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- (54) Title  
**Cosmetic compositions containing a vinyl dimethicone/dimethicone copolymer in aqueous emulsion and an associative thickener, and uses thereof**
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**ABSTRACT**

**COSMETIC COMPOSITIONS CONTAINING A VINYL  
DIMETHICONE/DIMETHICONE COPOLYMER IN AQUEOUS  
EMULSION AND AN ASSOCIATIVE THICKENER,  
AND USES THEREOF**

The invention relates to novel cosmetic compositions comprising, in a cosmetically acceptable medium, at least one dimethicone containing ethylenic unsaturation/dimethicone copolymer with a viscosity of between  $10^6$  and  $100 \times 10^6$  cP in aqueous emulsion and at least one associative thickener.

This combination gives cosmetic properties (smoothness, lightness, softness) without the phenomenon of regreasing keratin fibres.

These compositions are used in particular for washing and/or conditioning keratin materials such as the hair or the skin.

AUSTRALIA  
Patents Act 1990

**COMPLETE SPECIFICATION**  
**STANDARD PATENT**



**Applicant(s):**

L'OREAL

**Invention Title:**

COSMETIC COMPOSITIONS CONTAINING A VINYL  
DIMETHICONE/DIMETHICONE COPOLYMER IN AQUEOUS EMULSION  
AND AN ASSOCIATIVE THICKENER, AND USES THEREOF

The following statement is a full description of this invention, including the best method of performing it known to me/us:

**COSMETIC COMPOSITIONS CONTAINING A VINYL  
DIMETHICONE/DIMETHICONE COPOLYMER IN AQUEOUS  
EMULSION AND AN ASSOCIATIVE THICKENER,  
5 AND USES THEREOF**

The present invention relates to novel cosmetic compositions comprising, in a cosmetically acceptable medium, at least one copolymer of  
10 dimethicone containing ethylenic unsaturation/  
dimethicone with a viscosity of between  $10^6$  and  
 $100 \times 10^6$  cP, as an aqueous emulsion, and at least one  
associative thickener.

It is well known that hair which has been  
15 sensitized (i.e. damaged and/or embrittled) to varying  
degrees under the action of atmospheric agents or under  
the action of mechanical or chemical treatments, such  
as dyes, bleaches and/or permanent-waving, is often  
difficult to disentangle and to style, and lacks  
20 softness.

It has already been recommended to use conditioners, in particular silicones, in compositions for washing or caring for keratin materials such as the hair, in order to facilitate the disentangling of the  
25 hair and to give it softness and suppleness. However, the cosmetic advantages mentioned above are also unfortunately accompanied, on dried hair, by certain cosmetic effects considered as being undesirable, i.e.

lankness of the hairstyle (lack of lightness of the hair), lack of smoothness (hair not uniform from the root to the tip, an unpleasant, charged feel, stiffness of the hair, and inter-fibre adhesion having an adverse effect on the styling, in particular when used repeatedly. These drawbacks are accentuated in the case of fine hair, which lacks liveliness and body.

In summary, it is found that the current cosmetic compositions containing silicones are not entirely satisfactory.

The Applicant has now discovered that the combination of at least one specific silicone copolymer, with a viscosity of between  $10^6$  and  $100 \times 10^6$  cP in aqueous emulsion, with associative thickeners makes it possible to overcome these drawbacks.

Thus, after considerable research conducted in this matter, it has now been found by the Applicant that by using a combination of at least one specific silicone copolymer with a viscosity of between  $10^6$  and  $100 \times 10^6$  cP, as an aqueous emulsion, with associative thickeners in a composition, in particular a hair composition, it is possible to limit, or even eliminate, the problems generally associated with the use of such compositions, i.e. in particular, the lankness (charged feel following repeated applications) and the lack of smoothness and softness of the hair, while at the same time retaining the other advantageous

cosmetic properties which are associated with conditioner-based compositions.

This combination gives cosmetic properties (smoothness, lightness and softness) without any phenomenon of regreasing of the keratin fibres.

Moreover, when applied to the skin, in particular in the form of a bubble bath or shower gel, the compositions of the invention provide an improvement in the softness of the skin.

Thus, according to the present invention, novel cosmetic compositions are now proposed comprising, in a cosmetically acceptable medium, at least one silicone copolymer defined below, the said copolymer having a viscosity of between  $10^6$  and  $100 \times 10^6$  cP, and at least one associative thickener.

Another subject of the invention relates to the use of an aqueous emulsion of at least one silicone copolymer defined below, with a viscosity of between  $10^6$  and  $100 \times 10^6$  cP, in, or for the manufacture of, a cosmetic composition [lacuna] an associative thickener.

The various subjects of the invention will now be described in detail. All the meanings and definitions of the compounds used in the present invention given below are valid for all the subjects of the invention.

The silicone copolymer generally has a dynamic viscosity, measured at a temperature of about  $25^\circ\text{C}$  and at a shear rate of 0.01 Hz for a stress of

1500 Pa, of between  $10^6$  and  $100 \times 10^6$  cP and preferably between  $5 \times 10^6$  cP and  $30 \times 10^6$  cP.

All the dynamic viscosity measurements given in the present patent application were carried out at a temperature of about  $25^\circ\text{C}$ , on a Carri-Med CSL2-500 machine.

The silicone copolymer present in the composition according to the invention is in the form of an aqueous emulsion.

10           The expression "aqueous emulsion" means an emulsion of oil-in-water type in which the silicone copolymer is dispersed in the form of particles or droplets in the aqueous phase forming the continuous phase of the emulsion.

15           This emulsion can be stabilized with a common emulsifying system.

This silicone emulsion can have a silicone droplet or particle size ranging from 10 nm to 50  $\mu\text{m}$  and preferably from 0.3  $\mu\text{m}$  to 20  $\mu\text{m}$ .

20           The particle size is measured by laser granulometry.

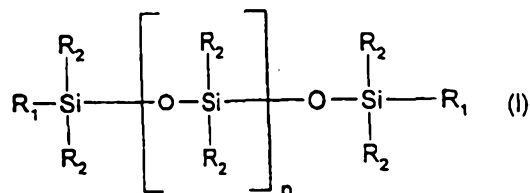
The emulsifying system comprises surfactants usually used in silicone emulsions. These surfactants may be nonionic, cationic, anionic or amphoteric, or  
25 mixtures thereof, such as those described below.

The emulsifying system represents from 0.5% to 10% by weight relative to the total weight of the emulsion.

The silicone copolymer results from the addition reaction, in the presence of a catalyst, of at least:

- (a) one polysiloxane of formula (I):

5



in which:

R<sub>1</sub> denotes a group which can react by chain addition  
 10 reaction such as, for example, a hydrogen atom or an  
 aliphatic group containing an ethylenic unsaturation,  
 in particular vinyl, allyl or hexenyl.

The groups R<sub>2</sub> in formula (I) can represent in  
 particular alkyl, cycloalkyl, aryl, alkylaryl or  
 15 hydroxyl groups and can also comprise functional groups  
 such as ethers, amines, carboxyls, hydroxyls, thiols,  
 esters, sulphonates or sulphates.

The alkyl groups contain, for example, 1 to  
 20 carbon atoms; the cycloalkyl groups contain, for  
 20 example, 5 or 6 carbon atoms; the aryl groups are in  
 particular phenyl groups; the alkylaryl groups may  
 contain from 7 to 20 carbon atoms.

R<sub>2</sub> more particularly denotes methyl.

n is an integer such that the polysiloxane of  
 25 formula (I) preferably has a kinetic viscosity of



between 1 and  $1 \times 10^6$  mm<sup>2</sup>/s, n ranging in particular from 5 to 5000.

- (b) and of at least one silicone compound comprising at least one and not more than two groups capable of reacting with the groups R<sub>1</sub> of the polysiloxane (a), at least one of the compounds of type (a) or (b) contains an aliphatic group containing an ethylenic unsaturation.

The compounds of type (b) are another polysiloxane of type (a) in which the groups R<sub>1</sub> of the polysiloxane (b) can react with the groups R<sub>1</sub> of the polysiloxane (a).

Preferably, the silicone copolymers are obtained in particular by addition reaction, in the presence of a hydrosilylation catalyst (for example a platinum catalyst), of at least:

- (a) one  $\alpha,\omega$ -divinylpolydimethylsiloxane, and
- (b) one  $\alpha,\omega$ -dihydrogenopolydimethylsiloxane.

The kinetic viscosity is measured, for example, at 25°C according to ASTM standard 445 Appendix C.

The silicone copolymers according to the invention are essentially non-crosslinked.

The synthesis of these silicone emulsions is described in particular in patent application EP-A-874 017.

Such emulsions are sold in particular under the name DC2-1997 Cationic Emulsion by the company

Dow Corning. This emulsion comprises an  $\alpha,\omega$ -divinyl-dimethicone/ $\alpha,\omega$ -dihydrogenodimethicone copolymer having a dynamic viscosity of about  $15 \times 10^6$  cP, an emulsifier of cationic type such as cetyltrimethylammonium chloride, a stabilizer such as hydroxyethylcellulose, and water.

The silicone copolymer is preferably used in an amount of between 0.05% and 10% by weight relative to the total weight of the composition. This amount is more preferably between 0.1% and 5% by weight relative to the total weight of the composition.

The aqueous emulsion of the silicone copolymer represents from 0.5% to 15% by weight relative to the total weight of the composition.

According to the invention, the expression "associative thickener" means an amphiphilic thickener comprising both hydrophilic units and hydrophobic units.

Associative thickeners according to the invention which may be used are associative polymers chosen from:

- (i) nonionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit;
- (ii) anionic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

(iii) cationic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

(iv) amphoteric amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

the fatty chains containing from 8 to 30 carbon atoms.

The nonionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit are preferably chosen from:

(1) Celluloses modified with groups comprising at least one fatty chain;

mention may be made, for example, of:

- hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups, or mixtures thereof, and in which the alkyl groups are preferably  $C_8-C_{22}$ , such as the product Natrosol Plus Grade 330 CS ( $C_{16}$  alkyls) sold by the company Aqualon, or the product Bermocoll EHM 100 sold by the company Berol Nobel,

- those modified with polyalkylene glycol alkylphenyl ether groups, such as the product Amercell Polymer HM-1500 (polyethylene glycol (15) nonylphenyl ether) sold by the company Amerchol.

(2) Hydroxypropyl guar modified with groups comprising at least one fatty chain, such as the product Esaflor HM 22 ( $C_{22}$  alkyl chain) sold by the company Lamberti, and the products Miracare XC95-3 ( $C_{14}$

alkyl chain) and RE205-1 (C<sub>20</sub> alkyl chain) sold by the company Rhone-Poulenc.

(3) Polyether urethanes comprising at least one fatty chain, such as C<sub>8</sub>-C<sub>30</sub> alkyl or alkenyl groups, for instance the products Dapral T 210 and Dapral T 212 sold by the company Akzo or the products Aculyn 44 and Aculyn 46 sold by the company Rohm & Haas.

(4) Copolymers of vinylpyrrolidone and of hydrophobic monomers containing a fatty chain;

10 mention may be made, for example, of:

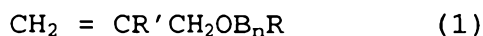
- the products Antaron V216 or Ganex V216 (vinylpyrrolidone/hexadecene copolymer) sold by the company I.S.P.,

- the products Antaron V220 or Ganex V220  
15 (vinylpyrrolidone/eicosene copolymer) sold by the company I.S.P.

(5) Copolymers of C<sub>1</sub>-C<sub>6</sub> alkyl acrylates or methacrylates and of amphiphilic monomers comprising at least one fatty chain, such as, for example, the  
20 oxyethylenated methyl methacrylate/stearyl acrylate copolymer sold by the company Goldschmidt under the name Antil 208.

(6) Copolymers of hydrophilic acrylates or methacrylates and of hydrophobic monomers comprising at  
25 least one fatty chain, such as, for example, the polyethylene glycol methacrylate/lauryl methacrylate copolymer.

Among the anionic amphiphilic polymers according to the invention comprising at least one hydrophilic unit and at least one unit containing a fatty chain, the ones which are preferred are those comprising at least one allyl ether unit containing a fatty chain and at least one hydrophilic unit consisting of an ethylenic unsaturated anionic monomer, more particularly a vinylcarboxylic acid and most particularly an acrylic acid, a methacrylic acid or mixtures thereof, the allyl ether unit containing a fatty chain corresponding to the monomer of formula (1) below:



in which R' denotes H or CH<sub>3</sub>, B denotes an ethyleneoxy radical, n is zero or denotes an integer ranging from 1 to 100, R denotes a hydrocarbon-based radical chosen from alkyl, arylalkyl, aryl, alkylaryl and cycloalkyl radicals, containing 8 to 30 carbon atoms, preferably 10 to 24 carbon atoms and even more particularly from 12 to 18 carbon atoms. A unit of formula (I) which is more particularly preferred according to the present invention is a unit in which R' denotes H, n is equal to 10 and R denotes a stearyl (C<sub>18</sub>) radical.

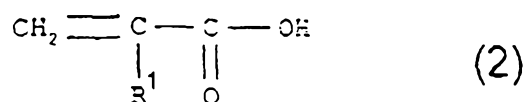
Anionic amphiphilic polymers of this type are described and prepared, according to an emulsion polymerization process, in patent EP-0 216 479 B2.

Among these anionic amphiphilic polymers that are particularly preferred according to the invention

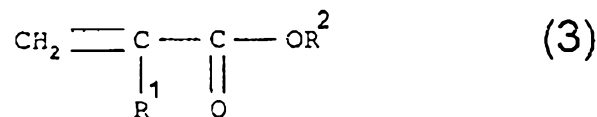
are polymers formed from 20% to 60% by weight of acrylic acid and/or of methacrylic acid, from 5% to 60% by weight of lower alkyl (meth)acrylates, from 2% to 50% by weight of allyl ether containing a fatty chain of formula (I), and from 0% to 1% by weight of a crosslinking agent which is a well-known copolymerizable unsaturated polyethylenic monomer, for instance diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate or  
10 methylenebisacrylamide.

Among the latter polymers, those most particularly preferred are crosslinked terpolymers of methacrylic acid, of ethyl acrylate and of polyethylene glycol (10 EO) stearyl ether (Steareth-10), in  
15 particular those sold by the company Allied Colloids under the names Salcare SC 80 and Salcare SC 90, which are aqueous 30% emulsions of a crosslinked terpolymer of methacrylic acid, of ethyl acrylate and of steareth-10 allyl ether (40/50/10).

20 The anionic amphiphilic polymers can also be chosen from those comprising at least one hydrophilic unit such as an unsaturated olefinic carboxylic acid, and at least one hydrophobic unit exclusively such as a (C<sub>10</sub>-C<sub>30</sub>) alkylester of an unsaturated carboxylic acid,  
25 which are used according to the invention, preferably chosen from those in which the hydrophilic unit of unsaturated olefinic carboxylic acid type corresponds to the monomer of formula (2) below:



in which formula  $\text{R}^1$  denotes H or  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ , i.e. acrylic acid, methacrylic acid or ethacrylic acid units, and in which the hydrophobic unit such as the  
 5  $(\text{C}_{10}\text{-C}_{30})$  alkyl ester of an unsaturated carboxylic acid corresponds to the monomer of formula (3) below:



in which formula  $\text{R}^1$  denotes H or  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$  (i.e. acrylate, methacrylate or ethacrylate units) and  
 10 preferably H (acrylate units) or  $\text{CH}_3$  (methacrylate units),  $\text{R}^2$  denoting a  $\text{C}_{10}\text{-C}_{30}$  and preferably  $\text{C}_{12}\text{-C}_{22}$  alkyl radical.

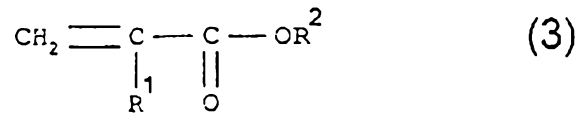
$(\text{C}_{10}\text{-C}_{30})$  Alkyl esters of unsaturated carboxylic acids in accordance with the invention comprise, for  
 15 example, lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate, and dodecyl acrylate, and the corresponding methacrylates, lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate.

20 Anionic amphiphilic polymers of this type are disclosed and prepared, for example, according to US patents 3 915 921 and 4 509 949.

The anionic amphiphilic polymers which can be used in the context of the present invention may more

particularly denote polymers formed from a mixture of monomers comprising:

(i) essentially acrylic acid, an ester of formula (3) below:

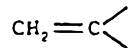


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in which R<sup>1</sup> denotes H or CH<sub>3</sub>, R<sup>2</sup> denoting an alkyl radical containing from 12 to 22 carbon atoms, and a crosslinking agent, such as, for example, those consisting of from 95% to 60% by weight of acrylic acid (hydrophilic unit), 4% to 40% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit), and 0% to 6% by weight of crosslinking polymerizable monomer, or 98% to 96% by weight of acrylic acid (hydrophilic unit), 1% to 4% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit) and 0.1% to 0.6% by weight of crosslinking polymerizable monomer,

(ii) essentially acrylic acid and lauryl methacrylate, such as the product formed from 66% by weight of acrylic acid and 34% by weight of lauryl methacrylate.

20 The said crosslinking agent is a monomer



containing a group with at least one other polymerizable group whose unsaturated bonds are not conjugated. Mention may be made in particular of polyallyl ethers such as, in particular,

25 polyallylsucrose and polyallylpentaerythritol.



Among the said polymers above, the ones most particularly preferred according to the present invention are the products sold by the company Goodrich under the trade names Pemulen TR1, Pemulen TR2, 5 Carbopol 1382, and even more preferably Pemulen TR1, and the product sold by the company S.E.P.C. under the name Coatex SX.

As anionic amphiphilic polymers containing fatty chains, mention may also be made of the 10 ethoxylated copolymer of methacrylic acid/methyl acrylate/alkyl dimethyl-meta-isopropenylbenzyl-isocyanate sold under the name Viscophobe DB 1000 by the company Amerchol.

The cationic amphiphilic polymers used in the 15 present invention are preferably chosen from quaternized cellulose derivatives and polyacrylates containing amine side groups.

The quaternized cellulose derivatives are, in particular,

- 20 - quaternized celluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups containing at least 8 carbon atoms, or mixtures thereof,
- quaternized hydroxyethylcelluloses modified with 25 groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups containing at least 8 carbon atoms, or mixtures thereof.

Quaternized or non-quaternized polyacrylates containing amine side groups, have, for example, hydrophobic groups, such as Steareth 20 (polyoxy-ethylenated(20) stearyl alcohol) or (C<sub>10</sub>-C<sub>30</sub>)alkyl PEG-20  
5 itaconate.

The alkyl radicals borne by the above quaternized celluloses or hydroxyethylcelluloses preferably contain from 8 to 30 carbon atoms.

The aryl radicals preferably denote phenyl,  
10 benzyl, naphthyl or anthryl groups.

Examples of quaternized alkylhydroxyethyl-celluloses containing C<sub>8</sub>-C<sub>30</sub> fatty chains which may be indicated are the products Quatrisoft LM 200,  
Quatrisoft LM-X 529-18-A, Quatrisoft LM-X 529-18B  
15 (C<sub>12</sub>alkyl) and Quatrisoft LM-X 529-8 (C<sub>18</sub>alkyl) sold by the company Amerchol, and the products Crodacel QM, Crodacel QL (C<sub>12</sub>alkyl) and Crodacel QS (C<sub>18</sub>alkyl) sold by the company Croda.

Examples of polyacrylates containing amine  
20 side chains which may be mentioned are the polymers 8781-124B or 9492-103 or Structure Plus from the company National Starch.

As amphoteric amphiphilic polymers containing at least one fatty chain, mention may be made of  
25 copolymers of methacrylamidopropyltrimethylammonium chloride/acrylic acid/C<sub>10</sub>-C<sub>30</sub> alkyl methacrylate, the alkyl radical preferably being a stearyl radical.

Preferably, the associative thickeners in the cosmetic compositions in accordance with the present invention advantageously have, in solution or in dispersion at a concentration of 1% active material in 5 water, a viscosity, measured using a Rheomat RM 180 rheometer at 25°C, of greater than 0.1 ps and even more advantageously of greater than 0.2 cp, at a shear rate of 200 s<sup>-1</sup>.

According to the invention, the thickener(s) 10 can represent from 0.001% to 20% by weight, preferably from 0.01% to 10% by weight and more particularly from 0.1% to 3% by weight, relative to the total weight of the final composition.

The compositions of the invention also 15 advantageously contain at least one surfactant chosen from anionic, amphoteric and nonionic surfactants, or mixtures thereof, which is generally present in an amount of between 0.1% and 60% by weight approximately, preferably between 3% and 40% and even more preferably 20 between 5% and 30%, relative to the total weight of the composition.

The surfactants which are suitable for carrying out the present invention are, in particular, the following:

25 (i) Anionic surfactant(s):

In the context of the present invention, their nature is not of critical importance.

Thus, as examples of anionic surfactants which can be used, alone or as mixtures, in the context of the present invention, mention may be made in particular (non-limiting list) of salts (in particular

5 alkaline salts, especially sodium salts, ammonium salts, amine salts, amino alcohol salts or magnesium salts) of the following compounds: alkyl sulphates, alkyl ether sulphates, alkylamidoether sulphates, alkylarylpolyether sulphates, monoglyceride sulphates;

10 alkyl sulphonates, alkyl phosphates, alkylamide sulphonates, alkylaryl sulphonates,  $\alpha$ -olefin sulphonates, paraffin sulphonates; alkyl sulphosuccinates, alkyl ether sulphosuccinates, alkylamide sulphosuccinates; alkyl sulphosuccinamates;

15 alkyl sulphoacetates; alkyl ether phosphates; acyl sarcosinates; acyl isethionates and N-acyltaurates, the alkyl or acyl radical of all of these various compounds preferably containing from 8 to 24 carbon atoms, and the aryl radical preferably denoting a phenyl or benzyl

20 group. Among the anionic surfactants which can also be used, mention may also be made of fatty acid salts such as the salts of oleic, ricinoleic, palmitic and stearic acids, coconut oil acid or hydrogenated coconut oil acid; acyl lactylates in which the acyl radical

25 contains 8 to 20 carbon atoms. Weakly anionic surfactants can also be used, such as alkyl-D-galactosiduronic acids and their salts, as well as polyoxyalkylenated (C<sub>6</sub>-C<sub>24</sub>) alkyl ether carboxylic

acids, polyoxyalkylenated (C<sub>6</sub>-C<sub>24</sub>) alkylaryl ether  
carboxylic acids, polyoxyalkylenated (C<sub>6</sub>-C<sub>24</sub>) alkylamido  
ether carboxylic acids and their salts, in particular  
those containing from 2 to 50 ethylene oxide groups,  
5 and mixtures thereof.

Among the anionic surfactants, it is  
preferred according to the invention to use alkyl  
sulphate salts and alkyl ether sulphate salts and  
mixtures thereof.

10 (ii) Nonionic surfactant(s):

The nonionic surfactants are, themselves  
also, compounds that are well known per se (see in  
particular in this respect "Handbook of Surfactants" by  
M.R. Porter, published by Blackie & Son (Glasgow and  
15 London), 1991, pp. 116-178) and, in the context of the  
present invention, their nature is not a critical  
feature. Thus, they can be chosen in particular from  
(non-limiting list) polyethoxylated, polypropoxylated  
or polyglycerolated fatty acids, alkylphenols,  $\alpha$ -diols  
20 or alcohols having a fatty chain containing, for  
example, 8 to 18 carbon atoms, it being possible for  
the number of ethylene oxide or propylene oxide groups  
to range in particular from 2 to 50 and for the number  
of glycerol groups to range in particular from 2 to 30.  
25 Mention may also be made of copolymers of ethylene  
oxide and of propylene oxide, condensates of ethylene  
oxide and of propylene oxide with fatty alcohols;  
polyethoxylated fatty amides preferably having from 2

to 30 mol of ethylene oxide, polyglycerolated fatty amides containing on average 1 to 5, and in particular 1.5 to 4, glycerol groups; polyethoxylated fatty amines preferably having 2 to 30 mol of ethylene oxide;

5 oxyethylenated fatty acid esters of sorbitan having from 2 to 30 mol of ethylene oxide; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, amine oxides such as (C<sub>10</sub>-C<sub>14</sub>)alkylamine oxides or

10 N-acylamino-propylmorpholine oxides. It will be noted that the alkylpolyglycosides constitute nonionic surfactants that are particularly suitable in the context of the present invention.

(iii) Amphoteric surfactant(s):

15 The amphoteric surfactants, whose nature is not a critical feature in the context of the present invention, can be, in particular (non-limiting list), aliphatic secondary or tertiary amine derivatives in which the aliphatic radical is a linear or branched

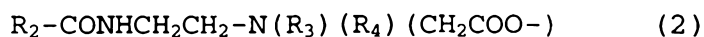
20 chain containing 8 to 22 carbon atoms and containing at least one water-soluble anionic group (for example carboxylate, sulphonate, sulphate, phosphate or phosphonate); mention may also be made of

(C<sub>8</sub>-C<sub>20</sub>)alkylbetaines, sulphobetaines,

25 (C<sub>8</sub>-C<sub>20</sub>)alkylamido(C<sub>1</sub>-C<sub>6</sub>)alkylbetaines or (C<sub>8</sub>-C<sub>20</sub>)alkylamido(C<sub>1</sub>-C<sub>6</sub>)alkylsulphobetaines.

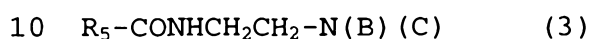
Among the amine derivatives, mention may be made of the products sold under the name Miranol, as

described in US patents 2,528,378 and 2,781,354 and having the structures:



in which:  $R_2$  denotes an alkyl radical derived from an acid  $R_2\text{-COOH}$  present in hydrolysed coconut oil, a heptyl, nonyl or undecyl radical,  $R_3$  denotes a  $\beta$ -hydroxyethyl group and  $R_4$  denotes a carboxymethyl group;

and



in which:

B represents  $\text{-CH}_2\text{CH}_2\text{OX}'$ , C represents  $\text{-(CH}_2\text{)}_z\text{-Y}'$ , with  $z = 1$  or  $2$ ,

$X'$  denotes the  $\text{-CH}_2\text{CH}_2\text{-COOH}$  group or a hydrogen atom,

15  $Y'$  denotes  $\text{-COOH}$  or the  $\text{-CH}_2\text{-CHOH-SO}_3\text{H}$  radical,

$R_5$  denotes an alkyl radical of an acid  $R_9\text{-COOH}$  present in coconut oil or in hydrolysed linseed oil, an alkyl radical, in particular a  $C_7$ ,  $C_9$ ,  $C_{11}$  or  $C_{13}$  alkyl radical, a  $C_{17}$  alkyl radical and its iso form, an

20 unsaturated  $C_{17}$  radical.

These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, disodium capryloampho-

dipropionate, lauroamphodipropionic acid,  
cocoamphodipropionic acid.

By way of example, mention may be made of the  
cocoamphodiacetate sold under the trade name Miranol  
5 C2M Concentrate by the company Rhône-Poulenc.

In the compositions in accordance with the  
invention, mixtures of surfactants are preferably used,  
and in particular mixtures of anionic surfactants and  
mixtures of anionic surfactants and of amphoteric or  
10 nonionic surfactants. A particularly preferred mixture  
is a mixture consisting of at least one anionic  
surfactant and of at least one amphoteric surfactant.

The anionic surfactant used is preferably  
chosen from (C<sub>12</sub>-C<sub>14</sub>)alkyl sulphates of sodium, of  
15 triethanolamine or of ammonium, the (C<sub>12</sub>-C<sub>14</sub>)alkyl ether  
sulphates of sodium, of triethanolamine or of ammonium  
oxyethylenated with 2.2 mol of ethylene oxide, sodium  
cocoyl isethionate and sodium (C<sub>14</sub>-C<sub>16</sub>)- $\alpha$ -olefin  
sulphonate, and mixtures thereof, with:

- 20 - either an amphoteric surfactant such as the amine  
derivatives known as disodium cocoamphodipropionate or  
sodium cocoamphopropionate, sold in particular by the  
company Rhône-Poulenc under the trade name "Miranol C2M  
Conc." as an aqueous solution containing 38% active  
25 material, or under the name Miranol C32;  
- or an amphoteric surfactant of zwitterionic type,  
such as alkylbetaines, in particular the cocobetaine

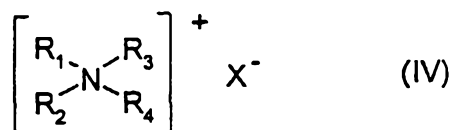


sold under the name "Dehyton AB 30" as an aqueous solution containing 32% AM by the company Henkel.

Even more preferably, the compositions according to the invention can also contain at least  
5 one cationic surfactant.

The cationic surfactants may be chosen from:

A) the quaternary ammonium salts of general formula (IV) below:



10

in which X is an anion chosen from the group of halides (chloride, bromide or iodide) or (C<sub>2</sub>-C<sub>6</sub>)alkyl sulphates, more particularly methyl sulphate, phosphates, alkyl or  
15 alkylaryl sulphonates, anions derived from organic acids, such as acetate or lactate, and

i) the radicals R<sub>1</sub> to R<sub>3</sub>, which may be identical or different, represent a linear or branched aliphatic radical containing from 1 to 4 carbon atoms, or an  
20 aromatic radical such as aryl or alkylaryl. The aliphatic radicals can comprise hetero atoms such as, in particular, oxygen, nitrogen, sulphur or halogens. The aliphatic radicals are chosen, for example, from alkyl, alkoxy and alkylamide radicals,  
25 R<sub>4</sub> denotes a linear or branched alkyl radical containing from 16 to 30 carbon atoms.

The cationic surfactant is preferably a behenyltrimethylammonium salt (for example chloride).

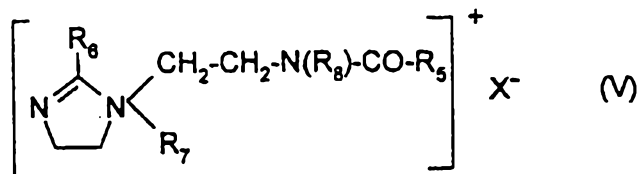
ii) the radicals  $R_1$  and  $R_2$ , which may be identical or different, represent a linear or branched aliphatic radical containing from 1 to 4 carbon atoms, or an aromatic radical such as aryl or alkylaryl. The aliphatic radicals can comprise hetero atoms such as, in particular, oxygen, nitrogen, sulphur or halogens. The aliphatic radicals are chosen, for example, from alkyl, alkoxy, alkylamide and hydroxyalkyl radicals containing from about 1 to 4 carbon atoms;

$R_3$  and  $R_4$ , which may be identical or different, denote a linear or branched alkyl radical containing from 12 to 30 carbon atoms, the said radical comprising at least one ester or amide function.

$R_3$  and  $R_4$  are chosen in particular from  $(C_{12}-C_{22})$ alkylamido  $(C_2-C_6)$ alkyl and  $(C_{12}-C_{22})$ alkylacetate radicals.

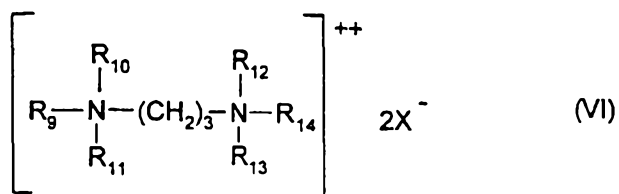
The cationic surfactant is preferably a stearamidopropyldimethyl(myristyl acetate)ammonium salt (for example chloride);

B) - quaternary ammonium salts of imidazolinium, such as, for example, that of formula (V) below:



in which R<sub>5</sub> represents an alkenyl or alkyl radical containing from 8 to 30 carbon atoms, for example fatty acid derivatives of tallow, R<sub>6</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical or an alkenyl or alkyl radical containing from 8 to 30 carbon atoms, R<sub>7</sub> represents a C<sub>1</sub>-C<sub>4</sub> alkyl radical, R<sub>8</sub> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical, and X is an anion chosen from the group of halides, phosphates, acetates, lactates, alkyl sulphates, alkyl sulphonates or alkylaryl sulphonates. R<sub>5</sub> and R<sub>6</sub> preferably denote a mixture of alkenyl or alkyl radicals containing from 12 to 21 carbon atoms, such as, for example, fatty acid derivatives of tallow, R<sub>7</sub> denotes methyl and R<sub>8</sub> denotes hydrogen. Such a product is, for example, Quaternium-27 (CTFA 1997) or Quaternium-83 (CTFA 1997), which are sold under the names "Rewoquat" W75, W90, W75PG and W75HPG by the company Witco,

C) - diquaternary ammonium salts of formula (VI):



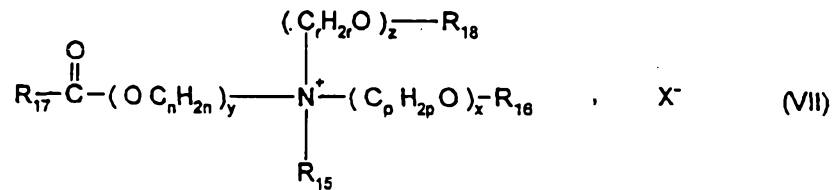
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in which R<sub>9</sub> denotes an aliphatic radical containing from about 16 to 30 carbon atoms, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub> and R<sub>14</sub>, which may be identical or different, are chosen from hydrogen and an alkyl radical containing from 1 to

25

4 carbon atoms, and X is an anion chosen from the group of halides, acetates, phosphates, nitrates and methyl sulphates. Such diquatertiary ammonium salts in particular comprise propanetallowdiammonium  
5 dichloride.

D) - quaternary ammonium salts containing at least one ester function, of formula (VII) below:



10

in which:

- R<sub>15</sub> is chosen from C<sub>1</sub>-C<sub>6</sub> alkyl radicals and C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl or dihydroxyalkyl radicals;

- R<sub>16</sub> is chosen from:

15 - a radical  $\text{R}_{19}-\overset{\text{O}}{\parallel}{\text{C}}-$

- linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>22</sub> hydrocarbon-based radicals R<sub>20</sub>,

- a hydrogen atom,

- R<sub>18</sub> is chosen from:

20 - a radical  $\text{R}_{21}-\overset{\text{O}}{\parallel}{\text{C}}-$

- linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>6</sub> hydrocarbon-based radicals R<sub>22</sub>,

- a hydrogen atom,

- $R_{17}$ ,  $R_{19}$  and  $R_{21}$ , which may be identical or different, are chosen from linear or branched, saturated or unsaturated  $C_7$ - $C_{21}$  hydrocarbon-based radicals;
  - $n$ ,  $p$  and  $r$ , which may be identical or different, are 5 integers ranging from 2 to 6;
  - $y$  is an integer ranging from 1 to 10;
  - $x$  and  $z$ , which may be identical or different, are integers ranging from 0 to 10;
  - $X^-$  is a simple or complex organic or inorganic anion;
- 10 with the proviso that the sum  $x + y + z$  is from 1 to 15, that when  $x$  is 0, then  $R_{16}$  denotes  $R_{20}$  and that when  $z$  is 0, then  $R_{18}$  denotes  $R_{22}$ .

Use is made more particularly of the ammonium salts of formula (VII) in which:

- 15 -  $R_{15}$  denotes a methyl or ethyl radical,
- $x$  and  $y$  are equal to 1;
- $z$  is equal to 0 or 1;
- $n$ ,  $p$  and  $r$  are equal to 2;
- $R_{16}$  is chosen from:
  - 20 - a radical  $R_{19}\overset{\text{O}}{\parallel}\text{C}-$
  - methyl, ethyl or  $C_{14}$ - $C_{22}$  hydrocarbon-based radicals,
  - a hydrogen atom;
- $R_{17}$ ,  $R_{19}$  and  $R_{21}$ , which may be identical or different,
- 25 are chosen from linear or branched, saturated or unsaturated  $C_7$ - $C_{21}$  hydrocarbon-based radicals;
- $R_{18}$  is chosen from:

- a radical  $R_{21}\overset{\text{O}}{\parallel}{\text{C}}-$
- a hydrogen atom.

Such compounds are sold, for example, under the names Dehyquart by the company Henkel, Stepanquat  
 5 by the company Stepan, Noxamium by the company Ceca, and Rewoquat WE 18 by the company Rewo-Witco.

Among the quaternary ammonium salts that are preferred are behenyltrimethylammonium chloride and  
 stearamidopropylmethyl(myristyl acetate)ammonium  
 10 chloride, sold under the name "Ceraphyl 70" by the company Van Dyk, and Quaternium-27 or Quaternium-83 sold by the company Witco.

The cationic surfactant is generally present in concentrations ranging from 0.1% to 10% by weight  
 15 relative to the total weight of the composition, and preferably from 0.5% to 7% by weight and more preferably between 1% and 5% by weight.

The composition of the invention can also contain at least one additive chosen from fragrances,  
 20 nacreous agents, preserving agents, silicone or non-silicone sunscreens, vitamins, provitamins, amphoteric, anionic or nonionic polymers, proteins, protein hydrolysates, 18-methyleicosanoic acid, hydroxy acids, panthenol, volatile or non-volatile, cyclic or linear  
 25 or crosslinked, modified or non-modified silicones, ceramides, pseudoceramides, plant, animal, mineral or synthetic oils and any other additive conventionally

used in cosmetics which does not affect the properties of the compositions according to the invention.

These additives are present in the composition according to the invention in proportions 5 which can range from 0 to 20% by weight relative to the total weight of the composition. The precise amount of each additive is readily determined by those skilled in the art depending on its nature and its function.

The compositions in accordance with the 10 invention can be used more particularly for washing or treating keratin materials such as the hair, the skin, the eyelashes, the eyebrows, the nails, the lips or the scalp, and more particularly the hair.

The compositions according to the invention 15 can be rinse-out or leave-in conditioner compositions.

The compositions according to the invention can also be detergent compositions such as shampoos, shower gels or bubble baths and can also be make-up-removing products. In this embodiment of the invention, 20 the compositions comprise a washing base, which is generally aqueous.

The surfactant(s) forming the washing base can be chosen, indifferently, alone or as mixtures, from the anionic, amphoteric and nonionic surfactants 25 as defined above.

The quantity and quality of the washing base are those which are sufficient to give the final

composition satisfactory foaming and/or detergent power.

Thus, according to the invention, the washing base can represent from 4% to 50% by weight, preferably 5 from 6% to 35% by weight and even more preferably from 8% to 25% by weight, of the total weight of the final composition.

The subject of the invention is also a process for treating keratin materials such as the skin 10 or the hair, characterized in that it consists in applying a cosmetic composition as defined above to the keratin materials and then in optionally rinsing it out with water.

Thus, this process according to the invention 15 allows maintenance of the hairstyle and treatment of, care of, washing of or removal of make-up from the skin, the hair or any other keratin material.

The compositions of the invention can also be in the form of permanent-waving, straightening, dyeing 20 or bleaching compositions, or alternatively in the form of rinse-out compositions to be applied before or after dyeing, bleaching, permanent-waving or straightening the hair, or alternatively between the two steps of a permanent-waving or hair-straightening operation.

25 The compositions according to the invention can also be in the form of aqueous or aqueous-alcoholic lotions for skin care and/or hair care.



The cosmetic compositions according to the invention can be in the form of a gel, a milk, a cream, an emulsion, a thickened lotion or a mousse and can be used for the skin, the nails, the eyelashes, the lips  
5 and, more particularly, the hair.

The compositions can be packaged in various forms, in particular in vaporizers, pump-dispenser bottles or in aerosol containers in order to ensure application of the composition in vaporized form or in  
10 the form of a mousse. Such packaging forms are indicated, for example, when it is desired to obtain a spray, a lacquer or a mousse for treating the hair.

In all of the text hereinabove and hereinbelow, the percentages expressed are on a weight  
15 basis.

The invention will now be illustrated more fully with the aid of the examples which follow, which should not be considered as limiting it to the embodiments described. In the examples, AM means active  
20 material.

In the examples, the commercial names have the following definitions:

[lacuna]

EXAMPLE 1

25 A conditioner in accordance with the invention, having the following composition, was prepared:

- Cationic emulsion containing 67% AM of

- copolymer of polydimethylsiloxane containing  $\alpha, \omega$ -vinyl groups/polydimethylsiloxane containing  $\alpha, \omega$ -hydrogeno groups (DC-1997 from Dow Corning) 4 gMA
- 5 - SMDI/polyethylene glycol/alkyl (methyl/C18) endings copolymer at a concentration of 15% in a maltodextrin/water matrix (Aculyn 46 from Rohm & Haas) 0.6 gAM
- crosslinked ethyltrimethylammonium
- 10 methacrylate chloride homopolymer as a reverse emulsion at a concentration of 50% in mineral oil (Salcare SC 95 from Ciba Geigy) 0.55 gAM
- Mixture of cetyl alcohol and of stearyl alcohol (50/50 by weight) 2 g
- Fragrance, preserving agents qs
- Water qs 100 g

This composition is applied to washed and dried hair. It is left to stand on the hair for 20 2 minutes and is then rinsed off thoroughly with water.

Hair treated with this conditioner is soft, smooth and disentangles easily.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

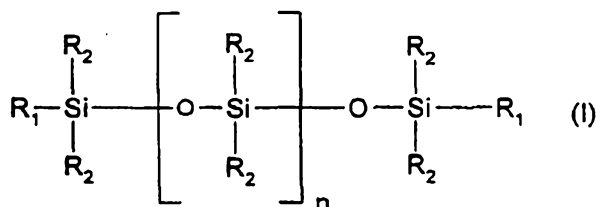
For the purposes of this specification it will be clearly understood that the word "comprising" means "including but not limited to", and that the word "comprises" has a corresponding meaning.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Cosmetic composition, characterized in that it comprises, in a cosmetically acceptable medium, at least one associative thickener and at least one aqueous emulsion comprising:

at least one silicone copolymer with a viscosity of between  $10^6$  and  $100 \times 10^6$  cP, resulting from the addition reaction, in the presence of a catalyst, of at least:

- (a) one polysiloxane of formula (I):



in which:

$R_1$  denotes a group which can react by chain addition reaction;

the groups  $R_2$  in formula (I) represent alkyl groups containing from 1 to 20 carbon atoms, cycloalkyl groups containing from 5 to 6 carbon atoms, aryl groups, alkylaryl groups containing from 7 to 20 carbon atoms or hydroxyl groups and can also comprise functional groups such as ethers, amines, carboxyls, hydroxyls, thiols, esters, sulphonates or sulphates;

$n$  is an integer such that the polysiloxane of formula (I) preferably has a kinetic viscosity of between 1 and  $1 \times 10^6$  mm<sup>2</sup>/s;



- (b) and at least one silicone compound comprising at least one and not more than two groups capable of reacting with the groups  $R_1$  of the polysiloxane (a), at least one of the compounds of type (a) or (b) containing an ethylenic  
5 unsaturation.

2. Composition according to claim 1, wherein  $R_1$  denotes a hydrogen atom or an aliphatic group containing an ethylenic unsaturation.  
10

3. Composition according to claim 1 or claim 2 characterized in that  $R_2$  denotes methyl.

4. Composition according to any one of claims 1 to  
15 3, characterized in that the compound of type (b) is another polysiloxane of type (a) in which the groups  $R_1$  of the polysiloxane (b) can react with the groups  $R_1$  of the polysiloxane (a).

20 5. Composition according to any one of claims 1 to 4, characterized in that the silicone copolymer is obtained by addition reaction, in the presence of a hydrosilylation catalyst, of at least:

- 25 - (a) one  $\alpha, \omega$ -divinylpolydimethylsiloxane, and  
- (b) one  $\alpha, \omega$ -dihydrogenopolydimethylsiloxane.

6. Composition according to any one of claims 1 to  
30 5, characterized in that the said emulsion of the silicone copolymer has a silicone droplet or particle size in the range of from 10 nm to 50  $\mu\text{m}$ .

7. Composition according to any one of claims 1 to  
35 5, characterized in that the said emulsion of the silicone copolymer has a silicone droplet or particle size in the range of from 10 nm to 50  $\mu\text{m}$ .



8. Composition according to any one of claims 1 to 7, characterized in that the aqueous emulsion of the silicone copolymer represents from 0.5% to 15% by weight relative to the total weight of the composition.

5

9. Composition according to any one of claims 1 to 8, characterized in that the silicone copolymer is present at a concentration of between 0.05% and 10% by weight relative to the total weight of the composition.

10

10. Composition according to any one of claims 1 to 9, characterized in that the said associative thickener is an associative polymer chosen from:

15 (i) nonionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit;

(ii) anionic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

20

(iii) cationic amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

(iv) amphoterteric amphiphilic polymers comprising at least one hydrophilic unit and at least one unit containing a fatty chain;

25

11. Composition according to claim 10, characterized in that the nonionic amphiphilic polymers comprising at least one fatty chain and at least one hydrophilic unit are chosen from:

30

(1) celluloses modified with groups comprising at least one fatty chain;

35 (2) hydroxypropyl guar modified with groups comprising at least one fatty chain;

(3) polyether urethanes comprising at least one fatty



chain;

- (4) copolymers of vinylpyrrolidone and of hydrophobic monomers containing a fatty chain;
- (5) copolymers of C<sub>1</sub>-C<sub>6</sub> alkyl acrylates or methacrylates and of amphiphilic monomers comprising at least one fatty chain;
- (6) copolymers of hydrophilic acrylates or methacrylates and of hydrophobic monomers comprising at least one fatty chain.

10

12. Composition according to claim 10, characterized in that the anionic amphiphilic polymers comprising at least one hydrophilic unit, and at least one unit containing a fatty chain are chosen from those comprising at least one allyl ether unit containing a fatty chain and at least one hydrophilic unit consisting of an unsaturated ethylenic anionic monomer, those comprising at least one hydrophilic unit such as an unsaturated olefinic carboxylic acid, and at least one hydrophobic unit exclusively such as a (C<sub>10</sub>-C<sub>10</sub>) alkyl ester of an unsaturated carboxylic acid, and ethoxylated methacrylic acid/methyl acrylate/alkyl dimethyl-meta-isopropenylbenzylisocyanate copolymers.

13. Composition according to claim 10, characterized in that the cationic amphiphilic polymers used in the present invention are chosen from quaternized cellulose derivatives and polyacrylates containing amine side groups.

14. Composition according to claim 10, characterized in that the amphoteric amphiphilic polymers containing at least one fatty chain are chosen from copolymers of methacrylamidopropyltrimethyl-ammonium chloride/acrylic acid/C<sub>10</sub>-C<sub>30</sub> alkyl methacrylate.

15. Composition according to any one of the preceding



claims, characterized in that the thickener is present at a concentration of between 0.001% and 20% by weight relative to the total weight of the composition.

5 16. Composition according to any one of the preceding claims, characterized in that the thickener is present at a concentration of between 0.01% and 10% by weight relative to the total weight of the composition.

10 17. Composition according to any one of the preceding claims, characterized in that the composition also comprises at least one surfactant chosen from anionic, nonionic and amphoteric surfactants, and mixtures thereof.

15 18. Composition according to claim 17, characterized in that the surfactant(s) is (are) present at a concentration of between 0.1% and 60% by weight.

19. Composition according to claim 17, characterized  
20 in that the surfactant(s) is (are) present at a concentration of between 3% and 40% by weight.

20. Composition according to claim 17, characterized  
25 in that the surfactant(s) is (are) present at a concentration of between 5% and 30% by weight.

21. Composition according to any one of the preceding  
claims, characterized in that the composition also  
comprises at least one cationic surfactant.

30 22. Composition according to claim 21, characterized in that the cationic surfactant is present at a concentration of from 0.1% to 10% by weight relative to the total weight of the composition.

35 23. Composition according to claim 21, characterized in that the cationic surfactant is present at a concentration of from 0.5% to 7% by weight relative to the



total weight of the composition.

24. Composition according to claim 21, characterized  
in that the cationic surfactant is present at a  
5 concentration of from 1% to 5% by weight relative to the  
total weight of the composition.

25. Composition substantially as herein described  
with reference to the accompanying examples.

10

26. Composition according to any one of the preceding  
claims, characterized in that the composition is in the  
form of a shampoo, a rinse-out or leave-in conditioner, a  
composition for permanent-waving, straightening, dyeing or  
15 bleaching the hair, a rinse-out composition to be applied  
between the two steps of a permanent-waving or hair-  
straightening operation, or washing compositions for the  
body.

20 27. Use of a composition as defined in any one of the  
preceding claims, for washing or caring for keratin  
materials.

28. Process for treating keratin materials, such as  
25 the hair, characterized in that it consists in applying a  
cosmetic composition according to one of claims 1 to 26,  
to the said keratin materials, and then in optionally  
rinsing it out with water.





29. Use of a silicone copolymer as defined in one of claims 1 to 7, in, or for the manufacture of, a cosmetic composition comprising an associative thickener.

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Dated this 24th day of January 2002

L'OREAL

By their Patent Attorneys

GRIFFITH HACK

10 Fellows Institute of Patent and  
Trade Mark Attorneys of Australia

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