



(51) International Patent Classification:

A61Q 5/00 (2006.01) A61K 8/98 (2006.01)

(21) International Application Number:

PCT/EP2017/074531

(22) International Filing Date:

27 September 2017 (27.09.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16192683.7 06 October 2016 (06.10.2016) EP

(71) **Applicant** (for AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, JO, KE, KN, KW, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; a company registered in England and Wales under company no. 41424 of Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).

(71) **Applicant** (for all designated States except AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, JO, KE, KN, KW, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER N.V.** [NL/NL]; Weena 455, 3013 AL Rotterdam (NL).

(71) **Applicant** (for US only): **CONOPCO, INC., D/B/A UNILEVER** [US/US]; 800 Sylvan Avenue AG West, S. Wing, Englewood Cliffs, New Jersey 07632 (US).

(72) **Inventors**: **PAUL, Prem, Kumar, Cheyalazhagan**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **PYE, Susan**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **RAUT, Janhavi, Sanjay**; Hindustan Unilever Ltd, Research Centre, 64, Main Road, Whitefield, Bangalore 560 066 (IN).

(74) **Agent**: **JAMES, Helen, Sarah**; Unilever PLC Patent Group Colworth House, Sharnbrook, Bedford Bedfordshire MK44 1LQ (GB).

(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).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))
- with sequence listing part of description (Rule 5.2(a))

(54) **Title:** METHOD OF TREATING HAIR

(57) **Abstract:** The invention provides a method of treating hair by sequential topical application of: (i) an aqueous composition comprising one or more silk sericins dissolved or dispersed in an aqueous continuous phase; and (ii) a hair oil composition comprising one or more oily liquid hair conditioning agents selected from oily liquid hydrocarbons, oily liquid glycerides and mixtures thereof. The method is especially suitable for treating oxidatively damaged hair to provide benefits to the fibre such as fibre strengthening, damage repair, hair shape smoothing and frizz control.

5

METHOD OF TREATING HAIRField of the Invention

This invention relates to a method of treating hair. More particularly this invention relates to a method of treating oxidatively damaged hair.

10

Background of the Invention

The purpose of bleaching is to eliminate or lighten the natural hair colour by the reaction of an oxidizing agent with the melanin pigment. Examples of oxidizing agents that can be used are hydrogen peroxide, potassium, sodium or ammonium salts of

15

perborate, percarbonate, persulfate and percarbamide, and mixtures thereof. Bleaches are also used during oxidative dyeing treatments. Oxidative (or "permanent") dye compositions comprise "precursor dyes" which are small molecules capable of diffusing into the hair. These molecules mainly belong to three classes of aromatic compounds: diamines, aminophenols and phenols. They are sufficiently small to diffuse

20

in the hair shaft where, once activated by an oxidizing agent such as hydrogen peroxide, they further react with other precursors to form larger coloured complexes.

Oxidative treatments of hair are very popular with consumers since they provide good results which are relatively unaffected by light, shampooing and perspiration. However

25

the process is not without drawbacks. Repeated oxidative treatments over prolonged periods may damage or weaken hair, making it prone to breakage and reduced lustre.

Since the hair fibre is a multilayer structure, once hair is damaged, treatments must intervene on several levels to treat it - from the middle of the core to the surface of the

30

cuticle.

Film-forming polymers are often used in treatments for damaged hair because they alter hair surface properties, imparting smoothing and gliding effects and shine, and have a significant impact on the macroscopic behavior of the hair array. However, film-

35

forming polymers are by nature designed to provide hair fibres with a hydrophobic coating that may slow or prevent the penetration of actives. Therefore such treatments

- 5 may not provide multilayer benefits to the fibre such as fibre strengthening, damage repair, hair shape smoothing and frizz control.

The present invention addresses this problem.

10 Summary of the Invention

The present invention provides a method of treating oxidatively damaged hair by sequential topical application of:

- (i) an aqueous composition comprising one or more silk sericins dissolved or
15 dispersed in an aqueous continuous phase; and
(ii) a hair oil composition comprising one or more oily liquid hair conditioning agents selected from oily liquid hydrocarbons, oily liquid glycerides and mixtures thereof.

20 Detailed Description and Preferred Embodiments

All molecular weights as used herein are weight average molecular weights, unless otherwise specified.

- The composition (i) for use in the invention comprises one or more silk sericins
25 dissolved or dispersed in an aqueous continuous phase.

By "aqueous continuous phase" is meant a continuous phase which has water as its basis.

- 30 A composition (i) for use in the invention will generally comprise from about 50 to about 98% water, preferably from about 60 to about 90% water (by weight based on the total weight of the composition).

- Other organic solvents may also be present, such as lower alkyl alcohols and
35 polyhydric alcohols. Examples of lower alkyl alcohols include C1 to C6 monohydric alcohols such as ethanol and isopropanol. Examples of polyhydric alcohols include

- 5 propylene glycol, hexylene glycol, glycerol and propanediol. Mixtures of any of the above-described organic solvents may also be used.

The composition (i) for use in the invention comprises one or more silk sericins.

- 10 Silks can be broadly defined as externally spun fibrous protein secretions, made by arthropods for a variety of task-specific applications. Silk fibres are typically composite materials formed of silk protein and other associated molecules such as glycoproteins and lipids.
- 15 Silkworms produce silk cocoons to protect themselves during their metamorphosis into moths, and humans have harvested silk fibres from these cocoons for centuries to produce textiles. Of all natural silk-producing animals, mulberry silkworms (*Bombyx mori*) are of the most economic importance, because it is possible to rear them in captivity. Other than the domesticated *B.mori*, silk fibre production is reported from the
- 20 wild non-mulberry saturniid variety of silkworms, such as tasar (*Antheraea mylitta*), muga (*Antheraea assamensis*) and eri (*Philosamia ricini*).

- Silkworm (e.g. *B.mori*) silks are composed of two groups of proteins. The fibroins, which constitute the silk thread, are synthesized in the posterior part of the silk gland
- 25 (PSG). The sericins are produced by the middle silk gland (MSG), and are a family of globular, water-soluble proteins which ensure the cohesion of the cocoon by sticking the fibroin fibres together. The sericins are characterized by their high serine content, where serine represents at least about 20 mol% of the total amino acid residues. Typically serine represents from about 20 to about 40 mol%, preferably from about 30
- 30 to about 40 mol% of the total amino acid residues.

- A peptide consisting of 38 amino acids has been identified as a highly conserved and internally repetitive sequence of *B.mori* silk sericins. The consensus sequence of this peptide (Ser-Ser-Thr-Gly-Ser-Ser-Ser-Asn-Thr-Asp-Ser-Asn-Ser-Asn-Ser-Ala-Gly-Ser-
- 35 Ser-Thr-Ser-Gly-Gly-Ser-Ser-Thr-Tyr-Gly-Tyr-Ser-Ser-Asn-Ser-Arg-Asp-Gly-Ser-Val) is characterized by its similarity to the average amino acid composition of silk sericin and its high hydrophilic amino acid content.

- 5 Native *B.mori* silk sericins range in molecular weight from about 10 to about 400 kDa, depending on gene coding and post-translational modifications. Three major fractions of silk sericin have been isolated from the *B.mori* cocoon, with molecular weights of about 150, 250, and 400 kDa respectively.
- 10 Silk sericins for use in the invention may be naturally derived, typically by extraction from silkworm (e.g. *B.mori*) cocoons or by extraction from raw silk. During the extraction process, the silk sericin may be hydrolysed to a certain extent, depending on the extraction method, temperature, pH and processing time. Accordingly, the molecular weight which is quoted for such materials will represent the average
- 15 molecular weight of the various protein, polypeptide, oligopeptide and amino acid constituents present. The average molecular weight of silk sericins derived by boiling water extraction of cocoons generally ranges from about 65 kDa to about 400 kDa. If an alkaline solution is used, such as one containing sodium hydroxide, the average molecular weight of the derived silk sericin generally ranges from about 1 kDa to about
- 20 50 kDa.

Silk sericins for use in the invention may also be artificially synthesized using conventionally known biological methods, for example, by inserting the silk sericin gene sequence into *E. coli*, in which the *E. coli* produces recombinant silk sericin, or by

25 conventionally known chemical methods such as Fmoc/tBu solid-phase peptide synthesis.

Artificially synthesized silk sericins will generally contain several repeats of the 38 amino acid consensus sequence described above (Ser-Ser-Thr-Gly-Ser-Ser-Ser-Asn-

30 Thr-Asp-Ser-Asn-Ser-Asn-Ser-Ala-Gly-Ser-Ser-Thr-Ser-Gly-Gly-Ser-Ser-Thr-Tyr-Gly-Tyr-Ser-Ser-Asn-Ser-Arg-Asp-Gly-Ser-Val), for example 2 to 8 repeats, more preferably 2 to 6 repeats.

Mixtures of any of the above described types of silk sericins may also be used in the

35 invention.

- 5 Preferred silk sericins for use in the invention are naturally derived, and have an average molecular weight ranging from about 1 kDa to about 50 kDa, more preferably from about 5 to about 30 kDa and most preferably from about 10 kDa to about 30 kDa,

10 An example of a preferred silk sericin for use in the invention is silk sericin extracted from silkworm (e.g. *B.mori*) cocoons or raw silk, and containing serine at a level of from about 30 to about 40 mol% of the total amino acid residues, and having an average molecular weight ranging from about 1 kDa to about 50 kDa, more preferably from about 5 to about 30 kDa and most preferably from about 10 kDa to about 30 kDa.

- 15 In a typical composition (i) for use in the invention, the level of silk sericin(s) generally ranges from about 0.5 to about 6% and preferably ranges from 1 to 3%, more preferably from 1.5 to 2.5% (by weight based on the total weight of the composition).

20 The composition (i) for use in the invention is intended for topical application to the hair and may be formulated as a rinse-off product or a leave-on product.

Rinse-off products are intended to be substantially rinsed off the hair of the user with water after use, such as shampoos. Rinse-off products also include conditioners which are intended for application to the hair post-wash and which may be rinsed immediately
25 after application or (for more intensive conditioning), left on the hair for up to 2 hours, e.g. 5 minutes to 2 hours.

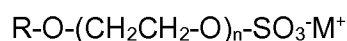
Leave-on products are intended not to be rinsed off the hair of the user immediately after use (i.e. within at least the first 2 hours, preferably at least four hours, after
30 application of the product). Leave-on products include for example lotions, creams and serums for use in-between washes, and leave-on conditioners for application to the hair post-wash.

Examples of suitable product forms are shampoos and conditioners.
35

- 5 A shampoo for use as composition (i) in the invention will typically include one or more anionic surfactants which are cosmetically acceptable and suitable for topical application to the hair.

10 Typical anionic surfactants for use in the invention include those surface active agents which contain an organic hydrophobic group with from 8 to 14 carbon atoms, preferably from 10 to 14 carbon atoms in their molecular structure; and at least one water-solubilising group which is preferably selected from sulphate, sulphonate, sarcosinate and isethionate.

- 15 A preferred class of anionic surfactants for use in the invention are alkyl ether sulphates of general formula:



- 20 in which R is a straight or branched chain alkyl group having 10 to 14 carbon atoms, n is a number that represents the average degree of ethoxylation and ranges from 1 to 5, preferably from 1 to 3.5, and M is an alkali metal, ammonium or alkanolammonium cation, preferably sodium, potassium, monoethanolammonium or triethanolammonium, or a mixture thereof.

25

Specific examples of such preferred anionic surfactants include the sodium, potassium, ammonium or ethanolamine salts of C₁₀ to C₁₂ alkyl sulphates and C₁₀ to C₁₂ alkyl ether sulphates (for example sodium lauryl ether sulphate (nEO) in which n ranges from 1 to 3.5).

30

The level of anionic surfactant will generally range from about 5 to 26%, and preferably ranges from 10 to 16% (by weight based on the total weight of the composition (i)).

- 35 A shampoo for use as composition (i) in the invention can optionally include co-surfactants, to help impart aesthetic, physical or cleansing properties to the composition.

- 5 A preferred type of co-surfactant is an amphoteric surfactant. Suitable amphoteric surfactants are betaines, such as those having the general formula $R(\text{CH}_3)_2\text{N}^+\text{CH}_2\text{COO}^-$, where R is an alkyl or alkylamidoalkyl group, the alkyl group preferably having 10 to 16 carbon atoms. Particularly suitable betaines are oleyl betaine, caprylamidopropyl betaine, lauramidopropyl betaine, isostearylamidopropyl
10 betaine, and cocoamidopropyl betaine.

Mixtures of any of the above described materials may also be used.

- When included, the total level of amphoteric surfactant is generally from 0.1% to 20%,
15 preferably from 1% to 10%, more preferably from 1% to 5% (by weight based on the total weight of the composition (i)).

- A shampoo for use as composition (i) in the invention may include one or more cationic deposition polymers which are selected from cationic polygalactomannans having a
20 mean charge density at pH7 from 0.2 to 2 meq/g, preferably from 0.5 to 1.8 meq/g. Such polymers may serve to enhance the delivery of conditioning agents from the composition to the skin and/or hair surface during consumer use, thereby improving the conditioning benefits obtained.

- 25 The term "charge density" in the context of this invention refers to the ratio of the number of positive charges on a monomeric unit of which a polymer is comprised to the molecular weight of the monomeric unit. The charge density multiplied by the polymer molecular weight determines the number of positively charged sites on a given polymer chain. The charge density is suitably determined via the Kjeldahl method as described
30 in the US Pharmacopoeia under chemical tests for nitrogen determination.

Preferred cationic polygalactomannans for use in the invention include guar hydroxypropyltrimethylammonium chlorides.

- 35 Guar hydroxypropyltrimethylammonium chlorides for use in the invention are generally comprised of a nonionic guar gum backbone that is functionalized with ether-linked 2-

- 5 hydroxypropyltrimethylammonium chloride groups, and are typically prepared by the reaction of guar gum with N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride.

Cationic polygalactomannans for use in the invention (preferably guar hydroxypropyltrimethylammonium chlorides) generally have an average molecular weight
10 (weight average molecular mass (Mw) determined by size exclusion chromatography) in the range 500,000 to 3 million g/mol, more preferably 800,000 to 2.5 million g/mol.

Cationic polygalactomannans for use in the invention are commercially available from Rhodia as JAGUAR ® C13S, JAGUAR ® C14 and JAGUAR ® C17.

Mixtures of any of the above described materials may also be used.

When included, the total level of cationic polygalactomannan will generally range from
15 0.05 to 0.25%, and preferably ranges from 0.15 to 0.2% (by weight based on the total weight of the composition (i)).

A shampoo for use as composition (i) in the invention may include one or more suspending agents. Suitable suspending agents include polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer,
20 copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives.

Mixtures of any of the above suspending agents may be used. Preferred is a mixture of
25 cross-linked polymer of acrylic acid and crystalline long chain acyl derivative.

When included, the total level of suspending agent is generally 0.1 to 10%, preferably from 0.5 to 6%, more preferably from 0.9 to 4% (by weight based on the total weight of the composition (i)).

30 A conditioner for use as composition (i) in the invention may suitably include a structured liquid phase, which may be characterized as a lamellar gel network formed from cationic surfactant and fatty alcohol bilayers. The bilayers may grow, swell or fold

- 5 to form extended sheets or spherical vesicles in the aqueous continuous phase of the composition (i).

Examples of suitable cationic surfactants include cetyltrimethylammonium chloride (CTAC), behenyltrimethylammonium chloride (BTAC) and mixtures thereof.

10

The level of cationic surfactant suitably ranges from 0.1 to 10%, preferably from 0.2 to 5% and more preferably from 0.25 to 4% (by total weight of cationic surfactant based on the total weight of the composition (i)).

- 15 Examples of suitable fatty alcohols include cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The level of fatty alcohol suitably ranges from 0.01 to 10%, preferably from 0.1 to 8%, more preferably from 0.2 to 7% and most preferably from 0.3 to 6% (by weight based on the total weight of the composition (i)).

20

The weight ratio of cationic surfactant to fatty alcohol is suitably from 1:1 to 1:10, preferably from 1:1.5 to 1:8, optimally from 1:2 to 1:5.

- 25 A composition (i) for use in the invention may also incorporate other optional ingredients to enhance performance and/or consumer acceptability. Suitable optional ingredients include: preservatives, colouring agents, chelating agents, antioxidants, fragrances, antimicrobials, antidandruff agents, cationic conditioning polymers, styling ingredients, sunscreens, proteins and hydrolysed proteins. Each of these optional i will be present in an amount effective to accomplish its purpose. Generally these optional ingredients are included individually at a level of up to about 5% by weight of the total composition (i).

30

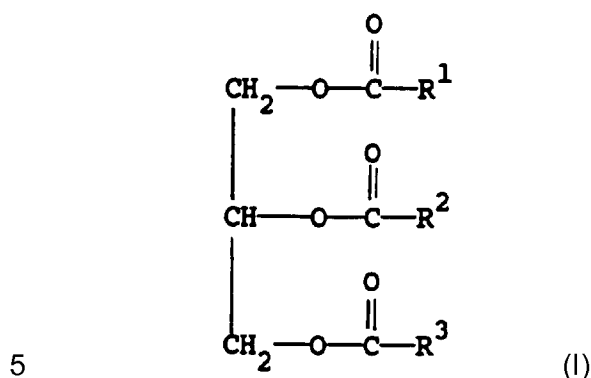
The hair oil composition (ii) for use in the invention comprises one or more oily liquid hair conditioning agents selected from oily liquid hydrocarbons, oily liquid glycerides and mixtures thereof.

35

- 5 For the purposes of the present invention, the term “oil” means a non-aqueous compound which is immiscible with water (distilled or equivalent) at a concentration of 0.1wt%, at 25°C. The term “oily liquid” means an oil that is capable of flowing under its own weight under ambient conditions (1 atmosphere, 25°C).
- 10 Oily liquid hydrocarbons suitable for use in the invention will generally have a kinematic viscosity at 40°C of 1000 cS ($\text{mm}^2.\text{s}^{-1}$) or less, preferably 500 cS ($\text{mm}^2.\text{s}^{-1}$) or less, more preferably 50 cS ($\text{mm}^2.\text{s}^{-1}$) or less, and most preferably 10 cS ($\text{mm}^2.\text{s}^{-1}$) or less, such as from 0.5 to 10 cS ($\text{mm}^2.\text{s}^{-1}$).
- 15 Examples of such materials include C_4 - C_{50} straight or branched chain, saturated or unsaturated aliphatic or cycloaliphatic hydrocarbons and mixtures thereof. Straight chain hydrocarbons will preferably contain from about 12 to about 30 carbon atoms. Branched chain hydrocarbons can and typically may contain higher numbers of carbon atoms. Also suitable are polymeric hydrocarbons, such as polymers of C_{2-6} alkenyl
- 20 monomers (e.g. polyisobutene, polybutene) and poly α -olefin oils derived from 1-alkene monomers having from about 6 to about 16 carbons, preferably from about 6 to about 12 carbon atoms (e.g. polymers derived from 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and mixtures thereof). Polymeric hydrocarbons for use in the invention can be straight or branched chain polymers, and may be hydrogenated.
- 25 The number average molecular weight of such polymeric materials can vary widely, but will typically range from about 200 up to about 3000.

- Preferred oily liquid hydrocarbons for use in the invention include mineral oils. The term “mineral oil” in the context of this invention generally denotes an oily liquid mixture
- 30 of saturated hydrocarbons with boiling points greater than 200°C, and which is obtained from petroleum (i.e. a mineral source). Mineral oil saturated hydrocarbons include straight chain (paraffinic), branched chain (isoparaffinic) and cyclic (naphthenic) structures, and molecules containing all three configurations, with the number of carbon atoms per hydrocarbon molecule generally ranging from about C_{15} to about C_{50} .
- 35 Mineral oils suitable for use in the invention are typically obtained from petroleum through various refining steps (e.g. distillation, extraction and/or crystallisation) and subsequent purification (e.g. acid treatment and/or catalytic hydrotreatment).

- 5 Mineral oils may also be characterised in terms of their viscosity. "Light" mineral oils will generally have a kinematic viscosity of about 34 cS ($\text{mm}^2.\text{s}^{-1}$) or less at 40°C and "heavy" mineral oils will generally have a kinematic viscosity ranging from about 35 cS ($\text{mm}^2.\text{s}^{-1}$) up to about 240 cS ($\text{mm}^2.\text{s}^{-1}$) at 40°C.
- 10 Light mineral oils (as defined above) are preferred for use in the invention. More preferably such light mineral oils have a kinematic viscosity of about 10 cS ($\text{mm}^2.\text{s}^{-1}$) or less at 40°C. Most preferably the kinematic viscosity ranges from about 3 to about 5 cS ($\text{mm}^2.\text{s}^{-1}$) at 40°C. Materials of this type are commercially available from Sonneborn Inc. under the brand name Lytol®.
- 15 Mixtures of any of the above-described materials may also be used.
- Oily liquid glycerides suitable for use in the invention will generally have a viscosity at ambient temperature (25 to 30°C) of from 0.01 to 0.8 Pa.s, preferably from 0.015 to 0.6
- 20 Pa.s, more preferably from 0.02 to 0.065 Pa.s, as measured by a Carri-Med CSL2 100 controlled stress rheometer, from TA Instruments Inc., New Castle, Del. (USA).
- Examples of such materials include mono-, di- and triglycerides (and mixtures thereof) formed between glycerol and long chain carboxylic acids having at least 8 carbon atoms, preferably from 8 to 22 carbon atoms and more preferably from 8 to 18 carbon
- 25 atoms. The carboxylic acids may be saturated or unsaturated, linear or branched chain, or contain hydrophilic groups such as hydroxyl.
- Preferred oily liquid glycerides for use in the invention include triglycerides corresponding to the following general formula (I):



in which R¹, R² and R³ are each independently selected from linear alkyl groups having from 7 to 17 carbon atoms and 0, 1, 2 or 3 double bonds.

10 Oily liquid glycerides for use in the invention may be chemically synthesized by a condensation reaction, but are preferably derived from natural, particularly plant, sources.

Naturally-derived oily liquid glycerides suitable for use in the invention include almond oil, castor oil, coconut oil, sesame oil, sunflower oil and soybean oil. Coconut oil is particularly preferred.

15 Coconut oil generally contains a mixture of triglycerides of general formula (I), with varying chain lengths of the R¹, R² and R³ groups. Typically at least about 85% of the R¹, R² and R³ groups have from 7 to 17 carbon atoms; and at least about 50% of the R¹, R² and R³ groups have from 7 to 11 carbon atoms (by weight based on total weight of the R¹, R² and R³ groups)

20 A representative carbon chain length distribution for the R¹, R² and R³ groups in coconut oil triglycerides of general formula (I) is as follows:

C ₇	5 to 10 wt%
C ₉	5 to 10 wt%
C ₁₁	48 to 56 wt%
25 C ₁₃	15 to 23 wt%

5	C ₁₅	7 to 12 wt%
	C ₁₇	1 to 5 wt%
	C _{17:1}	4 to 12 wt%
	C _{17:2}	1 to 4 wt%

- 10 The hair oil composition (ii) for use in the invention is intended for topical application to the hair.

Preferably, the level of oily liquid hair conditioning agents selected from oily liquid hydrocarbons, oily liquid glycerides and mixtures thereof is at least 95%, more
15 preferably at least 98% (by weight based on the total weight of the hair oil composition (ii)).

A particularly preferred hair oil composition (ii) for use in the invention comprises at least 95%, more preferably at least 98% light mineral oil and/or coconut oil (by weight
20 based on the total weight of the hair oil composition (ii)).

Alternatively, a hair oil composition (ii) for use in the invention may be formulated as a shampoo, or more preferably a conditioner, with additional ingredients as described above with respect to composition (i).

25 A hair oil composition (ii) for use in the invention may also incorporate other optional ingredients to enhance performance and/or consumer acceptability. Suitable optional ingredients include: preservatives, colouring agents, antioxidants, fragrances, sunscreens and antimicrobials. Each of these optional ingredients will be present in an
30 amount effective to accomplish its purpose. Generally these optional ingredients are included individually at a level of up to about 5% by weight of the total hair oil composition (ii).

Advantageously, the method of the invention does not require the use of reducing
35 agents, and compositions (i) and (ii) for use in the invention are generally substantially free of such materials.

- 5 The term “substantially free” in the context of this invention means that reducing agents are absent or included in trace quantities only, such as no more than 0.1%, preferably no more than 0.01%, and more preferably from 0 to 0.001% by weight based on the total weight of the respective composition.
- 10 The term “reducing agent” in the context of this invention means an agent which is effective to break hair disulfide bonds when applied to hair for a period ranging from about 3 to 15 minutes and at a temperature ranging from about 20 to 30°C. Examples of such reducing agents are ammonium thioglycolate (in a solution having a pH of between about 7 and 10.5), glyceryl monothioglycolate (employed at a pH of less than
- 15 7), thioglycolic acid, dithioglycolic acid, mercaptoethyl amine, mercaptopropionic acid, dithioglycolate and alkali metal or ammonium sulfites or bisulfites.

A preferred method of treating hair according to the invention is a two-stage method in which aqueous composition (i) is topically applied to the hair and then hair oil

20 composition (ii) is topically applied to the hair.

The aqueous composition (i) may suitably be topically applied to dry hair. The term “dry hair” in the context of this invention generally means hair from which free water (i.e. water disposed as a film or droplets on the cuticle surface) has been substantially

25 removed. Hair may be dried by exposure to air, by use of a heated hair drying appliance, by rubbing with a water- absorbent article, or by a combination of any of these methods. Preferably, the dry hair will not have been washed or actively wetted, (such as by shampooing, conditioning, rinsing or otherwise treating with an aqueous composition) in the preceding 2 hours and more preferably in the preceding 3 hours

30 prior to topical application of the aqueous composition (i), and will have been permitted to acclimatise to atmospheric conditions. In such circumstances there is substantially no free water present which interferes with the adsorption of the aqueous composition (i) on application. A suitable indicator of dry hair in the context of this invention would be a hair fibre whose calculated water content does not exceed 25% by weight based

35 on the total weight of the hair fibre.

- 5 Preferably, the aqueous composition (i) is topically applied to the hair at a temperature from 15 to 40°C, and more preferably at a temperature from 20 to 30°C.

Subsequent to its topical application, the aqueous composition (i) is suitably allowed to remain in contact with the hair without rinsing for a period ranging from 1 to 60 minutes,
10 more preferably from 3 to 45 minutes. The hair oil composition (ii) is then topically applied to the hair.

Generally, the aqueous composition (i) is not rinsed off the hair prior to application of hair oil composition (ii). Suitably, the aqueous composition (i) is not rinsed off the hair
15 and the hair so treated is dried or allowed to dry prior to application of hair oil composition(ii). The hair so treated may be dried naturally by exposure to air, by use of a heated hair drying appliance, by rubbing with a water-absorbent article, or by a combination of any of these methods.

- 20 Preferably, the hair oil composition (ii) is topically applied to the hair at a temperature from 15 to 40°C, and more preferably at a temperature from 20 to 30°C.

Preferably the hair oil composition (ii) is massaged into the hair for a period which typically ranges from 30 seconds to 5 minutes and preferably ranges from 1 to 3
25 minutes. The hair oil composition (ii) may then be rinsed from the hair with water or cleansing shampoo if required, and the hair dried and styled.

The method of this invention is suitable for application to hair to improve properties such as smoothness, frizz control and volume-down. The term “volume-down” in the
30 context of this invention generally means reduced visible bulkiness of the hair. For many consumers, improved hair volume-down provides a number of associated benefits, such as improved straightness, manageability and style retention.

The method of this invention is suitable for application to damaged hair, such as
35 oxidatively-treated hair. The method is especially suitable for treating oxidatively damaged hair to provide benefits to the fibre such as fibre strengthening, damage repair, hair shape smoothing and frizz control.

5 As used herein, the term "oxidatively-treated hair" means hair which has been subjected to any treatment comprising at least one step of contacting the hair with at least one oxidizing composition. Examples of oxidative treatments for human hair are bleaching, dyeing or perming.

10 As used herein, the term "oxidizing composition" means a composition comprising at least one oxidizing agent suitable for use on hair, such as hydrogen peroxide, potassium, sodium or ammonium salts of perborate, percarbonate, persulfate and percarbamide, and mixtures thereof. Examples of such compositions are oxidative dye compositions and bleaching compositions.

15

The invention is further illustrated with reference to the following, non-limiting Examples.

EXAMPLES

20 In the Examples, all ingredients are expressed by weight percent of the total formulation, and as level of active ingredient.

Comparative Examples (not according to the invention) are indicated by letter; Examples according to the invention are indicated by number.

25

Experiment 1

Twice-bleached dark brown European wavy#6 switches of length 25 cm and weight 2gms, were treated as follows:

30 Control: Soaked for 30 minutes in water

Example A: Soaked for 30 minutes in an aqueous solution of 2% silk sericin*

Example 1: Soaked for 30 minutes in an aqueous solution of 2% silk sericin* then when dry treated with coconut oil at a level of 0.1gm per gm of hair

Example B: Soaked for 30 minutes in water then when dry treated with coconut oil at
35 a level of 0.1gm per gm of hair

- 5 * *Sericin powder molecular weight 20 kDa, ex Huzhou Xintiansi Bio-tech Co., Ltd., China*

A few fibres from all the switches were removed and prepared for wet DSC measurements. The denaturation temperature Td was measured and the results are
10 shown in Table 1.

Table 1

Treatment	Td	SD	Significance
Control (water)	144.54	0.17	A
Example A	146.56	0.09	B
Example 1	148.06	0.83	C
Example B	145.11	0.52	A

- 15 The last column shows that switches not connected by a letter are significantly different (>95%).

The Td increase from control for the combination of Example 1 (according to the invention) is seen to be synergistic. It is much greater in real and percent terms
20 compared to the simple addition of the effects of silk sericin and coconut oil on their own (Examples A and B respectively).

Experiment 2

Switches were treated as in Experiment 1 and washed once in a stripping shampoo. It
25 was found that the Example 1 switches showed excellent smoothing, volume down and frizz control compared to the other switches.

Experiment 3

Experiments 1 & 2 were repeated with the coconut oil substituted for an equivalent
30 quantity of light mineral oil (Lytol, CAS No. : 8042-47-5, ex Sonneborn) . The mineral oil was observed to have an equivalent effect to the coconut oil in terms of smoothing,

- 5 frizz control and damage repair, when combined with silk sericin in accordance with the invention.

5 CLAIMS

1. A method of treating oxidatively damaged hair by sequential topical application of:
 - (i) an aqueous composition comprising one or more silk sericins dissolved or
10 dispersed in an aqueous continuous phase; and
 - (ii) a hair oil composition comprising at least 99% light mineral oil and/or coconut oil (by weight based on the total weight of the hair oil composition (ii)),wherein the aqueous composition (i) is suitably allowed to remain in contact
15 with the hair without rinsing for a period ranging from 1 to 60 minutes.
2. A method according to claim 1, in which the silk sericin (s) are extracted from *B.mori* cocoons or raw silk, and contain serine at a level of from 30 to 40 mol% of the total amino acid residues, and have an average molecular weight
20 ranging from 1 kDa to 50 kDa.
3. A method according to claim 1 or claim 2, in which the average molecular weight of the silk sericin (s) ranges from 10 kDa to 30 kDa.
- 25 4. A method according to any one of claims 1 to 3, in which the level of silk sericin(s) ranges from 1.5 to 2.5% (by weight based on the total weight of the aqueous composition (i)).
5. A method according to any one of claims 1 to 4, in which aqueous composition
30 (i) is topically applied to the hair and then hair oil composition (ii) is topically applied to the hair.
6. A method according to claim 5, in which the aqueous composition (i) is not rinsed off the hair and the hair so treated is dried or allowed to dry prior to
35 application of hair oil composition(ii).

- 5 7. A method according to any one of claims 1 to 6, in which the hair is oxidatively-treated hair.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/074531

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61Q5/00 A61K8/98
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, EMBASE, 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	DE 10 2005 063096 A1 (HENKEL KGAA [DE]) 5 July 2007 (2007-07-05)	1-7
Y	page 1 example 1 examples 11, 16, 62, 65	1-7
X	JP 2011 037778 A (CREIDA KK) 24 February 2011 (2011-02-24)	1-7
Y	paragraph [0001] paragraph [0011] paragraph [0017] paragraph [0039]	1-7
X	WO 2004/024176 A1 (HENKEL KGAA [DE]) 25 March 2004 (2004-03-25)	1-7
Y	page 88 - page 90	1-7
	----- -/-	



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

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

12 December 2017

Date of mailing of the international search report

22/12/2017

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

Steinheimer, K

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/074531

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 32 33 388 A1 (BEIERSDORF AG [DE]) 15 March 1984 (1984-03-15)	1-7
Y	examples 7, 9 -----	1-7
X	US 2011/311655 A1 (ROSS VALERIE MARIE [US]) 22 December 2011 (2011-12-22)	1-7
Y	paragraph [0010] - paragraph [0020] -----	1-7
X	JP 2006 131579 A (KANEBO LTD) 25 May 2006 (2006-05-25)	1-7
Y	paragraph [0027]; example 6 -----	1-7
X	JP 2010 013405 A (KRACIE HOME PRODUCTS LTD) 21 January 2010 (2010-01-21)	1-7
Y	paragraph [0030] - paragraph [0031]; example 10 example 12 -----	1-7
X	WO 2009/056275 A1 (BIOPHIL SRL [IT]; SANTUS GIACOMO [IT]; BARBERI LAURA [IT]; SCHUBERT CR) 7 May 2009 (2009-05-07)	1-7
Y	page 13 - page 14 -----	1-7
Y	WO 2016/005184 A1 (HENKEL AG & CO KGAA [DE]) 14 January 2016 (2016-01-14) the whole document -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/074531

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102005063096 A1	05-07-2007	DE 102005063096 A1 WO 2007079793 A1	05-07-2007 19-07-2007
JP 2011037778 A	24-02-2011	NONE	
WO 2004024176 A1	25-03-2004	AT 355073 T AU 2003280329 A1 CN 1678339 A EC SP055712 A EP 1531853 A1 JP 2006508919 A KR 20050054924 A RU 2342924 C2 WO 2004024176 A1	15-03-2006 30-04-2004 05-10-2005 06-07-2005 25-05-2005 16-03-2006 10-06-2005 10-01-2009 25-03-2004
DE 3233388 A1	15-03-1984	DE 3233388 A1 JP S5965008 A	15-03-1984 13-04-1984
US 2011311655 A1	22-12-2011	US 2011311655 A1 US 2015209261 A1	22-12-2011 30-07-2015
JP 2006131579 A	25-05-2006	NONE	
JP 2010013405 A	21-01-2010	NONE	
WO 2009056275 A1	07-05-2009	EP 2211828 A1 US 2010297047 A1 WO 2009056275 A1	04-08-2010 25-11-2010 07-05-2009
WO 2016005184 A1	14-01-2016	EP 3166689 A1 US 2017112738 A1 WO 2016005184 A1	17-05-2017 27-04-2017 14-01-2016