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

Non-limiting examples of product formulations disclosed in the present specification are summarized below.

Example 1: Synthesis of metathesized canola oil

Prior to the metathesis reaction, the RBD (refined, bleached, and deodorized) canola oil is pre-treated by mixing the oil with 2% (by weight) bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) and heating to 120°C with a nitrogen sweep for 1.5 hours. The oil is cooled to room temperature, filtered through a bed of Celite® 545 diatomaceous earth (EMD, Billerica, MA), and stored under inert gas until ready to use.

To a round-bottomed flask, the oil is added and sub-surface sparged with inert gas while mixing and heating to 55°C. The catalyst is dissolved in 1,2-dichloroethane ([107-06-2], EMD, Billerica, MA) that is stored over 4 Å molecular sieves and sub-surface sparged with inert gas prior to use. After catalyst addition to the reaction flask, a vacuum is applied to remove volatile olefins that are generated. After the defined reaction time, the vacuum is broken and the metathesized unsaturated polyol ester is cooled to room temperature.

The metathesized canola oil is diluted in hexanes ([110-54-3], EMD, Billerica, MA). To the diluted material, 2% bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) is added and

mixed for ~6 hours. The oil is filtered through a bed of Celite® 545 diatomaceous earth. The oil is treated a second time with 2% bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) for ~6 hours. The oil is filtered through a bed of Celite® 545 diatomaceous earth and then rotary evaporated to concentrate.

- 5 The metathesized canola oil is then passed through a wipe film evaporator at 180°C and <0.5 Torr vacuum to remove olefins up to and including C-18 chain lengths. Representative examples are summarized in Table 4 below.

Table 4

Example	Pretreated Canola Oil (g) ^a	Catalyst	Catalyst (g)	Max Temperature (°C)	Max Vacuum (Torr)	Reaction Time (min)
1A	500	1 ^b	0.25	61	7.9	87
1B	500	2 ^c	0.25	62	0.6	45
1C	500	2 ^c	0.025	90	0.1	60
1D	13,000	2 ^c	0.65	80	>1	120

^a Canola oil from J. Edwards, Braintree, MA.

- 10 ^b Catalyst 1 is Tricyclohexylphosphine [4,5-dimethyl-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] [2-thienylmethylene]ruthenium (II) dichloride [1190427-50-9] available as CatMETium RF-3 from Evonik Corporation, Parsippany, NJ.

- 15 ^c Catalyst 2 is Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene][2-thienylmethylene] ruthenium(II) dichloride [1190427-49-6] available as CatMETium RF-2 from Evonik Corporation, Parsippany, NJ.

The samples 1A, 1B, 1C and 1D are analyzed for weight average molecular weight (Mw), and free hydrocarbon content, and samples 1A and 1B are analyzed for iodine value and oligomer index, using methods described previously, and are found to approximately have the following values:

Example	Mw (g/mol)	Iodine Value (cg/g)	Free Hydrocarbon content (wt%)	Oligomer Index
1A	5,400	85	0.5	0.05
1B	3,900	85	0.5	0.04
1C	21,000	Not measured	0.5	Not measured
1D	10,000	Not measured	0.2	Not measured

Example 2: Remetathesis of metathesized unsaturated polyol ester

Metathesized canola oil, sufficiently stripped of residual olefins (176.28 g from Example 1A) is blended with pretreated canola oil (350.96 g, pretreated as described in Example 1) in a round-bottomed flask. The blend is sub-surface sparged with inert gas while mixing and heating to 55°C. The catalyst is dissolved in 1,2-dichloroethane ([107-06-2], EMD, Billerica, MA) that is stored over 4 Å molecular sieves and sub-surface sparged with inert gas prior to use. After catalyst addition to the reaction flask, a vacuum is applied to remove volatile olefins that are generated. After -100 minutes of reaction time, the vacuum is broken and the metathesized unsaturated polyol ester is cooled to room temperature.

The metathesized canola oil is diluted in hexanes ([110-54-3], EMD, Billerica, MA). To the diluted material, 2% bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) is added and mixed for - 6 hours. The oil is filtered through a bed of Celite® 545 diatomaceous earth. The oil is treated a second time with 2% bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) for - 6 hours. The oil is filtered through a bed of Celite® 545 diatomaceous earth and then rotary evaporated to concentrate.

The remetathesized canola oil is then passed through a wipe film evaporator at 180°C and <0.5 Torr vacuum to remove olefins up to and including C-18 chain lengths. A representative example is summarized in Table 5 below.

Table 5

Example	Oil Blend (g)	Catalyst ^a (g)	Max Temp (°C)	Max Vacuum (Torr)
2	500	0.27	65	0.2

^a Tricyclohexylphosphine [4,5-dimethyl-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] [2-thienylmethylene]ruthenium (II) dichloride [1190427-50-9] available as CatMETium RF-3 from Evonik Corporation, Parsippany, NJ.

The sample 2 is analyzed for weight average molecular weight, iodine value, free hydrocarbon content and oligomer index, using methods described previously, and is found to approximately have the following values:

Example	Mw (g/mol)	Iodine Value (cg/g)	Free Hydrocarbon content (wt%)	Oligomer Index
2	13,000	80	0.5	0.07

Example 3: Synthesis of metathesized unsaturated polyol esters

Prior to the metathesis reaction, the RBD (refined, bleached, and deodorized) oil is pre-treated by mixing the oil with 2% (by weight) bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) and heating to 120°C with a nitrogen sweep for 1.5 hours. The oil is cooled to room temperature, filtered through a bed of Celite® 545 diatomaceous earth (EMD, Billerica, MA), and stored under inert gas until ready to use.

To a round-bottomed flask, the oil is added and sub-surface sparged with inert gas while mixing and heating to 55°C. The catalyst is dissolved in 1,2-dichloroethane ([107-06-2], EMD, Billerica, MA) that is stored over 4 Å molecular sieves and sub-surface sparged with inert gas prior to use. After catalyst addition to the reaction flask, a vacuum is applied to remove volatile olefins that are generated. After ~4 hours reaction time, the vacuum is broken and the metathesized unsaturated polyol ester is cooled to room temperature.

The metathesized oil is diluted in hexanes ([110-54-3], EMD, Billerica, MA). To the diluted material, 2% bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) is added and mixed for ~6 hours. The metathesized oil is filtered through a bed of Celite® 545 diatomaceous earth. The metathesized oil is treated a second time with 2% bleaching clay (Filtrol F-160, BASF, Florham Park, NJ) for ~6 hours. The metathesized oil is filtered through a bed of Celite® 545 diatomaceous earth and then rotary evaporated to concentrate.

The metathesized unsaturated polyol ester is then passed through a wipe film evaporator at 180°C and <0.5 Torr vacuum to remove olefins up to and including C-18 chain lengths. Representative examples are summarized in Table 6 below.

Table 6

Example	Starting unsaturated polyol ester	Pretreated Oil (g)	Catalyst^a (g)	Max Temp (°C)	Max Vacuum (Torr)
3A	High erucic acid rapeseed oil	500	0.25	61	7.9
3B	Blend of High erucic acid rapeseed oil and canola oil, 50/50 by weight	500 (250g HEAR oil and 250g canola oil)	0.25	61	7.9
3C	High oleic soybean oil	500	0.25	61	7.9

^a Tricyclohexylphosphine [4,5-dimethyl-13-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] [2-thienylmethylene]ruthenium (II) dichloride [1190427-50-9] available as CatMETium RF-3 from Evonik Corporation, Parsippany, NJ.

5 Example 4

Hydrogenations are performed in a T316 stainless steel, 600 ml Parr reactor (Model Number 4563) containing internal cooling coils and a stir shaft with 2 impellers comprised of 4 blades each.

The metathesized unsaturated polyol ester (approximately 200 g) is dissolved in hexanes
10 (120 ml, [110-54-3], EMD, Billerica Ma). To this solution is added a slurry of Nickel on Silica
(20 g, [7440-02-0], Catalog #28-1900, Strem Chemicals, Inc., Newburyport, MA). The slurried
mixture is transferred via vacuum to the Parr reactor. The mixture is degassed with several
vacuum/nitrogen fill cycles. Then with stirring (800-900 rpm), hydrogen gas (550-650 psig,
[1333-74-0], UHP grade, Wright Brothers, Inc., Montgomery, OH) is charged to the reactor. The
15 reaction is heated at 150°C and hydrogen gas pressure reduction monitored until constant (-12
hours).

The reaction is cooled to 60°C and drained from the reactor. The reactor is rinsed with
methyl tert-butyl ether ([1634-04-4], EMD, Billerica, MA) and combined with the solid
hydrogenated metathesized polyol ester. A hot filtration is then performed to remove the catalyst,
20 followed by vacuum to remove all residual solvent. Fully hydrogenated materials are obtained
using the method above. Lower hydrogenation levels are obtained by decreasing the reaction
temperature to 125 degrees Celsius using 5 grams of catalyst and reducing the reaction time and
hydrogen consumed. Iodine Value (IV) is measured, as described elsewhere.

25 Example 5

A round bottom flask is charged with palm oil (approximately 500g), heated to 60°C to
melt the oil and sparged with nitrogen for one hour using a gas dispersion tube. The nitrogen sparge
tube is lifted above the surface of the liquid to blanket the oil and Filtrol F-160 (2%) is charged to
the flask under rapid agitation and the reactor is heated to 120°C for one hour. The flask is cooled
30 to 90°C and toluene is added to reduce the nonvolatile content to 70%. The solution is filtered with
a Buchner funnel containing a pile of Whatman Grade 1 filter paper, glass microfiber pad, filter
paper and Celite 454.

Treated palm oil solution is transferred to a 4 neck round bottom flask equipped with a
central mechanical agitator, thermometer, glass stopper and a connecting tube with a vacuum take-

off and a chilled receiver for metathesis reaction. The flask is sparged with dry nitrogen for 1 hour and the flask is heated to 90°C. A separate oven-dried flask is charged with CatMETium RF2 catalyst (50 ppm) and 1,2-Dichloroethane (kept over sieves, sparged for 45 min with nitrogen). The nitrogen sparge tube is raised to blanket the oil and the catalyst solution is added to the 90°C palm oil using a cannula. Vacuum is immediately applied through a chilled 2L trap and reaches 2 mm within a few minutes ultimately reaching 0.11 mm as distillate removal slows. Vacuum and temperature are held for 4 hours. The flask is cooled to room temperature.

The catalyst is removed by stirring the palm polyoil solution with Filtrol F-160 (2%) at 50°C overnight followed by filtration using a Buchner funnel containing a pile of filter paper, a piece of glass wool pad, a piece of filter paper and Celite 454. This treatment is performed twice. High boiling olefin such as 9-octadecene and residual toluene are removed by a vacuum stripping procedure using a 3 neck flask containing a thermometer, mechanical agitation and a connecting tube with a vacuum takeoff and chilled receiver. The temperature is set for 130°C. Toluene is removed quickly and olefin begins to be removed at about 105°C. Vacuum improves as the olefin removal slows and reaches 0.06 mm when olefin removal is very slow. The final palm polyoil is discharged at 60°C.

The palm polyoil of Example 5 is analyzed for weight average molecular weight, iodine value, free hydrocarbon content, and oligomer index using methods described previously, and is found to approximately have the following values:

Example	Mw (g/mol)	Iodine Value (cg/g)	Free Hydrocarbon content (wt%)	Oligomer Index
5	4000	43	1.6	0.13

Example 6

The metathesis monomers, dimers, trimers, tetramers, pentamers, and higher order oligomers from the product in Example 2 are fully separated by SFC using the method described above. The individual SFC fractions are collected and trimers, tetramers, and higher order oligomers are combined. The oligomer index of this sample is about 1.

The following Tables 7 through 10 include examples that are representative of hair care compositions of the present invention. Tables 7, 9 and 10 also include certain comparative examples. The compositions of Table 10 comprise fatty alcohol gel networks. A key difference between the inventive examples and corresponding comparative examples is the properties of metathesized oils, as represented in Table 11 below for those specific materials. The comparative material has a weight average molecular weight of less than 5,000 Daltons, an Iodine value of less

Dimethiconol ¹⁰	--	--	--	--	--	--	0.5	0.5	1.0	1.0
Fragrance	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Preservatives, pH, viscosity adjustment	Up to 3%	Up to 3%	Up to 3%							

¹ Guar Hydroxypropyltrimonium Chloride, available as Jaguar Excel, from Rhodia

² Sodium Laureth Sulfate, from P&G

³ Sodium Lauryl Sulfate, from P&G

⁴ Ninol Comf, from Stepan

⁵ Amphosol HCA-B, from Stepan

⁶ Example 1A in Table 4 above

⁷ Example 2 in Table 5 above

⁸ Elevance Smooth CS-1 10, available from Elevance Renewable Sciences,
Woodridge, IL.

⁹ Elevance Soft CG-100, available from Elevance Renewable Sciences,
Woodridge, IL.

¹⁰ SLM28 104 from Wacker

Table 8

Ingredient	Inventive							
	Ex. K	Ex. L	Ex. M	Ex. N	Ex. O	Ex. P	Ex. Q	Ex. R
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Cationic Guar ¹	0.25	–	–	–	0.25	–	–	–
Cationic Cassia ²	–	0.25	–	–	–	0.25	–	–
PQ-10 ³	–	–	0.25	–	–	–	0.25	–
PQ-76 ⁴	–	–	–	0.25	–	–	–	0.25
Sodium Laureth (El) Sulfate ⁵	10.5	10.5	10.5	10.5	12	12	12	12
Sodium Lauryl Sulfate ⁶	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CMEA ⁷	0.8	0.8	0.8	0.8	–	–	–	–
Cocoamidopropyl Betaine ⁸	1.0	1.0	1.0	1.0	2.0	2.0	2.0	2.0
Metathesized oil ⁹	0.5	–	0.5	–	1.0	–	1.0	–
Metathesized oil ¹⁰	–	0.5	–	0.5	–	1.0	–	1.0
Dimethicone ¹¹	0.5	0.5	0.5	0.5	–	–	–	–

Dimethicone ¹²	--	--			0.5	0.5	0.5	0.5
Ethylene Glycol Distearate ¹³	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Fragrance	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Preservatives, pH, viscosity adjustment	Up to 3%							

¹ Guar Hydroxypropyltrimonium Chloride, available as Jaguar C-500, from Rhodia

² Cationic Cassia, MW=300,000; 4.25% Nitrogen, from Lubrizol Advanced Materials

³ LR400, from Amerchol

⁴ Copolymer of acrylamide and 1,3-Propanediaminium,N-[2-[[[dimethyl[3-(2-methyl-1-oxo-2-propenyl)amino]propyl]ammonio]acetyl]amino]ethyl]2-hydroxy-N,N,N',N',N'-pentamethyl-, trichloride, available as Mirapol AT-1, from Rhodia

⁵ Sodium Laureth Sulfate, from P&G

⁶ Sodium Lauryl Sulfate, from P&G

⁷ Ninol Comf, from Stepan

⁸ Amphosol HCA-B, from Stepan

⁹ Example 3A in Table 6 above

¹⁰ Example 3B in Table 6 above

¹¹ DC-1664, from Dow Corning

¹² Viscasil 330M, from Momentive

¹³ EGDS pure, from Evonik

Table 9

Ingredient	Inventive				Comparative		Inventive	
	Ex. S	Ex. T	Ex. U	Ex. V	Ex. W	Ex. X	Ex. Y	Ex. Z
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Cationic Guar ¹	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Polyquaternium-6 ²	0.075	0.075	0.075	0.075	0.075	0.075	0.075	0.075
Sodium Laureth (El) Sulfate ³	12	12	12	12	12	12	12	12
Cocoamidopropyl Betaine ⁴	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Trihydroxystearin ⁵	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Metathesized canola oil ⁶	1.0	0	0	0	0	0	0	0
Metathesized canola oil ⁷	0	1.0	0	0	0	0	0	0

Metathesized canola oil ⁸	0	0	1.0	0	0	0	0.5	0
Metathesized Palm oil ⁹	0	0	0	1.0	0	0	0	0.5
Hydrogenated soybean oil (and) Hydrogenated soy polyglycerides (and) C ₁₅₋₂₃ alkane ¹⁰	0	0	0	0	1.0	0	0	0
Ceteth-20 ¹¹	0.047	0.047	0.047	0	0.020	0	0.023	0
Glyceryl Monooleate ¹²	0.103	0.103	0.103	0	0.105	0	0.051	0
Sorbitan Stearate ¹³	0	0	0	0.097	0	0	0	0.048
Polysorbate 60 ¹⁴	0	0	0	0.028	0	0	0	0.014
Preservatives, pH, viscosity adjustment, fragrance	Up to 5%							

¹ Guar Hydroxypropyltrimonium Chloride, available as NHance 3196, from Ashland

² Poly (Dially) Dimethyl Ammonium Chloride, available as Mirapol 100S, from Rhodia

³ Sodium Laureth Sulfate, from P&G

⁴ Amphosol HCA-B, from Stepan

⁵ Thixcin R, available from Elementis Specialties

⁶ Example IB in Table 4 above. The metathesized oil is emulsified with Ceteth-20 and Glyceryl monooleate to a median particle size of about 0.23 microns prior to incorporation to the shampoo.

⁷ Example 1C in Table 4 above. The metathesized oil is emulsified with Ceteth-20 and Glyceryl monooleate to a median particle size of about 0.76 microns prior to incorporation to the shampoo.

⁸ Example ID in Table 4 above. The metathesized oil is emulsified with Ceteth-20 and Glyceryl monooleate to a median particle size of about 0.42 microns prior to incorporation to the shampoo.

⁹ Example 5. The metathesized palm oil is emulsified with Sorbitan stearate and Polysorbate 60 to a median particle size of about 0.20 microns prior to incorporation to the shampoo.

¹⁰ Elevance Soft CG-100, available from Elevance Renewable Sciences, Woodridge, IL. The oil is emulsified with Ceteth-20 and Glyceryl monooleate to a median particle size of about 0.36 microns prior to incorporation to the shampoo.

¹¹ Brij C20, available from Croda

¹² Capmul GMO-50, available from Abitec

¹³ Span 60, available from Croda

¹⁴ Tween 60, available from Croda

Ingredient	Inventive	Comparative	Inventive		Comparative	Inventive		
	Ex.AA	Ex.BB	Ex.CC	Ex.DD	Ex.EE	Ex.FF	Ex.GG	Ex.HH
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Cationic Guar ¹	0.15	0.15	0.15	0.15	0.15	0.15	0.20	0.20
Polyquaternium-6 ²	0.1	0.1	0.1	0.1	0.1	0.1	0.20	0.20
Sodium Laureth (El) Sulfate ³	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1
Sodium Lauryl Sulfate ⁴	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Cocoamidopropyl Betaine ⁵	2.0	2.0	2.0	2.0	2.0	2.0	1.0	1.0
Trihydroxystearin ⁶	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Metathesized canola oil ⁷	0.5	--	--	0.5	--	--	1.0	1.0
Metathesized Palm oil ⁸	--	--	0.5	--	--	1.0	--	--
Hydrogenated soybean oil (and) Hydrogenated soy polyglycerides (and) C ₁₅₋₂₃ alkane ⁹	--	0.5	--	--	1.0	--	--	--
Silicone ¹⁰	0.5	--	--	--	--	--	--	--
Steary alcohol ¹¹	0.32	0.32	0.32	0.32	0.32	0.32	0.32	1.16
Cetyl alcohol ¹²	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.64
Fragrance	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Polysorbate 20 ¹³	0.04	--	0.04	0.04	0.08	0.08	0.08	0.08
Sorbitan Stearate ¹⁴	0.02	--	0.02	0.02	0.04	0.04	0.04	0.04
Preservatives, pH, viscosity adjustment	Up to 5%	Up to 5%	Up to 5%	Up to 5%	Up to 5%	Up to 5%	Up to 5%	Up to 5%

¹ Guar Hydroxypropyltrimonium Chloride, available as NHance 3196, from Ashland

² Poly (Dially) Dimethyl Ammonium Chloride, available as Mirapol 100S, from Rhodia

³ Sodium Laureth Sulfate, from P&G

⁴ Sodium Lauryl Sulfate, from P&G

⁵ Amphosol HCA-B, from Stepan

⁶ Thixcin R, available from Elementis Specialties

⁷ Example ID in Table 4 above. The metathesized oil is emulsified with Polysorbate 20 and Sorbitan stearate to a median particle size of about 0.3 microns prior to incorporation to the shampoo.

⁸ Example 5. The metathesized palm oil is emulsified with Sorbitan stearate and Polysorbate 20 to a median particle size of about 0.3 microns prior to incorporation to the shampoo.

- ⁹ Elevance Soft CG-100, available from Elevance Renewable Sciences, Woodridge, IL. The oil is emulsified with sorbitan stearate and Polysorbate 20 to a median particle size of about 0.3 microns prior to incorporation to the shampoo.
- ¹⁰ Belsil DM5500 silicone emulsion, available from Wacker Chemie AG
- ¹¹ Stearyl alcohol, available from P&G
- ¹² Cetyl alcohol, available from P&G
- ¹³ Polysorbate 20, available from Croda
- ¹⁴ Sorbitan stearate, available from Croda

Table 11

	Metathesized oils	Mw	IV	Free hydrocarbons, %
Comparative	Hydrogenated soy polyglycerides (and) C ₁₅₋₂₃ alkane ¹	3,900	4.4	6-11
Inventive	Metathesized canola oil ²	3,900	85	0.5
	Metathesized canola oil ³	21,000	Not measured	0.5
	Metathesized canola oil ⁴	10,000	Not measured	0.2
	Metathesized Palm oil ⁵	4,000	43	1.6

- ¹ Elevance Smooth SC-1 10, available from Elevance Renewable Sciences, Woodridge, IL.
- ² Example IB in Table 4.
- ³ Example 1C in Table 4.
- ⁴ Example 1D in Table 4.
- ⁵ Example 5.

Wet Conditioning Tests

This rinse friction test determines the amount of conditioning provided by shampoo products as measured by the force required to pull hair through an Instron while wet. The operator ranks and balances the 4g, 8 in. hair switches for base line condition by using the Instron machine to determine a baseline force. The operator then applies a measured amount of shampoo and/or conditioner to a hair switch, distributes the product evenly through the switch. The wet forces are then measured as the product is rinsed using the Instron machine. Each test product is applied to a total of 4 switches. The data is then analyzed using standard statistical methods.

Dry Conditioning Tests

This inter-fiber friction test determines the amount of friction on the hair provided by shampoo as measured by the force required to move hair up and down past each other. This method emulates the motion of rubbing hair between the thumb and index finger in an up and down direction the treated hair switch. The operator ranks and balances the 4g, 8 in. hair switches for base line condition by using an Instron machine. The operator then applies a measured amount of shampoo to a hair switch, distributes the product evenly through the switch and rinses as per the protocol. Wet switches are then allowed to dry overnight and evaluated the next day for friction force using the Instron machine. Each test product is applied to a total of 4 switches. The data is then analyzed using standard statistical methods.

5

10

Comparative Data

Using the abovementioned test protocols, the wet and dry conditioning benefits of selected formulations were measured. The data in Table 12A (single treatment) and 12B (multicycle treatment) reflect improved wet conditioning benefits provided by compositions containing the metathesized unsaturated polyols esters described herein. The data in Table 13 demonstrate the described metathesized oils provide significantly lower hair friction benefit in dry conditioning with multicycle cycle treatment versus comparative examples.

15

Table 12A

	Formulation (1 Treatment)	Final Rinse Friction (grams-force) Mean ± STD
Comparative	Example W in Table 9	1450 ± 84
Inventive	Example S in Table 9	1367 ± 40
	Example T in Table 9	1328 ± 102
	Example V in Table 9	1284 ± 87
	Example U in Table 9	1193 ± 54

20

Table 12B

	Formulation (6 cycle treatment)	Final Rinse Friction (grams-force) Mean ± STD
Comparative	Example BB in Table 10	2001 ± 100
Inventive	Example DD in Table 10	1738 ± 142
Comparative	Example EE in Table 10	2025 ± 146
Inventive	Example GG in Table 10	1710 ± 155

Table 13

	Formulation (6 cycle treatment)	Peak Sum Friction (grams-force) Mean \pm STD
Comparative	Example BB in Table 10	2004 \pm 78
Inventive	Example DD in Table 10	1794 \pm 61
Comparative	Example EE in Table 10	1778 \pm 67
Inventive	Example GG in Table 10	1633 \pm 34

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

According to one embodiment, the hair care compositions may be provided in the form of a porous, dissolvable solid structure, such as those disclosed in U.S. Patent Application Publication Nos. 2009/0232873; and 2010/0179083, which are incorporated herein by reference in their entirety. As described in these references, such dissolvable solid structure embodiments will typically have a water content well below the at least about 20% aqueous carrier element of certain embodiments described above.

The hair care compositions are generally prepared by conventional methods such as those known in the art of making the compositions. Such methods typically involve mixing of the ingredients in one or more steps to a relatively uniform state, with or without heating, cooling, application of vacuum, and the like. The compositions are prepared such as to optimize stability (physical stability, chemical stability, photostability) and/or delivery of the active materials. The hair care composition may be in a single phase or a single product, or the hair care composition may be in a separate phases or separate products. If two products are used, the products may be used together, at the same time or sequentially. Sequential use may occur in a short period of time, such as immediately after the use of one product, or it may occur over a period of hours or days.

The composition provided by the formula above is made by combining such ingredients in accordance with the method of making provided in this specification.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such

dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

All documents cited in the Detailed Description of the Invention are, in relevant part,
5 incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention. To the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

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

15 **Examples/Combinations**

A. A hair care composition comprising: a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having one or more of the following properties: (i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%; (ii) a weight average molecular weight of from about 5,000 Daltons to about 50,000 Daltons; (iii) an iodine value of from about 30 to about 200; b) from about 5% to about 50% of one or more anionic surfactants, by weight of said hair care composition; and c) at least about 20% of an aqueous carrier, by weight of said hair care composition.

B. The hair care composition of paragraph A, wherein the metathesized unsaturated polyol ester has a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%.

C. The hair care composition of paragraph A or B, wherein the metathesized unsaturated polyol ester has a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0.1% to about 4%.

D. The hair care composition of any of paragraphs A-C, wherein the metathesized unsaturated polyol ester has a weight average molecular weight of from about 5,000 Daltons to about 50,000 Daltons.

- E. The hair care composition of any of paragraphs A-D, wherein the metathesized unsaturated polyol ester has a weight average molecular weight of from about 6,000 Daltons to about 30,000 Daltons.
- F. The hair care composition of any of paragraphs A-E, wherein the metathesized unsaturated polyol ester has a weight average molecular weight of from about 5,000 Daltons to about 50,000 Daltons.
- G. The hair care composition of any of paragraphs A-F, wherein the metathesized unsaturated polyol ester has an iodine value of from about 30 to about 200.
- H. The hair care composition of any of paragraphs A-G, wherein the metathesized unsaturated polyol ester has an iodine value of from about 30 to about 120.
- I. The hair care composition of any of paragraphs A-H, wherein the metathesized unsaturated polyol ester has an iodine value of from about 30 to about 200.
- J. The hair care composition of any of paragraphs A-I, wherein the metathesized unsaturated polyol ester has a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%.
- K. The hair care composition of any of paragraphs A-J, wherein said metathesized unsaturated polyol ester is selected from the group consisting of metathesized abyssinian oil, metathesized almond oil, metathesized apricot oil, metathesized apricot kernel oil, metathesized argan oil, metathesized avocado oil, metathesized babassu oil, metathesized baobab oil, metathesized black cumin oil, metathesized black currant oil, metathesized borage oil, metathesized camelina oil, metathesized carinata oil, metathesized canola oil, metathesized castor oil, metathesized cherry kernel oil, metathesized coconut oil, metathesized corn oil, metathesized cottonseed oil, metathesized echium oil, metathesized evening primrose oil, metathesized flax seed oil, metathesized grape seed oil, metathesized grapefruit seed oil, metathesized hazelnut oil, metathesized hemp seed oil, metathesized jatropha oil, metathesized jojoba oil, metathesized kukui nut oil, metathesized linseed oil, metathesized macadamia nut oil, metathesized meadowfoam seed oil, metathesized moringa oil, metathesized neem oil, metathesized olive oil, metathesized palm oil, metathesized palm kernel oil, metathesized peach kernel oil, metathesized peanut oil, metathesized pecan oil, metathesized pennycress oil, metathesized perilla seed oil, metathesized pistachio oil, metathesized pomegranate seed oil, metathesized pongamia oil, metathesized pumpkin seed oil, metathesized raspberry oil, metathesized red palm olein, metathesized rice bran oil, metathesized rosehip oil, metathesized safflower oil, metathesized seabuckthorn fruit oil,

metathesized sesame seed oil, metathesized shea glein, metathesized sunflower oil, metathesized soybean oil, metathesized tonka bean oil, metathesized tung oil, metathesized walnut oil, metathesized wheat germ oil, metathesized high oleoyl soybean oil, metathesized high oleoyl sunflower oil, metathesized high oleoyl safflower oil, metathesized high erucic acid rapeseed oil, metathesized lard, metathesized tallow, metathesized poultry fat, metathesized yellow grease, metathesized fish oil, and mixtures thereof.

L. A hair care composition comprising: a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having a weight average molecular weight of from about 2,000 Daltons to about 50,000 Daltons; and one or more of the following properties: (i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%; or (ii) an iodine value of from about 8 to about 200; b) from about 5% to about 50% of one or more anionic surfactants, by weight of said hair care composition; and c) at least about 20% of an aqueous carrier, by weight of said hair care composition.

M. The hair care composition of paragraph L, wherein said metathesized unsaturated polyol ester has a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%.

N. The hair care composition of paragraph L or M, wherein said metathesized unsaturated polyol ester has a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0.1% to about 4%.

O. The hair care composition of any of paragraphs L-N, wherein said metathesized unsaturated polyol ester has an iodine value of from about 8 to about 200.

P. The hair care composition of any of paragraphs L-O, wherein said metathesized unsaturated polyol ester has an iodine value of from about 30 to about 120.

Q. The hair care composition of any of paragraphs L-P, wherein said metathesized unsaturated polyol ester has a weight average molecular weight of from about 4,000 Daltons to about 30,000 Daltons.

R. The hair care composition of any of paragraphs L-Q, comprising a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having i) a weight average molecular weight of from about 2,000 Daltons to about 30,000 Daltons; ii) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0.1 to about 3%; and (iii) an iodine value of from about 30 to about 120.

S. The hair care composition of any of paragraphs L-R, wherein said metathesized unsaturated polyol ester is selected from the group consisting of metathesized abyssinian oil, metathesized almond oil, metathesized apricot oil, metathesized apricot kernel oil, metathesized argan oil, metathesized avocado oil, metathesized babassu oil, metathesized baobab oil, metathesized black cumin oil, metathesized black currant oil, metathesized borage oil, metathesized camelina oil, metathesized carinata oil, metathesized canola oil, metathesized castor oil, metathesized cherry kernel oil, metathesized coconut oil, metathesized corn oil, metathesized cottonseed oil, metathesized echium oil, metathesized evening primrose oil, metathesized flax seed oil, metathesized grape seed oil, metathesized grapefruit seed oil, metathesized hazelnut oil, metathesized hemp seed oil, metathesized jatropha oil, metathesized jojoba oil, metathesized kukui nut oil, metathesized linseed oil, metathesized macadamia nut oil, metathesized meadowfoam seed oil, metathesized moringa oil, metathesized neem oil, metathesized olive oil, metathesized palm oil, metathesized palm kernel oil, metathesized peach kernel oil, metathesized peanut oil, metathesized pecan oil, metathesized pennycress oil, metathesized perilla seed oil, metathesized pistachio oil, metathesized pomegranate seed oil, metathesized pongamia oil, metathesized pumpkin seed oil, metathesized raspberry oil, metathesized red palm olein, metathesized rice bran oil, metathesized rosehip oil, metathesized safflower oil, metathesized seabuckthorn fruit oil, metathesized sesame seed oil, metathesized shea glein, metathesized sunflower oil, metathesized soybean oil, metathesized tonka bean oil, metathesized tung oil, metathesized walnut oil, metathesized wheat germ oil, metathesized high oleoyl soybean oil, metathesized high oleoyl sunflower oil, metathesized high oleoyl safflower oil, metathesized high erucic acid rapeseed oil, metathesized lard, metathesized tallow, metathesized poultry fat, metathesized yellow grease, metathesized fish oil, and mixtures thereof.

T. The hair care composition of any of paragraphs A-S, wherein said metathesized unsaturated polyol ester is selected from the group consisting of metathesized canola oil, metathesized palm oil, metathesized soybean oil, and mixtures thereof.

CLAIMS

What is claimed is:

1. A hair care composition comprising: a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having one or more of the following properties: (i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%; (ii) a weight average molecular weight of from about 5,000 Daltons to about 50,000 Daltons; (iii) an iodine value of from about 30 to about 200; b) from about 5% to about 50% of one or more anionic surfactants, by weight of said hair care composition; and c) at least about 20% of an aqueous carrier, by weight of said hair care composition.
2. A hair care composition comprising: a) a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having a weight average molecular weight of from about 2,000 Daltons to about 50,000 Daltons; and one or more of the following properties: (i) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%; or (ii) an iodine value of from about 8 to about 200.
3. The hair care composition according to claim 1 or 2, wherein the metathesized unsaturated polyol ester has a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0% to about 5%.
4. The hair care composition according to any of claims 1-3, wherein the metathesized unsaturated polyol ester has a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0.1% to about 4%.
5. The hair care composition according to any of claims 1-4, wherein the metathesized unsaturated polyol ester has a weight average molecular weight of from about 6,000 Daltons to about 30,000 Daltons.
6. The hair care composition according to any of claims 1-5, wherein the metathesized unsaturated polyol ester has an iodine value of from about 30 to about 200.
7. The hair care composition according to any of claims 1-6, wherein the metathesized unsaturated polyol ester has an iodine value of from about 30 to about 120.

8. The hair care composition according to any of claims 1-7, wherein said metathesized unsaturated polyol ester is selected from the group consisting of metathesized abyssinian oil, metathesized almond oil, metathesized apricot oil, metathesized apricot kernel oil, metathesized argan oil, metathesized avocado oil, metathesized babassu oil, metathesized baobab oil, metathesized black cumin oil, metathesized black currant oil, metathesized borage oil, metathesized camelina oil, metathesized carinata oil, metathesized canola oil, metathesized castor oil, metathesized cherry kernel oil, metathesized coconut oil, metathesized corn oil, metathesized cottonseed oil, metathesized echium oil, metathesized evening primrose oil, metathesized flax seed oil, metathesized grape seed oil, metathesized grapefruit seed oil, metathesized hazelnut oil, metathesized hemp seed oil, metathesized jatropha oil, metathesized jojoba oil, metathesized kukui nut oil, metathesized linseed oil, metathesized macadamia nut oil, metathesized meadowfoam seed oil, metathesized moringa oil, metathesized neem oil, metathesized olive oil, metathesized palm oil, metathesized palm kernel oil, metathesized peach kernel oil, metathesized peanut oil, metathesized pecan oil, metathesized pennycress oil, metathesized perilla seed oil, metathesized pistachio oil, metathesized pomegranate seed oil, metathesized pongamia oil, metathesized pumpkin seed oil, metathesized raspberry oil, metathesized red palm olein, metathesized rice bran oil, metathesized rosehip oil, metathesized safflower oil, metathesized seabuckthorn fruit oil, metathesized sesame seed oil, metathesized shea glein, metathesized sunflower oil, metathesized soybean oil, metathesized tonka bean oil, metathesized tung oil, metathesized walnut oil, metathesized wheat germ oil, metathesized high oleoyl soybean oil, metathesized high oleoyl sunflower oil, metathesized high oleoyl safflower oil, metathesized high erucic acid rapeseed oil, metathesized lard, metathesized tallow, metathesized poultry fat, metathesized yellow grease, metathesized fish oil, and mixtures thereof.

9. The hair care composition according to claim 2 wherein said metathesized unsaturated polyol ester has a weight average molecular weight of from about 4,000 Daltons to about 30,000 Daltons.

10. The hair care composition according to claim 2 or claim 9 comprising a metathesized unsaturated polyol ester, said metathesized unsaturated polyol ester having i) a weight average molecular weight of from about 2,000 Daltons to about 30,000 Daltons; ii) a free hydrocarbon content, based on total weight of metathesized unsaturated polyol ester, of from about 0.1 to about 3%; and (iii) an iodine value of from about 30 to about 120.

11. The hair care composition according to claim 10 wherein said metathesized unsaturated polyol ester is selected from the group consisting of metathesized abyssinian oil, metathesized almond oil, metathesized apricot oil, metathesized apricot kernel oil, metathesized argan oil, metathesized avocado oil, metathesized babassu oil, metathesized baobab oil, metathesized black cumin oil, metathesized black currant oil, metathesized borage oil, metathesized camelina oil, metathesized carinata oil, metathesized canola oil, metathesized castor oil, metathesized cherry kernel oil, metathesized coconut oil, metathesized corn oil, metathesized cottonseed oil, metathesized echium oil, metathesized evening primrose oil, metathesized flax seed oil, metathesized grape seed oil, metathesized grapefruit seed oil, metathesized hazelnut oil, metathesized hemp seed oil, metathesized jatropha oil, metathesized jojoba oil, metathesized kukui nut oil, metathesized linseed oil, metathesized macadamia nut oil, metathesized meadowfoam seed oil, metathesized moringa oil, metathesized neem oil, metathesized olive oil, metathesized palm oil, metathesized palm kernel oil, metathesized peach kernel oil, metathesized peanut oil, metathesized pecan oil, metathesized pennycress oil, metathesized perilla seed oil, metathesized pistachio oil, metathesized pomegranate seed oil, metathesized pongamia oil, metathesized pumpkin seed oil, metathesized raspberry oil, metathesized red palm olein, metathesized rice bran oil, metathesized rosehip oil, metathesized safflower oil, metathesized seabuckthorn fruit oil, metathesized sesame seed oil, metathesized shea glein, metathesized sunflower oil, metathesized soybean oil, metathesized tonka bean oil, metathesized tung oil, metathesized walnut oil, metathesized wheat germ oil, metathesized high oleoyl soybean oil, metathesized high oleoyl sunflower oil, metathesized high oleoyl safflower oil, metathesized high erucic acid rapeseed oil, metathesized lard, metathesized tallow, metathesized poultry fat, metathesized yellow grease, metathesized fish oil, and mixtures thereof.

12. The hair care composition according to claim 11 wherein said metathesized unsaturated polyol ester is selected from the group consisting of metathesized canola oil, metathesized palm oil, metathesized soybean oil, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/045677

A. CLASSIFICATION OF SUBJECT MATTER
 INV. A61Q5/02 A61Q5/12 A61K8/92
 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)
 A61Q A61K

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	wo 2013/158380 A2 (PROCTER & GAMBLE [US]) 24 October 2013 (2013-10-24)	1-12
Y	the whole document	1-12
A	- & UNIVAR: "Dow Corni ng HY-3050 Soy Wax" , INTERNET CITATION, 4 October 2008 (2008-10-04) , pages 1-3 , XP002727611 , Retri eved from the Internet: URL: http://www. uni var. com/US/ Industri es/ " / medi a/PDFs/US%20Corp%20Regi on%20PDFs/PC/Na tural s/DC%20HY-3050%20Soy%20Wax%20from%20U ni var.ashx [retri eved on 2014-07-22] ----- -/- .	1-12

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 12 October 2017	Date of mailing of the international search report 20/10/2017
--	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Nopper, Agathe
--	--

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/045677

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MICHAEL STARCH: "New Cosmeti c Ingredi ents Based on Soybean Oi l", I P.COM JOURNAL, I P.COM INC. , WEST HENRI ET TA, NY, US, 15 June 2007 (2007-06-15) , XP013120951 , ISSN: 1533-0001 page 14	1-12
A	----- wo 2014/165788 AI (PROCTER & GAMBLE [US]) 9 October 2014 (2014-10-09) cited in the appl icati on page 4, line 28 claim 1; exampl es A-B, I-4,CEx. i	1-12
X	----- wo 2016/054347 AI (PROCTER & GAMBLE [US]) 7 Apri l 2016 (2016-04-07) claim 1; exampl es A-B, I-4,CEx. i; tabl es 1-2	1-12
X,P	----- wo 2017/011249 AI (PROCTER & GAMBLE [US]) 19 January 2017 (2017-01-19) claims 1,4; exampl es 1-5 ,7A-F	2-12
Y	----- wo 2013/192384 AI (ELEVANCE RENEWABLE SCI ENCES [US]) 27 December 2013 (2013-12-27) "Methathesi s of Canol a Oi l to generate FAMR and di esters" ; page 34, paragraph 0093 - page 37 claims 1, 14-15	1-12
A	----- wo 2007/103398 AI (CARGI LL INC [US] ; BRAKSMAYER DIZA PEARL [US] ; MURPHY TIMOTHY A [US] ; R) 13 September 2007 (2007-09-13) the whol e document	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/045677

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013158380	A2	24-10-2013	CA 2869957 AI 24-10-2013
			CN 104220040 A 17-12-2014
			EP 2838496 A2 25-02-2015
			HK 1202818 AI 09-10-2015
			JP 5986290 B2 06-09-2016
			JP 2015514763 A 21-05-2015
			US 2013280192 AI 24-10-2013
			Wo 2013158380 A2 24-10-2013

WO 2014165788	AI	09-10-2014	CN 105050567 A 11-11-2015
			EP 2981245 AI 10-02-2016
			JP 2016515629 A 30-05-2016
			US 2014309154 AI 16-10-2014
			wo 2014165788 AI 09-10-2014

WO 2016054347	AI	07-04-2016	CN 106999416 A 01-08-2017
			EP 3200757 AI 09-08-2017
			US 2016095808 AI 07-04-2016
			wo 2016054347 AI 07-04-2016

WO 2017011249	AI	19-01-2017	AR 105299 AI 20-09-2017
			US 2017009184 AI 12-01-2017
			US 2017009402 AI 12-01-2017
			wo 2017011249 AI 19-01-2017
			wo 2017011253 AI 19-01-2017

WO 2013192384	AI	27-12-2013	AU 2013277107 AI 22-01-2015
			CA 2876675 AI 27-12-2013
			CN 104583369 A 29-04-2015
			EA 201492139 AI 30-04-2015
			EP 2864447 AI 29-04-2015
			JP 2015523440 A 13-08-2015
			JP 2017115156 A 29-06-2017
			KR 20150132068 A 25-11-2015
			US 2013344012 AI 26-12-2013
			US 2015105566 AI 16-04-2015
			wo 2013192384 AI 27-12-2013

WO 2007103398	AI	13-09-2007	AU 2007223922 AI 13-09-2007
			BR PI0708675 A2 07-06-2011
			CA 2646879 AI 13-09-2007
			CN 101522160 A 02-09-2009
			CN 102525829 A 04-07-2012
			EP 1996149 AI 03-12-2008
			JP 2009529092 A 13-08-2009
			KR 20090003302 A 09-01-2009
			PL 220777 B1 29-01-2016
			RU 2008138824 A 20-04-2010
			US 2009220443 AI 03-09-2009
			US 2014357714 AI 04-12-2014
			wo 2007103398 AI 13-09-2007
