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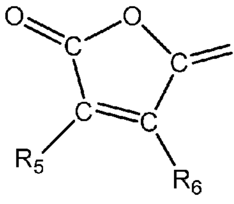
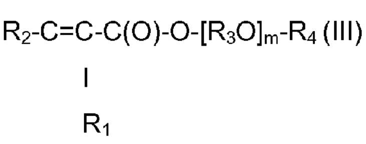
(54) Title: COMPOSITION


(II)


(III)

$$R_2\text{-}\underset{\substack{|\\R_1}}{C}\text{=C-C(O)-O-}[R_3O]_m\text{-}R_4$$

(57) Abstract: An aqueous composition comprising: A) a transparent cleansing base composition comprising: i) at least 0.5 wt.% of the total composition of a cleansing surfactant; ii) at least 0.05 wt.% of the total composition of an addition polymerization product of: a. from 0.1 to 5 wt.% of a first unsaturated monomer A of a ethylenically unsaturated diacid of formula (I): $HOOC\text{-}CR_5\text{=}CR_6\text{-}COOH$ or an unsaturated cyclic anhydride precursor of such an ethylenically unsaturated cis diacid, the anhydride having formula (II) where R_5 and R_6 are individually selected from H, C_1-C_3 alkyl, phenyl, chlorine and bromine; b. from 1 to 60 wt.% of a second ethylenically unsaturated monomer B selected from acrylic acid, methacrylic acid and combinations thereof, c. from 30 to 75 wt.% a (meth)acrylate monomer C selected from C_1 to C_8 alkyl esters of (meth)acrylic acid and C_1 to C_8 alkyl esters of methacrylic acid and combinations thereof, d. from 1 to 25 wt.% of an associative monomer D of the formula (III) where R_1 and R_2 are each independently selected from H, and $C_{1\text{-}3}$ alkyl; R_3 is C_2-C_4 and mixtures thereof, preferably C_2; m, the average number of alkoxy units R_3O, is from 6 to 40; R_4 is alkyl or alkylaryl where the alkyl part is linear or branched; and the total number of carbons is from 6 to 40; e. from 0 to 1.0 wt.% of a cross linking monomer E for introducing branching and controlling molecular weight, the cross linking monomer comprising polyfunctional units carrying multiple reactive functionalization groups selected from the group consisting of vinyl, allylic and functional mixtures thereof; in which any particulate material if present in the base phase has a particle size of less than 0.1 microns; and B) optionally particles having a particle size larger than 200 microns.

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Composition

This invention relates to compositions in the form of structured liquids which are transparent and, more particularly, to cleansing compositions such as shampoos, body washes, and other detersive products for personal care applications

Background

Cleansing compositions comprise anionic surfactants, compositions comprising anionic cleansing surfactants are formulated to provide a microstructure of entangled elongated or rod-like micelles. However, the native yield stress of such compositions is very low so there is a need for an additional suspending agent if it is desired to include colloidal benefit agents such as oily emulsion droplets such as silicones or particulates such as coated mica or insoluble anti-dandruff agents. Traditionally, suspension in shampoo formulations has been achieved either by adding associative thickeners (polymers that build structure by cross-linking the surfactant micelles) or space-filling particles.

The former class of suspending agent is typified by the Hydrophically-modified Alkali Swellable Emulsion (HASE) polymers such as Aculyn 28 ex Rohm & Haas or Carbopol Aqua SF1 ex-Lubrizol. These polymers comprise a polyacrylate backbone, whose solubility is controlled by pH, and hydrophobic pendant groups that associate with surfactant micelles to form a network. Such networks are typically optically transluscent and hence offer a combination of clarity and suspending power. However it has been found that the clarity of the product can be distorted by the presence of additional ingredients, especially particulate materials which are not visible to the naked eye.

Thus there remains the need for improved suspending agents that create a transparent base that can suspend materials such as silicone conditioning materials, such transparent bases are particularly advantageous for suspending visible particulates.

The present invention relates to a way of solving this problem.

Description of the Invention

The present invention relates to an aqueous composition comprising:

A) a transparent cleansing base composition comprising

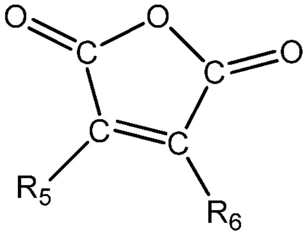
i) at least 0.5 wt. % of the total composition of a cleansing surfactant

ii) at least 0.05 wt. % of the total composition of an addition polymerization product of:

a. from 0.1 to 5 wt. % of a first unsaturated monomer **A** of a ethylenically unsaturated diacid of formula (I):

$$HOOC\text{-}CR_5{=}CR_6\text{-}COOH \qquad (I)$$

or an unsaturated cyclic anhydride precursor of such an ethylenically unsaturated cis diacid, the anhydride having formula (II)



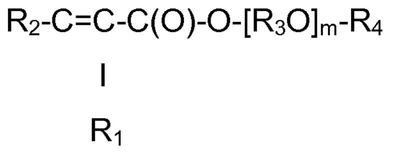
(II)

where R_5 and R_6 are individually selected from H, C_1-C_3 alkyl, phenyl, chlorine and bromine;

b. from 1 to 60 wt. % of a second ethylenically unsaturated monomer **B** selected from acrylic acid, methacrylic acid and combinations thereof,

c. from 30 to 75 wt. % a (meth)acrylate monomer **C** selected from C_1 to C_8 alkyl esters of (meth)acrylic acid and C_1 to C_8 alkyl esters of methacrylic acid and combinations thereof,

d. from 1 to 25 wt. % of an associative monomer **D** of the formula III:



$$R_2\text{-}\underset{\substack{|\\ R_1}}{C}\text{=C-C(O)-O-}[R_3O]_m\text{-}R_4 \qquad \text{(III)}$$

where R_1 and R_2 are each independently selected from H, and $C_{1\text{-}3}$ alkyl; R_3 is C_2-C_4 and mixtures thereof, preferably C_2;
m, the average number of alkoxy units R_3O, is from 6 to 40;
R_4 is alkyl or alkylaryl where the alkyl part is linear or branched; and the total number of carbons is from 6 to 40;

e. from 0 to 1.0 wt. % of a cross linking monomer E for introducing branching and controlling molecular weight, the cross linking monomer comprising polyfunctional units carrying multiple reactive functionalization groups selected from the group consisting of vinyl, allylic and functional mixtures thereof;

in which any particulate material if present in the base phase has a particle size of less than 0.1 microns; and

B) optionally visible particles having a particle size larger than 200 microns.

The invention also relates to a method of cleansing the hair and/or the skin with the above mentioned composition.

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

Detailed Description of the Invention

Copolymer

The copolymers of the invention are based on a combination of monomers that include an ethylenically unsaturated polyacidic monomer such as a maleic derivative, a monoacid ethylenically unsaturated monomer such as an acrylic or methacrylic acid, an acrylate ester monomer an associative monomer and optionally a cross-linker.

Preferably the level of copolymer in the invention is from 0.05 to 1 wt. % of the total composition; more preferably from 0.1 to 0.7 wt. %, most preferably from 0.2 to 0.5 wt. %.

Preferably the copolymer is swollen, more preferably fully swollen in an aqueous solution. The term swollen means an increase in the structured volume of a solution associated with the uptake of a liquid. The term fully swollen means that no further liquid can be uptaken (and hence no increase in viscosity occurs). To obtain such a fully swollen polymer it is preferable if the polymer is dissolved in water and the pH increased until no further change in viscosity occurs. The fully swollen polymer can then be added to the formulation or the formulation is built around the fully swollen polymer. It is preferred if the polymer is swollen before addition of the surfactant.

It is preferable if ranges of the monomeric units in the polymer are as follows:
Monomer A ranges from 0.2 to 1 % by weight of the copolymer;
Monomer B ranges from 25 to 50 % by weight of the copolymer;
Monomer C ranges from 30 to 65 % by weight of the copolymer; and

Monomer D ranges from 2 to 12 % by weight of the copolymer.

In the context of the present invention the weight % of monomer within the copolymer relates to the non-neutralized monomer (not it salt form).

Preferably the weight ratio of monomer A to monomer D is from 1:3 to 1:30; more preferably from 1:5 to 1:25; most preferably from 1:7 to 1:22. These weight ratios are particularly advantageous with the preferred monomers of A and D listed below.

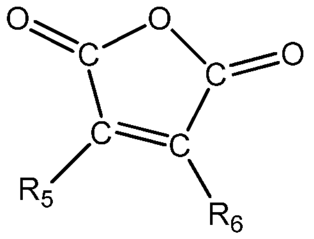
Preferably the copolymer includes neutralized and partially neutralized (non-protonated) forms.

Monomer A

Monomer **A** is an ethylenically unsaturated diacid, preferably cis diacid of formula (I):

$$HOOC\text{-}CR_5\text{=}CR_6\text{-}COOH \qquad (I)$$

or an unsaturated cyclic anhydride precursor of such an ethylenically unsaturated diacid, the anhydride having formula (II)



(II)

where R_5 and R_6 are individually selected from H, C_1-C_3 alkyl, phenyl, chlorine and bromine;

Preferably the copolymer will include a first ethylenically unsaturated monomer which may be maleic, fumaric, itaconic and citraconic acids and anhydrides thereof as well as combinations of these. Most preferred are maleic derivatives. Accordingly, the most preferred species are maleic acid, maleic anhydride or a combination thereof. Preferably maleic acid can be generated from maleic anhydride as starting material and hydrolyzing this to the di acid in the emulsion polymerization.

While both fumaric and itaconic acid are contemplated for use herein, in one or more embodiments, it is preferred the itaconic acid and, in further embodiments, both itaconic and fumaric acid, are absent from the subject copolymers or are individually present in only minor amounts, i.e., less than 0.05 wt. %, preferably less than 0.005 wt. %, based on the total weight of monomer. While both fumaric and itaconic acid are contemplated for use herein, in one or more embodiments, it is preferred the itaconic acid and, in further embodiments, both itaconic and fumaric acid, are absent from the subject copolymers or are individually present in only minor amounts, i.e., less than 0.05 wt. %, preferably less than 0.005 wt. %, based on the total weight of monomer.

The first ethylenically unsaturated acid monomer may be employed in amounts of from 0.1 to 5 wt. %, preferably from 0.2 to 4 wt. %, more preferably from 0.2 to 1 wt. %, and, in one or more embodiments, from 0.3 to 0.6 wt. %, based on the total weight of monomer. In one or more embodiments of particular interest, maleic acid accounts for at least 50 % by weight, more preferably at least 80 % by weight, even more preferably, at least 95 % by weight, based on the total weight of the first ethylenically unsaturated acid monomer.

Monomer B

The second ethylenically unsaturated acid monomer B is selected from acrylic acid, methacrylic acid and combinations thereof.

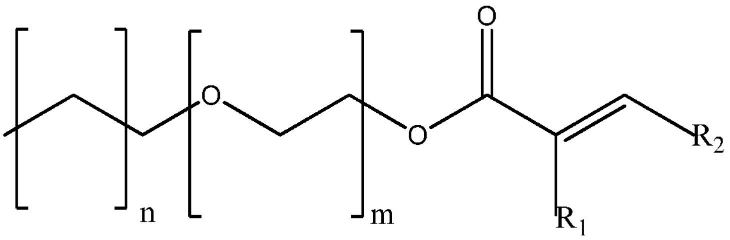
The second ethylenically unsaturated acid monomer may be employed in amounts of from 15 to 60 wt. %, preferably from 20 to 55 wt. %, more preferably from 25 to 50 wt. %, based on total monomer. In one or more embodiments of interest the amount of second ethylenically unsaturated acid monomer is from 40 to 50 wt. % based on total monomer; in one or more other embodiments of interest, the amount of second ethylenically unsaturated acid monomer is from 20 to 40 wt. % based on total monomer. In one or more embodiments of particular interest methacrylic acid accounts for at least 50 % by weight, more preferably at least 70 % by weight, even more preferably, at least 90 % by weight, of the total weight of the second ethylenically unsaturated acid monomer.

Monomer C

The (meth)acrylate monomer C may be selected from C_1 to C_8 alkyl esters of (meth)acrylic acid and C_1 to C_8 alkyl esters of methacrylic acid and combinations thereof, with C_1 to C_4 alkyl esters of such acids, being particularly preferred. Preferred ester monomers are ethyl acrylate, methyl acrylate, ethyl methacrylate, methyl methacrylate, butyl acrylate, and butyl methacrylate, ethyl acrylates is particularly preferred. In one or more embodiments of particular interest, C_1 to C_4 alkyl esters of acrylic acid, preferably ethyl acrylate, account, for at least 50 % by weight, more preferably at least 70 % by weight, even more preferably, at least 90 % by weight of the (meth)acrylate monomer.

Monomer D

D is preferably an associative monomer of formula (I)



(I)

in which each R_1 and R_2 are independently selected from H, C_1 to C_3 alkyl

Preferably R_1 is a methyl group and R_2 is H.

n ranges from 6 to 40 and m ranges from 6 to 40, more preferably n ranges from 10 to 30 and m ranges 15 to 35 most preferably n ranges from 12 to 22 and m ranges from 20 to 30. It is preferable if m is greater or equal to n.

The associative monomer may be employed in amounts of from 1 to 25 wt. %, preferably from 2 to 20 wt. %, and more preferably from 2 to12 wt. %, based on total monomer. In one or more embodiments of particular interest the amount of associate monomer employed is from 5 to 10 wt. %, based on total monomer.

Monomer E

One or more cross linking monomers E may be present in the copolymer for purposes of introducing branching and controlling molecular weight. These monomers will be polyunsaturated. Illustrative but not limiting examples are divinyl benzene, divinyl naphthalene, trivinyl benzene, triallyl pentaerythritol, diallyl pentaerythritol, diallyl sucrose, octaallyl sucrose, trimethylol propane diallyl ether, 1,6-hexanediol di(meth) acrylate, tetramethylene tri(meth) acrylate, trimethylol propane tri(meth)acrylate, polyethoxylated glycol di(meth) acrylate, alkylene bisacrylamides, bisphenol A polyethyoxylated dimethacrylate, trimethylolpropane polyethoxylated trimethacrylate and similar materials. Preferred for the present invention is bisphenol A polyethoxylated glycol diacrylate, diallyl pentaerythritol and trimethylolpropane triacrylate.

Amounts of the cross linking monomer may range from 0 to 1 wt. %, preferably from about 0 to 3 %, more preferably from about 0 to 2 % based on total monomer, optimally the copolymer is free from cross linking polymer.

In some embodiments, one or more the acid groups of the starting acid monomers may be neutralized to salt form. Typical salt counter-ions to the acid groups are alkali metals, especially sodium and potassium, and ammonium and triethanolammonium cations.

Other Ingredients

Compositions in accordance with the invention are preferably formulated as compositions for washing the hair and subsequent rinsing.

Cleansing Surfactant

Compositions of the invention comprise one or more cleansing surfactants which are cosmetically acceptable and suitable for topical application to the hair. Further surfactants may be present as emulsifiers.

Suitable cleansing surfactants are selected from anionic, amphoteric and zwitterionic surfactants, and mixtures thereof. The cleansing surfactant may be the same surfactant as the emulsifier, or may be different.

Compositions of the invention comprise anionic surfactant. Examples of suitable anionic cleansing surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, alkyl ether sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, and alkyl ether carboxylic acids and salts thereof, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18, preferably from 10 to 16 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether sulphosuccinates, alkyl ether phosphates and alkyl ether carboxylic acids and salts thereof may contain from 1 to 20 ethylene oxide or propylene oxide units per molecule.

Typical anionic cleansing surfactants for use in compositions of the invention include sodium oleyl succinate, ammonium lauryl sulphosuccinate, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium lauryl ether sulphosuccinate, ammonium lauryl sulphate, ammonium lauryl ether sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauryl isethionate, lauryl ether carboxylic acid and sodium N-lauryl sarcosinate.

Preferred anionic surfactants are the alkyl sulfates and alkyl ether sulfates. These materials have the respective formulae R_2OSO_3M and $R_1O(C_2H_4O)_xSO_3M$, wherein R_2 is alkyl or alkenyl of from 8 to 18 carbon atoms, x is an integer having a value of from about 1 to about 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium. Most preferably R_2 has 12 to 14 carbon atoms, in a linear rather than branched chain.

Preferred anionic cleansing surfactants are selected from sodium lauryl sulphate and sodium lauryl ether sulphate(n)EO, (where n is from 1 to 3); more preferably sodium lauryl ether sulphate(n)EO, (where n is from 1 to 3); most preferably sodium lauryl ether sulphate(n)EO where n=1.

Preferably the level of alkyl ether sulphate is from 0.5 wt. % to 25 wt. % of the total composition, more preferably from 3 wt. % to 18 wt. %, most preferably from 6 wt. % to 15 wt. % of the total composition.

The total amount of anionic cleansing surfactant in compositions of the invention generally ranges from 0.5 wt. % to 45 wt. %, more preferably from 1.5 wt. % to 20 wt. %.

Compositions of the invention may comprise fatty acyl isethionate, if present preferably at a level of from 1 to 10 wt. %, more preferably from 2 to 8 wt. %, most preferably from 2.5 to 7.5 wt. %.

A preferred fatty acyl isethionate product comprises fatty acyl isethionate surfactant at a level of from 40 to 80 wt. % of the product, as well as free fatty acid and/or fatty acid salt at a level of from 15 to 50 %.

Preferably, greater than 20 wt. % and less than 45 wt. %, more preferably greater than 25 wt. % and less than 45 wt. % of the fatty acyl isethionate are of chain length greater than or equal to C_{16}; and greater than 50 wt. %, preferably greater than 60 wt. % of the free fatty acid/soap is of chain length C_{16} to C_{20}.

In addition, the product may contain isethionates salts which are present typically at levels less than 5 wt. %, and traces (less than 2 wt. %) of other impurities.

Preferably, a mixture of aliphatic fatty acids is used for the preparation of commercial fatty acyl isethionates surfactants. The resulting fatty acyl isethionate surfactants (e.g., resulting from reaction of alkali metal isethionate and aliphatic fatty acid) preferably should have more than 20 wt. %, preferably more than 25 wt. %, but no more than 45 wt. %, preferably 35 % (on basis of fatty acyl isethionates reaction product) of fatty acyl group with 16 or greater carbon atoms to provide both excellent lather and mildness of the resulting fatty acyl isethionate product. These longer chain fatty acyl isethionate surfactants and fatty acids, i.e. fatty acyl group and fatty acid with 16 or more carbons, can typically form insoluble surfactant/fatty acid crystals in water at ambient temperatures.

Examples of commercial fatty acyl isethionate products that are particularly useful in the subject invention are DEFI flakes and Dove® cleansing bar noodles produced by Unilever. DEFI (Direct Esterification of Fatty Isethionate) flakes typically contain about 68 to 80 wt. % of sodium fatty acyl isethionate and 15 to 30 wt. % free fatty acid. More than 25 wt. % and no more than 35 % of fatty acyl group of the resulting fatty acyl isethionate have 16 to 18 carbon atoms. Dove® cleansing bar noodles are mixtures of DEFI flakes described above and long chain (mainly C_{16} and C_{18}) fatty acid and fatty soap which contain about 40 to 55 wt. % of fatty acyl isethionate and 30 to 40 wt. % of fatty acid and fatty soap.

Compositions of the invention may contain non-ionic surfactant. Most preferably non-ionic surfactants are present in the range 0 to 5 wt. %.

Nonionic surfactants that can be included in compositions of the invention include condensation products of aliphatic (C_8 - C_{18}) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups. Alkyl ethoxylates are particularly preferred. Most preferred are alkyl ethoxylates having the formula $R-(OCH_2CH_2)_nOH$, where R is an alkyl chain of C12 to C15, and n is 5 to 9.

Other suitable nonionic surfactants include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

Further nonionic surfactants which can be included in compositions of the invention are the alkyl polyglycosides (APGs). Typically, APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:

$$RO - (G)_n$$

wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about C_5 to about C_{20}. Preferably R represents a mean alkyl chain length of from about C_8 to about C_{12}. G may be selected from C_5 or C_6 monosaccharide residues, and is preferably a glucoside. G may be selected from the group comprising glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably G is glucose.

The degree of polymerisation, n, may have a value of from about 1 to about 10 or more. Most preferably the value of n lies from about 1.3 to about 1.5.

Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.

Other sugar-derived nonionic surfactants which can be included in compositions of the invention include the C_{10}-C_{18} N-alkyl (C_l-C_6) polyhydroxy fatty acid amides, such as the C_{12}-C_{18} N-methyl glucamides, as described for example in WO 92 06154 and US 5 194 639, and the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3-methoxypropyl) glucamide.

Amphoteric or zwitterionic surfactant can be included in an amount ranging from 0.5 wt. % to about 8 wt. %, preferably from 1 wt. % to 4 wt. % of the total composition.

Examples of amphoteric or zwitterionic surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphoacetates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Typical amphoteric and zwitterionic surfactants for use in shampoos of the invention include lauryl amine oxide, cocodimethyl sulphopropyl betaine, lauryl betaine, cocamidopropyl betaine and sodium cocoamphoacetate.

A particularly preferred amphoteric or zwitterionic surfactant is cocamidopropyl betaine.

Mixtures of any of the foregoing amphoteric or zwitterionic surfactants may also be suitable. Preferred mixtures are those of cocamidopropyl betaine with further amphoteric or zwitterionic surfactants as described above. A preferred further amphoteric or zwitterionic surfactant is sodium cocoamphoacetate.

Silicone Conditioning Agents

The compositions of the invention may contain silicone conditioning agents preferably these are emulsified droplets of a silicone conditioning agent, for enhancing conditioning performance.

Suitable silicones include polydiorganosiloxanes, in particular polydimethylsiloxanes which have the CTFA designation dimethicone.

The viscosity of the emulsified silicone itself (not the emulsion or the final hair conditioning composition) 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.

Emulsified silicones if used in the shampoo compositions of the invention will have an average silicone droplet size in the composition of less than 0.15 microns . Preferabley less than 0.1 micron, most preferably less than 0.08 microns. Silicone emulsions having an average silicone droplet size of less than 0.15 micron are generally termed microemulsions.

Examples of suitable pre-formed emulsions include microemulsions DC2-1865 and DC21870,available from Dow Corning (each having an average silicone particle size in the microemulsion of less than 0.15 microns). Also suitable for use with the invention is DC X2-1391 from Dow Corning, which is a microemulsion of cross-linked dimethiconol gum having an average silicone particle size in the microemulsion of 0.045 microns.

The conditioning performance of small particle size emulsified silicone in a surfactant-based shampoo composition can be significantly boosted by the presence of an amino functionalised silicone.

The weight ratio of amino functionalised silicone to nonamino functionalised silicone is generally 1: 2 or less.

Suitably, the ratio of amino functionalised silicone to nonamino functionalised silicone ranges from 1: 2 to 1: 20, preferably 1: 3 to 1: 20, more preferably 1: 3 to 1: 8, optimally around 1: 4

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

The total amount of silicone is preferably from 0.01 wt. % to 10 wt. % of the total composition more preferably from 0.1 wt. % to 5 wt. %, most preferably 0.5 wt. % to 3 wt. %.

Cationic Deposition Polymer

Cationic polymers may be present in the composition of the invention for further enhancing deposition performance.

Suitable cationic polymers may be homopolymers which are cationically substituted or may be formed from two or more types of monomers. The weight average (M_w) molecular weight of the polymers will generally be between 100 000 and 2 million g/mol. The polymers will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof. If the molecular weight of the polymer is too low, then the conditioning effect is poor. If too high, then there may be problems of high extensional viscosity leading to stringiness of the composition when it is poured.

The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the cationic polymer. Thus when the polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition. The ratio of the cationic to non-cationic monomer units is selected to give polymers having a cationic charge density in the required range, which is generally from 0.2 to 3.0 meq/gm. 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.

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the composition. In general secondary and tertiary amines, especially tertiary, are preferred.

Amine substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

The cationic polymers can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic polymers include, for example:

- cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Salcare SC60;

Other cationic polymers that can be used include cationic polysaccharide polymers, such as cationic cellulose derivatives, cationic starch derivatives, and cationic guar gum derivatives. Particularly preferred hydroxyethyl celluloses include Polqquatrnium 10 Polymer JR30M, Polymer JR400, Polymer LR30M and Polymer LR400 (all ex-Amerchol).

Further cationic polysaccharide polymers suitable for use in compositions of the invention include monomers of the formula:

$$A\text{-}O\text{-}[R\text{-}N^{+}(R^{1})(R^{2})(R^{3})X^{-}],$$

wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual. R is an alkylene, oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof. R^1, R^2 and R^3 independently represent alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms. The total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R^1, R^2 and R^3) is preferably about 20 or less, and X is an anionic counterion.

Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24.

Other suitable cationic polysaccharide polymers include quaternary nitrogen-containing cellulose ethers (e.g. as described in U.S. Patent 3,962,418), and copolymers of etherified cellulose and starch (e.g. as described in U.S. Patent 3,958,581).

A particularly suitable type of cationic polysaccharide polymer that can be used is a cationic guar gum derivative, such as guar hydroxypropyltrimethylammonium chloride (commercially available from Rhodia in their JAGUAR trademark series). Particularly preferred for transparent formulations is JAGUAR EXCEL.

Mixtures of any of the above cationic polymers may be used.

Cationic polymer will generally be present in a shampoo composition of the invention at levels of from 0.01 to 5 %, preferably from 0.05 to 1 %, more preferably from 0.08 to 0.5 % by total weight of cationic polymer based on the total weight of the composition.

Particulates

Compositions of the invention may comprise particles having a particle size larger than 200 microns, preferably greater than 300 microns. Such particles are preferably visible to the naked eye and are suspended in the transparent base.

Further Optional Ingredients

The compositions of the present invention may also contain adjuncts suitable for hair care. Generally such ingredients are included individually at a level of up to 2, preferably up to 1 wt. % of the total composition.

Suitable hair care adjuncts include perfumes, fibre actives, antidandruff agents, amino acids, sugars, preservatives, pH adjusters and ceramides.

Preferably salt is present at levels from 0.1 to 1 wt. % of the total composition to adjust the product viscosity.

Preferably NaOH is present at levels from 0.1 to 1 wt. % of the total composition to to initially swell the polymer.

Preferably the PH of the formulation is below 7, as this gives greater clarity. Preferably citric acid is used to adjust the pH of the formulation

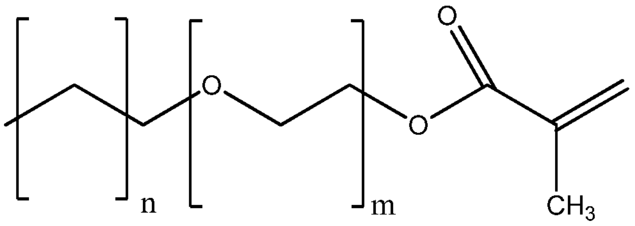
The invention will now be further illustrated by the following, non-limiting Examples. Examples of the invention are illustrated by a number, comparative Examples are illustrated by a letter.

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

Examples

Example 1

Associative Monomer Synthesis



n = 12

m = 23

Brij® 35P (150g) was dissolved in 500ml anhydrous dichloromethane under a nitrogen atmosphere and cooled in an ice bath to 5°C. Triethylamine (18.6g) was added via syringe before methacryloyl chloride (20.9g) was added dropwise over a 30 minute period. After complete addition, the solution was allowed to warm to room temperature and the reaction stirred for 4 weeks. The solution was then filtered to remove the resulting precipitate and washed once with saturated sodium hydrogen carbonate solution (200ml) and once with saturated brine (200ml). The solution was then passed through a column containing basic alumina before the product was dried with anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. In subsequent examples the product is referred to as Surfmer D1.

HASE copolymer synthesis

A round bottom flask was charged with ethyl acrylate (66.8g), methacrylic acid (37.7g), maleic anhydride (0.515g) and SurmerD1(10.0g). The mixture was sealed and purged with nitrogen for 60 minutes before sodium dodecyl sulfonate (1.03 g) and deoxygenated water (26.5g) was added and stirred forming a pre-emulsion. A multineck round bottom flask was fitted with a nitrogen sparge and overhead stirrer. Deoxygenated water (181g) and sodium dodecyl sulfonate (0.298g) were added, stirred at 250 rpm and heated to 90°C. Ammonium persulfate (0.073g) in water (1ml) was added via syringe. The pre-emulsion was fed into the surfactant solution via peristaltic pump over 150 minutes. After complete addition, ammonium persulfate (0.033g) in water (1ml) was added and the reaction stirred for a further 240 minutes. Copolymers in Table 1 were synthesised by using suitable adaptations of this process.

Table 1

	Raw Material Charge (Weight in Grams)			
Component	Polymer 1.1	Polymer 1.2	Polymer 1.3	Polymer 1.4
Pre-emulsion				
Ethyl Acrylate	66.8	74.0	70.7	54.2
Methacrylic Acid	37.7	41.7	43.1	30.6
Maleic anhydride	0.515	0.57	0.71	0.506
Surfmer D1	10.0	4.26	7.91	8.12
Water	26.5	29.3	36.0	21.5
Sodium Dodecyl Sulphonate	1.03	1.14	1.18	0.84
Surfactant solution				
Deoxygenated Water	181.0	200.6	207.3	147.1
Sodium Dodecyl Sulphonate	0.298	0.33	0.341	0.242
Ammonium Persulfate Solution	0.073	0.081	0.084	0.059
Post Addition				
Ammonium Persulfate Solution	0.033	0.036	0.037	0.026

Table 2

Polymer composition	MAA w%	MA w%	EA w%	Surfmer w%
Copolymer 1	32.8	0.45	58.1	8.7

Preparation of shampoo formulations

Polymer solution (13.33 g)(Copolymer 1 or Carbopol Aqua SF1) was added to water (391.88 g) aided by mixing with an overhead stirrer. The pH was adjusted to pH 12.00 using sodium hydroxide (50w%) before Sodium Lauryl Ether Sulfate

(428.57 g) (Aqueous solution containing 28 wt. % active; herein abbreviated as SLES). Tegobetaine® CK KB 5 (53.33 g) (Cocoamidopropyl Betaine (aqueous solution containing 30 wt. % active; herein abbreviated as CAPB), EDTA 4Na soln versene 100A (1.28 g), Nipaguard DMDM H/Glydant Ltd (1.00 g) and preservative (0.6 ml) were added. The pH was adjusted with citric acid. The solution was split into 90 g aliquots and the appropriate level of sodium chloride added as in Table 3.

Clarity was measured using a SpectraMax Microplate Spectrophotometer for UV/VIS absorbance measurements at 420nm. Nunc Nuclon D microtitre plates with well capacity of 200 microlitres were used for the measurements. Each well was loaded with 60 microlitres of sample and four wells were used for each sample with an average value being taken. The value for demineralized water was then deducted from the sample value and the following results obtained:

Table 3

Example	**Polymer type/pH/NaCl**	**Absorbance**
Example 1	Copolymer 1/PH6.5 0% NaCL	0.17
Example A	Carbopol Aqua SF1 1/PH6.5 0% NaCL	0.20
Example 2	Copolymer 1/PH6.5 0.5% NaCL	0.16
Example B	Carbopol Aqua SF1 1/PH6.5 0.5% NaCL	0.25
Example 3	Copolymer 1/PH6.5 1% NaCL	0.14
Example C	Carbopol Aqua SF1 1/PH6.5 1.% NaCL	0.35
Example 4	Copolymer 1/PH6.5 1.5% NaCL	0.20
Example D	Carbopol Aqua SF1 1/PH6.5 1.5% NaCL	0.52
Example 5	Copolymer 1/PH6.5 2% NaCL	0.29
Example E	Carbopol Aqua SF1 1/PH6.5 2% NaCL	0.73

High absorbance indicates less transparency. Thus the formulations according to the invention are more transparent than the comparative examples.

Preparation of body wash formulations

Base formuation Copolymer solution (30 ml) was added to water (745.2 g) aided by mixing with an overhead stirrer. The pH was adjusted to pH 12.00 using sodium hydroxide (50w%) before Sodium Lauryl Ether Sulfate (107.1 g), Tegobetaine® CK KB 5 (83.3 g) and Kathon CG/ICP II (1.0 ml) were added. The solution was split into 96.7 g aliquots from which base formulations were prepared. Examples were made up as in table 4 by adjusting the pH and adding the appropriate level of sodium chloride:

Clarity was measured using a SpectraMax Microplate Spectrophotometer for UV/VIS absorbance measurements at 420nm. Nunc Nuclon D microtitre plates with well capacity of 200 microlitres were used for the measurements. Each well was loaded with 60 microlitres of sample and four wells were used for each sample with an average value being taken. The value for demineralized water was then deducted from the sample value and the following results obtained:

Table 4

Example	Formulation	Absorbance
F	Carbopol Aqua SF1 pH 5, 0% NaCl	1.00
6	Copolymer 1 pH 5, 0% NaCl	0.41
G	Carbopol Aqua SF1 pH 5, 1% NaCl	1.50
7	Copolymer 1 pH 5, 1% NaCl	0.55
H	Carbopol Aqua SF1 pH 6, 0% NaCl	0.82
8	Copolymer 1 pH 6, 0% NaCl	0.45
I	Carbopol Aqua SF1 pH 6, 1% NaCl	1.10
9	Copolymer 1 pH 6, 1% NaCl	0.54
J	Carbopol Aqua SF1 pH 6.75, 0% NaCl	0.21
10	Copolymer 1 pH 6.75, 0% NaCl	0.14
K	Carbopol Aqua SF1 pH 6.75, 2% NaCl	0.45
11	Copolymer 1 pH 6.75, 2% NaCl	0.10

Body wash formulations according to the invention are more transparent than the comparative formulations.

Claims

1. An aqueous composition comprising:

A) a transparent cleansing base composition comprising

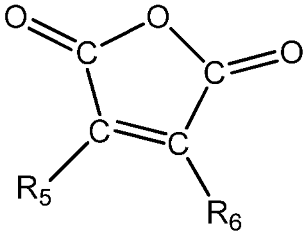
i) at least 0.5 wt. % of the total composition of a cleansing surfactant

ii) at least 0.05 wt. % of the total composition of an addition polymerization product of:

a. from 0.1 to 5 wt. % of a first unsaturated monomer **A** of a ethylenically unsaturated diacid of formula (I):

a. $HOOC\text{-}CR_5\text{=}CR_6\text{-}COOH$ (I)

or an unsaturated cyclic anhydride precursor of such an ethylenically unsaturated cis diacid, the anhydride having formula (II)



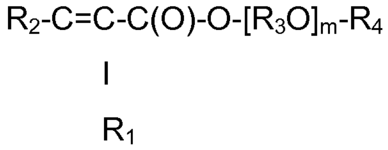
(II)

where R_5 and R_6 are individually selected from H, C_1-C_3 alkyl, phenyl, chlorine and bromine;

b. from 1 to 60 wt. % of a second ethylenically unsaturated monomer **B** selected from acrylic acid, methacrylic acid and combinations thereof,

c. from 30 to 75 wt. % a (meth)acrylate monomer **C** selected from C_1 to C_8 alkyl esters of (meth)acrylic acid and C_1 to C_8 alkyl esters of methacrylic acid and combinations thereof,

d. from 1 to 25 wt. % of an associative monomer **D** of the formula III:



$$R_2\text{-}C\text{=}\underset{\substack{|\\ R_1}}{C}\text{-}C(O)\text{-}O\text{-}[R_3O]_m\text{-}R_4 \quad \text{(III)}$$

where R_1 and R_2 are each independently selected from H, and C_{1-3} alkyl; R_3 is C_2-C_4 and mixtures thereof, preferably C_2; m, the average number of alkoxy units R_3O, is from 6 to 40; R_4 is alkyl or alkylaryl where the alkyl part is linear or branched; and the total number of carbons is from 6 to 40;

e. from 0 to 1.0 wt. % of a cross linking monomer E for introducing branching and controlling molecular weight, the cross linking monomer comprising polyfunctional units carrying multiple reactive functionalization groups selected from the group consisting of vinyl, allylic and functional mixtures thereof;

in which any particulate material if present in the base phase has a particle size of less than 0.1 microns; and

B) optionally particles having a particle size larger than 200 microns.

2. A composition according to any preceding claim in which the copolymer is at least partially neutralized.

3. A composition according to any preceding claim in which cross linking monomer E is not present.

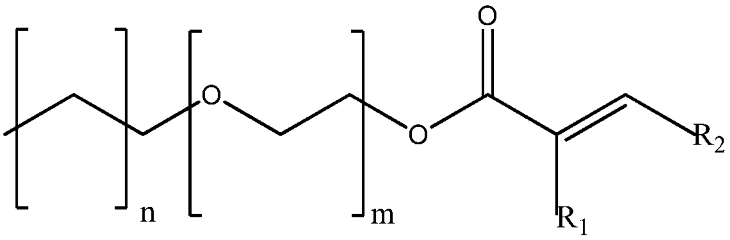
4. A composition according to any preceding claim in which the monomer A is selected from the group consisting of maleic anhydride, maleic acid and salts thereof.

5. A composition according to any preceding claim in which the monomer B is methacrylic acid.

6. A composition according to any preceding claim in which monomer C of the copolymer is ethylacrylate or butyl acrylate.

7. A composition according to any preceding claim in which the monomer E is not present.

8. A composition according to any preceding claim in which associative monomer **D** is of the formula:



(I)

in which each R_1 and R_2 are independently H, C_1 to C_3 alkyl

n ranges from 6 to 40 and m ranges from 6 to 40.

9. A composition according to any preceding claim in which for monomer D n ranges from 12 to 22 and m ranges from 20 to 30.

10. A composition according to any preceding claim in which in monomer D is R_1 is H or methyl and R_2 is H.

12. A composition according to any preceding claim in which for the copolymer:
    a ranges from 0.2 to 1 % by weight of the copolymer;
    b ranges from 25 to 50 % by weight of the copolymer;
    c ranges from 40 to 65 % by weight of the copolymer; and
    d ranges from 5 to 15 % by weight of the copolymer
    e ranges from 0.01 to 5 wt. % by weight of the copolymer.

13. A composition according to any preceding claim in which the level of copolymer is from 0.05 to 1.0 wt. % of the total composition.

14. A composition according to any preceding claim in which the level of anionic surfactant is from 1.5 wt. % to 20 wt. % of the total composition.

15. A composition according to any preceding claim in which the particulate material in the base phase A) comprises a silicone conditioning agent.

16. A composition according to any preceding claim in which the silicone conditioning agent has an average silicone droplet size of less than 0.15 micron.

17. A composition according to any preceding claim which further comprises a cationic deposition aid.

18. A method of cleansing the hair or skin comprising the step of applying to the hair and/or skin a composition according to any preceding claim.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/051400

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/81 A61Q19/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K A61Q

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 5 266 646 A (EISENHART ERIC K [US] ET AL) 30 November 1993 (1993-11-30) column 1, line 10 - column 11, line 9; claims; examples 1,30; table IV -----	1-10, 12-14,18 15,16
Y	WO 2007/090759 A1 (CIBA SC HOLDING AG [CH]; WESTON RACHEL CLARE [GB]; DUNGWORTH HOWARD RO) 16 August 2007 (2007-08-16) page 1, line 1 - page 8, line 14 page 12, line 13 - page 15, line 15 page 19, line 29 - page 20, line 19 page 27, line 14 - line 25; examples A,1-4; table 1 ----- -/--	15,16

☒ 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 13 March 2014	Date of mailing of the international search report 21/03/2014
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 Loloiu, Teodora

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/051400

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/045646 A1 (TAMARESELVY KRISHNAN [US] ET AL) 21 February 2008 (2008-02-21) paragraph [0010] - paragraph [0027]; claims; examples 1-8,51,53-55,60,61.65 paragraph [0103] - paragraph [0109] -----	15,16
X,P	WO 2013/045377 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; CONOPCO) 4 April 2013 (2013-04-04) page 9, line 11 - line 23; examples 1,2; tables I,II page 3, line 10 - page 8, line 24 -----	1,2,4,5, 8-10, 12-14,17

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/051400

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5266646	A	30-11-1993	NONE		
WO 2007090759	A1	16-08-2007	NONE		
US 2008045646	A1	21-02-2008	AR 038162	A1	29-12-2004
			AT 400594	T	15-07-2008
			AU 2003209240	A1	02-09-2003
			BR 0306975	A	09-11-2004
			CA 2473241	A1	31-07-2003
			EP 1465932	A1	13-10-2004
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			MX 261407	B	15-10-2008
			TW 200302232	A	01-08-2003
			US 2003207988	A1	06-11-2003
			US 2008045646	A1	21-02-2008
			WO 03062288	A1	31-07-2003
WO 2013045377	A1	04-04-2013	NONE		