



(51) International Patent Classification:

A61K 8/73 (2006.01) A61Q 5/02 (2006.01)

A61K 8/81 (2006.01) A61Q 5/12 (2006.01)

A61K 8/89 (2006.01)

(21) International Application Number:

PCT/EP2020/066615

(22) International Filing Date:

16 June 2020 (16.06.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

19181766.7 21 June 2019 (21.06.2019) 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]; 700 Sylvan Avenue (A4), Englewood Cliffs, New Jersey 07632 (US).

(72) Inventors: **MACHEN, Robert**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **MOGHADAM, Arash, Mohajer**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **MUSCAT, Joseph**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **RILEY, Robert, George**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **STARCK, Pierre**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB).

(74) Agent: **CHISEM, Janet**; Unilever Patent Group, Bronland 14, 6708 WH Wageningen (NL).

(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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, 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,

(54) Title: CLEANSING COMPOSITION

(57) Abstract: An aqueous, sulphate free shampoo composition for hair and scalp comprising:- a. a pre-formed emulsified silicone; b. a cationic deposition polymer; c. a hair substantive cationic conditioning polymer which is an APTAC polymer having a molecular weight of less than 1 million Daltons, preferably selected from a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride and a (3- acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer; d. a total amount of anionic surfactant, amphoteric surfactant and zwitterionic surfactant consisting of: (i) from 3 wt % to 13 wt %, by weight of the total composition at 100 % activity, of an alpha olefin sulfonate anionic surfactant of general formula (I): $R^1-CH=CH-CH_2-SO_3^{-M^+}$ (I) in which R^1 is selected from linear or branched alkyl groups having from 11 to 13 carbon atoms and mixtures thereof; and M is a solubilizing cation; (ii) from 1 to 6%, by weight of an amphoteric or zwitterionic surfactant, selected from an alkyl betaine of general formula (II) $R^2-N^+(CH_3)_2-CH_2-COO^-M^+$ (II) wherein R^2 = C12 (Lauryl) or Coco derived; an alkyl hydroxy sultaine of general formula (III), $R^3-N^+(CH_3)_2-CH_2-CH(OH)-CH_2-SO_3^-M^+$ (III) wherein R^3 = C12 (Lauryl) or Coco derived; an alkyl aminopropyl hydroxy sultaine of general formula (IV), $R^4-CO-NH-(CH_2)_3-N^+(CH_3)_2-CH_2-CH(OH)-CH_2-SO_3^-M^+$ (IV) wherein R^4 = C12 (Lauryl) or Coco derived; an alkyl amphotacetate of general formula (V), $R^5-CO-NH-(CH_2)_2-N(CH_2-CH_2-OH)(CH_2-COO^-M^+)$ (V) wherein R^5 = C12 (Lauryl) or Coco derived; and mixtures thereof; and e. a suspending agent in which the weight ratio of (i) to (ii) ranges from 1:1 to 6:1 and the pH of the composition is from 3 to 6.5; and wherein the composition has a viscosity from 3,500 to 15,000 mPa.s, preferably from 4,000 to 12,000 mPa.s when measured using a Brookfield V2 viscometer using a spindle RTV5, for 1 minute at 20rpm at 30°C. results in superior deposition and retention of silicone on hair.

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))*

CLEANSING COMPOSITION

Field of the Invention

- 5 The present invention relates to mild sulphate free cleansing compositions for hair and scalp.

Background and Prior Art

10 US 2012/276210 relates to shampoo compositions containing polyacrylate microcapsules, wherein the polyacrylate microcapsules have increased deposition onto hair. A shampoo composition is disclosed comprising:

- (a) from about 0.001% to about 10% of an anionic charged polyacrylate microcapsule;
- (b) from about 0.01% to about 2% of a cationic deposition polymer; and
- (c) from about 2% to about 25% of a deterative surfactant; and
- 15 (d) a carrier.

WO 2007/065537 addresses a problem associated with the use of cationic deposition polymers in that it is difficult to obtain a good balance of conditioning benefits at different stages of the shampooing process, and discloses an aqueous shampoo composition

20 comprising:

- (i) one or more anionic cleansing surfactants;
- (ii) discrete, dispersed droplets of a water-insoluble conditioning agent with a mean droplet diameter ($D_{3,2}$) of 4 micrometres or less;
- (iii) one or more cationic polymers (A) selected from cationically modified acrylamide
- 25 polymers having a cationic charge density at pH7 of less than 1.0 meq per gram, cationically modified celluloses and mixtures thereof, and
- (iv) one or more cationic polymers (B) selected from cationically modified acrylamide polymers having a cationic charge density at pH7 of greater than 1.0 meq per gram, cationically modified polygalactomannans, and mixtures thereof, wherein the composition
- 30 comprises a cationic polymer other than a cationically modified acrylamide polymer.

WO 2013/122861 discloses a conditioning composition additive for providing immediate and prolonged benefit to a keratin surface comprising:

- 2 -

a) a hydrophobically modified poly(acrylamido-N-propyltrimethylammonium chloride) (polyAPTAC) and b) water;

wherein the hydrophobically modified polyAPTAC is present in an amount of from 0.1 wt % to 20 wt % of the total weight of the conditioning composition additive and has a cationic charge density in the range of about 1 to 8 meq/g.

US2012/0076747 discloses a surfactant-based cleansing composition comprising, a surfactant, cationic, water-soluble polyelectrolytes and the use of the composition in personal care and household care cleansing compositions for treating keratinous substrates, textile substance and hard-surface substrates.

US2018/015009 discloses a microcapsule and a copolymer of acrylamide and acrylamidopropyltrimonium chloride as a first deposition aid to facilitate the deposition of the microcapsule onto a hard surface such as skin, hair, fabric and floor.

WO2018/007332 discloses personal cleansing composition comprising: (i) an aqueous continuous phase including cleansing surfactant; (ii) one or more oily liquid conditioning agents for skin and/or hair wherein the agent is solubilized in wormlike micelles in the aqueous continuous phase via the incorporation of at least one inorganic electrolyte and at least one linker molecule; (iii) one or more cationic deposition polymers which are selected from cationic polygalactomannans having a mean charge density at pH7 from 0.2 to 2 meq per gram; and (iv) a hair substantive cationic conditioning polymer which is a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride.

Many cleansing and conditioning products for use on hair contain silicones. It is desirable to deposit silicone onto hair in order to confer conditioning and sensory benefits. A typical hair wash process involves first washing hair with a shampoo and rinsing, followed by applying a conditioner product and rinsing.

Silicone can be deposited onto hair from a shampoo.

However, we have found that this silicone is largely deterged when the hair is subsequently washed with a conditioner as part of a typical washing process. A consequence of this is that it is necessary to include silicone in the conditioner in order to provide conditioning benefits that are apparent when the hair has dried.

- 3 -

We have now found that a shampoo comprising a conditioning polymer which is an APTAC polymer, preferably selected from a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride and a (3-acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer can enhance the adhesion of the silicone delivered from shampoo and help retain it on hair during and after washing with a conditioner.

When the hair is washed with a shampoo containing a conditioning polymer which is an APTAC polymer, preferably selected from a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride and a (3-acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer and then a silicone free conditioner, it has a significantly higher disposition of silicone compared to hair that is washed with a 1% silicone containing shampoo and then a silicone free conditioner.

In dry friction data, the hair that is washed with a shampoo containing which is an APTAC polymer, preferably selected from a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride and a (3-acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer and then a silicone free conditioner has a significantly lower dry friction compared to the hair that is washed with a 1% silicone containing shampoo and then a silicone free conditioner.

Addition of silicone to a shampoo formulation is known to have a detrimental effect on the foaming properties, for example flash foam and foam height.

The inventors have identified Alpha Olefin Sulfonate (AOS) as a sulfate free, primary surfactant. As with sulfate based chassis a secondary surfactant is required to help build viscosity using salt, control the foam and aid in the delivery of mildness benefits through lower CMC.

It is desirable to reduce the level of surfactant used in formulations (for mildness and environmental benefits). We have found that if you reduce the amount of surfactant, then the viscosity of the formulation falls undesirably.

- 4 -

However, the typical secondary surfactant, cocamidopropyl betaine (CAPB) does not allow viscosity to be built at low total surfactant concentrations with Alpha Olefin Sulfonate (AOS) as the primary surfactant.

- 5 The inventors have now found that a combination of AOS, at a specified ratio, with at least one of an alkyl betaine, an alkyl hydroxy sultaine, an alkyl aminopropyl hydroxy sultaine or an alkyl amphotacetate can afford viscosity builds with salt addition at low total concentrations of surfactant. This negates the need for other thickening agents, for example, polymers and other secondary surfactants.

10

Use of such APTAC polymers in a shampoo composition having a combination of anionic and amphoteric sulfate free surfactants at enriched amphoteric ratios; reduced surfactant concentrations; specific primary sulfate free surfactant levels, a cationic conditioning polymer and a silicone emulsion to provide good foamability, dry lubrication that provides silky,
15 smooth feel and desirable rheological characteristics, whilst maintaining mildness to skin and hair protein as well as increased silicone delivery and retention.

Summary of the Invention

20

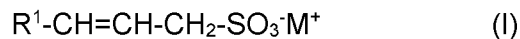
In a first aspect the present invention provides an aqueous, sulphate free shampoo for hair and scalp comprising:-

- a. a pre-formed emulsified silicone;
- b. a cationic deposition polymer;
- c. a hair substantive cationic conditioning polymer which is an APTAC polymer having
25 a molecular weight of less than 1 million Daltons, preferably selected from a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride and a (3-acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer;
- d. a total amount of anionic surfactant, amphoteric surfactant and zwitterionic surfactant consisting of:

30

(i) from 3 wt % to 13 wt %, by weight of the total composition at 100 % activity, of an alpha olefin sulfonate anionic surfactant of general formula (I):

- 5 -



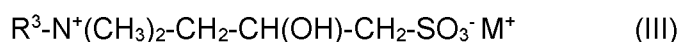
in which R^1 is selected from linear or branched alkyl groups having from 11 to 13 carbon atoms and mixtures thereof; and M is a solubilizing cation;

(ii) from 1 to 6%, by weight of an amphoteric or zwitterionic surfactant, selected from an alkyl betaine of general formula (II)



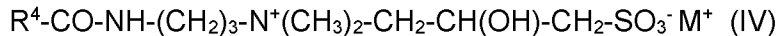
wherein R^2 = C12 (Lauryl) or Coco derived;

an alkyl hydroxy sultaine of general formula (III),



wherein R^3 = C12 (Lauryl) or Coco derived;

an alkyl aminopropyl hydroxy sultaine of general formula (IV),



wherein R^4 = C12 (Lauryl) or Coco derived;

an alkyl amphotoacetate of general formula (V),



wherein R^5 = C12 (Lauryl) or Coco derived;

and mixtures thereof; and

e. a suspending agent

in which the weight ratio of (i) to (ii) ranges from 1:1 to 6:1 and the pH of the composition is from 3 to 6.5

and wherein the composition has a viscosity from 3,500 to 15,000 mPa.s, preferably from 4,000 to 12,000 mPa.s when measured using a Brookfield V2 viscometer using a spindle RTV5, for 1 minute at 20 rpm at 30°C.

- 6 -

In a second aspect, the present invention provides a method of treating hair comprising the steps of applying to hair the composition of the first aspect and performing a first rinse with water.

- 5 Silicone is deposited onto the hair from the composition of the invention, during the method of the invention.

Preferably, the method comprises a subsequent steps of applying a conditioner composition and then performing a second rinse with water. Following these subsequent steps, the
10 silicone that is deposited on the hair from the composition of the invention remains on the hair.

Some or all of the silicone is retained on the hair following rinse with water, and/or following treatment with a hair conditioner and a second rinse. By “retained” on the hair is meant that
15 the silicone remains on the hair.

Detailed Description and Preferred Embodiments

The Emulsified Silicone

- 20 The composition of the invention comprises a pre-formed emulsified silicone. Mixtures of emulsified silicones can be used.

Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone. Also suitable for use compositions of the invention
25 are polydimethyl siloxanes having hydroxyl end groups, which have the CTFA designation dimethiconol. Also suitable for use in compositions of the invention are silicone gums having a slight degree of cross-linking, as are described for example in WO 96/31188.

The viscosity of the emulsified silicone itself (not the emulsion or the final hair composition)
30 is typically at least 10,000 cst at 25 °C the viscosity of the silicone itself is preferably at least 60,000 cst, most preferably at least 500,000 cst, ideally at least 1,000,000 cst. Preferably the viscosity does not exceed 10^9 cst for ease of formulation.

- 7 -

Emulsified silicones for use in the compositions of the invention will typically have a D90 silicone droplet size in the composition of less than 30, preferably less than 20, more preferably less than 10 micron, ideally from 0.01 to 1 micron. Silicone emulsions having an average silicone droplet size (D50) of 0.15 micron are generally termed microemulsions.

5

Silicone particle size may be measured by means of a laser light scattering technique, for example using a 2600D Particle Sizer from Malvern Instruments.

Examples of suitable pre-formed emulsions include Xiameter MEM 1785 and microemulsion DC2-1865 available from Dow Corning. These are emulsions /microemulsions of

10 dimethiconol. Cross-linked silicone gums are also available in a pre-emulsified form, which is advantageous for ease of formulation.

A further preferred class of emulsified silicones for inclusion in compositions of the invention are amino functional silicones. By "amino functional silicone" is meant a silicone containing

15 at least one primary, secondary or tertiary amine group, or a quaternary ammonium group.

Examples of suitable amino functional silicones include: polysiloxanes having the CTFA designation "amodimethicone".

Specific examples of amino functional silicones suitable for use in the invention are the aminosilicone oils DC2-8220, DC2-8166 and DC2-8566 (all ex Dow Corning).

20

Suitable quaternary silicone polymers are described in EP-A-0 530 974. A preferred quaternary silicone polymer is K3474, ex Goldschmidt.

Also suitable are emulsions of amino functional silicone oils with non ionic and/or cationic surfactant.

25

Pre-formed emulsions of amino functional silicone are also available from suppliers of silicone oils such as Dow Corning and General Electric. Specific examples include DC939 Cationic Emulsion and the non-ionic emulsions DC2-7224, DC2-8467, DC2-8177 and DC2-8154 (all ex Dow Corning).

30

Preferably, the silicone is selected from the group consisting of dimethicone, dimethiconol, amodimethicone and mixtures thereof. Also preferred are blends of amino-functionalised silicones with dimethicones.

- 8 -

The amount of silicone in compositions of the invention may suitably range from 0.05 to 10%, preferably from 0.1 to 8%, more preferably 0.5 to 6.5 %, most preferably 1 to 3 % at 100 % activity, based on the total weight of the composition).

5 The cationic deposition polymer

The composition of the invention includes a cationic deposition polymers which may be selected from cationic polygalactomannans having a mean charge density at pH7 from 0.2 to 2 meq per gram. Such polymers may serve to enhance the delivery of conditioning agents
10 from the composition to the skin and/or hair surface during consumer use, thereby improving the conditioning benefits obtained. Mixtures of cationic deposition polymers may be employed.

The term "charge density" in the context of this invention refers to the ratio of the number of
15 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 polygalactomannans are polysaccharides composed principally of galactose and mannose units and are usually found in the endosperm of leguminous seeds, such as guar,
20 locust bean, honey locust, flame tree, and the like. Guar flour is composed mostly of a galactomannan which is essentially a straight chain mannan with single membered galactose branches. The mannose units are linked in a 1-4- β -glycosidic linkage and the galactose branching takes place by means of a 1-6 linkage on alternate mannose units. The ratio of galactose to mannose in the guar polymer is therefore one to two.

25 Suitable cationic polygalactomannans for use in the invention include polygalactomannans, such as guar, and polygalactomannan derivatives, such as hydroxyalkyl guar (for example hydroxyethyl guar or hydroxypropyl guar), that have been cationically modified by chemical reaction with one or more derivatizing agents.

30 Derivatizing agents typically contain a reactive functional group, such as an epoxy group, a halide group, an ester group, an anhydride group or an ethylenically unsaturated group, and at least one cationic group such as a cationic nitrogen group, more typically a quaternary ammonium group. The derivatization reaction typically introduces lateral cationic groups on

- 9 -

the polygalactomannan backbone, generally linked via ether bonds in which the oxygen atom corresponds to hydroxyl groups on the polygalactomannan backbone which have reacted.

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

Guar hydroxypropyltrimethylammonium chlorides for use in the invention are generally comprised of a nonionic guar gum backbone that is functionalized with ether-linked 2-
10 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
15 (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 generally have a charge density ranging from 0.5 to 1.8 meq/g.
20

Preferably the cationic polygalactomannans are selected from guar hydroxypropyltrimethylammonium chlorides having a charge density ranging from 0.5 to 1.8 meq/g (and mixtures thereof).

- 25 The cationic charge density of the polymer is suitably determined via the Kjeldahl method as described in the US Pharmacopoeia under chemical tests for nitrogen determination.

Specific examples of preferred cationic polygalactomannans are guar hydroxypropyltrimonium chlorides having a cationic charge density from 0.5 to 1.1 meq/g.
30

Also suitable are mixtures of cationic polygalactomannans in which one has a cationic charge density from 0.5 to 1.1 meq/g, and one has a cationic charge density from 1.1 to 1.8 meq per gram.

- 10 -

Specific examples of preferred mixtures of cationic polygalactomannans are mixtures of guar hydroxypropyltrimonium chlorides in which one has a cationic charge density from 0.5 to 1.1 meq/g, and one has a cationic charge density from 1.1 to 1.8 meq per gram.

Cationic polygalactomannans for use in the invention are commercially available from Solvay as JAGUAR ® C13S, JAGUAR ® C14 and JAGUAR ® C17. Also Esaflor 0X 14B from Lamberti.

- 5 In a preferred composition according to the invention the cationic polygalactomannans are selected from guar hydroxypropyltrimethylammonium chlorides having a charge density ranging from 0.5 to 1.8 meq/g (and mixtures thereof), at a level ranging from 0.15 to 0.2% by weight based on the total weight of the composition.
- 10 The cationic deposition polymer is preferably present in an amount of from 0.05 to 1 wt %, preferably from 0.1 to 0.5 wt %, most preferably from 0.15 to 0.2 wt % based on the total weight of the composition.

The hair substantive cationic conditioning polymer

15

The composition of the invention includes a hair substantive cationic conditioning polymer which is an APTAC polymer having a molecular weight of less than 1 million Daltons, preferably selected from a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride and a (3-acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer.

20

WO2013/122861 describes the synthesis of (3-acrylamidopropyl) trimethyl ammonium chloride (APTAC) homopolymers of varying molecular weights, using a radical polymerisation reaction. According to the described method, APTAC monomer is polymerised in an aqueous medium by a discontinuous adiabatic process using an azo or persulfate radical initiator. The APTAC homopolymers so obtained have molecular weights ranging from about 100,000 g/mol to about 1,000,000 g/mol. The molecular weight can be determined by using standard analytical measurements, such as size exclusion chromatography (SEC).

25

30

A polymer suitable for use in the invention is commercially available from Ashland, Inc.

- 11 -

as N-DurHance™ A-1000 Conditioning Polymer (supplied as a 20% a.i. aqueous solution of the polymer). A suitable copolymer of (3-acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer is available from Ashland as N-DurHance AA2000.

- 5 The APTAC polymer for use in the invention, preferably has a charge density at pH 7 of greater than 3, most preferably from 4 to 6.

The APTAC polymer for use in the invention has a molecular weight of less than 1 million Daltons, more preferably 100,000 to 950,000 Daltons, most preferably from 200,000 to
10 900,000 Daltons.

In a preferred embodiment the APTAC polymer has a charge density at pH 7 of from 4 to 6. and a molecular weight of 100,000 to 950,000 Daltons.

- 15 Suitable methods of measuring charge density and molecular weight are as given above.

In a typical composition according to the invention the level of polymer (*per se* as active ingredient) generally ranges from 0.05 to 5 %, more preferably from 0.1 to 2%, most preferably from 0.15 to 1 % (by weight based on the total weight of the composition).

20

Preferably the composition comprises an isotropic surfactant phase, where under dilution, isotropic micelles provide higher availability of monomers to the air/water interface, whereas anisotropic may diffuse at a slower rate, resulting in lower flash foam properties. Thus, the isotropic phase is advantageous for product appearance, clarity and good flash foam
25 properties.

The surfactants

- 30 All amounts referred to herein are based on 100 % activity (or “active”) unless otherwise stated. By 100 % activity (or “active”) is meant that the material is not diluted and is at 100 % v/v or wt/wt. Many materials used in personal care formulations are commercially available at different active concentrations, for example at 70 % active or 60 % active. For example, 100 ml of 70 % active surfactant provides the same amount of active material as 70 ml of

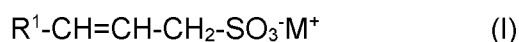
- 12 -

100 % active surfactant. Therefore, in order to provide for variations in activities of materials, all amounts are based on 100 % active materials.

The composition comprises a total amount of anionic, amphoteric and zwitterionic surfactant consisting of (i) and (ii) below. That is to say, no further anionic, amphoteric and zwitterionic surfactants are present in the compositions of the invention. Preferably, no other surfactants, for example, nonionic surfactants are present in the compositions of the invention.

(i) The alpha olefin sulfonate anionic surfactant

The composition of the invention comprises (i) one or more alpha olefin sulfonate anionic surfactants of general formula (I)



in which R^1 is selected from linear or branched alkyl groups having from 11 to 13 carbon atoms and mixtures thereof; and M is a solubilizing cation;

Preferably R^1 in general formula (I) is a C_{14} or C_{16} linear alkyl group.

Preferably M in general formula (I) is selected from alkali metal cations (such as sodium or potassium), ammonium cations and substituted ammonium cations (such as alkylammonium, alkanolammonium or glucammonium).

Commercially produced alpha olefin sulfonate anionic surfactants of general formula (I) may be made by sulfating C_{14} - C_{16} olefins derived from natural gas. The process can also yield mixtures of homologues and low levels of unreacted olefins.

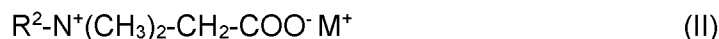
Particularly preferred is alpha olefin sulfonate with an average of 14-16 carbons. A suitable example of such a material is Bioterge AS40 (ex Stepan).

The amount of alpha olefin sulfonate anionic surfactant, at 100 % activity, of general formula (I) ranges from 3 to 13 %, for example from 3 to 12.85 %, preferably from 3.5 to 12%, more preferably from 3 to 10%, still more preferably from 3 to 9% and most preferably from 3.25 to 8% (by weight based on the total weight of the composition).

- 13 -

(ii) The amphoteric or zwitterionic surfactant of general formulae (II), (III), (IV) or (V)

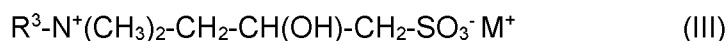
The composition of the invention comprises (ii) an amphoteric or zwitterionic surfactant, selected from an alkyl betaine of general formula (II)



5

wherein R^2 = C12 (Lauryl) or Coco derived;

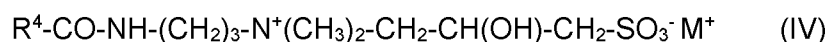
an alkyl hydroxy sultaine of general formula (III),



10

wherein R^3 = C12 (Lauryl) or Coco derived;

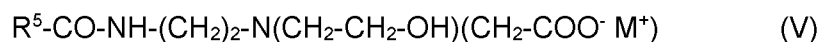
an alkyl aminopropyl hydroxy sultaine of general formula (IV),



15

wherein R^4 = C12 (Lauryl) or Coco derived;

an alkyl amphotoacetate of general formula (V),



20

wherein R^5 = C12 (Lauryl) or Coco derived;

and mixtures thereof.

25 The preferred surfactant (ii) is selected from coco betaine, lauryl hydroxy sultaine, coco aminopropyl hydroxy sultaine, lauryl amphotoacetate and mixtures thereof, most preferably selected from coco betaine, lauryl hydroxy sultaine and mixtures thereof.

30 The amount of amphoteric or zwitterionic surfactants of general formula (II), (III), (IV) or (V) or mixtures thereof, preferably ranges from 1 to 6%, more preferably from 1 to 5%, most preferably from 1.2 to 4 % (based on the total weight of the composition and 100 % activity).

In a preferred composition according to the invention the amphoteric or zwitterionic surfactant (ii) is selected from coco betaine, lauryl hydroxy sultaine, coco aminopropyl

- 14 -

hydroxy sultaine, lauryl amphoacetate and mixtures thereof, in an amount ranging from 1 to 4 % (by weight based on the total weight of the composition and 100 % activity).

In a more preferred composition the amphoteric or zwitterionic surfactant (ii) is selected from a betaine amphoteric surfactant of general formula (II), which is coco betaine, an amphoteric surfactant of general formula (III), which is lauryl hydroxy sultaine, and mixtures thereof, in an amount of from 1 to 4 % (by weight based on the total weight of the composition and 100 % activity).

An especially preferred composition according to the invention comprises (i) alpha olefin sulfonate in an amount ranging from 3.25 to 8% (by weight based on the total weight of the composition and 100 % active material); and (ii) an amphoteric or zwitterionic surfactant selected from coco betaine, lauryl hydroxy sultaine, coco aminopropyl hydroxy sultaine, lauryl amphoacetate or mixtures thereof, in an amount ranging from 1 to 4 % (by weight based on the total weight of the composition and 100 % active material).

The combined amount of (i) and (ii) ranges from 4 to 19 wt %, preferably from 5 to 15 wt %, most preferably from 5 to 11 wt % (based on the total weight of the composition and 100 % activity).

The weight ratio of the alpha olefin sulfonate anionic surfactant (i) to the amphoteric surfactant (ii) ranges from 1:1 to 6:1, preferably from 1.5:1 to 4.5:1 and most preferably 2:1 to 4:1.

The pH of the composition of the invention ranges from 3 to 6.5, preferably from 3.5 to 5.1, more preferably from 4 to 5.

A protonating agent may be used for achieving the low pH. Suitable protonating agents are acids. Suitable acids useful herein include hydrochloric acid, citric acid, acetic acid, tartaric acid, fumaric acid, lactic acid, malic acid, succinic acid, and mixtures thereof. Preferably, the acid is selected from the group consisting of citric acid, acetic acid, tartaric acid, hydrochloric acid, fumaric acid, lactic acid and mixtures thereof.

- 15 -

The Suspending agent

The composition of the invention includes one or more suspending agents. Suitable suspending agents are selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearate, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof. Ethylene glycol distearate and polyethylene glycol 3 distearate are preferred long chain acyl derivatives, since these impart pearlescence to the composition. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used; they are available commercially as Carbopol 910, Carbopol 934, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing monomer and acrylic acid esters is Carbopol 1342. All Carbopol (trademark) materials are available from Goodrich.

Suitable cross-linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

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

The suspending agent will generally be present in a shampoo composition for use in the invention at levels of from 0.1 to 10%, preferably from 0.15 to 6%, more preferably from 0.2 to 4% by total weight of suspending agent based on the total weight of the composition

Water

The aqueous composition of the invention preferably comprises from about 50 to about 90%, preferably from about 55 to about 85%, more preferably from about 60 to about 85%, most preferably from about 65 to about 83% water (by weight based on the total weight of the composition).

- 16 -

The inorganic electrolyte

We have found that, surprisingly, the compositions of the invention are amenable to building viscosity very well. It is thus possible to build viscosity at lower concentrations at enriched
5 surfactant ratios. This is further advantage of the invention.

The composition of the invention preferably includes at least one inorganic electrolyte. The inorganic electrolyte provides viscosity to the composition.

10 The viscosity of the composition ranges from 2,500 to 25,000 mPa.s, preferably from 3,000 to 20,000 mPa.s, more preferably from 3,500 to 15,000 mPa.s, most preferably from 4,000 to 12,000 mPa.s when measured using a Brookfield V2 viscometer (spindle RTV5, 1 minute, 20rpm) at 30°C.

15 At these ranges our products are pourable yet thick enough to satisfy the consumer desire for thick compositions.

Suitable inorganic electrolytes include metal chlorides (such as sodium chloride, potassium chloride, calcium chloride, magnesium chloride, zinc chloride, ferric chloride and aluminium
20 chloride) and metal sulfates (such as sodium sulfate and magnesium sulfate).

It is intended that the inorganic electrolyte is separate from any inorganic electrolytes that may be present in the raw materials of the invention.

Examples of preferred inorganic electrolytes for use in the invention include sodium chloride,
25 potassium chloride, magnesium sulfate and mixtures thereof.

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

The amount of inorganic electrolyte in compositions of the invention preferably ranges from 0.5
30 to 10 %, more preferably from 0.75 to 7 %, even more preferably from 1 to 5 % and most preferably from 1 to 3 % (by weight based on the total weight of the composition).

A preferred composition of the invention has a weight ratio of (i) an alpha olefin sulfonate anionic surfactant of general formula (I) to (ii) an amphoteric or zwitterionic surfactant of

- 17 -

general formula (II), (III), (IV), (V) or mixtures thereof, of from 2:1 to 4:1 and comprises an amount of inorganic electrolyte of from 1 to 3 wt % based on total weight of the composition.

A further preferred composition of the invention has a weight ratio of (i) an alpha olefin sulfonate anionic surfactant of general formula (I) to (ii) an amphoteric or zwitterionic surfactant of general formula (II), (III), (IV), (V) or mixtures thereof, of from greater than 4:1 to 6:1, preferably 5:1 to 6:1 and comprises an amount of inorganic electrolyte of from 1 to 5, preferably from greater than 3 to 5 wt %, more preferably 4 to 5 wt % based on total weight of the composition.

Preferably, the compositions of the invention are free from thickening agents selected from thickening polymers and secondary surfactants not included in (ii). In the context of the invention, by free from is meant having less than 0.4 weight %, more preferably less than 0.1 weight %, even more preferably less than 0.05 weight %, still more preferably less than 0.001 weight %, yet preferably less than 0.0001 weight %, and most preferably 0 weight % of thickening agents by weight of the total composition. For the sake of clarity, the cationic polymer (iii) of the invention is not intended to be a thickening polymer.

A preservative

The composition of the invention preferably comprises one or more preservatives, selected from sodium benzoate, sodium salicylate, benzyl alcohol, phenoxyethanol, 1,2-alkanediols, lodopropynyl butylcarbamate (IPBC), 5-chloro-2-methyl-2H-isothiazol-3-one, 2-methyl-2H-isothiazol-3-one, or mixtures thereof. Preferably the preservative is an organic acid, most preferably the preservative is sodium benzoate.

A preferred composition has a pH of from 3 to 5.8, preferably 4 to 5 and comprises a preservative that is sodium benzoate.

Other ingredients

Preferably, the composition of the invention further comprises one or more structurants to assist in the suspension of dispersed benefit agent and provide phase stability. Suitable structurants include polyacrylic acids, polymethacrylic acids, cross-linked polymers of acrylic

- 18 -

acid, cross-linked polymers of methacrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of methacrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, copolymers of carboxylic acid-containing monomers and methacrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, cross-linked copolymers of methacrylic acid and acrylate esters heteropolysaccharide gums and crystalline long chain acyl derivatives.

Preferred structurants are selected from polyacrylic acids, polymethacrylic acids, cross-linked polymers of acrylic acid, cross-linked polymers of methacrylic acid and mixtures thereof.

Mixtures of any of the above structurants may be used.

When included, the total amount of structurant is generally 0.1 to 10 %, preferably from 0.1 to 3 %, more preferably from 0.2 to 2 %, most preferably from 0.3 to 0.9 % (by weight based on the total weight of the composition).

A preferred composition comprises a structurant selected from polyacrylic acids, polymethacrylic acids, cross-linked polymers of acrylic acid, cross-linked polymers of methacrylic acid and mixtures thereof in an amount of from 0.1 to 10 %, preferably from 0.1 to 3 %, more preferably from 0.2 to 2 %, most preferably from 0.3 to 0.9 % (by weight based on the total weight of the composition).

A composition of the invention may contain further optional ingredients to enhance performance and/or consumer acceptability. Examples of such ingredients include fragrance, dyes and pigments. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally, these optional ingredients are included individually at an amount of up to 5% (by weight based on the total weight of the composition).

The composition of the invention is primarily intended for topical application to the hair and scalp.

- 19 -

Most preferably the composition of the invention is topically applied to the hair and then massaged into the hair and scalp. The composition is then rinsed off the hair and scalp with water prior to drying the hair.

- 5 The invention will be further illustrated by the following, non-limiting Examples.

EXAMPLES

Example 1: Preparation of Compositions 1 to 2 in accordance with the invention

- 10 Rinse-off aqueous hair cleansing shampoo formulations may be prepared, having ingredients as shown in Table 1 below.

The shampoos may suitably be prepared using the following method:

- 15 1. A vessel was charged with water. Surfactants and any structurant were added with stirring.
2. The mixture was heated to 30° C and mixed until completely homogenous.
3. The silicone emulsion was then added and mixed well.
4. The Acrylamidopropyltrimonium Chloride/Acrylamide Copolymer was then added and
20 mixed well.
5. The pH was adjusted to pH 4.5 using citric acid.

- 20 -

Table 1: Compositions 1 and 2 in accordance with the invention

INCI and/or Trade Name	% active	1	2
Alpha Olefin Sulfonate (Bioterge AS-40)	38.5	19.09	19.09
Coco betaine / Genagen KB	30	8.83	-
Lauryl Hydroxy Sultaine / Mackam LHS E	50	-	5.30
Acrylamidopropyltrimonium Chloride/Acrylamide Copolymer ¹	20	1	1
Guar Hydroxypropyltrimonium Chloride	100	0.185	0.185
Citric acid	100	to pH 4.5	to pH 4.5
Carbomer	100	0.3	0.3
Perfume	100	0.5	0.5
Dimethiconol / TEA-dodecylbenzene sulfonate	50	3	3
Water	to 100	to 100%	to 100%

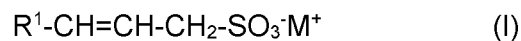
¹N-DurHance™ AA2000 ex Ashland

CLAIMS

1. An aqueous, sulphate free shampoo composition for hair and scalp comprising:-
- a. a pre-formed emulsified silicone;
 - 5 b. a cationic deposition polymer;
 - c. a hair substantive cationic conditioning polymer which is an APTAC polymer having a molecular weight of less than 1 million Daltons, preferably selected from a homopolymer of (3-acrylamidopropyl) trimethyl ammonium chloride and a (3-acrylamidopropyl) trimethyl ammonium chloride/acrylamide copolymer; wherein the
 - 10 APTAC polymer;
 - d. a total amount of anionic surfactant, amphoteric surfactant and zwitterionic surfactant consisting of:

(i) from 3 wt % to 13 wt %, by weight of the total composition at 100 % activity, of an

15 alpha olefin sulfonate anionic surfactant of general formula (I):



in which R¹ is selected from linear or branched alkyl groups having from 11 to 13

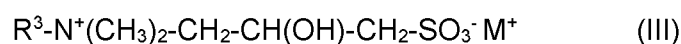
20 carbon atoms and mixtures thereof; and M is a solubilizing cation;

(ii) from 1 to 6%, by weight of an amphoteric or zwitterionic surfactant, selected from an alkyl betaine of general formula (II)



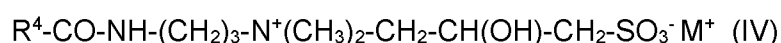
wherein R² = C12 (Lauryl) or Coco derived;

an alkyl hydroxy sultaine of general formula (III),



wherein R³ = C12 (Lauryl) or Coco derived;

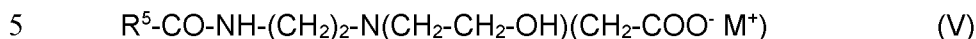
an alkyl aminopropyl hydroxy sultaine of general formula (IV),



- 22 -

wherein R^4 = C12 (Lauryl) or Coco derived;

an alkyl amphoacetate of general formula (V),



wherein R^5 = C12 (Lauryl) or Coco derived;

and mixtures thereof; and

- 10 e. a suspending agent in which the weight ratio of (i) to (ii) ranges from 1:1 to 6:1 and the pH of the composition is from 3 to 6.5;
and wherein the composition has a viscosity from 3,500 to 15,000 mPa.s, preferably from 4,000 to 12,000 mPa.s when measured using a Brookfield V2 viscometer using a spindle RTV5, for 1 minute at 20rpm at 30°C.
- 15 2. A composition as claimed in claim 1, wherein the amount of emulsified silicone is from 0.01 to 10 wt % based on the total weight of the composition and 100 % activity.
- 20 3. A composition according to claim 1 or claim 2, wherein the amount of alpha olefin sulfonate anionic surfactant of general formula (I) is from 3 to 12.85 %, preferably from 3.5 to 12 % by weight based on the total weight of the composition and at 100 % activity.
- 25 4. A composition according to any preceding claim, wherein the amount of amphoteric or zwitterionic surfactants of general formula (II), (III), (IV) or (V) is from 1 to 4 % (based on the total weight of the composition and 100 % activity).
- 30 5. A composition according to any preceding claim, in which the combined amount of (i) and (ii) ranges from 5 wt % to 15 wt % (by weight based on the total weight of the composition).

- 23 -

6. A composition according to any preceding claim, wherein the weight ratio of the alpha olefin sulfonate anionic surfactant (i) to the amphoteric or zwitterionic surfactant (ii) is from 1.5:1 to 4.5:1.
- 5 7. A composition according to any preceding claim, wherein the amphoteric or zwitterionic surfactant (ii) is selected from a betaine amphoteric surfactant of general formula (II), which is coco betaine, an amphoteric surfactant of general formula (III), which is lauryl hydroxy sultaine, and mixtures thereof, in an amount of from 1 to 4 % (by weight based on the total weight of the composition and 100 % activity).
- 10 8. A composition according to any preceding claim, in which the cationic deposition polymer is a cationic polygalactomannan selected from guar hydroxypropyltrimethylammonium chlorides with a charge density ranging from 0.5 to 1.8 meq/g (and mixtures thereof).
- 15 9. A composition according to claim 8, in which the level of the guar hydroxypropyltrimethylammonium chloride(s) ranges from 0.15 to 0.2% by weight based on the total weight of the composition.
- 20 10. A composition as claimed in any preceding claim, wherein the suspending agent is selected from polyacrylic acids, cross-linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and long chain acyl derivatives.
- 25 11. A composition as claimed in any preceding claim, wherein the suspending agent is present at levels of from 0.1 to 10 wt % by total weight of suspending agent based on the total weight of the composition.
- 30 12. A composition as claimed in any preceding claim, wherein the APTAC polymer has a charge density at pH 7 of greater than 3, preferably from 4 to 6.
13. A composition as claimed in any preceding claim, wherein the APTAC polymer has a molecular weight of 100,000 to 950,000 Daltons.

- 24 -

14. A method of treating hair comprising the steps of applying to hair the composition as defined in any one of claims 1 to 11, and performing a first rinse with water.

5 15. A method as claimed in claim 14, which comprises the subsequent steps of applying a conditioner composition and performing a second rinse with water.

16. A composition according to any preceding claim, which is free from thickening agents selected from thickening polymers and secondary surfactants not defined in (ii).

10

17. A composition according to any preceding claim, which comprises an inorganic electrolyte, preferably in amount of inorganic electrolyte of from 0.5 to 3 wt % based on total weight of the composition, and wherein the weight ratio of (i) to (ii) is from 2:1 to 4:1.

15

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/066615

A. CLASSIFICATION OF SUBJECT MATTER		
INV. A61K8/73	A61K8/81	A61K8/89 A61Q5/02 A61Q5/12
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/076747 A1 (BIERGANNIS PATRIC [DE] ET AL) 29 March 2012 (2012-03-29) paragraph [0002] table 8A	1-17
A	----- US 2018/015009 A1 (SOUBIRAN LAURENCE [FR] ET AL) 18 January 2018 (2018-01-18) paragraph [0011] example 7; table 7	1-16
A	----- WO 2018/007332 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC D/B/A UNILEVER [US]) 11 January 2018 (2018-01-11) page 1, lines 5-6 example 1 ----- -/-	1-16
☒ 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 31 August 2020		Date of mailing of the international search report 08/09/2020
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 Durand-Oral, Ilknur

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/066615

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/002868 A1 (BIERGANNNS PATRIC [DE] ET AL) 6 January 2011 (2011-01-06) the whole document -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/066615

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012076747	A1	29-03-2012	NONE
US 2018015009	A1	18-01-2018	NONE
WO 2018007332	A1	11-01-2018	AR 108953 A1 10-10-2018
		BR 112018074602 A2 19-03-2019	
		CN 109328054 A 12-02-2019	
		EA 201892433 A1 31-07-2019	
		EP 3481363 A1 15-05-2019	
		JP 2019519551 A 11-07-2019	
		PH 12018502552 A1 14-10-2019	
		US 2019231672 A1 01-08-2019	
		WO 2018007332 A1 11-01-2018	
		ZA 201808055 B 26-02-2020	
US 2011002868	A1	06-01-2011	BR PI1015950 A2 26-04-2016
		CN 102471734 A 23-05-2012	
		EP 2449079 A1 09-05-2012	
		ES 2657681 T3 06-03-2018	
		JP 5656990 B2 21-01-2015	
		JP 2012532223 A 13-12-2012	
		KR 20120107067 A 28-09-2012	
		RU 2012103385 A 10-08-2013	
		US 2011002868 A1 06-01-2011	
		WO 2011003068 A1 06-01-2011	