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(54) Title: COMPOSITION FOR TREATING KERATIN FIBRES COMPRISING A BLOCK COPOLYMER, A SILOXANE RESIN AND A VOLATILE SOLVENT

(57) Abstract: The present invention relates to a composition for treating keratin fibres comprising one or more ethylenic block copolymers, containing at least one first block having a glass transition temperature (T_g) greater than or equal to 40°C and being derived wholly or partly from one or more first monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature greater than or equal to 40°C, and at least one second block having a glass transition temperature less than or equal to 20°C and being derived wholly or partly from one or more second monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature less than or equal to 20°C, said first block and said second block being joined together by a random intermediate segment comprising at least one of said first monomers constituting the first block and at least one of said second monomers constituting the second block, and said block copolymer having a polydispersity index I greater than 2, a siloxane resin with propyl radicals comprising the units, and one or more volatile solvents, the weight ratio of the volatile solvent to the ethylenic block copolymer being greater than 2.



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**COMPOSITION FOR TREATING KERATIN FIBRES COMPRISING A BLOCK
COPOLYMER, A SILOXANE RESIN AND A VOLATILE SOLVENT**

5 The present invention relates to a composition for treating
keratin fibres, and in particular human keratin fibres such as
the hair as well as a composition for colouring the hair based
on a pigment.

10 It is customary to use styling products that permit
conditioning of the hair, notably by giving it body, mass or
volume.

These styling products are generally hair cosmetic
compositions comprising one or more polymers that have strong
affinity for the hair and whose function is most often to form
a film on the surface of the hair in order to modify its
15 surface properties, and notably for conditioning the hair.

A drawback associated with the use of these hair-care
compositions is that hair treated with said compositions has a
tendency to dry slowly when rewetted, notably by rain.
Moreover, the styling effects provided disappear when the hair
20 is exposed to high humidity.

The use of film-forming polymers of the ethylenic block
copolymer type for treatment of the hair is known from patent
application EP 1411069.

25 These polymers form a surface coating which provides a
beneficial cosmetic effect by giving the hair body and volume
as well as a deposit of the homogeneous. However, they do not
solve the problems mentioned above.

30 Thus, the aim of the present invention is to provide a
composition for treating keratin fibres, and in particular the
hair, permitting quick drying of wetted hair and displaying
resistance of the styling effects to external agents such as
humidity.

This aim is achieved with the present invention, which
relates to a composition for treating keratin fibres, and in
35 particular the hair, comprising

- one or more ethylenic block copolymers, containing at least
one first block having a glass transition temperature (T_g)
greater than or equal to 40°C and being derived wholly or

partly from one or more first monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature greater than or equal to 40°C, and at least one second block having a glass transition temperature less than or equal to 20°C and being derived wholly or partly from one or more second monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature less than or equal to 20°C, said first block and said second block being joined together by a random intermediate segment comprising at least one of said first monomers constituting the first block and at least one of said second monomers constituting the second block, and said block copolymer having a polydispersity index I greater than 2,

• one or more siloxane resins comprising the units:

- (i) $(R^1_3SiO_{1/2})_a$
 (ii) $(R^2_2SiO_{2/2})_b$
 (iii) $(R^3_3SiO_{3/2})_c$ and
 (iv) $(SiO_{4/2})_d$

with

R^1 , R^2 and R^3 representing independently an alkyl or hydroxyalkyl group having from 1 to 8 carbon atoms, an aryl group or an amino group,
 a being between 0.05 and 0.5,
 b being between zero and 0.3,
 c being greater than zero,
 d being between 0.05 and 0.6,
 $a + b + c + d = 1$,

and more than 40 mol.% of the groups R^3 of the siloxane resin are propyl groups, and

• one or more volatile solvents, the weight ratio of the volatile solvent to the ethylenic block copolymer being greater than 2, and preferably between 2 and 90.

The composition according to the present invention makes it possible to obtain, on keratin fibres, treatments that can withstand humidity. Very quick drying of the hair when rewetted is also observed. The resultant drying can be even quicker than the drying of untreated natural hair. This treatment also gives

a smooth and homogeneous deposit with the individual hairs perfectly separated, which can be styled without any problem.

"Individual hairs perfectly separated" means that after application of the composition and drying, the individual hairs are not stuck together (i.e. are all kept separate from one another) and therefore do not form clumps of hair, the surface coating being formed around practically every individual hair.

The present invention also relates to a method for treating keratin fibres, and the hair in particular, employing this composition.

Siloxane resin

Preferably the siloxane resin comprises the units:

- (i) $(R^1_3SiO_{1/2})_a$
- (ii) $(R^2_2SiO_{2/2})_b$
- (iii) $(R^3SiO_{3/2})_c$ and
- (iv) $(SiO_{4/2})_d$

with

- R^1 , R^2 and R^3 representing independently an alkyl or hydroxyalkyl group having from 1 to 8 carbon atoms, an aryl group or an amino group, R^1 preferably being a methyl group and R^3 preferably being a propyl group,
- a being between 0.05 and 0.5, preferably between 0.15 and 0.4,
- b being between zero and 0.3,
- c being greater than zero, preferably between 0.15 and 0.4,
- d being between 0.05 and 0.6, preferably between 0.2 and 0.6, or between 0.2 and 0.55,
- $a + b + c + d = 1$,

and more than 40 mol.% of the groups R^3 of the siloxane resin are propyl groups.

The siloxane resins usable according to the invention can be obtained by a method comprising the reaction of:

- A) a resin MQ comprising at least 80 mol.% of units $(R^1_3SiO_{1/2})_a$ and $(SiO_{4/2})_d$

R¹ representing an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group or an amino group,

a and d being greater than zero,

the ratio a/d being between 0.5 and 1.5;

and of

B) a propyl resin T comprising at least 80 mol.% of units (R³SiO_{3/2})_c,

R³ representing an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group or an amino group,

c being greater than zero,

provided that at least 40 mol.% of the groups R³ are propyl groups,

where the mass ratio A/B is between 95:5 and 15:85, preferably the mass ratio A/B is less than or equal to 70:30.

The resins usable according to the invention are notably those described in application WO 2005/075542.

The composition according to the invention preferably comprises less than 0.1 to 40 wt.% of siloxane resin, and advantageously from 0.5 to 30 wt.%, notably from 0.5 to 20 wt.% of active substance relative to the total weight of the composition.

ETHYLENIC BLOCK COPOLYMER

The composition according to the present invention contains at least one ethylenic block copolymer (also called ethylenic block polymer), containing at least one first block having a glass transition temperature (T_g) greater than or equal to 40°C and being derived wholly or partly from one or more first monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature greater than or equal to 40°C, and at least one second block having a glass transition temperature less than or equal to 20°C and being derived wholly or partly from one or more second monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature less than or equal to 20°C, said first block and said second block being joined

together by a random intermediate segment comprising at least one of said first monomers constituting the first block and at least one of said second monomers constituting the second block, and said block copolymer having a polydispersity index I greater than 2.

The block polymer used according to the invention thus comprises at least one first block and at least one second block.

"At least" one block means one or more blocks.

"Block" polymer means a polymer comprising at least 2 separate blocks, preferably at least 3 separate blocks.

"Ethylene" polymer means a polymer obtained by polymerization of monomers comprising an ethylenic unsaturation.

The ethylenic block polymer used according to the invention is prepared exclusively from monofunctional monomers.

This signifies that the ethylenic block polymer used according to the present invention does not contain multifunctional monomers, which would make it possible to break the linearity of a polymer to obtain a branched or even crosslinked polymer, depending on the proportion of multifunctional monomer. The polymer used according to the invention does not contain macromonomers either ("macromonomer" means a monofunctional monomer having a pendent group of polymeric nature, and preferably having a molecular weight greater than 500 g/mol, or else a polymer having, at just one of its ends, a polymerizable end group (or having an ethylenic unsaturation)), which are used in the preparation of a graft polymer.

Note that in the foregoing and hereinafter the terms "first" and "second" blocks do not in any way define the order of said blocks (or sequences) in the structure of the polymer.

The first block and the second block of the polymer used in the invention can advantageously be incompatible with one another.

"Blocks incompatible with one another" means that the mixture formed from a polymer corresponding to the first block and from a polymer corresponding to the second block is not

miscible in the polymerization solvent, the main proportion by weight, of the block polymer, at room temperature (25°C) and atmospheric pressure (105 Pa), for a content of the mixture of said polymers greater than or equal to 5 wt.%, relative to the total weight of the mixture of said polymers and of said polymerization solvent, it being understood that:

i) said polymers are present in the mixture in a content such that the respective weight ratio is in the range from 10/90 to 90/10, and that

ii) each of the polymers corresponding to the first and second blocks has a (weight-average or number-average) molecular weight equal to that of the block polymer $\pm 15\%$.

In the case of a mixture of polymerization solvents, assuming that two or more solvents are present in identical proportions by weight, said mixture of polymers is not miscible in at least one of them.

Of course, in the case of polymerization carried out in a single solvent, the latter is the principal solvent.

The block polymer according to the invention comprises at least one first block and at least one second block joined together by an intermediate segment comprising at least one monomer constituting the first block and at least one monomer constituting the second block. The intermediate segment (also called intermediate block) has a glass transition temperature T_g between the glass transition temperatures of the first and second blocks.

The intermediate segment is a block comprising at least one monomer constituting the first block and at least one monomer constituting the second block of the polymer and makes it possible to "compatibilize" these blocks.

Advantageously, the intermediate segment comprising at least one monomer constituting the first block and at least one monomer constituting the second block of the polymer is a random polymer.

Preferably, the intermediate block is derived essentially from monomers constituting the first block and the second block.

"Essentially" means at least to 85%, preferably at least to 90%, more preferably to 95% and even more preferably to 100%.

The block polymer according to the invention is advantageously a film-forming ethylenic block polymer.

5 "Ethylenic" polymer means a polymer obtained by polymerization of monomers comprising an ethylenic unsaturation.

"Film-forming" polymer means a polymer that is able to form, on its own or in the presence of a film-forming auxiliary, a continuous deposit on a substrate, notably on keratinous materials.

10 Preferably, the polymer according to the invention does not comprise silicon atoms in its backbone. "Backbone" means the main chain of the polymer, as opposed to the pendent side chains.

15 Preferably, the polymer according to the invention is not water-soluble, i.e. the polymer is not soluble in water or in a mixture of water and linear or branched lower monohydric alcohols having from 2 to 5 carbon atoms such as ethanol, isopropanol or n-propanol, without change of pH, at a content of active substance of at least 1 wt.%, at room temperature (25°C).

20 Preferably, the polymer according to the invention is not an elastomer.

25 "Non-elastomeric polymer" means a polymer which, when it is submitted to a stress with the aim of stretching it (for example by 30% relative to its initial length), does not return to a length almost identical to its initial length when the stress is removed.

30 More specifically, "non-elastomeric polymer" denotes a polymer having an instantaneous recovery $R_i < 50\%$ and a delayed recovery $R_{2h} < 70\%$ after undergoing elongation of 30%. Preferably, R_i is $< 30\%$, and $R_{2h} < 50\%$.

35 More precisely, the non-elastomeric character of the polymer is determined according to the following protocol:

A polymer film is prepared by pouring a solution of the polymer in a PTFE-coated mould, followed by drying for 7 days

in controlled conditions at $23\pm 5^{\circ}\text{C}$ and $50\pm 10\%$ relative humidity.

A film with thickness of about $100\ \mu\text{m}$ is obtained, from which rectangular test specimens are cut (for example with a punch) with width of 15 mm and length of 80 mm.

A tensile force is applied to this specimen by means of apparatus marketed under the reference Zwick, in the same conditions of temperature and humidity as for drying.

The test specimens are stretched at a speed of 50 mm/min and the distance between the jaws is 50 mm, which corresponds to the initial length (I_0) of the test specimen.

The instantaneous recovery R_i is determined as follows:

- the test specimen is stretched by 30% (ϵ_{max}) i.e. about 0.3 times its initial length (I_0)
- the stress is relieved by setting a return speed equal to the pulling speed, i.e. 50 mm/min and the residual elongation of the test specimen is measured as a percentage, after returning to zero loading stress (ϵ_i).

The percentage instantaneous recovery (R_i) is given by the following formula:

$$R_i = (\epsilon_{\text{max}} - \epsilon_i) / \epsilon_{\text{max}} \times 100$$

To determine the delayed recovery, after 2 hours the extent of residual elongation of the test specimen is measured as a percentage ($\epsilon_{2\text{h}}$), 2 hours after return to zero loading stress.

The percentage delayed recovery ($R_{2\text{h}}$) is given by the following formula:

$$R_{2\text{h}} = (\epsilon_{\text{max}} - \epsilon_{2\text{h}}) / \epsilon_{\text{max}} \times 100$$

Purely as a guide, a polymer according to one embodiment of the invention preferably has an instantaneous recovery R_i of 10% and a delayed recovery $R_{2\text{h}}$ of 30%.

The polydispersity index of the polymer of the invention is greater than 2.

Advantageously, the block polymer used in the compositions according to the invention has a polydispersity index I greater than 2, for example in the range from 2 to 9, preferably greater than or equal to 2.5, for example in the range from 2.5 to 8, and more preferably greater than or equal to 2.8 and notably in the range from 2.8 to 6.

The polydispersity index I of the polymer is equal to the ratio of the weight-average molecular weight Mw to the number-average molecular weight Mn.

5 The weight-average molecular weight (Mw) and the number-average molecular weight (Mn) are determined by gel-permeation liquid chromatography (solvent THF, calibration curve established with reference standards of linear polystyrene, refractometric detector).

10 The weight-average molecular weight (Mw) of the polymer according to the invention is preferably less than or equal to 300 000, it ranges for example from 35 000 to 200 000, and preferably from 45 000 to 150 000 g/mol.

15 The number-average molecular weight (Mn) of the polymer according to the invention is preferably less than or equal to 70 000, it ranges for example from 10 000 to 60 000, and preferably from 12 000 to 50 000 g/mol.

20 Preferably, the polydispersity index of the polymer according to the invention is greater than 2, for example in the range from 2 to 9, preferably greater than or equal to 2.5, for example in the range from 2.5 to 8, and more preferably greater than or equal to 2.8 and notably in the range from 2.8 to 6.

First block having a Tg greater than or equal to 40°C

25 The block having a Tg greater than or equal to 40°C has for example a Tg in the range from 40 to 150°C, preferably greater than or equal to 50°C, ranging for example from 50°C to 120°C, and more preferably greater than or equal to 60°C, ranging for example from 60°C to 120°C.

30 The stated glass transition temperatures of the first and second blocks can be theoretical Tg's determined from the theoretical Tg's of the monomers constituting each of the blocks, which can be found in a reference manual such as the Polymer Handbook, 3rd ed., 1989, John Wiley, according to the following relation, called the Fox Law:

$$1/T_g = \sum_i (\omega_i / T_{g_i}),$$

i

w_i being the mass fraction of monomer i in the block in question and T_{gi} being the glass transition temperature of the homopolymer of monomer i .

Unless stated otherwise, the T_g 's stated for the first and second blocks in the present application are theoretical T_g 's.

The difference between the glass transition temperatures of the first and second blocks is generally greater than 10°C , preferably greater than 20°C , and more preferably greater than 30°C .

In the present invention, the expression "between ... and ..." means a range of values whose stated limits are excluded, and "from ... to ..." and "in the range from ... to ..." mean a range of values whose limits are included.

The block having a T_g greater than or equal to 40°C can be a homopolymer or a copolymer.

The block having a T_g greater than or equal to 40°C can be derived wholly or partly from one or more monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature greater than or equal to 40°C . This block can also be called "rigid block".

In the case when this block is a homopolymer, it is derived from monomers, which are such that the homopolymers prepared from these monomers have glass transition temperatures greater than or equal to 40°C . This first block can be a homopolymer, constituted of a single type of monomer (where the T_g of the corresponding homopolymer is greater than or equal to 40°C).

In the case when the first block is a copolymer, it can be derived wholly or partly from one or more monomers, whose nature and concentration are selected so that the T_g of the resultant copolymer is greater than or equal to 40°C . The copolymer can for example comprise:

- monomers which are such that the homopolymers prepared from these monomers have T_g 's greater than or equal to 40°C , for example a T_g in the range from 40°C to 150°C , preferably greater than or equal to 50°C , ranging for example from 50°C to 120°C , and more preferably greater than or equal to 60°C , ranging for example from 60°C to 120°C , and

- monomers which are such that the homopolymers prepared from these monomers have Tg's below 40°C, selected from the monomers having a Tg between 20°C to 40°C and/or the monomers having a Tg less than or equal to 20°C, for example a Tg in the range from -100°C to 20°C, preferably below 15°C, notably in the range from -80°C to 15°C and more preferably below 10°C, for example in the range from -50°C to 0°C, as described later.

The first monomers whose homopolymers have a glass transition temperature greater than or equal to 40°C are, preferably, selected from the following monomers, also called principal monomers:

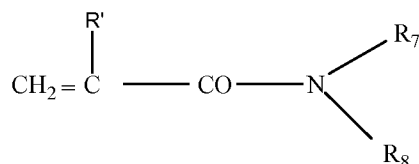
- the methacrylates of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_4$

in which R4 represents an unsubstituted, linear or branched alkyl group, containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group or R1 represents a C₄ to C₁₂ cycloalkyl group, preferably a C₈ to C₁₂ cycloalkyl, such as isobornyl methacrylate,

- the acrylates of formula $\text{CH}_2=\text{CH}-\text{COOR}_5$

in which R5 represents a C₄ to C₁₂ cycloalkyl group such as an isobornyl group or a tert-butyl group,

- the (meth)acrylamides of formula:



where R7 and R8, which may be identical or different, each represent a hydrogen atom or a linear or branched C₁ to C₁₂ alkyl group, such as an n-butyl, t-butyl, isopropyl, isohexyl, isooctyl, or isononyl group; or R7 represents H and R8 represents a 1,1-dimethyl-3-oxobutyl group,

and R' denotes H or methyl. As examples of monomers, we may mention N-butylacrylamide, N-t-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide,

- and mixtures thereof.

The first block is advantageously obtained from at least one acrylate monomer of formula $\text{CH}_2=\text{CH}-\text{COOR}_5$ and at least one methacrylate monomer of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_4$ in which R5

and R4 represent a C₄ to C₁₂ cycloalkyl group, preferably a C₈ to C₁₂ cycloalkyl, such as isobornyl. The monomers and their proportions are preferably selected in such a way that the glass transition temperature of the first block is greater than or equal to 40°C.

According to one embodiment, the first block is obtained from:

i) at least one acrylate monomer of formula CH₂=CH-COOR₅ in which R₅ represents a C₄ to C₁₂ cycloalkyl group, preferably a C₈ to C₁₂ cycloalkyl group, such as isobornyl,

- ii) and at least one methacrylate monomer of formula CH₂=C(CH₃)-COOR₄ in which R₄ represents a C₄ to C₁₂ cycloalkyl group, preferably a C₈ to C₁₂ cycloalkyl group, such as isobornyl.

According to one embodiment, the first block is obtained from at least one acrylate monomer of formula CH₂=CH-COOR₅ in which R₅ represents a C₈ to C₁₂ cycloalkyl group, such as isobornyl, and at least one methacrylate monomer of formula CH₂=C(CH₃)-COOR₄ in which R₄ represents a C₈ to C₁₂ cycloalkyl group, such as isobornyl.

Preferably, R₅ and R₄ represent, independently or simultaneously, an isobornyl group.

Preferably, the block copolymer comprises from 50 to 80 wt.% of isobornyl methacrylate/acrylate, from 10 to 30 wt.% of isobutyl acrylate and from 2 to 10 wt.% of acrylic acid.

The first block can be obtained exclusively from said acrylate monomer and said methacrylate monomer.

The acrylate monomer and the methacrylate monomer are preferably in weight ratios between 30:70 and 70:30, preferably between 40:60 and 60:40, notably of the order of 50:50.

The proportion of the first block is advantageously in the range from 20 to 90 wt.% of the polymer, preferably from 30 to 80% and more preferably from 60 to 80%.

According to one embodiment, the first block is obtained by polymerization of isobornyl methacrylate and isobornyl acrylate.

Second block with glass transition temperature below 20°C

The second block advantageously has a glass transition temperature T_g less than or equal to 20°C for example a T_g in the range from -100°C to 20°C, preferably less than or equal to 15°C, notably in the range from -80°C to 15°C and more preferably less than or equal to 10°C, for example in the range from -100°C to 10°C, notably in the range from -30°C to 10°C.

The second block is derived wholly or partly from one or more second monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature less than or equal to 20°C.

This block can also be called "flexible block".

The monomer having a T_g less than or equal to 20°C (called second monomer) is, preferably, selected from the following monomers:

- the acrylates of formula $\text{CH}_2=\text{CHCOOR}_9$,
R₉ representing an unsubstituted, linear or branched C₁ to C₁₂ alkyl group, with the exception of the tert-butyl group, in which optionally one or more heteroatoms selected from O, N, S are intercalated,
- the methacrylates of formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COOR}_{10}$,
R₁₀ representing an unsubstituted, linear or branched C₆ to C₁₂ alkyl group, in which optionally one or more heteroatoms selected from O, N and S are intercalated;
- the vinyl esters of formula $\text{R}_{11}\text{-CO-O-CH=CH}_2$
where R₁₁ represents a linear or branched C₄ to C₁₂ alkyl group;
- the ethers of vinyl alcohol and of C₄ to C₁₂ alcohol,
- the C₄ to C₁₂ N-alkyl acrylamides, such as N-octylacrylamide,
- and mixtures thereof.

The monomers having a T_g less than or equal to 20°C that are preferred are isobutyl acrylate, ethyl-2 hexyl acrylate or mixtures thereof in all proportions.

Each of the first and second blocks can contain, in smaller proportion, at least one monomer constituting the other block.

Thus, the first block can contain at least one monomer constituting the second block and vice versa.

The first and/or second block can each comprise, apart from the monomers stated above, one or more other monomers called additional monomers, different from the principal monomers mentioned previously.

The nature and the amount of this or these additional monomers are selected so that the block in which they reside has the desired glass transition temperature.

10 This additional monomer is for example selected from:

- monomers with ethylenic unsaturation(s) comprising at least one tertiary amine function such as 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminopropyl methacrylamide and salts thereof,

- methacrylates of formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COOR}_{12}$

in which R₁₂ represents a linear or branched alkyl group, containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group, said alkyl group being substituted with one or more substituents selected from hydroxyl groups (such as 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate) and halogen atoms (Cl, Br, I, F), such as trifluoroethyl methacrylate,

- methacrylates of formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COOR}_{13}$,
R₁₃ representing a linear or branched C₆ to C₁₂ alkyl group, in which optionally one or more heteroatoms selected from O, N and S are intercalated, said alkyl group being substituted with one or more substituents selected from hydroxyl groups and halogen atoms (Cl, Br, I, F);

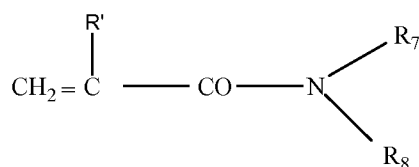
- acrylates of formula $\text{CH}_2=\text{CHCOOR}_{14}$,

R₁₄ representing a linear or branched C₁ to C₁₂ alkyl group substituted with one or more substituents selected from hydroxyl groups and halogen atoms (Cl, Br, I and F), such as 2-hydroxypropyl acrylate and 2-hydroxyethyl acrylate, or R₁₀ represents a C₁ to C₁₂ alkyl O-POE (polyoxyethylene) with repetition of the oxyethylene unit 5 to 10 times, for example methoxy-POE, or R₈ represents a

polyoxyethylene group comprising 5 to 10 ethylene oxide units.

In particular, the first block can comprise as additional monomer:

- 5 - (meth)acrylic acid, preferably acrylic acid,
 - tert-butyl acrylate
 - the methacrylates of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_4$
 in which R_1 represents an unsubstituted, linear or
 branched alkyl group, containing from 1 to 4 carbon atoms,
 10 such as a methyl, ethyl, propyl or isobutyl group,
 - the (meth)acrylamides of formula:



where R_7 and R_8 , which may be identical or different, each represent a hydrogen atom or a linear or branched C_1 to C_{12} alkyl group, such as an n-butyl, t-butyl, isopropyl, isohexyl, isooctyl, or isononyl group; or R_7 represents H and R_8 represents a 1,1-dimethyl-3-oxobutyl group, and R' denotes H or methyl. As examples of monomers, we may mention N-butylacrylamide, N-t-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide,

- and mixtures thereof.

The additional monomer can represent 0.5 to 30 wt.% of the weight of the polymer. According to one embodiment, the polymer of the invention does not contain an additional monomer.

Preferably, the polymer of the invention comprises at least isobornyl acrylate and isobornyl methacrylate monomers in the first block and isobutyl acrylate and acrylic acid monomers in the second block.

Preferably, the polymer comprises at least isobornyl acrylate and isobornyl methacrylate monomers in equivalent proportions by weight in the first block and isobutyl acrylate and acrylic acid monomers in the second block.

Preferably, the polymer comprises at least isobornyl acrylate and isobornyl methacrylate monomers in equivalent

proportion by weight in the first block, and isobutyl acrylate and acrylic acid monomers in the second block, the first block representing 70 wt.% of the polymer.

Preferably, the polymer comprises at least isobornyl acrylate and isobornyl methacrylate monomers in equivalent proportion by weight in the first block, and isobutyl acrylate and acrylic acid monomers in the second block. Preferably, the block with Tg above 40°C represents 70 wt.% of the polymer, and the acrylic acid represents 5 wt.% of the polymer.

According to one embodiment, the first block does not comprise any additional monomer.

According to a preferred embodiment, the second block comprises acrylic acid as additional monomer. In particular, the second block is advantageously obtained from an acrylic acid monomer and at least one other monomer having a Tg less than or equal to 20°C.

The block copolymer can advantageously comprise more than 2 wt.% of acrylic acid monomers, and notably from 2 to 15 wt.%, for example from 3 to 15 wt.%, in particular from 4 to 15 wt.%, or even from 4 to 10 wt.% of acrylic acid monomers, relative to the total weight of said copolymer.

The monomers constituting the second block and their proportions are selected in such a way that the glass transition temperature of the second block is less than or equal to 20°C.

Intermediate segment

The intermediate segment (also called intermediate block) joins together the first block and the second block of the polymer used according to the present invention. The intermediate segment results from the polymerization:

- i) of the first monomer(s), and optionally of the additional monomer(s), remaining available after their polymerization at a degree of conversion of at most 90% to form the first block,
- ii) and of the second monomer(s), and optionally of the additional monomer(s), added to the reaction mixture.

Formation of the second block is initiated when the first monomers no longer react or are no longer incorporated in the

polymer chain either because they have all been consumed or because their reactivity no longer permits them to exist.

Thus, the intermediate segment comprises the first monomers available, resulting from a degree of conversion of these first monomers less than or equal to 90%, at the time of introduction of the second monomer(s) during synthesis of the polymer.

The intermediate segment of the block polymer is a random polymer (it can also be called a random block). This means that it comprises a random distribution of the first monomer(s) and of the second monomer(s) as well as of the additional monomer(s) optionally present.

Thus, the intermediate segment is a random block, as are the first block and the second block if they are not homopolymers (i.e. if they are both formed from at least two different monomers).

Method of preparation of the copolymer:

The ethylenic block copolymer according to the invention is prepared by free radical polymerization, according to the well known techniques of this type of polymerization.

Free radical polymerization is carried out in the presence of an initiator, the nature of which depends, as is well known, on the desired polymerization temperature and on the polymerization solvent. In particular, the initiator can be selected from initiators with a peroxide function, redox couples, or other initiators of radical polymerization known by a person skilled in the art.

In particular, as initiator with a peroxide function, we may mention for example:

- a. peroxyesters, such as tert-butyl-peroxyacetate, tert-butyl perbenzoate, tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S from Akzo Nobel), 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox 141 from Akzo Nobel);
- b. peroxydicarbonates, such as diisopropylperoxydicarbonate;
- c. peroxyketones, such as methyl ethyl ketone peroxide;

- d. hydroperoxides, such as hydrogen peroxide (H_2O_2), tert-butylhydroperoxide;
- e. diacyl peroxides, such as acetyl peroxide, benzoyl peroxide;
- 5 f. dialkyl peroxides, such as di-tert-butyl peroxide;
- g. inorganic peroxides, such as potassium peroxodisulphate ($K_2S_2O_8$);

As initiator in the form of redox couple, we may mention the potassium thiosulphate + potassium peroxodisulphate couple,
10 for example.

According to a preferred embodiment, the initiator is selected from the organic peroxides comprising 8 to 30 carbon atoms. Preferably, the initiator used is 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane marketed under the
15 reference Trigonox® 141 by the company Akzo Nobel.

The block copolymer used according to the invention is prepared by free radical polymerization and not by controlled or living polymerization. In particular, the polymerization of the ethylenic block copolymer is carried out in the absence of
20 controlling agents, and in particular in the absence of controlling agents used conventionally in the methods of living or controlled polymerization such as nitroxides, alkoxyamines, dithioesters, dithiocarbamates, dithiocarbonates or xanthates, trithiocarbonates, copper-based catalysts, for
25 example.

As stated previously, the intermediate segment is a random block, as are the first block and the second block if they are not homopolymers (i.e. if they are both formed from at least two different monomers).

30 The block copolymer can be prepared by free radical polymerization, and in particular by a method consisting of mixing, in one and the same reactor, a polymerization solvent, an initiator, at least one monomer with glass transition greater than or equal to $40^\circ C$, at least one monomer with glass
35 transition less than or equal to $20^\circ C$ according to the following sequence:

- a portion of the polymerization solvent and optionally a portion of the initiator and of the monomers of

the first melt are poured into the reactor, and this mixture is heated to a reaction temperature between 60 and 120°C,

- then, in a first melt, said at least one first monomer with Tg greater than or equal to 40°C and optionally a portion of the initiator are poured in and left to react for a time T corresponding to a degree of conversion of said monomers of max. 90%,

- then, in a second melt, once again polymerization initiator, and said at least one second monomer with glass transition less than or equal to 20°C are poured into the reactor, and left to react for a time T', after which the degree of conversion of said monomers reaches a plateau,

- the reaction mixture is brought back to room temperature.

Preferably, the copolymer can be prepared by free radical polymerization, in particular by a method consisting of mixing, in one and the same reactor, a polymerization solvent, an initiator, an acrylic acid monomer, at least one monomer with glass transition less than or equal to 20°C, at least one acrylate monomer of formula $\text{CH}_2=\text{CH}-\text{COOR}_9$ in which R9 represents a C₄ to C₁₂ cycloalkyl group, and at least one methacrylate monomer of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_{10}$ in which R10 represents a C₄ to C₁₂ cycloalkyl group, according to the following sequence of steps:

- a portion of the polymerization solvent and optionally a portion of the initiator and of the monomers of the first melt are poured into the reactor, this mixture being heated to a reaction temperature between 60 and 120°C,

- then, in a first melt, said at least acrylate monomer of formula $\text{CH}_2=\text{CH}-\text{COOR}_5$ and said at least methacrylate monomer of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_4$ as monomers with Tg greater than or equal to 40°C, and optionally a portion of the initiator are poured in, and left to react for a time T corresponding to a degree of conversion of said monomers of max. 90%,

- then, in a second melt, once again polymerization initiator, the acrylic acid monomer and said at least monomer with glass transition less than or equal to 20°C, are poured

into the reactor, and left to react for a time T', after which the degree of conversion of said monomers reaches a plateau,

- the reaction mixture is brought back to room temperature.

5 "Polymerization solvent" means a solvent or a mixture of solvents. In particular, as polymerization solvent that can be used, we may mention:

- 10 - ketones that are liquid at room temperature, such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone, acetone;
- ethers of propylene glycol that are liquid at room temperature, such as propylene glycol, propylene glycol monomethyl ether acetate, dipropylene glycol mono-n-butyl ether;
- 15 - short-chain esters (having from 3 to 8 carbon atoms in total) such as ethyl acetate, methyl acetate, propyl acetate, n-butyl acetate, isopentyl acetate;
- ethers that are liquid at room temperature such as 20 diethyl ether, dimethyl ether or dichlorodiethyl ether;
- alkanes that are liquid at room temperature such as decane, heptane, dodecane, isododecane, cyclohexane, isohexadecane;
- 25 - aromatic cyclic compounds that are liquid at room temperature such as toluene and xylene; aldehydes that are liquid at room temperature such as benzaldehyde, acetaldehyde and mixtures thereof.

Conventionally, the polymerization solvent is a volatile oil 30 with flash point below 80°C. The flash point is measured in particular according to standard ISO 3679.

The polymerization solvent can be selected notably from ethyl acetate, butyl acetate, alcohols such as isopropanol, ethanol, aliphatic alkanes such as isododecane and mixtures 35 thereof. Preferably, the polymerization solvent is a mixture of butyl acetate and isopropanol or isododecane.

According to another embodiment, the copolymer can be prepared by free radical polymerization according to a method

of preparation, consisting of mixing, in one and the same reactor, a polymerization solvent, an initiator, at least one monomer with glass transition less than or equal to 20°C, and at least one monomer with Tg greater than or equal to 40°C, according to the following sequence of steps:

- a portion of the polymerization solvent and optionally a portion of the initiator and of the monomers of the first melt are poured into the reactor, and the mixture is heated to a reaction temperature between 60 and 120°C,

- then, in a first melt, said at least one monomer with glass transition less than or equal to 20°C and optionally a portion of the initiator are poured in, and left to react for a time T corresponding to a degree of conversion of said monomers of max. 90%,

- then, in a second melt, once again polymerization initiator, and said at least one monomer with Tg greater than or equal to 40°C, are poured into the reactor, and left to react for a time T', after which the degree of conversion of said monomers reaches a plateau,

- the reaction mixture is brought back to room temperature.

According to a preferred embodiment, the copolymer can be prepared by free radical polymerization according to a method of preparation consisting of mixing, in one and the same reactor, a polymerization solvent, an initiator, an acrylic acid monomer, at least one monomer with glass transition less than or equal to 20°C, at least one monomer with Tg greater than or equal to 40°C, and in particular as monomers with Tg greater than or equal to 40°C, at least one acrylate monomer of formula $\text{CH}_2=\text{CH}-\text{COOR}_5$ in which R5 represents a C₄ to C₁₂ cycloalkyl group, and at least one methacrylate monomer of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_4$ in which R4 represents a C₄ to C₁₂ cycloalkyl group, according to the following sequence of steps:

- a portion of the polymerization solvent and optionally a portion of the initiator and of the monomers of the first melt are poured into the reactor, and the mixture is heated to a reaction temperature between 60 and 120°C,

- then, in a first melt, the acrylic acid monomer and said at least monomer with glass transition less than or equal to 20°C and optionally a portion of the initiator are poured in, and left to react for a time T corresponding to a degree of conversion of said monomers of max. 90%,

- then, in a second melt, once again polymerization initiator, said at least one acrylate monomer of formula $\text{CH}_2=\text{CH}-\text{COOR}_5$ and said at least one methacrylate monomer of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_4$, as monomer with T_g greater than or equal to 40°C, are poured into the reactor, and left to react for a time T', after which the degree of conversion of said monomers reaches a plateau,

- the reaction mixture is brought back to room temperature.

The polymerization temperature is preferably of the order of 90°C.

The reaction time after the second melt is preferably between 3 and 6 hours.

Distillation of the synthesis solvent

For application of the block polymer in a composition according to the invention, and when the polymer is prepared in a volatile solvent or a volatile oil having a flash point below 80°C, it is necessary to proceed to a stage of total or partial removal of said volatile solvent or volatile oil. This is done in particular by distillation, optionally under vacuum, and addition of non-volatile hydrocarbon ester oil comprising at least 16 carbon atoms and having a molar mass below 650 g/mol.

This technique is known by a person skilled in the art. The distillation of the synthesis solvent (conventionally isododecane) is carried out with simultaneous addition, or with presence in the mixture before distillation, of a non-volatile hydrocarbon ester oil comprising at least 16 carbon atoms and having a molar mass below 650 g/mol. This stage is carried out hot and optionally under vacuum for maximum distillation of isododecane (and more generally of synthesis solvent), if the latter was used as polymerization solvent, or

more generally for maximum distillation of volatile oil with flash point below 80°C. The non-volatile oil ester can also be added partly or wholly to the polymer in the volatile solvent prior to distillation.

5 Removal of the volatile oil with flash point below 80°C (conventionally isododecane) makes it possible to limit the content of the latter in the solution of block copolymer and thus produce a cosmetic composition containing less than 10 wt.% of isododecane (and more generally of volatile
10 solvent) and preferably less than 5 wt.% of isododecane (and more generally of volatile solvent), relative to the total weight of the composition.

The composition according to the invention preferably comprises less than 0.1 to 40 wt.% of ethylenic block
15 copolymer, and advantageously from 0.5 to 30 wt.%, notably from 1 to 20 wt.% of active substance relative to the total weight of the composition.

Volatile solvent

20 According to the invention, the composition contains one or more volatile solvents.

Within the scope of the invention, "volatile solvent" means a compound that is liquid at room temperature (20°C) and at atmospheric pressure (760 mmHg) having a vapour pressure at
25 20°C greater than 0.1 mmHg and preferably between 0.1 and 300 mmHg, even more preferably between 0.5 and 200 mmHg.

This volatile solvent can be water, a non-silicone organic solvent, a silicone organic solvent or mixtures thereof.

As non-volatile silicone organic solvent, we may mention:

- 30
- volatile C₁-C₄ alkanols such as ethanol, isopropanol;
 - volatile C₅-C₇ alkanes such as n-pentane, hexane, cyclopentane, 2,3-dimethylbutane, 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane;
 - esters of liquid C₁-C₂₀ acids and of volatile C₁-C₈
35 alcohols such as methyl acetate, n-butyl acetate, ethyl acetate, propyl acetate, isopentyl acetate, ethyl 3-ethoxypropionate;

- ketones that are liquid at room temperature and volatile such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone, acetone;

- volatile polyols such as propylene glycol;

5 - volatile ethers such as dimethoxymethane, diethoxyethane, diethyl ether;

- volatile glycol ethers such as 2-butoxyethanol, butyl diglycol, diethylene glycol monomethyl ether, propylene glycol n-butyl ether, propylene glycol monomethyl ether acetate;

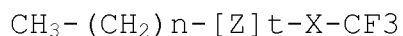
10 - volatile hydrocarbon oils such as volatile hydrocarbon oils having from 8 to 16 carbon atoms and mixtures thereof, and notably branched C₈-C₁₆ alkanes such as C₈-C₁₆ isoalkanes (also called isoparaffins), isododecane, isodecane, and for example oils sold under the trade names Isopars or
15 Permetyls, and mixtures thereof. We may also mention isohexyl or isodecyl neopentanoates.

The volatile hydrocarbon oil can also be a linear volatile alkane selected from linear volatile alkanes comprising from 8
20 to 17 carbon atoms, and in particular from 9 to 15 carbon atoms, and more particularly from 11 to 13 carbon atoms, notably of vegetable origin.

- volatile C₄-C₁₀ perfluoroalkanes such as dodecafluoropentane, tetradecafluorohexane, decafluoropentane;

25 - volatile perfluorocycloalkyls such as perfluoromethylcyclopentane, 1,3-perfluorodimethylcyclohexane and perfluorodecalin, sold respectively under the names "Flutec PC1®", "Flutec PC3®" and "Flutec PC6®" by the company F2 Chemicals, as well as perfluorodimethylcyclobutane and perfluoromorpholine;

30 - volatile fluoroalkyl or heterofluoroalkyl compounds corresponding to the following formula:



in which t is 0 or 1; n is 0, 1, 2 or 3; X is a linear or branched divalent perfluoroalkyl radical, having from 2 to
35 5 carbon atoms, and Z represents O, S, or NR, R being a hydrogen atom, a radical $-(\text{CH}_2)_n-\text{CH}_3$ or a radical $-(\text{CF}_2)_m-\text{CF}_3$, m being 2, 3, 4 or 5.

Among the volatile fluoroalkyl or heterofluoroalkyl compounds, we may notably mention methoxynonafluorobutane sold under the name "MSX 4518®", "HFE-7100®" by the 3M Company and ethoxynonafluorobutane sold under the name "HFE-7200®" by the 3M Company.

Preferably, the solvent is selected so that its boiling point is below 200°C.

According to a particular embodiment, the non-silicone organic solvent is selected from ethanol, isopropanol, acetone, and alkanes that are liquid at 25°C and at atmospheric pressure (760 mmHg) such as isododecane.

As volatile silicone solvent, we may mention the silicone compounds of low viscosity selected from the linear or cyclic silicones having from 2 to 7 silicon atoms, these silicones optionally having alkyl or alkoxy groups having from 1 to 10 carbon atoms, for example octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethylethyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, and mixtures thereof. According to a particular embodiment, the silicone compound is selected from cyclopentadimethylsiloxane, dodecamethylcyclohexasiloxane, octamethyltrisiloxane and decamethyltetrasiloxane.

According to a particular embodiment, the volatile silicone solvent has a viscosity below 50 centistokes.

Preferably, the volatile silicone is selected from decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, octamethyltrisiloxane and decamethyltetrasiloxane.

As examples, we may mention decamethylcyclopentasiloxane marketed under the name DC-245 by the company Dow Corning, dodecamethylcyclohexasiloxane marketed under the name DC-246 by the company Dow Corning, octamethyltrisiloxane marketed under the name DC-200 Fluid 1 cst by the company Dow Corning and decamethyltetrasiloxane marketed under the name DC-200 Fluid 1.5 cst by the company Dow Corning.

According to a particular embodiment of the invention, the volatile solvent(s) are selected from water, ethanol, isopropanol, acetone, the volatile alkanes as defined

previously and in particular isododecane, decamethylcyclopentasiloxane, octamethyltrisiloxane and decamethyltetrasiloxane and mixtures thereof.

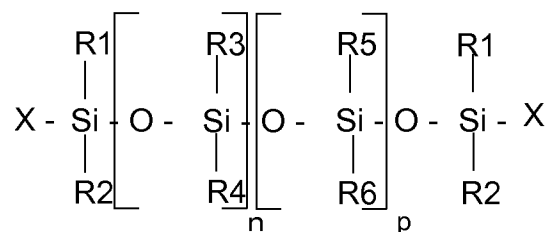
The volatile solvent(s) can be present in the composition of the invention at a content in the range from 0.1 to 95 wt.% relative to the total weight of the composition, preferably in the range from 1 to 90 wt.%, and preferably in the range from 5 to 90 wt.%.

10 Additional silicone compounds

To obtain better spreading of the composition of the invention as well as an improved surface coating, the composition of the invention can also contain one or more polysiloxanes having a viscosity greater than 100 cSt, preferably greater than 300 cSt. The viscosity of these polysiloxanes can be measured according to standard ASTM D-445. Said polysiloxanes can be silicone oils, gums or resins, and crosslinked silicones.

As polysiloxanes with viscosity greater than 100 cSt, we may notably mention polydimethylsiloxanes; alkyldimethicones; polyphenylmethylsiloxanes such as phenyldimethicones, phenyltrimethicones, and vinylmethylmethicones; as well as silicones modified with aliphatic and/or aromatic groups, optionally fluorinated, or with functional groups such as hydroxyl, thiol and/or amine groups.

Said polysiloxanes can be selected from the silicones of formula (I):



(I)

in which:

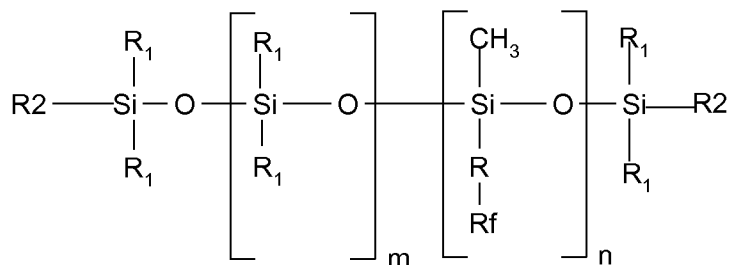
30 R₁, R₂, R₅ and R₆ are, together or separately, an alkyl radical having 1 to 6 carbon atoms, R₃ and R₄ are, together or separately, an alkyl radical having from 1 to 6 carbon atoms, a vinyl radical, an aryl radical, an aminoalkyl radical having

from 1 to 6 carbon atoms optionally substituted, a hydroxyl radical, a thioalkyl radical having from 1 to 6 carbon atoms, X is an alkyl radical having from 1 to 6 carbon atoms, a hydroxyl radical, a vinyl radical, an aminoalkyl radical having from 1 to 6 carbon atoms optionally substituted, a thioalkyl radical having from 1 to 6 carbon atoms, n and p being integers selected so as to obtain a viscosity greater than 300 cSt.

As examples, we may mention the following polydimethylsiloxanes:

- the substituents R_1 to R_6 and X represent a methyl group, such as that sold under the name Baysilicone TP 3898 by the company General Electric, and that sold under the name AK 500000 by the company Wacker,
- the substituents R_1 to R_6 and X represent a methyl group, p and n are such that the molecular weight is 120 000 g/mol, such as that sold under the name Dow Corning 200 Fluid 60000 CS by the company Dow Corning,
- the substituents R_1 to R_6 and X represent a methyl group, p and n are such that the molecular weight is 250 000 g/mol, such as that sold under the name Mirasil DM 500.000 by the company Rhodia and that sold under the name Dow Corning 200 Fluid 500.000 cst by the company Dow Corning,
- the substituents R_1 to R_6 represent a methyl group, the group X represents a hydroxyl group, n and p are such that the molecular weight of the polymer is 600 000 g/mol, such as that sold under the name SGM 36 by the company Dow Corning,
- the dimethicones of the (polydimethylsiloxane) (methylvinylsiloxane) type such as SE63 marketed by GE BAYER Silicones, the poly(dimethylsiloxane) (diphenyl) (methylvinylsiloxane) copolymers, and mixtures thereof.

In the case when the polysiloxane comprises a fluorinated group, we can select the copolymers with the following structure:



in which:

R represents a linear or branched divalent alkyl group, having 1 to 6 carbon atoms, preferably a methyl, ethyl, propyl or butyl divalent group, R_f represents a fluoroalkyl radical, notably a perfluoroalkyl radical, having 1 to 12 carbon atoms, preferably 1 to 9 carbon atoms, R₁ represents, independently of one another, a C₁-C₂₀ alkyl radical, a hydroxyl radical, a phenyl radical, R₂ represents R₁ or R_f,
 5 m is selected from 0 to 500, preferably from 0 to 200, and n is selected from 1 to 1000, preferably from 1 to 500.

Preferably, the groups R₁ are identical and represent a methyl radical.

Such polysiloxanes are notably those marketed by the company Shin-Etsu under the names 'FL-5', 'FL-10', 'X22-821' and 'X22-822' or 'FL-100', by the company Dow Corning under the name FS-1265 Fluid, by the company Phoenix Chemical in the range Pecosil FS under the names Pecosil FSL-150, Pecosil FSL-300, Pecosil FSH-150, Pecosil FSH-300, Pecosil FSU-150, Pecosil FSU-300.
 15 20

The weight-average molecular weight of the polysiloxane(s) can be between 1000 and 1 500 000 g/mol, notably between 20 000 and 1 000 000 g/mol.

The polysiloxane can be in the form of resin different from the siloxane resins of the invention. The term "resin" means a three-dimensional structure crosslinked or not crosslinked. As examples of polysiloxane resin, we may mention silsesquioxanes and siloxysilicates.
 25

The nomenclature of the silicone resins is known by the name "MDTQ", the resin being described in relation to the various siloxane monomer units that it comprises, each of the letters "MDTQ" characterizing a type of unit.
 30

The letter M represents the monofunctional unit of formula $(\text{CH}_3)_3\text{SiO}_{1/2}$, the silicon atom being attached to just one oxygen atom in the polymer comprising said unit.

The letter D signifies a bifunctional unit $(\text{CH}_3)_2\text{SiO}_{2/2}$ in which the silicon atom is attached to two oxygen atoms.

The letter T represents a trifunctional unit of formula $(\text{CH}_3)\text{SiO}_{3/2}$.

In the units M, D, T defined above, at least one of the methyl groups can be substituted with a group R different from the methyl group, such as a hydrocarbon radical (notably alkyl) having from 2 to 10 carbon atoms or a phenyl group or else a hydroxyl group.

Finally, the letter Q signifies a tetrafunctional unit $\text{SiO}_{4/2}$ in which the silicon atom is attached to four hydrogen atoms, which are in their turn attached to the rest of the polymer.

Various resins with different properties can be obtained from these various units, the properties of these polymers varying depending on the type of monomers (or units), type and number of radicals substituted, length of the polymer chain, degree of branching and the size of the pendent chains.

As examples of these silicone resins, we may mention:

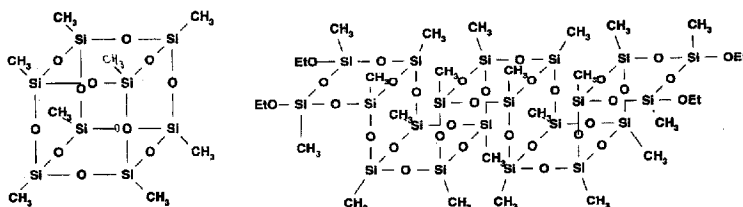
- the siloxysilicates, which can be trimethylsiloxysilicate of formula $[(\text{CH}_3)_3\text{SiO}]_x(\text{SiO}_{4/2})_y$ (units MQ) in which x and y are integers in the range from 50 to 80,
- the polysilsesquioxanes of formula $(\text{CH}_3\text{SiO}_{3/2})_x$ (units T) in which at least one of the methyl radicals can be substituted with a group R as defined above. Preferably the number x of units T of the silsesquioxane is less than or equal to 500, and more preferably it is between 50 and 500. The molecular weight of the silicone resin according to the invention is therefore preferably between 500 and 50 000 g/mol, more preferably between 500 and 20 000 g/mol and even more preferably between 500 and 10 000 g/mol;
- the polymethylsilsesquioxanes, which are polysilsesquioxanes in which none of the methyl radicals is substituted with another group. Said polymethylsilsesquioxanes are described in document US 5 246 694, the contents of which are incorporated by reference;

- the polypropylsilsesquioxanes, for which the methyl radicals are replaced with propyl radicals. These compounds as well as their synthesis are notably described in patent application WO 2005/075567;

5 - the polyphenylsilsesquioxanes, for which the methyl radicals are replaced with phenyl radicals. These compounds as well as their synthesis are notably described in patent application US 2004/0180011.

As examples of commercially available
10 polymethylsilsesquioxane resins, we may mention those that are marketed:

- by the company Wacker under the reference Resin MK such as Belsil PMS MK: polymer comprising $\text{CH}_3\text{SiO}_{3/2}$ repeating units (units T), which can also comprise up to 1 wt.% of $(\text{CH}_3)_2\text{SiO}_{2/2}$ units (units D) and have an average molecular weight of about 10 000 g/mol. It is thought that the polymer is in a "cage" and "ladder" configuration as shown in the figures below. The average molecular weight of the units in the "cage" configuration was calculated as 536 g/mol. Most of
20 the polymer is in the "ladder" configuration with ethoxy groups at the ends. These ethoxy groups represent 4.5 wt.% of the polymer. As these ends can react with water, a small, variable proportion of SiOH groups may also be present.



25 Cage

Ladder

- by the company SHIN-ETSU under the references KR-220L which are composed of units T of formula $\text{CH}_3\text{SiO}_{3/2}$ and have Si-OH (silanol) end groups, under the reference KR-242A which comprise 98% of units T and 2% of dimethyl units D and have
30 Si-OH end groups or under the reference KR-251 comprising 88% of units T and 12% of dimethyl units D and have Si-OH end groups.

As examples of commercially available polypropylsilsesquioxane resins, we may mention those that are marketed:

5 - by the company DOW CORNING under the reference Dow Corning 670 Fluid, which is a polypropylsilsesquioxane diluted in D5.

As examples of commercially available polyphenylsilsesquioxane resins, we may mention those that are marketed:

10 - by the company DOW CORNING under the reference Dow Corning 217 Flake Resin, which is a polyphenylsilsesquioxane with silanol ends;

- by the company WACKER under the reference Belsil SPR 45 VP.

15 As siloxysilicate resins, we may mention the trimethylsiloxysilicate (TMS) resins optionally in the form of powders. Such resins are marketed under the reference SR1000 by the company General Electric or under the reference TMS 803 by the company Wacker. We may also mention the
20 trimethylsiloxysilicate resins marketed in a solvent such as cyclomethicone, sold under the name "KF-7312J" by the company Shin-Etsu, "DC 749", "DC 593" by the company Dow Corning.

The silicone resin according to the invention is preferably film-forming. In fact, not all of the silsesquioxanes are film-
25 forming, for example the highly polymerized polymethylsilsesquioxanes such as TospearlTM from Toshiba or KMP590 from Shin-Etsu are insoluble and are not film-forming.

In one embodiment of the invention, the silicone resin(s) are soluble or dispersible in the composition of the invention.
30 Preferably, the silicone resins according to the invention are soluble in volatile silicones and organic solvents. In one embodiment, the silicone resin is solid at 25°C.

The silicone resins that are preferred according to the invention are the trimethylsiloxysilicate resins, the
35 polymethylsilsesquioxane resins and the polypropylsilsesquioxane resins.

The composition of the invention can also contain a crosslinked silicone such as a crosslinked elastomeric

organopolysiloxane, a silicone compound of high molecular weight having a three-dimensional structure, with the viscoelastic properties of a flexible solid material. These organopolysiloxanes can thus be in the form of dry powder, or
5 in swollen form, in a solvent, the resultant product generally being a gel. These products can also be in dispersed form in an aqueous solution.

The synthesis of these organopolysiloxane is described in the following patents:

- 10 - US 5 266 321 of Kobayashi Kose,
- US 4 742 142 of Toray Silicone,
- US 5 654 362 of Dow Corning Corp,
- patent application FR 2 864 784.

The elastomeric organopolysiloxanes used in the composition
15 can be partially or fully crosslinked. They are generally in the form of particles. In particular, the particles of elastomeric organopolysiloxane have a number-average size in the range from 0.1 to 500 μm . These particles can be of any shape and can for example be spherical, flat or amorphous.

The crosslinked organopolysiloxane obtained can be a non-
20 emulsifying compound or an emulsifying compound. The term "non-emulsifying" defines crosslinked organopolysiloxanes not containing polyoxyalkylene units. The term "emulsifying" denotes crosslinked organopolsiloxane compounds having at least
25 one polyoxyalkylene unit, notably polyoxyethylene or polyoxypropylene.

The particles of crosslinked organopolysiloxane can be carried in the form of gel constituted of a crosslinked organopolysiloxane included in at least one hydrocarbon oil
30 and/or one silicone oil. In these gels, the particles of organopolysiloxane are often non-spherical particles. The particles of crosslinked organopolysiloxane can also be in the form of powder, notably in the form of spherical powder.

Non-emulsifying crosslinked organopolysiloxanes are notably
35 described in patents US 4 970 252, US 4 987 169, US 5 412 004, US 5 654 362, US 5 760 116, and in application JP-A-61-194009.

As non-emulsifying crosslinked organopolysiloxanes, those sold under the names "KSG-6", "KSG-15", "KSG-16", "KSG-18",

"KSG-31", "KSG-32", "KSG-33", "KSG-41", "KSG-42", "KSG-43", "KSG-44", "USG-103" by the company Shin Etsu, "DC 9040", "DC9041", "DC 9509", "DC9505", "DC 9506", "DC 9045" by the company Dow Corning, "GRANSIL" by the company Grant Industries, "SFE 839" by the company General Electric can be used.

Advantageously, the emulsifying crosslinked organopolysiloxanes comprise the polyoxyalkylene modified organopolysiloxanes formed from divinyllic compounds, in particular polysiloxanes having at least two vinyl groups, reacting with Si-H bonds of a polysiloxane. Emulsifying crosslinked organopolysiloxanes are notably described in patents US 5 236 986, US 5 412 004, US 5 837 793, US 5 811 487.

As emulsifying crosslinked organopolysiloxanes, those marketed under the names "KSG-21", "KSG-20", "KSG-30" by the company Shin-Etsu, and "DC9010", "DC9011" by the company Dow Corning, can be used.

The particles of elastomeric crosslinked organopolysiloxane can also be in the form of powder of elastomeric crosslinked organopolysiloxane coated with silicone resin, notably with silsesquioxane resin, as described for example in patent US 5 538 793.

Such elastomers are sold under the name "KSP-100", "KSP-101", "KSP-102", "KSP-103", "KSP-104", "KSP-105" by the company Shin-Etsu.

Preferably the crosslinked organopolysiloxane is non-emulsifying.

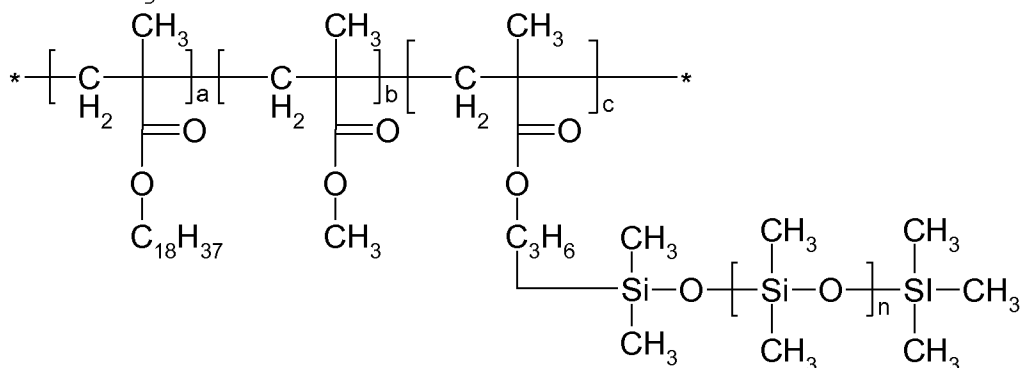
The composition of the invention can also contain a silicone graft polymer. Within the scope of the invention, silicone graft polymer means a polymer comprising a polysiloxane portion and a portion constituted of a non-silicone organic chain, one of the two portions constituting the main chain of the polymer and the other being grafted on said main chain.

The silicone graft polymers used in the cosmetic composition according to the invention are preferably selected from the group comprising polymers with an organic non-silicone backbone grafted with monomers containing a polysiloxane, polymers with a polysiloxane backbone grafted with non-silicone organic monomers and mixtures thereof.

The non-silicone organic monomers constituting the main chain of the silicone graft polymer can be selected from monomers with ethylenic unsaturation polymerizable by radical polymerization, monomers polymerizable by polycondensation such as those forming polyamides, polyesters, polyurethanes, ring-opening monomers such as those of the oxazoline or caprolactone type.

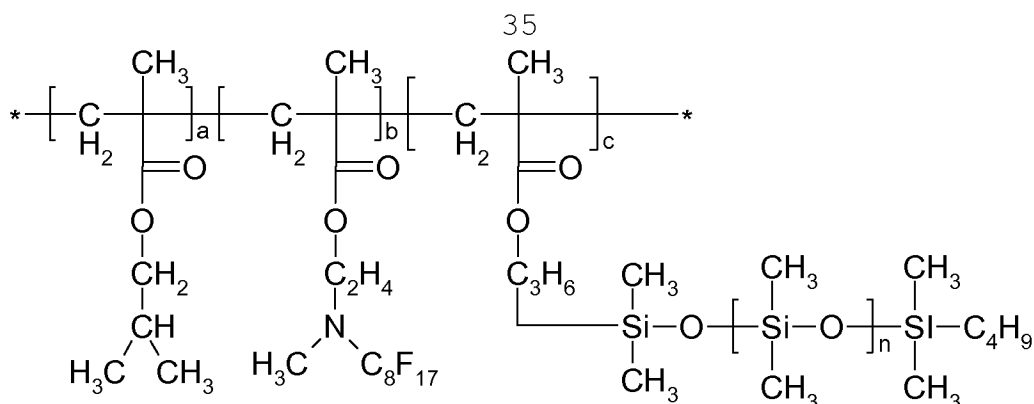
The polymers with a non-silicone organic backbone grafted with monomers containing a polysiloxane, according to the invention, can be selected from those described in patents US 4,693,935, US 4,728,571 and US 4,972,037 and patent applications EP-A-0 412 704, EP-A-0 412 707, EP-A-0 640 105 and WO 95/00578. They are copolymers obtained by radical polymerization from monomers with ethylenic unsaturation and silicone macromers having a vinyl end group or else copolymers obtained by reaction of a polyolefin comprising functionalized groups and a polysiloxane macromer having a terminal function that reacts with said functionalized groups.

The copolymer with non-silicone organic backbone grafted with monomers containing a polysiloxane can for example have the following structure:



Such a polymer is marketed under the name KP 561 by Shin-Etsu.

The copolymer with non-silicone organic backbone grafted with monomers containing a polysiloxane can also have the following structure:



Such a polymer, Polysilicone 7, is marketed under the name SA70 by 3M.

Other copolymers with a non-silicone organic backbone grafted with monomers containing a polysiloxane are also KP545, KP574 and KP575 marketed by Shin-Etsu.

As grafted silicone compound, we may also mention the isobutylmethacrylate / bis-hydroxypropyl dimethicone acrylate copolymer marketed by Grant Industrie under the name Granacrysil BMAS.

According to the present invention, the silicone graft polymer(s), with polysiloxane backbone grafted with non-silicone organic monomers comprise a main chain of silicone (or polysiloxane ($\equiv\text{Si-O-}$)_n), on which at least one organic group not containing silicone is grafted, within said chain as well as optionally on at least one of its ends.

Examples of silicone polymers corresponding to the definition are notably polydimethylsiloxanes (PDMS), on which mixed polymer units of the poly(meth)acrylic acid type and of the alkyl poly(meth)acrylate type are grafted, via a linking group of the thiopropylene type. As a compound corresponding to this definition, we may mention the poly dimethyl/methyl siloxane with propyl thio-3 methyl acrylate/methyl methacrylate/methacrylic acid groups or Polysilicone-8 marketed under the name VS80 by the 3M Company.

Other examples of silicone polymers are notably polydimethylsiloxanes (PDMS) on which polymer units of the isobutyl poly(meth)acrylate type are grafted, via a linking group of the thiopropylene type.

Preferably, the number-average molecular weight of the silicone polymers with polysiloxane backbone grafted with non-silicone organic monomers of the invention varies from about

10 000 to 1 000 000, and even more preferably from about 10 000 to 100 000.

Preferably, the silicone graft polymers are selected from the group comprising the alkyl methacrylate graft polydimethylsiloxane copolymer, the copolymers of methisobutyl acrylate, acrylic acid and silicone macromer, and the poly dimethyl/methyl siloxane with propyl methyl thio-3-acrylate/methyl methacrylate/methacrylic acid groups.

The preferred silicone compounds are the silicone oils and in particular those corresponding to formula (I).

When they are present in the composition of the invention, these silicone compounds that are different from the siloxane resins of the invention are introduced in an amount generally between 0.1 and 30 wt.%, notably between 0.1 and 20 wt.% and preferably between 0.1 and 15 wt.%.

Additional hydrophobic film-forming polymers

According to a particular embodiment, the composition of the invention comprises one or more hydrophobic film-forming polymers different from the polyethylene block polymers described previously and different from the silicone compounds described previously.

"Polymer" means a compound corresponding to the repetition of one or more units (these units being derived from compounds called monomers). This or these units are repeated at least twice and preferably at least 3 times.

"Hydrophobic polymer" means a polymer having a solubility in water at 25°C below 1 wt.%.

"Film-forming" polymer means a polymer able to form, on its own or in the presence of a film-forming auxiliary, a macroscopically continuous film on a substrate, notably on keratinous materials, and preferably a cohesive film.

In one embodiment, the hydrophobic film-forming organic polymer is at least one polymer selected from the group comprising:

- the film-forming polymers soluble in an organic solvent medium, in particular the fat-soluble polymers; this signifies that the polymer is soluble or miscible in the

organic medium and will form a single homogeneous phase when incorporated in the medium.

- the film-forming polymers dispersible in an organic solvent medium, this signifies that the polymer forms a phase that is insoluble in the organic medium, the polymer remaining stable and/or compatible once incorporated in this medium. In particular, such polymers can be in the form of non-aqueous dispersions of polymer particles, preferably dispersions in silicone or hydrocarbon oils; in one embodiment, the non-aqueous dispersions of polymer comprise polymer particles stabilized on their surface by at least one stabilizer; the abbreviation NAD is often used for these non-aqueous dispersions.

Among the hydrophobic film-forming polymers that can be used, we may mention the synthetic polymers, of the radical type or of the polycondensate type, the polymers of natural origin and mixtures thereof. As hydrophobic film-forming polymer, we may mention in particular acrylic polymers, polyurethanes, polyesters, polyamides, polyureas, cellulosic polymers such as nitrocellulose, polyurea-polyurethane silicone copolymer, copolymers based on silicone resin and fluid silicone, polyamide polymers and copolymers, polyisoprenes, polyalkylene-based supramolecular polymers.

The hydrophobic film-forming polymer can be selected from the film-forming polymers described in application WO 04/028487.

The hydrophobic film-forming polymer can notably be selected from:

a) The homopolymers and copolymers of olefins; of cycloolefins; of butadiene; of isoprene; of styrene; of ethers, of vinyl esters or amides; esters or amides of (meth)acrylic acid containing a linear, branched or cyclic C₁-C₂₀ alkyl group, a C₆-C₁₀ aryl group or a C₂-C₆ hydroxyalkyl group.

These homopolymers and copolymers can be obtained from monomers selected from the group comprising isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isopentyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl

(meth)acrylate, ethyl (meth)acrylate, methyl (meth)acrylate, tert-butyl (meth)acrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate, hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, benzyl or phenyl acrylate, or mixtures thereof.

5 As amides of acid monomers, we may mention the (meth)acrylamides, and notably the N-alkyl (meth)acrylamides, in particular of C₂-C₁₂ alkyl such as N-ethyl acrylamide, N-t-butyl acrylamide, N-octyl acrylamide; the N-dialkyl (C₁-C₄) (meth)acrylamides, perfluoroalkyl (meth)acrylates. The above
10 polymers can also contain, as monomers, small amounts of an unsaturated carboxylic or sulphonic acid such as the acrylic, methacrylic acids, AMPS, provided that the overall character of the polymer remains hydrophobic.

As other vinylic monomers that can be used, we may also
15 mention:

- N-vinylpyrrolidone, vinylcaprolactam, the vinyl N-alkyl (C₁-C₆) pyrroles, vinyl-oxazoles, vinyl-thiazoles, vinylpyrimidines, vinylimidazoles,

- the olefins such as ethylene, propylene, butenes,
20 isoprene, butadienes.

The vinylic polymer can be crosslinked by means of one or more bifunctional monomers, notably comprising at least two ethylenic unsaturations, such as ethylene glycol dimethacrylate or diallyl phthalate.

25 We may mention, for example, the alkyl acrylate/cycloalkyl acrylate copolymer marketed by PHOENIX CHEM. under the name GIOVAREZ AC-5099 ML, the vinylpyrrolidone copolymers, such as the copolymers of a C₂ to C₃₀ alkylene, such as C₃ to C₂₂, and combinations thereof, can be used. As examples of copolymers of
30 VP that can be used in the invention, we may also mention the copolymer of VP/vinyl laurate, of VP/vinyl stearate, butylated polyvinylpyrrolidone (PVP), of VP/hexadecene marketed by ISP under the name Ganex V216, of VP/eicosene marketed by ISP under the name Ganex V220, of VP/triacontene or of VP/acrylic
35 acid/lauryl methacrylate. We may also mention the copolymers whose CTFA name (4th Ed., 1991) is Octylacrylamide/acrylates/butylaminoethyl-methacrylate copolymer, such as the products sold under the name AMPHOMER®

or LOVOCRYL® 47 by the company NATIONAL STARCH as well as the copolymers whose CTFA name is Acrylates/octylacrylamide copolymer, such as the products sold under the name DERMACRYL® LT or DERMACRYL® 79 by the company NATIONAL STARCH.

5 As particular polymers, we may mention:

i) the polymers bearing fluorinated groups belonging to one of the classes described in the text above, in particular the Fomblins described in patent US 5 948 393, the alkyl (meth)acrylate/perfluoroalkyl (meth)acrylate copolymers
10 described in patents EP 0 815 836 and US 5 849 318.

ii) the polymers or copolymers resulting from the polymerization or the copolymerization of an ethylenic monomer, comprising one or more ethylene bonds, preferably conjugated (or dienes). As polymers or copolymers resulting from the
15 polymerization or the copolymerization of an ethylenic monomer, the vinylic, acrylic or methacrylic copolymers can be used.

In one embodiment, the film-forming polymer is a block copolymer comprising at least one block constituted of styrene units or styrene derivatives (for example methylstyrene, chlorostyrene or chloromethylstyrene). The copolymer comprising
20 at least one styrene block can be a diblock or triblock copolymer, or even a multiblock, star or radial copolymer. The copolymer comprising at least one styrene block can further comprise, for example, an alkylstyrene block (AS), an ethylene/butylene block (EB), an ethylene/propylene block (EP), a butadiene block (B), an isoprene block (I), an acrylate block (A), a methacrylate block (MA) or a combination of these
25 blocks. The copolymer comprising at least one block constituted of styrene units or styrene derivatives can be a diblock or triblock copolymer, and in particular of the
30 polystyrene/polyisoprene or polystyrene/polybutadiene type, such as those marketed or manufactured under the name "Luvitol HSB" by BASF and those of the polystyrene/copoly(ethylene-propylene) type or alternatively of the
35 polystyrene/copoly(ethylene/butylene) type, such as those marketed or manufactured under the brand "Kraton" by Shell Chemical Co. or Gelled Permethyl 99A by Penreco, can be used.

We may mention for example Kraton G1650 (SEBS), Kraton G1651 (SEBS), Kraton G1652 (SEBS), Kraton G1657X (SEBS), Kraton G1701X (SEP), Kraton G1702X (SEP), Kraton G1726X (SEB), Kraton D-1101 (SBS), Kraton D-1102 (SBS), Kraton D-1107 (SIS), Gelled Permethyl 99A-750, Gelled Permethyl 99A-753-58 (mixture of star block polymer and triblock polymer), Gelled Permethyl 99A-753-59 (mixture of star block polymer and triblock polymer), Versagel MD 970 and Versagel MD 960 from Penreco (mixture of star polymer and triblock polymer in isododecane).

Styrene-methacrylate copolymers can also be used, such as the polymers marketed under the reference OS 129880, OS 129881 and OS 84383 from Lubrizol (styrene-methacrylate copolymer).

In one embodiment, the film-forming polymer is selected from the copolymers of vinyl ester (the vinyl group being directly attached to the oxygen atom of the ester group and the vinyl ester having a linear or branched saturated hydrocarbon radical, with 1 to 19 carbon atoms, bound to the carbonyl of the ester group) and of at least one other monomer, selected from the vinyl esters (different from the vinyl ester already present), the α -olefins (having from 8 to 28 carbon atoms), the alkylvinyl ethers (whose alkyl group has from 2 to 18 carbon atoms), or the allylic or methallylic esters (having a linear or branched saturated hydrocarbon radical, with 1 to 19 carbon atoms, bound to the carbonyl of the ester group).

These copolymers can be partially crosslinked by means of crosslinking agents, which can either be of the vinylic type, or of the allylic or methallylic type, such as tetraallyloxyethane, divinylbenzene, divinyl octanedioate, divinyl dodecanedioate, and divinyl octadecanedioate.

As examples of these copolymers, we may mention the copolymers: vinyl acetate/allyl stearate, vinyl acetate/vinyl laurate, vinyl acetate/vinyl stearate, vinyl acetate/octadecene, vinyl acetate/octadecylvinyl ether, vinyl propionate/allyl laurate, vinyl propionate/vinyl laurate, vinyl stearate/octadecene-1, vinyl acetate/dodecene-1, vinyl stearate/ethylvinyl ether, vinyl propionate/cetylvinyl ether, vinyl stearate/allyl acetate, vinyl dimethyl-2,2-octanoate/vinyl laurate, allyl dimethyl-2,2-pentanoate/vinyl

laurate, dimethylvinyl propionate/vinyl stearate, allyl dimethyl propionate/vinyl stearate, vinyl propionate/vinyl stearate, crosslinked with 0.2% of divinylbenzene, dimethyl vinyl propionate/vinyl laurate, crosslinked with 0.2% of
5 divinylbenzene, vinyl acetate/octadecyl vinyl ether, crosslinked with 0.2% of tetraallyloxyethane, vinyl acetate/allyl stearate, crosslinked with 0.2% of divinylbenzene, vinyl acetate/octadecene-1 crosslinked with 0.2% of divinylbenzene and allyl propionate/allyl stearate
10 crosslinked with 0.2% of divinylbenzene.

iii) the polyalkylenes, the copolymers of C₂-C₂₀ alkylenes, in particular polybutylene.

iv) the polymers of natural origin, optionally modified, which can be selected from shellac resin, sandarac
15 gum, dammars, elemis, copals, polysaccharides comprising alkyl (ether or ester) side chains, in particular alkylcelluloses having a saturated or unsaturated, linear or branched C₁ to C₈ alkyl radical, such as ethylcellulose and propylcellulose.

The film-forming polymer of natural origin can be selected
20 in particular from cellulosic polymers such as nitrocellulose, cellulose acetate, cellulose acetobutyrate, cellulose acetopropionate. We may mention for example the ethyl cellulose marketed by Aqualon under the reference Aqualon Ethylcellulose N200, the cellulose acetobutyrate marketed by Eastman Chemical
25 under the reference CAB-381-0.5, the cellulose acetopropionates marketed by Eastman Chemical under the references CAP-482-20 and CAP-504-0.2.

v) the polycondensates

Among the polycondensates, we may mention non-ionic
30 polyurethanes, polyurethane-acrylics, polyurethane-polyvinylpyrrolidones, polyester-polyurethanes, polyether-polyurethanes, polyureas, polyurea/polyurethanes, and mixtures thereof.

The polyurethanes can be for example an aliphatic,
35 cycloaliphatic or aromatic polyurethane copolymer, or polyurea/polyurethane copolymer.

The polyurethanes as defined in the invention can also be obtained from branched or unbranched polyesters or from alkides

comprising mobile hydrogens, which are modified by polyaddition with a diisocyanate and a bifunctional organic co-reactant (for example dihydro, diamino or hydroxy-amino).

We may also mention the polyesters, the polyesteramides, the fatty-chain polyesters, the polyamides and the epoxyester resins.

The polyesters can be obtained in a known manner by the polycondensation of aliphatic or aromatic diacids with aliphatic or aromatic diols or with polyols. Succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid or sebacic acid can be used as aliphatic diacids. Terephthalic acid or isophthalic acid, or even a derivative such as phthalic anhydride, can be used as aromatic diacids. Ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, cyclohexanedimethanol and 4,4-N-(1-methylpropylidene)bisphenol, can be used as aliphatic diols.

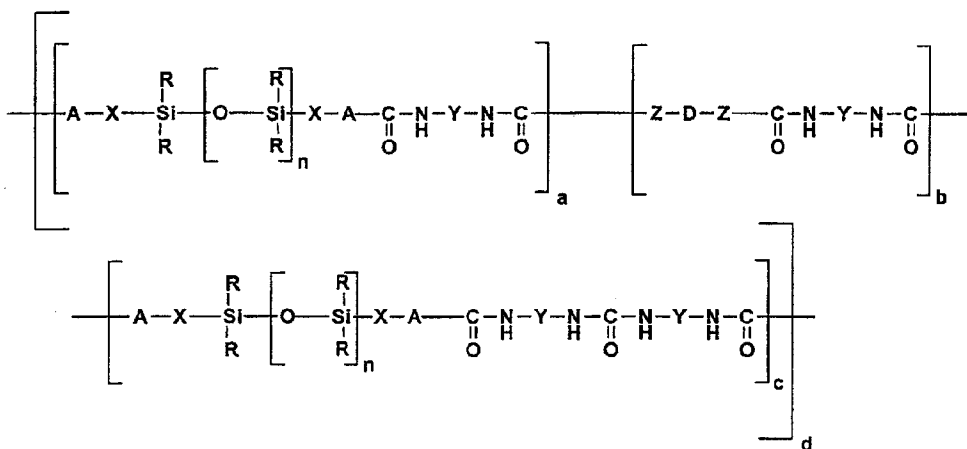
The polyester amides can be obtained similarly to the polyesters, by polycondensation of diacids with aminoalcohols. The polyamides can be obtained similarly to the polyesters, by polycondensation of diacids with diamines.

As particular polyesters, we may mention the aliphatic polyesters having C₄₋₅₀ alkyl side chains or else the polyesters resulting from the condensation of dimers of fatty acids, or even the polyesters comprising a silicone segment in the form of a block, graft or end group, such as defined in patent application FR 0113920.

b) The silicone polyamides of the polyorganosiloxane type such as those described in documents US A 5 874 069, US A 5 919 441, US A 6 051 216 and US A 5 981 680, the contents of which are incorporated in the present application by reference.

c) The polyurea/urethane silicone copolymers

These polyurea/polyurethane silicone copolymers correspond to the following general formula:



in which

R represents a monovalent hydrocarbon radical, if necessary substituted with fluorine or chlorine, having 1 to 20 carbon atoms,

X represents an alkylene radical having 1 to 20 carbon atoms, in which non-adjacent methylene units can be replaced with radicals -O-,

A represents an oxygen atom or an amino radical -NR'-,

Z represents an oxygen atom or an amino radical -NR'-,

R' represents hydrogen or an alkyl radical having 1 to 10 carbon atoms,

Y represents a bivalent hydrocarbon radical, if necessary substituted with fluorine or chlorine, having 1 to 20 carbon atoms,

D represents an alkylene radical, if necessary substituted with fluorine, chlorine, C₁-C₆ alkyl or C₁-C₆ alkyl ester, having 1 to 700 carbon atoms, in which non-adjacent methylene units can be replaced with radicals -O-, -COO-, -OCO- or -OCOO-,

n is a number in the range from 1 to 4000,

a is a number of at least 1,

b is a number in the range from 0 to 40,

c is a number in the range from 0 to 30, and

d is a number greater than 0,

provided that A represents, in at least one of the units (a), a radical NH.

Preferably, R represents a monovalent hydrocarbon radical with 1 to 6 carbon atoms, for example methyl, ethyl, vinyl and

phenyl. According to a particular embodiment, R is an unsubstituted alkyl radical.

Preferably, X represents an alkylene radical with 2 to 10 carbon atoms. Preferably, the alkylene radical X is not interrupted.

According to a particular embodiment, the group A in all the units (b) and (c), when they are present, represents NH.

According to a particularly preferred embodiment, all the groups A represent a radical NH.

Preferably, Z represents an oxygen atom or a radical NH.

Preferably, Y represents a hydrocarbon radical comprising 3 to 13 carbon atoms, which is preferably unsubstituted. Preferably, Y represents a linear or cyclic aralkylene, alkylene radical.

Preferably, D represents an alkylene radical with at least 2, in particular at least 4 carbon atoms and at most 12 carbon atoms.

Also preferably, D represents a polyoxyalkylene radical, in particular a polyoxyethylene or polyoxypropylene radical with at least 20, in particular at least 100 carbon atoms and at most 800, in particular at most 200 carbon atoms.

Preferably, the radical D is not substituted.

Preferably, n represents a number of at least 3, in particular at least 25 and preferably at most 800, in particular at most 400, and especially preferably at most 250.

Preferably, a represents a number greater than 50.

When b is different from 0, b preferably represents a number of at most 50, in particular at most 25.

Preferably, c represents a number of at most 10, in particular at most 5.

These copolymers can be obtained according to the methods of polymerization described in patent application US 2004/0254325 or application WO 03/014194.

As examples of copolymer, we may mention the dimethylpolysiloxane/urea copolymer, INCI name polyureadimethicone.

Said polymer can notably be obtained by copolymerization of an alpha, omega-aminosilicone with a di-isocyanate. Polymers

corresponding to these characteristics are for example the products marketed under the reference Wacker-Belsil® UD 60, Wacker-Belsil® UD 80, Wacker-Belsil® UD 140 and Wacker-Belsil® UD 200 by the company Wacker.

5 d) The copolymers based on silicone resin and fluid silicone

These silicone copolymers are obtained by reaction of a silicone resin and a fluid silicone.

Such copolymers are described for example in "Silicone
10 Pressure Sensitive Adhesive", Sobieski and Tangney, Handbook of Pressure Sensitive Adhesive Technology (D. Satas Ed.), Van Nostrand Reinhold, New York.

In the copolymer, the silicone resin is present in a proportion between 45 and 75% (relative to the total mass of
15 silicone) and the fluid silicone is present in a proportion between 25 and 55%, with the sum of the percentages of silicone resin and of fluid silicone being equal to 100. Preferably, the silicone resin is present in a proportion between 55 and 65% (relative to the total mass of silicone) and the fluid silicone
20 is present in a proportion between 35 and 45%, with the sum of the percentages of silicone resin and of fluid silicone being equal to 100.

Preferably, the silicone resin is the product of condensation of SiO_2 groups and $\text{R}_3(\text{SiO})_{1/2}$ groups
25 (triorganosilyl) for which each group R is selected independently from the methyl, ethyl, propyl or vinyl radicals and for which the ratio of the SiO_2 functions to the $\text{R}_3(\text{SiO})_{1/2}$ functions of the silicone resin is from 0.6 to 0.9. Triorganosilyl groups that can be used for forming the silicone
30 resin are trimethylsilyl, triethylsilyl, methylmethylpropylsilyl, and dimethylvinylsilyl units and mixtures thereof. The trimethylsilyl group is preferred within the scope of the invention.

Preferably, the fluid silicone is a diorganopolysiloxane
35 with terminal OH functions having a viscosity between 100 and 100 000 cSt at 25°C for which the substituents of the diorganopolysiloxane are selected independently from the methyl, ethyl, propyl or vinyl radicals. The diorganosiloxanes

are preferably linear polymers. Examples of diorganopolysiloxane can be, non-exhaustively, a polydimethylsiloxane, an ethylmethylpolysiloxane, a copolymer of dimethylsiloxane and methylvinylsiloxane, and mixtures of
5 said polymers or copolymers having OH end groups. The preferred diorganopolysiloxane is a polydimethylsiloxane.

Examples of synthesis of said copolymer are for example described in patent US5162410 or in patent CA711756.

The copolymers based on silicone resin and fluid silicone
10 that are preferred are marketed by Dow Corning under the reference BIO-PSA®, said BIO-PSA® being available in two forms, standard or amine-compatible, and being supplied in various solvents with various silicone resin/fluid silicone ratios. We may notably mention grades 7-4400, 7-4500, 7-4600. The BIO-PSA®
15 particularly preferred according to the invention is that of grade 7-4400.

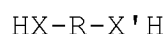
e) The supramolecular polymers based on polyalkylene

The supramolecular polymers based on polyalkylene comprise in their structure at least one polyalkylene part and at least
20 one part having at least one group capable of forming at least 3 hydrogen bonds, preferably 4 hydrogen bonds.

The polyalkylene is preferably selected from poly(ethylenebutylene), polybutadienes and polyisoprenes.

These supramolecular polymers can notably be derived from
25 the condensation of at least one polyalkylene polymer functionalized with at least one reactive group, with at least one graft functionalized with at least one reactive group able to react with the reactive group(s) of the functionalized polyalkylene polymer, said graft bearing at least one group
30 capable of forming at least 3 hydrogen bonds, preferably at least 4 hydrogen bonds.

Preferably, the functionalized polyalkylene polymer is of formula A:



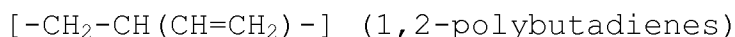
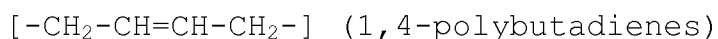
35 XH and X'H being reactive groups, with X and X', which may be identical or different, selected from O, S, NH, or NR_a, R_a representing a C₁-C₆ alkyl group; preferably, X and/or X' denote O; even more preferably, X and X' denote O;

R represents a homo- or copolymer derived from one or more mono- or polyunsaturated C₂-C₁₀ alkylenes, and preferably C₂-C₄; R preferably represents a poly(ethylenebutylene), a polybutadiene or a polyisoprene.

5 The poly(ethylenebutylene)s are copolymers of 1-butene and ethylene. They can be represented schematically by the sequence of units with the structures:



The polybutadienes can be 1,4-polybutadienes or 1,2-
10 polybutadienes, which can be represented schematically by the following sequences of units, respectively:



Preferably, the polybutadienes are 1,2-polybutadienes.

15 Functionalization preferably occurs at the chain ends. They are then called telechelic polymers. The functionalizing groups can be fixed to the polyalkylene polymer via linkers, preferably linear or branched C₁-C₄ alkylene groups.

These polyalkylenes can be partially or fully hydrogenated
20 to limit or prevent risks of crosslinking.

Their structure can include other units derived from other monomers. As comonomers, styrene may be mentioned in particular.

The polydienes, preferably hydrogenated, with hydroxyl end
25 groups and the polyolefins with hydroxyl end groups are the preferred polymer backbones according to the invention.

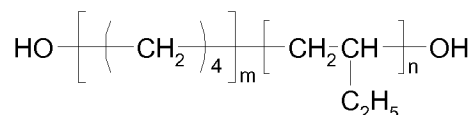
These polydienes with hydroxyl end groups are defined for example in patent FR 2 782 723 of ELF ATOCHEM. They are selected from the group comprising the homo- and copolymers of
30 polybutadiene, of polyisoprene and of poly(1,3-pentadiene). They are oligomers with number-average molecular weight below 7000, and preferably from 1000 to 5000, having a functionality of hydroxyl end groups from 1.8 to 3, and preferably close to 2.

35 We may mention in particular the hydroxylated polybutadienes marketed by the company ELF ATOCHEM under the brands POLY BD R-45HT and POLY BD R-20 LM, which will preferably be used in hydrogenated form. We may also mention the hydrogenated di-OH

(1,2-polybutadienes) such as GI3000 with Mn = 2600-3200 and GI2000 with Mn = 1800-2200 marketed by the company Nisso.

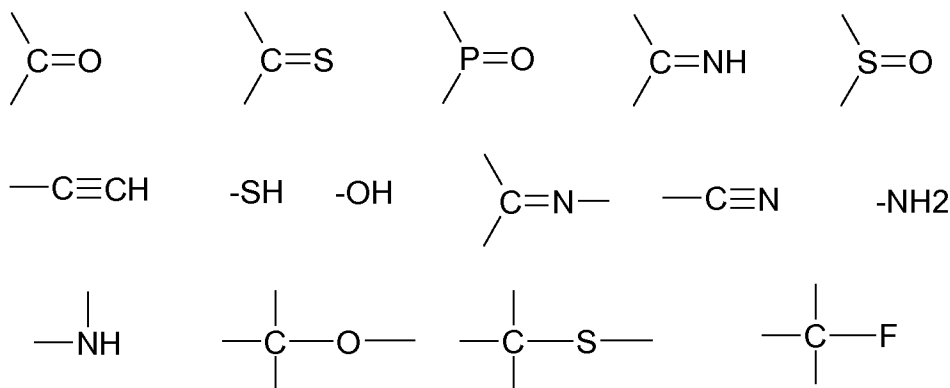
Homopolymeric or copolymeric polyolefins, with α, ω hydroxyl end groups, can also be used, such as:

- 5 • polyisobutylene oligomers with α, ω hydroxyl end groups;
- the copolymers marketed by the company Mitsubishi under the brand POLYTAIL, and in particular those corresponding to the formula:

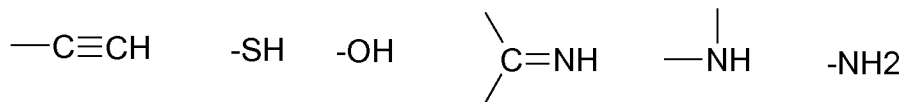


10 The supramolecular polymers possess in their structure at least one graft bearing at least one group capable of forming at least 3 hydrogen bonds, preferably at least 4 hydrogen bonds.

15 These groups capable of forming at least 3 hydrogen bonds can comprise for example at least 3 functional groups, preferably at least 4, selected from:

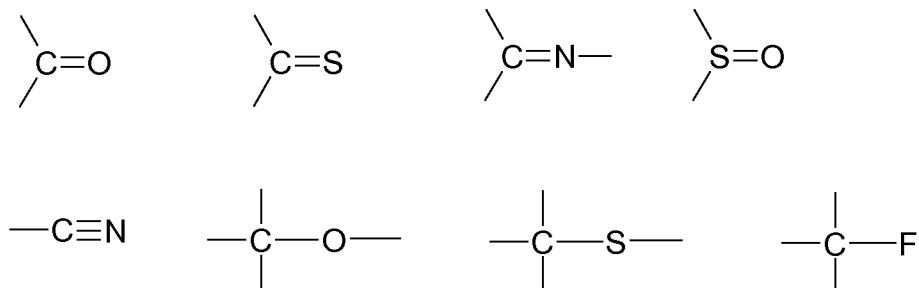


20 These functional groups can be classified in two categories:
 - the functional groups that are donors of hydrogen bonds such as the groups:

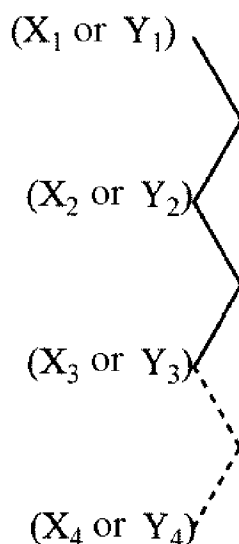


- and the functional groups that are acceptors of hydrogen bonds such as the groups:

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The groups capable of forming at least 3 hydrogen bonds form a basic structural element having at least 3, preferably at least 4 functional groups, and more preferably 4 functional groups, capable of establishing hydrogen bonds. The basic structural elements capable of establishing 3 or 4 hydrogen bonds can be represented schematically as follows:



where X_i (i being a natural integer) is a functional group that is an acceptor of hydrogen bonds and Y_i is a functional group that is a donor of hydrogen bonds.

Thus, each structural element must be able to establish hydrogen bonds with one or more partner structural elements, identical (i.e. self-complementary) or different, in such a way that each pairing of two partner structural elements takes place by formation of at least three hydrogen bonds, preferably at least four hydrogen bonds, and more preferably 4 hydrogen bonds.

A proton acceptor X will pair with a proton donor Y .

Several possibilities are offered, for example pairing of:

XXXX with YYYY;

XXXY with YYYY;

XXYX with YYXY;
 XYYX with YXXY;
 XXYY with YYXX self-complementary or not;
 XYYX with YXXY self-complementary or not.

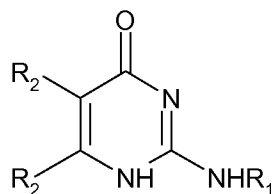
5 Preferably, the groups can establish 4 hydrogen bonds with an identical (or self-complementary) partner group including 2 donor bonds (for example NH) and 2 acceptor bonds (for example CO and -C=N-).

10 Preferably, the groups capable of forming at least 3 hydrogen bonds comprise rings with 5 or 6 atoms (unsaturated aromatic rings or heterocycles) very often constituted of C and/or N atoms and with conjugated double bonds for stabilizing and directing the H interactions.

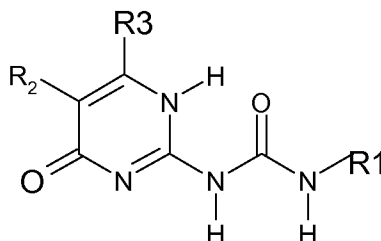
15 More preferably, the groups capable of forming at least 3 hydrogen bonds are included in rings with 6 atoms comprising C and/or N atoms and with conjugated double bonds for stabilizing and directing the H interactions.

20 According to a particular embodiment, the groups capable of forming 3 or 4 hydrogen bonds are selected from the following families, it being understood that all the tautomeric forms are included:

- (i) the aminopyrimidones of formula:



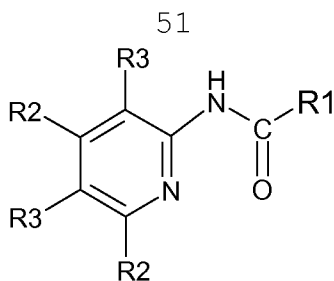
- (ii) the ureidopyrimidones of formula:



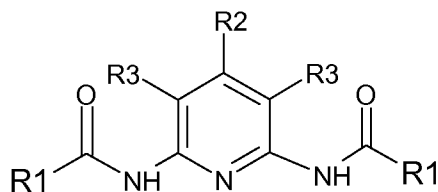
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- (iii) the acylaminopyridines and notably:

- the monoacylaminopyridines of structure:

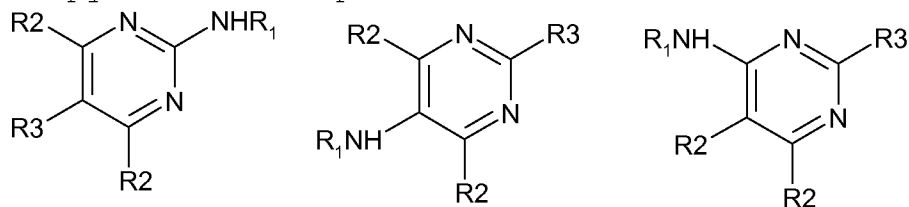


- the di(acylamino)pyridines and more particularly the 2,6-di(acylamino)pyridines of structure:

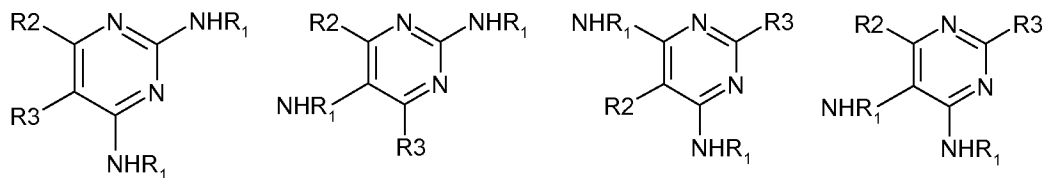


5 - (iv) the aminopyrimidines, and notably:

- the aminopyrimidine compounds:

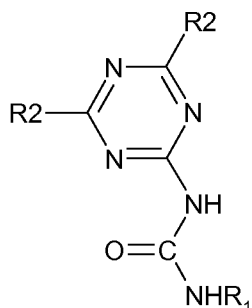


- the diaminopyrimidine compounds of structure:



10 - the triaminopyrimidine compounds;

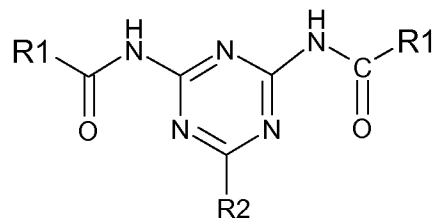
- (v) the ureidotriazines, and notably the mono-, di- and tri-ureidotriazines, and in particular the ureidoaminotriazines of structure:



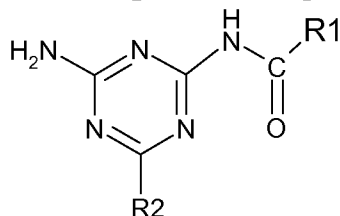
15 - (vi) the (acylamino)triazines, and notably the mono-, di- and tri-acylamino triazines, optionally amino (mono-, di- or tri-amino) and in particular:

- the di(acylamino)triazines of structure:

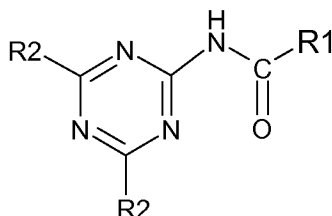
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- the acylamino, aminotriazines, (mono- or di-acylamino, and mono- or di-amino) and notably the compounds of structure:



5 - the acylaminotriazines of structure:

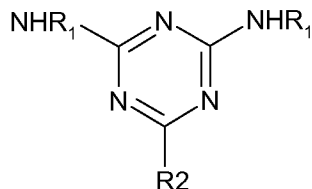


- the tri-acylamino-triazines;

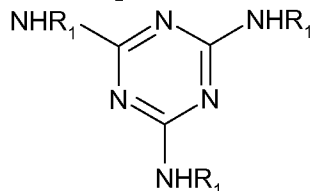
- (vii) the aminotriazines and notably:

- the monoaminotriazines;

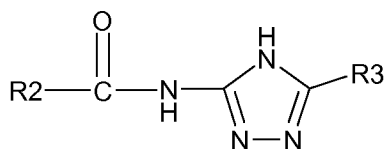
10 - the 2,6-diamino-s-triazines of structure:



- the triamino-s-triazine compounds of structure:

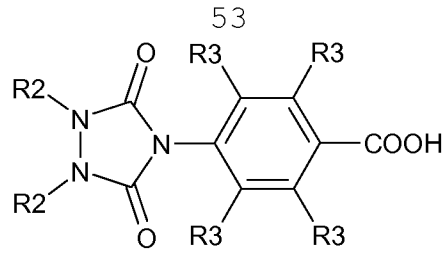


- (viii) the acylaminotriazoles of structure:

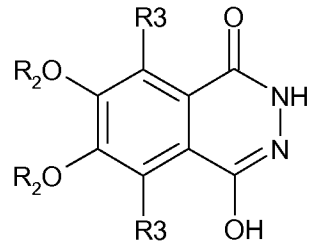


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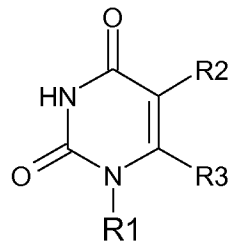
- (ix) the compounds of the urazoyl benzoic acid family of structure:



- (x) the phthalhydrazides of structure:

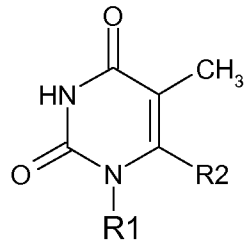


- (xi) the uracils of structure:

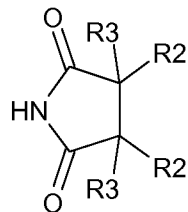


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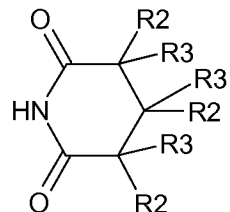
- (xii) the thymines of structure:



- (xiii) the succinimides of structure:

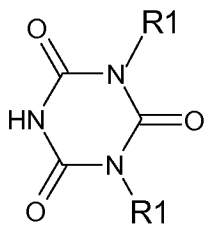


- 10
- (xiv) the glutarimides of structure:

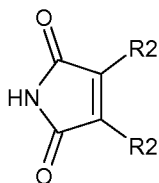


- (xv) the compounds of the cyanuric acid family of structure:

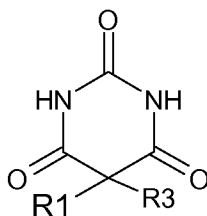
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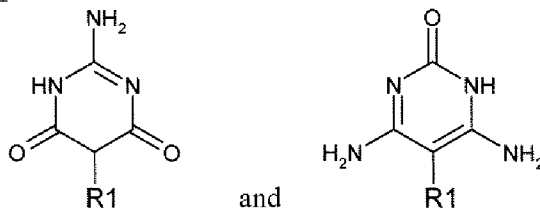
- (xvi) the maleimides:



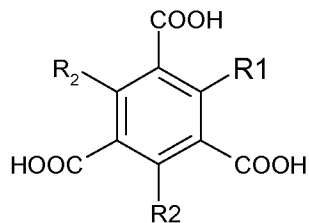
- (xvii) the compounds of the barbituric acid family, of structure:



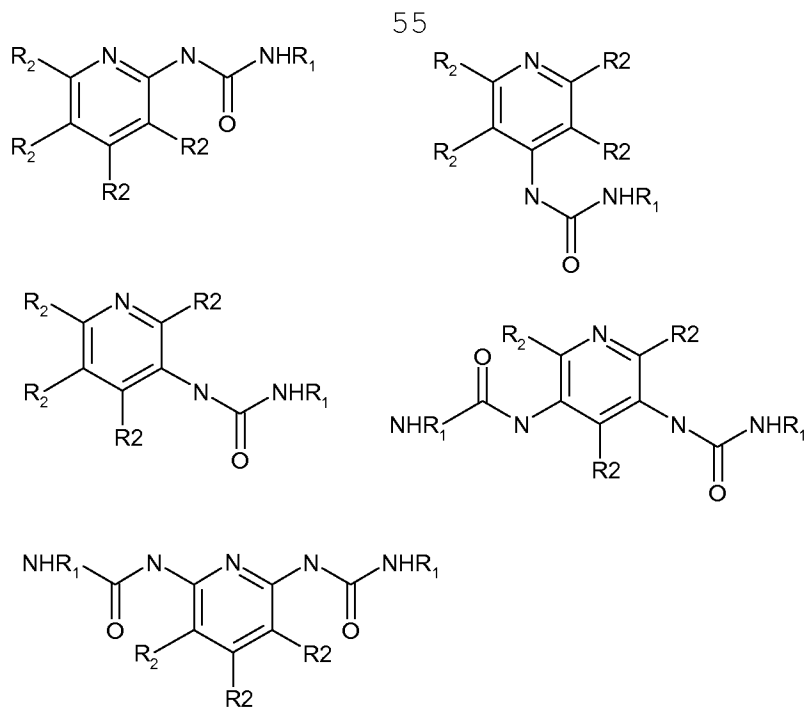
- (xviii) the compounds of structure:



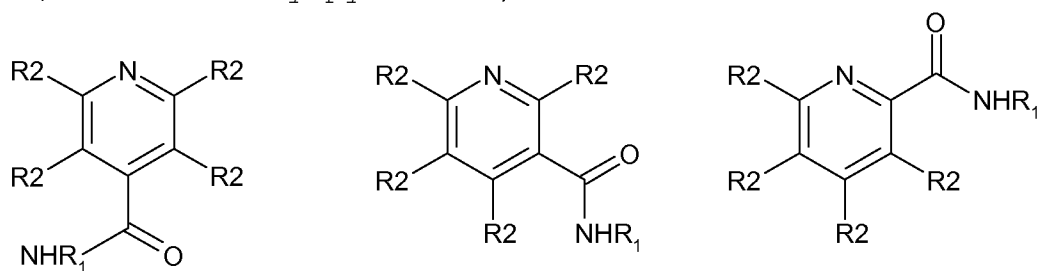
- (xix) the compounds of the trimellitic acid family, of formula:



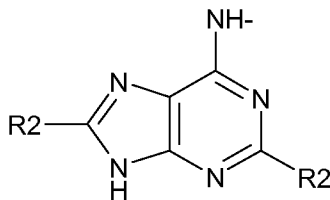
- (xx) the ureidopyridines, notably the mono- or di-ureidopyridines, and in particular those of formula:



- (xxi) the carbamoylpyridines, of formula:

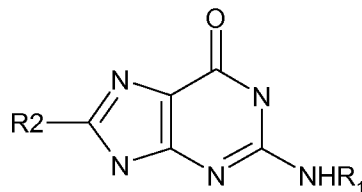


- (xxii) the adenines of formula:

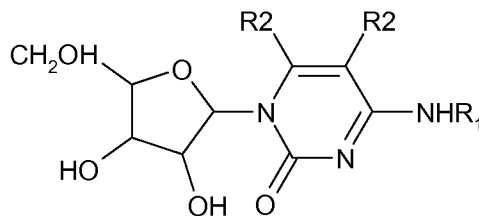


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- (xxiii) the guanines of formula:



- (xxiv) the cytidines of formula:



In all of these formulae, the meaning of the radicals is as follows:

- (a) the radicals R_1 , which may be identical or different, represent a single bond, a hydrogen atom, a halogen atom and/or a monovalent C_1-C_{6000} (notably alkyl) carbon-containing group, linear, branched or cyclic, saturated or unsaturated, optionally aromatic, which can contain one or more heteroatoms such as O, S, N, P, Cl, Br, Cl, Br, F; or a combination of these meanings.

The radical R_1 can notably be a C_4-C_{12} cycloalkyl group; a linear or branched C_1-C_{30} alkyl group or a C_4-C_{12} aryl group; optionally substituted with an amino, ester and/or hydroxy function.

The radical R_1 can also be a group: C_4H_9 ; phenyl; 1,4-nitrophenyl; 1,2-ethylene; 1,6-hexylene; 1,4-butylene; 1,6-(2,4,4-trimethylhexylene); 1,4-(4-methylpentylene); 1,5-(5-methylhexylene); 1,6-(6-methylheptylene); 1,5-(2,2,5-trimethylhexylene); 1,7-(3,7-dimethyloctylene); -isophorone-; 4,4'-methylene biscyclohexylene; tolylene; 2-methyl-1,3-phenylene; 4-methyl-1,3-phenylene; 4,4'-biphenylenemethylene; and preferably: -isophorone-; $-(CH_2)_2-$; $-(CH_2)_6-$; $-CH_2CH(CH_3)-CH_2-C(CH_3)_2-CH_2-CH_2$; 4,4'-methylene biscyclohexylene; 2-methyl-1,3-phenylene.

Even more preferably, R_1 is a single bond.

- (b) the radicals R_2 , which may be identical or different within one and the same formula, represent a single bond, a hydrogen atom, a halogen atom ($-Br$, $-Cl$, $-F$), a radical $-OH$, $-N(R)_2$ (with R being H or a linear or branched C_1-C_{12} , preferably C_1-C_4 , alkyl radical, and more preferably a methyl or ethyl radical); or a monovalent, linear, branched or cyclic, C_1-C_{6000} hydrocarbon group, saturated or unsaturated, optionally aromatic, which can contain one or more heteroatoms such as O, S, N, P, F; or a combination of these meanings.

The radicals R_2 can notably be H, CN, NH_2 or else:

- a C_1-C_{30} alkyl group;
- a C_4-C_{12} cycloalkyl group;
- a C_4-C_{12} aryl group;
- a C_1-C_{30} aryl(C_4-C_{12})alkyl group;

- a C₁-C₄ alkoxy group;
 - an arylalkoxy group, in particular an aryl(C₁-C₄)alkoxy group;
 - a C₄-C₁₂ heterocycle;
 - 5 - a thioalkoxy group;
 - a sulphony group;
- or mixtures thereof, these groups being optionally substituted with an amino, ester and/or hydroxy function.

Preferably, R₂ represents H, CH₃, C₁₃H₂₇, C₇H₁₅ or phenyl.

- 10 - (c) the radicals R₃, which may be identical or different within one and the same formula, represent a hydrogen atom or a monovalent, linear, branched or cyclic, C₁-C₆₀₀₀ hydrocarbon group, saturated or unsaturated, optionally aromatic, which can contain one or more heteroatoms such as O, S, N, P, F; or
- 15 a combination of these meanings.

The radical R₃ can notably be a C₄-C₁₂ cycloalkyl group; a linear or branched C₁-C₃₀ alkyl group or a C₄-C₁₂ aryl group; optionally substituted with an amino, ester and/or hydroxy function. Preferably, the radical R₃ represents a methyl

20 radical.

In all of these formulae, it is to be understood that at least one, notably one or two, groups R₁ and/or R₂ is a single bond constituting the point of attachment of the group capable of forming at least 3 hydrogen bonds on the rest of the graft.

25 Preferably, said point of attachment is carried by R₁ and/or R₂, and preferably it is carried by R₁.

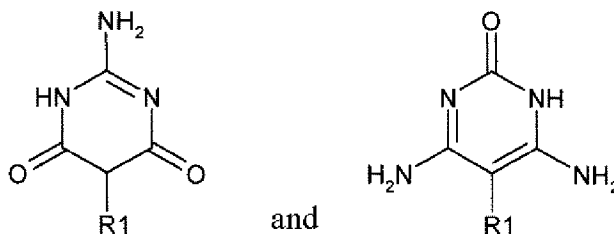
The groups capable of forming at least 3 hydrogen bonds can notably be selected from:

(a) the groups capable of forming at least 3 hydrogen bonds that are complementary and identical, i.e. self-complementary, and notably:

30

- the aminopyrimidones, the ureidopyrimidones,
- the compounds of the trimellitic acid family, or of the urazoyl benzoic acid family,
- 35 - the acylaminopyridines, the ureidopyridines, the carbamoylpyridines,
- the acylaminotriazines, the ureidotriazines and notably the ureidoaminotriazines, the diaminotriazines,

- the acylaminotriazoles,
- the phthalhydrazides,
- the compounds of formula:



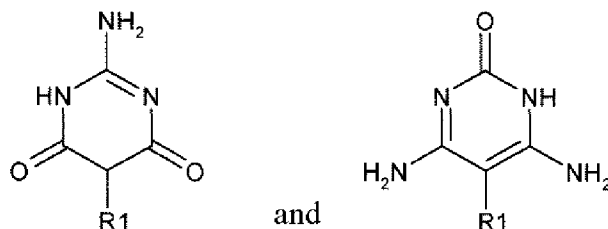
5 in which R₁ is a hydrogen atom or a monovalent, linear, branched or cyclic, C₁-C₆₀₀₀ hydrocarbon group, saturated or unsaturated, optionally aromatic, which can contain one or more heteroatoms such as O, S, N, P, F.

(b) the groups capable of forming at least 3 hydrogen bonds that are complementary but different, and notably:

- adenine complementary to guanine,
- cytidine complementary to thymine,
- triamino-s-triazine complementary to uracil or to succinimide or to glutarimide or to cyanuric acid or to thymine or to maleimide or to (di)aminopyrimidine or to barbituric acid,
- acylamino-amino-s-triazine complementary to uracil or to succinimide or to glutarimide or to cyanuric acid or to thymine or to maleimide or to (di)aminopyrimidine or to barbituric acid.

Preferably, the groups capable of forming at least 3 hydrogen bonds are selected from the groups capable of establishing at least three hydrogen bonds with themselves (self-complementary), notably at least four hydrogen bonds with themselves. Among these groups, we may mention in particular:

- the ureidopyrimidones;
- the ureidopyridines, the carbamoylpyridines;
- the acylamino-s-triazines and notably the acyl-diamino-s-triazines;
- the ureidotriazines;
- the phthalhydrazides;
- the compounds of formula:



in which the radicals R_1 , R_2 and R_3 have the meanings given above, in particular the meanings given as preferences.

Better still, we may mention, as preferred examples of groups capable of forming at least 3 hydrogen bonds, the groups derived from the ureidopyrimidones, and in particular from 2-ureidopyrimidone or from 6-methyl-2-ureidopyrimidone.

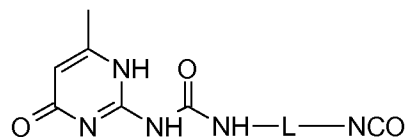
The rest of the graft is constituted of a linker L bearing at least one reactive group capable of reacting with the functionalized poly(alkylene) group(s).

This reactive group can be for example a carboxyl group or an isocyanate group. Preferably, it is a group $-N=C=O$ or $-N=C=S$, and even more preferably a group $-N=C=O$ (isocyanate).

Preferably, the linker L is a group: phenylene; 1,4-nitrophenyl; 1,2-ethylene; 1,6-hexylene; 1,4-butylene; 1,6-(2,4,4-trimethylhexylene); 1,4-(4-methylpentylene); 1,5-(5-methylhexylene); 1,6-(6-methylheptylene); 1,5-(2,2,5-trimethylhexylene); 1,7-(3,7-dimethyloctylene); -isophorone-; 4,4'-methylene biscyclohexylene; tolylene; 2-methyl-1,3-phenylene; 4-methyl-1,3-phenylene; 4,4-biphenylenemethylene;

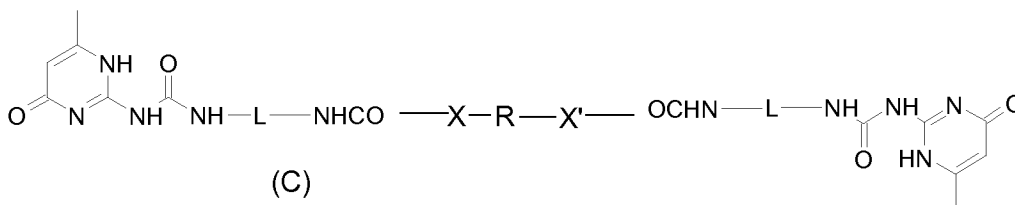
and preferably: -isophorone-; $-(CH_2)_2-$; $-(CH_2)_6-$; $-CH_2CH(CH_3)-CH_2-C(CH_3)_2-CH_2-CH_2-$; 4,4'-methylene biscyclohexylene; 2-methyl-1,3-phenylene.

In a particularly preferred version of the invention, the grafts are of formula (B):



L having the same meaning as above.

Even more preferably, the supramolecular polymer of the invention is of formula (C):



R, X, X', L having the meanings stated previously.

Preferably, in formula (C), X and X' denote an oxygen atom.

The supramolecular polymer(s) based on polyalkylene can also
 5 be obtained from a polymer (A1) having a polyalkylene moiety,
 said polymer being functionalized with at least one reactive
 group (B1), by condensation with at least one molecule (A3)
 having at least one reactive group (B2), said molecule being
 such that after reaction of groups (B1) and (B2) there is
 10 formation of an entity capable of forming at least 3 hydrogen
 bonds, preferably at least 4 hydrogen bonds.

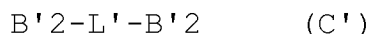
Preferably, these entities have the structures (i) to (xxiv)
 as defined previously with R₁ denoting a single bond.

The polymer (A1) can notably result from the action, on a
 15 polyalkylene polymer of formula A as defined previously, of
 compounds (A2) having two reactive groups (B'2) capable of
 reacting with the functionalized groups of the polyalkylene.

These reactive groups can be for example carboxyl groups or
 isocyanate groups. Preferably, they are groups -N=C=O or -
 20 N=C=S, and even more preferably groups -N=C=O (isocyanate).

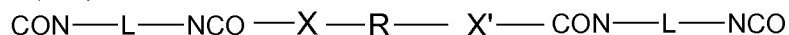
Preferably, the groups B2 are identical to the groups B'2.

Preferably, the compounds (A2) are of the following
 structure (C'):



25 the linker L' having the same meanings as L defined
 previously.

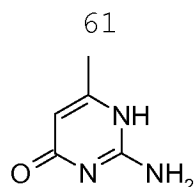
In a particularly preferred version, the polymers A1 have
 the formula (C1):



(C1)

30 in which L, X, X' and R have the same meanings as previously.

Preferably, the molecule (A3) is 6-methylisocytosine of
 formula:



When the hydrophobic film-forming polymer is dispersed in the organic solvent, the composition according to the invention advantageously comprises at least one stable dispersion of essentially spherical polymer particles of one or more polymers. Before their incorporation in the composition of the invention, the particles are generally dispersed in a physiologically acceptable liquid oil phase, such as hydrocarbon oils or silicone oils. According to one embodiment, these dispersions are generally known as "NAD" (non-aqueous dispersions) of polymer as opposed to the networks that are aqueous dispersions of polymer.

These dispersions can notably be in the form of nanopolymer particles in stable dispersion in said liquid organic phase. The nanoparticles are preferably of an average size between 5 and 800 nm, and more preferably between 50 and 500 nm. It is, however, possible to obtain sizes of polymer particles up to 1 μ m.

The polymers in dispersion that can be used in the composition of the invention preferably have a molecular weight in the range from about 2000 to 10 000 000 and a Tg in the range from -100°C to 300°C and preferably from -10°C to 80°C.

Among the film-forming polymers in dispersion, we may mention radical, acrylic or vinylic homopolymers or copolymers, preferably having a Tg less than or equal to 40°C and notably in the range from -10°C to 30°C, used alone or mixed.

According to one embodiment, the particles of polymer are stabilized with a stabilizer that is solid at room temperature, which can be a block polymer, a graft polymer, and/or a random polymer, alone or mixed. Stabilization can be carried out by any known means, and in particular by direct addition of the stabilizing polymer during polymerization.

When a dispersion of polymer particles is used, the dry matter content of said aqueous dispersion can be of the order of 3 to 60 wt.%, and preferably from 10 to 50%.

Non-exhaustively, the preferred hydrophobic film-forming polymers are selected from the polyurethanes; polyurethane-acrylics; polyureas; polyurea-polyurethanes; polyester-polyurethanes; polyether-polyurethanes; polyesters; polyester amides; acrylic and/or vinylic polymers or copolymers; polyacrylamides; acrylic polyesters; polymers or copolymers based on polyvinylpyrrolidone; silicone polymers comprising polyurethane, polyurea moieties; silicone resins; copolymers based on silicone resin and dimethiconol; fluorinated polymers; celluloses, polyalkylene-based supramolecular polymers and mixtures thereof. According to a particular embodiment, the hydrophobic film-forming polymer is selected from the acrylic polymers or copolymers, the acrylic polyesters, the polymers or copolymers based on polyvinylpyrrolidone, the copolymers based on silicone resin and dimethiconol, the silicone polymers comprising polyurethane, polyurea moieties; the celluloses, the supramolecular polymers based on polyalkylene and mixtures thereof.

According to a particular embodiment, the hydrophobic film-forming polymer is a non-ionic polymer. According to another embodiment, the film-forming polymer is solid at 25°C, in the sense that its flow is not observed with the naked eye after a period of one hour.

The film-forming polymer(s) for use in the composition of the invention can be present in the composition at a content in the range from 0.1 to 40 wt.%, relative to the total weight of the composition, preferably in the range from 0.2 to 20 wt.%, preferably in the range from 1 to 20 wt.%.

Pigments

According to one variant, the composition for treatment of the hair is a composition for colouring keratin fibres, which additionally comprises pigments. Said composition makes it possible to obtain long-lasting, colouring surface coatings, without degradation of the keratin fibres.

"Pigment" means all pigments that give colour to keratinous materials. Their solubility in water at 25°C and at atmospheric pressure (760 mmHg) is less than 0.05%, and preferably less than 0.01%.

The pigments that can be used are notably selected from the organic and/or mineral pigments known in the art, notably those described in the Kirk-Othmer encyclopaedia of chemical technology and in Ullmann's encyclopaedia of industrial chemistry.

These pigments can be in the form of powder or of pigment paste. They can be coated or uncoated.

The pigments can be selected for example from the mineral pigments, organic pigments, lakes, special-effect pigments such as nacres, metallic pigments or glitter, and mixtures thereof.

The pigment can be a mineral pigment. "Mineral pigment" means any pigment that meets the definition in the inorganic pigment chapter of Ullmann's encyclopaedia. Among the mineral pigments for use in the present invention, we may mention the iron or chromium oxides, manganese violet, ultramarine blue, chromium hydrate and ferric blue, titanium dioxide.

The pigment can be an organic pigment. "Organic pigment" means any pigment that meets the definition in the organic pigment chapter of Ullmann's encyclopaedia. The organic pigment can notably be selected from the nitroso, nitro, azo, xanthene, quinoline, anthraquinone, phthalocyanine, isoindolinone, isoindoline, quinacridone, perinone, perylene, diketopyrrolopyrrole, thioindigo, dioxazine, triphenylmethane, quinophthalone compounds.

In particular, the organic pigments can be selected from carmine, carbon black, aniline black, azo yellow, quinacridone, phthalocyanine blue, the blue pigments codified

in the Color Index under the references CI 42090, 69800, 69825, 73000, 74100, 74160, the yellow pigments codified in the Color Index under the references CI 11680, 11710, 15985, 19140, 20040, 21100, 21108, 47000, 47005, the green pigments
5 codified in the Color Index under the references CI 61565, 61570, 74260, the orange pigments codified in the Color Index under the references CI 11725, 15510, 45370, 71105, the red pigments codified in the Color Index under the references CI 12085, 12120, 12370, 12420, 12490, 14700, 15525, 15580, 15620,
10 15630, 15800, 15850, 15865, 15880, 17200, 26100, 45380, 45410, 58000, 73360, 73915, 75470, the pigments obtained by oxidative polymerization of indole and phenol derivatives such as those described in patent FR 2 679 771.

The pigments according to the invention can also be in the
15 form of composite pigments such as those described in patent EP 1 184 426. These composite pigments can be composed notably of particles having an inorganic core, at least one binder for fixing the organic pigments on the core, and at least one organic pigment at least partially covering the core.

20 The organic pigment can also be a lake. "Lake" means dyes adsorbed on insoluble particles, the whole thus obtained remaining insoluble during use.

The inorganic substrates on which the dyes are adsorbed are for example alumina, silica, calcium-sodium borosilicate or
25 calcium-aluminium borosilicate, and aluminium.

Among the dyes, we may mention carmine (from cochineal). We may also mention the dyes known by the following names: D & C Red 21 (CI 45 380), D & C Orange 5 (CI 45 370), D & C Red 27 (CI 45 410), D & C Orange 10 (CI 45 425), D & C Red 3 (CI 45
30 430), D & C Red 4 (CI 15 510), D & C Red 33 (CI 17 200), D & C Yellow 5 (CI 19 140), D & C Yellow 6 (CI 15 985), D & C Green (CI 61 570), D & C Yellow 10 (CI 77 002), D & C Green 3 (CI 42 053), D & C Blue 1 (CI 42 090).

As examples of lakes, we may mention the product known by
35 the following name: D & C Red 7 (CI 15 850:1).

The pigment can also be a special-effect pigment. Special-effect pigments are pigments that generally create a coloured appearance (characterized by a certain shade, a certain

vividness and a certain brightness) that is non-uniform and varies depending on the conditions of observation (light, temperature, angle of observation etc.). In that respect they differ from the coloured pigments that provide a conventional uniform opaque, semi-transparent or transparent hue.

There are several types of special-effect pigments: those with low refractive index such as the fluorescent, photochromic or thermochromic pigments, and those with higher refractive index such as nacres or glitter.

As examples of special-effect pigments, we may mention the nacreous pigments such as mica covered with titanium dioxide, or with bismuth oxychloride, coloured nacreous pigments such as mica covered with titanium dioxide and with iron oxides, mica covered with iron oxide, mica covered with titanium dioxide and notably with ferric blue or with chromium oxide, mica covered with titanium dioxide and with an organic pigment as defined previously as well as the nacreous pigments based on bismuth oxychloride. They may also be mica particles, on the surface of which at least two successive layers of metal oxides and/or organic colorants are superposed.

The nacres can more particularly possess a yellow, pink, red, bronze, orange, brown, gold and/or coppery colour or sheen.

As a guide to the nacres that can be employed within the scope of the present invention, we may notably mention the nacres of gold colour notably marketed by the company ENGELHARD under the name Gold 222C (Cloisonne), Sparkle gold (Timica), Gold 4504 (Chromalite) and Monarch gold 233X (Cloisonne); the bronze nacres notably marketed by the company MERCK under the name Bronze fine (17384) (Colorona) and Bronze (17353) (Colorona), by the company Eckart under the name Prestige Bronze and Prestige Soft Bronze and by the company ENGELHARD under the name Super bronze (Cloisonne); the orange nacres notably marketed by the company ENGELHARD under the name Orange 363C (Cloisonne) and Orange MCR 101 (Cosmica) and by the company MERCK under the name Passion orange (Colorona) and Matte orange (17449) (Microna); the nacres with a brown hue notably marketed by the company ENGELHARD under the name

Nu-antique copper 340XB (Cloisonne) and Brown CL4509 (Chromalite); the nacres with a copper sheen notably marketed by the company ENGELHARD under the name Copper 340A (Timica) and by the company Eckart under the name Prestige Copper and
5 Prestige soft Copper; the nacres with a red sheen notably marketed by the company MERCK under the name Sienna fine (17386) (Colorona); the nacres with a yellow sheen notably marketed by the company ENGELHARD under the name Yellow (4502) (Chromalite); the nacres of red hue with a gold sheen notably
10 marketed by the company ENGELHARD under the name Sunstone G012 (Gemtone); the black nacres with a gold sheen notably marketed by the company ENGELHARD under the name Nu antique bronze 240 AB (Timica), the blue nacres notably marketed by the company MERCK under the name Matte blue (17433) (Microna), Dark Blue
15 (117324) (Colorona), the white nacres with a silver sheen notably marketed by the company MERCK under the name Xirona Silver and the orange-pink-green golden nacres notably marketed by the company MERCK under the name Indian summer (Xirona) and mixtures thereof.

20 In addition to the nacres on a mica substrate, consideration may be given to multilayer pigments based on synthetic substrates such as alumina, silica, calcium-sodium borosilicate or calcium-aluminium borosilicate, and aluminium.

We may also mention the interference-effect pigments that
25 are not fixed on a substrate such as liquid crystals (Helicones HC from Wacker), holographic interference-effect glitter (Geometric Pigments or Spectra f/x from Spectratek). The special-effect pigments also comprise the fluorescent pigments, whether they are substances that fluoresce in
30 daylight or which produce an ultraviolet fluorescence, phosphorescent pigments, photochromic pigments, thermochromic pigments and quantum dots, marketed for example by the company Quantum Dots Corporation.

The variety of pigments that can be used in the present
35 invention makes it possible to obtain a rich palette of colours, as well as particular optical effects such as metallic and interference effects.

The particle size of the pigment used in the cosmetic composition according to the present invention is generally between 10 nm and 200 μm , preferably between 20 nm and 80 μm , and more preferably between 30 nm and 50 μm .

5 The pigments can be dispersed in the product with the aid of a dispersant.

The dispersant serves to prevent agglomeration or flocculation of the particles. Said dispersant can be a surfactant, an oligomer, a polymer or a mixture of several of
10 them, bearing a functionality or functionalities having a strong affinity for the surface of the particles to be dispersed. In particular, they can attach physically or chemically to the surface of the pigments. These dispersants have, moreover, at least one functional group compatible or
15 soluble in the continuous medium. In particular, it is possible to use the esters of hydroxy-12-stearic acid in particular and of C_8 to C_{20} fatty acid and of polyol such as glycerol, diglycerol, such as the stearate of poly(12-hydroxystearic) acid with molecular weight of about 750 g/mol
20 such as that sold under the name Solsperse 21 000 by the company Avecia, the polyglyceryl-2-dipolyhydroxystearate (CTFA name) sold under the reference Dehymyls PGPH by the company Henkel or polyhydroxystearic acid such as that sold under the reference Arlcel P100 by the company Uniqema and mixtures
25 thereof.

As other dispersants for use in the compositions of the invention, we may mention the quaternary ammonium derivatives of polycondensed fatty acids such as Solsperse 17 000 sold by the company Avecia, polydimethylsiloxane / oxypropylene
30 mixtures such as those sold by the company Dow Corning under the references DC2-5185, DC2-5225 C.

The pigments used in the cosmetic composition according to the invention can be surface-treated with an organic agent.

Thus, the previously surface-treated pigments that can be
35 used within the scope of the invention are pigments that have undergone, completely or partially, a surface treatment of chemical, electronic, electrochemical, mechano-chemical or mechanical nature, with an organic agent such as those that

are described notably in Cosmetics and Toiletries, February 1990, Vol. 105, p. 53-64 before being dispersed in the composition according to the invention. These organic agents can be selected for example from amino acids; waxes, for example carnauba wax and beeswax; fatty acids, fatty alcohols and their derivatives, such as stearic acid, hydroxystearic acid, stearyl alcohol, hydroxystearyl alcohol, lauric acid and their derivatives; anionic surfactants; lecithins; sodium, potassium, magnesium, iron, titanium, zinc or aluminium salts of fatty acids, for example aluminium stearate or laurate; metal alkoxides; polysaccharides, for example chitosan, cellulose and its derivatives; polyethylene; (meth)acrylic polymers, for example polymethylmethacrylates; polymers and copolymers containing acrylate units; proteins; alkanolamines; silicone compounds, for example silicones, polydimethylsiloxanes, alkoxy silanes, alkyl silanes, siloxysilicates; fluorinated organic compounds, for example perfluoroalkyl ethers; fluorosilicone compounds.

The surface-treated pigments for use in the cosmetic composition according to the invention can also have been treated with a mixture of these compounds and/or can have undergone several surface treatments.

The surface-treated pigments that can be used within the scope of the present invention can be prepared according to techniques of surface treatment that are well known by a person skilled in the art or can be obtained commercially as such.

Preferably, the surface-treated pigments are covered with an organic layer.

The organic agent with which the pigments are treated can be deposited on the pigments by solvent evaporation, chemical reaction between the molecules of the surface agent or creation of a covalent bond between the surface agent and the pigments.

The surface treatment can thus be carried out for example by chemical reaction of a surface agent with the surface of the pigments and creation of a covalent bond between the surface

agent and the pigments or the fillers. This method is notably described in patent US 4 578 266.

Preferably, an organic agent bound covalently to the pigments will be used.

5 The agent for the surface treatment can represent from 0.1 to 50 wt.% of the total weight of the surface-treated pigments, preferably from 0.5 to 30 wt.%, and even more preferably from 1 to 10 wt.%.

10 When they are present, the amount of pigments is generally between 0.1 to 40 wt.%, preferably 0.5 to 20 wt.% of the total weight of the composition.

Other additives

15 When the polymers for use in the composition of the invention have a glass transition temperature that is too high for the desired use, a plasticizer can be incorporated so as to lower said temperature of the mixture used. The plasticizer can be selected from the plasticizers usually employed in the field of application, and notably from the compounds that can
20 be solvents for the polymer.

Preferably, the plasticizer has a molecular weight less than or equal to 5000 g/mol, preferably less than or equal to 2000 g/mol, preferably less than or equal to 1000 g/mol. The plasticizer advantageously has a molecular weight greater than
25 or equal to 100 g/mol.

Thus, the composition can comprise, additionally, at least one plasticizer. In particular, we may mention, alone or mixed, the usual plasticizers, such as:

- the glycols and their derivatives, such as diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol butyl ether or diethylene glycol hexyl ether, ethylene glycol ethyl ether, ethylene glycol butyl ether, ethylene glycol hexyl ether;

- the polyethylene glycols, the polypropylene glycols, the polyethylene glycol-polypropylene glycol copolymers and mixtures thereof, notably the polypropylene glycols of high molecular weight, having for example a molecular weight in the range from 500 to 15000, for example

- the glycol esters;
- esters of acids, notably carboxylic, such as citrates, phthalates, adipates, carbonates, tartrates, phosphates, sebacates;
- 5 - esters derived from the reaction of a monocarboxylic acid of formula $R_{11}COOH$ with a diol of formula $HOR_{12}OH$ where R_{11} and R_{12} , which may be identical or different, represent a hydrocarbon chain, preferably comprising from 3 to 15 carbon atoms, linear, branched or cyclic, saturated or unsaturated
- 10 optionally comprising one or more heteroatoms such as N, O, S, in particular the monoester resulting from the reaction of isobutyric acid and octanediol such as trimethyl-2,2,4-pentane-1,3-diol, such as that marketed under the reference TEXANOL Ester Alcohol by the company Eastman Chemical,
- 15 - ethoxylated derivatives, such as the ethoxylated oils, notably the vegetable oils, such as castor oil;
- mixtures thereof.

Advantageously, the plasticizer can be present in the composition at a content such that the weight ratio of the hydrophobic film-forming polymer to the plasticizer is between 20 0.5 and 100, preferably between 1 and 50, preferably between 1 and 20.

The composition according to the invention can comprise one or more thickeners selected from polymeric thickeners, mineral 25 thickeners and mixtures thereof.

The thickener can be mineral or organic, polymeric or non-polymeric. The thickener can be selected for thickening an aqueous phase or an oil phase of the composition, as required.

"Thickener" means a compound that modifies the rheology of 30 the medium in which it is incorporated by increasing, by at least 100 cPs, the viscosity of the medium at 25°C and at a shear rate of 1 s^{-1} . This viscosity can be measured by means of a cone & plate viscosimeter (Haake R600 Rheometer or similar).

The thickener for aqueous medium can be selected from:

- 35 - hydrophilic clays,
- hydrophilic fumed silica,
- water-soluble cellulosic thickeners, such as hydroxyethylcellulose, methylcellulose,

hydroxypropylcellulose. Among the latter, we may notably mention the gums sold under the name Cellolize QP 4400 H by the company Amercol.

- non-ionic guar gums comprising C₁-C₆ hydroxyalkyl groups. As examples, we may mention hydroxymethyl, hydroxypropyl and hydroxybutyl groups. Such guar gums are notably sold under the trade names JAGUAR HP8, JAGUAR HP60, JAGUAR HP120, JAGUAR HP105 by the company MEYHALL or under the name GALACTASOL 40H4FD2 by the company AQUALON.
- carrageenans,
- carob gum, scleroglucan gum, gellan gum, rhamsan gum, karaya gum,
- alginates, maltodextrins, starch and its derivatives, hyaluronic acid and its salts,
- the glyceryl poly(meth)acrylate polymers sold under the names "Hispagel" or "Lubragel" by the companies Hispano Quimica or Guardian,
- polyvinyl alcohol,
- crosslinked acrylamide polymers and copolymers, such as those sold under the names "PAS 5161" or "Bozopol C" by the company Hoechst, "Sepigel 305" by the company Seppic by the company Allied Colloid, or,
- the crosslinked homopolymers of methacryloyloxyethyltrimethylammonium chloride sold under the name "Salcare SC95" by the company Allied Colloid,
- associative polymers and notably the associative polyurethanes.

Said thickeners are notably described in application EP-A-1400234, the contents of which are incorporated as reference.

The thickener for oily medium can be selected from

- organophilic clays,
- hydrophobic fumed silicas
- alkylated guar gums (with C₁-C₆ alkyl group), such as those described in EP-A-708114;
- oil-gelling polymers such as the triblock or star polymers resulting from polymerization or copolymerization of at least monomer with ethylenic group, such as the polymers sold under the name Kraton;

- polymers of weight-average molecular weight less than 100 000, having a) a polymer backbone having hydrocarbon repeating units provided with at least one heteroatom, and optionally b) at least one pendent fatty chain and/or at least one terminal fatty chain optionally functionalized, having from 6 to 120 carbon atoms and being bound to said hydrocarbon units, as described in applications WO-A-02/056847, WO-A-02/47619, the contents of which are incorporated as reference; in particular, the polyamide resins (notably comprising alkyl groups having from 12 to 22 carbon atoms) such as those described in US-A-5783657, the contents of which are incorporated as reference.

Said thickeners are notably described in application EP-A-1400234, the contents of which are incorporated as reference.

The thickener can be an organic gelling agent, i.e. an agent comprising at least one organic compound. The organic gelling agents can be selected from those described in application WO-A-03/105788, the contents of which are incorporated as reference.

More precisely, the polymeric thickener present in the composition according to the invention is an amorphous polymer formed by polymerization of an olefin. The olefin can notably be an elastomeric monomer with ethylenic unsaturation.

As examples of olefin, we may mention the ethylene carbide monomers, notably having one or two ethylenic unsaturations, having from 2 to 5 carbon atoms such as ethylene, propylene, butadiene, isoprene.

The polymeric thickener is capable of thickening or gelling the composition. "Amorphous polymer" means a polymer that is not in a crystalline form. The polymeric thickener can also be film-forming.

The polymeric thickener can notably be a diblock, triblock, multiblock, radial, or star copolymer or mixtures thereof.

Said polymeric thickeners are described in application US-A-2002/005562 and in patent US-A-5 221 534

Advantageously, the polymeric thickener is an amorphous block copolymer of styrene and olefin.

The polymeric thickener is preferably hydrogenated to reduce the residual ethylenic unsaturations after polymerization of the monomers.

In particular, the polymeric thickener is a copolymer, optionally hydrogenated, with styrene blocks and with ethylene/C₃-C₄ alkylene blocks.

As diblock copolymer, preferably hydrogenated, we may mention the styrene-ethylene/propylene copolymers, the styrene-ethylene/butadiene copolymers. Diblock polymers are notably sold under the name Kraton® G1701E by the company Kraton Polymers.

As triblock copolymer, preferably hydrogenated, we may mention the styrene-ethylene/propylene-styrene copolymers, the styrene-ethylene/butadiene-styrene copolymers, the styrene-isoprene-styrene copolymers, the styrene-butadiene-styrene copolymers. Triblock polymers are notably sold under the names Kraton® G1650, Kraton® G1652, Kraton® D1101, Kraton® D1102, Kraton® D1160 by the company Kraton Polymers.

It is also possible to use a mixture of hydrogenated styrene-butylene / ethylene-styrene triblock copolymer and of hydrogenated ethylene-propylene-styrene star polymer, said mixture notably being in isododecane. Said mixtures are for example sold by the company PENRECO under the trade names VERSAGEL® M5960 and VERSAGEL® M5670.

Advantageously, a diblock copolymer such as those described previously, in particular a styrene-ethylene / propylene diblock copolymer, is used as polymeric thickener.

More precisely, the organophilic clays are clays modified with chemical compounds rendering the clay swellable.

The clays are products that are already well known *per se*, which are described for example in the work "Minéralogie des argiles" (Mineralogy of the clays), S. Caillère, S. Hénin, M. Rautureau, 2nd edition 1982, Masson, the teaching of which is included here as reference.

The clays are silicates containing a cation, which can be selected from the cations of calcium, of magnesium, of aluminium, of sodium, of potassium, of lithium and mixtures thereof.

As examples of said products, we may mention the clays from the smectite family such as the montmorillonites, hectorites, bentonites, beidellites, saponites, as well as from the vermiculite family, stevensite, chlorites.

5 These clays can be of natural or synthetic origin. Preferably, clays are used that are cosmetically compatible and acceptable with keratinous materials.

The organophilic clay can be selected from montmorillonite, bentonite, hectorite, attapulgite, sepiolite, and mixtures
10 thereof. The clay is preferably a bentonite or a hectorite.

These clays can be modified with a chemical compound selected from the quaternary amines, tertiary amines, amine acetates, imidazolines, amine soaps, fatty sulphates, alkyl aryl sulphonates, amine oxides, and mixtures thereof.

15 As organophilic clays, we may mention the quaternium-18 bentonites such as those sold under the names Bentone 3, Bentone 38, Bentone 38V by the company Rheox, Tixogel VP by the company United Catalyst, Claytone 34, Claytone 40, Claytone XL by the company Southern Clay; the stearalkonium
20 bentonites such as those sold under the names Bentone 27 by the company Rheox, Tixogel LG by the company United Catalyst, Claytone AF, Claytone APA by the company Southern Clay; the quaternium-18/benzalkonium bentonites such as those sold under the names Claytone HT, Claytone PS by the company Southern
25 Clay.

The fumed silicas can be obtained by high-temperature hydrolysis of a volatile silicon compound in an oxyhydrogen flame, producing a finely divided silica. This method notably makes it possible to obtain hydrophilic silicas that have a
30 large number of silanol groups on their surface. These hydrophilic silicas are for example marketed under the names "AEROSIL 130®", "AEROSIL 200®", "AEROSIL 255®", "AEROSIL 300®", "AEROSIL 380®" by the company Degussa, "CAB-O-SIL HS-5®", "CAB-O-SIL EH-5®", "CAB-O-SIL LM-130®", "CAB-O-SIL MS-
35 55®", "CAB-O-SIL M-5®" by the company Cabot.

It is possible for the surface of said silica to be modified chemically, by chemical reaction causing a decrease in the number of silanol groups. Notably, the silanol groups can be

replaced with hydrophobic groups: a hydrophobic silica is then obtained.

They are for example marketed under the references "AEROSIL R812®" by the company Degussa, "CAB-O-SIL TS-530®" by the company Cabot, "AEROSIL R972®", "AEROSIL R974®" by the company Degussa, "CAB-O-SIL TS-610®", "CAB-O-SIL TS-720®" by the company Cabot.

The composition according to the invention can also comprise one or more surfactants. These surfactants are selected from the anionic, cationic, amphoteric and non-ionic surfactants.

The anionic surfactants that can be used in the compositions of the invention are notably selected from salts, in particular the salts of alkali metals such as the sodium salts, ammonium salts, amine salts, salts of aminoalcohols or salts of alkaline-earth metals, for example of magnesium, of the following types: alkylsulphates, alkylethersulphates, alkylamidoethersulphates, alkylarylpolyethersulphates, monoglyceride-sulphates, alkylsulphonates, alkylamide sulphonates, alkylarylsulphonates, -olefin sulphonates, paraffin sulphonates, alkylsulphosuccinates, alkylethersulphosuccinates, alkylamide sulphosuccinates, alkylsulpho-acetates, acylsarcosinates and acylglutamates, the alkyl and acyl groups of all of these compounds having from 6 to 24 carbon atoms and the aryl group preferably denoting a phenyl or benzyl group.

It is also possible to use the monoesters of C₆₋₂₄ alkyl and of polyglycoside-dicarboxylic acids such as the alkyl glucoside-citrates, the alkyl polyglycoside-tartrates and the alkyl polyglycoside-sulphosuccinates, the alkylsulphosuccinamates, the acylisethionates and the N-acyltaurates, the alkyl group or acyl of all these compounds having from 12 to 20 carbon atoms.

Another group of anionic surfactants that can be used in the compositions of the present invention is the acyl-lactylates, in which the acyl group has from 8 to 20 carbon atoms.

Moreover, we may also mention the alkyl-D-galactoside-uronic acids and their salts as well as the polyoxyalkylenated (C₆₋₂₄ alkyl)ether-carboxylic acids, the polyoxyalkylenated (C₆₋₂₄

alkyl)(C₆₋₂₄ aryl)ether-carboxylic acids, the polyoxyalkylenated (C₆₋₂₄ alkyl)amidoether-carboxylic acids and their salts, in particular those having from 2 to 50 ethylene oxide units, and mixtures thereof.

5 The alkylsulphates, the alkylethersulphates and mixtures thereof, in particular in the form of salts of alkali metals or alkaline-earth metals, of ammonium, of amine or of aminoalcohol, are preferably used.

10 Examples of additional non-ionic surfactants that can be used in the compositions of the present invention are described for example in "Handbook of Surfactants" by M.R. PORTER, publ. Blackie & Son (Glasgow and London), 1991, pp 116-178. They are selected notably from the alcohols, the alpha-diols, the alkyl(C₁₋₂₀)phenols or the polyethoxylated, 15 polypropoxylated or polyglycerolated fatty acids, having a fatty chain comprising, for example, from 8 to 18 carbon atoms, and the number of ethylene oxide or propylene oxide groups can notably be in the range from 2 to 50 and the number of glycerol groups can notably be from 2 to 30.

20 We may also mention the condensates of ethylene oxide and propylene oxide on fatty alcohols; the polyethoxylated fatty amides preferably having from 2 to 30 ethylene oxide units, the polyglycerolated fatty amides having on average from 1 to 5 glycerol groups and in particular from 1.5 to 4, the 25 ethoxylated sorbitan esters of fatty acids having from 2 to 30 ethylene oxide units, the sucrose esters of fatty acids, the polyethylene glycol esters of fatty acids, the (C₆₋₂₄ alkyl)polyglycosides, the derivatives of N-(C₆₋₂₄ alkyl)glucamine, the oxides of amines such as the oxides of 30 (C₁₀₋₁₄ alkyl)amines or the oxides of N-(C₁₀₋₁₄ acyl)-aminopropylmorpholine.

The amphoteric or zwitterionic surfactants that can be used in the present invention can notably be derivatives of 35 secondary or tertiary aliphatic amines, in which the aliphatic group is a linear or branched chain having from 8 to 22 carbon atoms and containing at least one anionic group such as, for example, a carboxylate, sulphonate, sulphate, phosphate or phosphonate group. We may mention in particular the alkyl(C₈₋

20)betaines, the sulphobetaines, the (C₈₋₂₀ alkyl)amido (C₆₋₈ alkyl)betaines or the (C₈₋₂₀ alkyl)amido (C₆₋₈ alkyl)sulphobetaines.

Among the derivatives of amines, we may mention the products marketed under the name MIRANOL®, such as described in patents US 2 528 378 and US 2 781 354 and classified in the CTFA Dictionary, 3rd edition, 1982, under the names Amphocarboxyglycinate and Amphocarboxypropionate of respective structures (A) and (B):

10 Ra-CONHCH₂CH₂-N(Rb) (Rc) (CH₂COO-) (A)

in which:

Ra represents an alkyl group derived from an acid Ra-COOH present in hydrolysed copra oil, a heptyl, nonyl or undecyl group,

15 Rb represents a beta-hydroxyethyl group, and

Rc represents a carboxymethyl group; and

Ra'-CONHCH₂CH₂-N(B) (B') (B)

in which:

B represents -CH₂CH₂OX',

20 B' represents -(CH₂)_z-Y', with z = 1 or 2,

X' represents the group -CH₂CH₂-COOH or a hydrogen atom,

Y' represents -COOH or the group -CH₂-CHOH-SO₃H,

25 Ra' represents an alkyl group of an acid Ra'-COOH present in copra oil or in hydrolysed linseed oil, an alkyl group, notably C₁₇ and its iso form, an unsaturated C₁₇ group.

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 capryloamphodipropionate, lauroamphodipropionic acid, cocoamphodipropionic acid.

35 As examples, we may mention the cocoamphodiacetate marketed by the company RHODIA under the trade name MIRANOL® C2M concentrated.

Among the amphoteric or zwitterionic surfactants mentioned above, the (C₈₋₂₀ alkyl)-betaines, the (C₈₋₂₀ alkyl)-amido(C₆₋₈ alkyl)betaines and mixtures thereof are preferably used.

As examples of cationic surfactants, we may notably mention
5 the salts of primary, secondary or tertiary fatty amines, optionally polyoxyalkylenated; the salts of quaternary ammonium such as the chlorides or the bromides of tetraalkylammonium, of alkylamidoalkyltrialkylammonium, of trialkylbenzylammonium, of trialkylhydroxyalkylammonium or of
10 alkylpyridinium; the derivatives of imidazoline.

In a first preferred variant, the composition according to the invention comprises one or more anionic surfactants and one or more amphoteric or zwitterionic surfactants.

In a second preferred variant, the composition according to
15 the invention comprises one or more cationic surfactants.

The surfactants are preferably present in an amount in the range from 0.01 to 30 wt.%, preferably from 0.1 to 20 wt.%, and even more preferably from 0.2 to 15 wt.% relative to the total weight of the cosmetic composition.

According to a particular embodiment, the composition
20 comprises one or more surfactants with a weight ratio of surfactant(s) to ethylenic block copolymer(s) greater than 0.4, preferably from 0.5 to 40 and more preferably from 0.7 to 20.

The composition according to the invention can also contain
25 one or more agents usually employed in cosmetics, selected for example from reducing agents, fats, softeners, anti-foaming agents, hydrating agents, UV filters, colloid minerals, peptizing agents, perfumes, proteins, vitamins, propellants,
30 waxes whether ethoxylated or not, paraffins, C₁₀-C₃₀ fatty acids such as stearic acid, lauric acid, C₁₀-C₃₀ fatty amides such as lauric diethanolamide, anionic, cationic, non-ionic or amphoteric polymers.

The above additives are generally present in an amount for
35 each of them between 0.01 and 20 wt.% relative to the weight of the composition.

Of course, a person skilled in the art will take care to select this or these optional additives in such a way that the

advantageous properties intrinsically linked to the formation of the surface coating according to the invention are unaffected, or substantially unaffected.

According to a particular embodiment, the composition of the invention comprises, in addition to the ethylenic block copolymer(s), the siloxane resin(s) and the volatile solvent(s), at least one or more hydrophobic film-forming supramolecular polymers. According to another embodiment, the composition comprises in addition to the ethylenic block polymers, the siloxane resin(s) and the volatile solvent(s), at least one or more hydrophobic film-forming supramolecular polymers and at least one or more additional polysiloxane compounds other than the siloxane resin. Preferably, the additional siloxane compound is a silicone oil of formula (I).

The composition according to the invention can notably be in the form of suspension, dispersion, solution, gel, emulsion, notably oil-in-water emulsion (O/W) or water-in-oil emulsion (W/O), or multiple (W/O/W or polyol/O/W or O/W/O), in the form of cream, mousse, stick, dispersion of vesicles notably of ionic or non-ionic lipids, biphasic or multiphase lotion, spray, powder, paste. The composition can also be in the form of lacquer.

A person skilled in the art will be able to select the appropriate galenic form, as well as its method of preparation, on the basis of his general knowledge, taking into account on the one hand the nature of the constituents used, notably of their solubility in the substrate, and on the other hand the intended application for the composition.

The composition can be an anhydrous composition, i.e. a composition containing less than 2 wt.% of water, or even less than 0.5% of water, notably water-free, water not being added during preparation of the composition but corresponding to the residual water supplied with the ingredients that are mixed together.

The composition described above can be applied on dry or wet hair as well as on all types of hair: light or dark, natural or coloured, permed, bleached or straightened.

According to a particular embodiment of the method of the invention, the hair is washed before application of the composition described above. Preferably, the composition is applied on clean hair.

5 It can be applied on dry or wet hair.

It can be applied on the hair for example using a comb, a brush or with the fingers.

According to a particular embodiment of the invention, application of the composition is followed by drying at a temperature above 40°C. Preferably, said temperature is above 45°C. Even more preferably, said temperature is above 45°C and below 220°C.

Drying can be carried out immediately after application or after a waiting time, which can be from 1 minute to 30 minutes.

Preferably, in addition to supply of heat, the hair is blow-dried. Blow-drying improves the individualization of the surface coating.

During drying, mechanical action can be exerted on the tresses of hair, such as combing, brushing, passing the fingers through.

The drying stage of the method of the invention can be carried out with a hood, a hair dryer, smoothing tongs, a climazone, etc.

25 When the drying stage is carried out with a hood or a hair dryer, the drying temperature is between 40 and 110 degrees, preferably between 50 and 90 degrees.

When the drying stage is carried out with smoothing tongs, the drying temperature is between 110 and 220 degrees, preferably between 140 and 200 degrees.

30 Once drying is completed, rinsing or a final shampooing can optionally be carried out.

The examples given below serve to illustrate the invention.

Example 1: Treatment composition

The following compositions are prepared:

Composition	A	A' (not of the invention)
Poly(isobornyl methacrylate-isobornyl co-acrylate-isobutyl co-acrylate-co-acrylic acid at 50% in isododecane as prepared in the above example	8 g	8 g
MQ-T propyl resin (30:70) at 30% in isododecane as prepared in the above example	16.6 g	-
Isododecane	Qs 100 g	Qs 100 g

1 g of composition A is applied on a 2.5 g hair tress with tone height 4, clean and wet. After waiting 2 minutes, the tress is dried with a hair dryer at a temperature of 80°C for 2 minutes. A tress is obtained in which the hair is well separated and has body. When the tress is wetted again it is very hydrophobic in water and it dries very quickly at room temperature. Moreover, the shaping produced by brushing stands up well to conditions of high humidity.

A tress treated with composition A' or a tress that has not been treated has poorer hydrophobic properties and the tress takes longer to dry at room temperature after it is wetted again. The shaping produced by brushing also stands up less well to conditions of high humidity

Example 2: Treatment composition:

The following composition is prepared:

Composition	B
Mixture of Polydimethylsiloxane alpha-omega dihydroxyl/Cyclopentadime-hylsiloxane (14.7/85.3) marketed by Dow Corning under the name DC1501 Fluid	14 g
Poly(isobornyl methacrylate-isobornyl co-acrylate-isobutyl co-acrylate-co-acrylic acid at 50% in isododecane as prepared in the above example	8 g
MQ-T propyl resin (30:70) at 30% in isododecane as	16.6

prepared in the above example	g
Isododecane	Qs 100 g

1 g of composition B is applied on a 2.5 g hair tress of tone height 4, clean and wet. After waiting 2 minutes, the tress is dried with a hair dryer at a temperature of 80°C for 2 minutes. A tress is obtained in which the hair is well separated and has body. When the tress is wetted again it is very hydrophobic in water and it dries very quickly at room temperature. Moreover, the shaping produced by brushing stands up well to conditions of high humidity.

10 **Example 3: Treatment composition:**

The following composition is prepared:

Composition	C
Mixture of Polydimethylsiloxane alpha-omega dihydroxyl / Cyclopentadimethylsiloxane (14.7 / 85.3) marketed by Dow Corning under the name DC1501 Fluid	14 g
Poly(isobornyl methacrylate-isobornyl co-acrylate-isobutyl co-acrylate-co-acrylic acid at 50% in isododecane as prepared in the above example	8 g
MQ-T propyl resin (30:70) at 30% in isododecane as prepared in the above example	16.6 g
Supramolecular polymer obtained from GI2000 as compound A and from a graft of formula B in which L denotes an isophorone radical at 25% in isododecane prepared as described below	24 g
Ethanol	5 g
Isododecane	Qs 100 g

0.5 g of composition C is applied on a 2.5 g hair tress of tone height 4, clean and wet. After waiting 2 minutes, the tress is dried with a hair dryer at a temperature of 80°C for 2 minutes. A tress is obtained in which the hair is well separated and has body. When the tress is wetted again it is very hydrophobic in water and it dries very quickly at room temperature. Moreover, the shaping produced by brushing stands

up well to conditions of high humidity. These effects resist shampooing.

Example 4: Colouring composition

5 The following composition is prepared:

Composition	D
Supramolecular polymer obtained from GI2000 as compound A and from a graft of formula B in which L denotes an isophorone radical at 25% in isododecane prepared as described below	24 g
Mixture of Polydimethylsiloxane alpha-omega dihydroxyl/Cyclopentadimethylsiloxane (14.7/85.3) marketed by Dow Corning under the name DC1501 Fluid	14 g
Mica nacre coated with brown iron oxide marketed by Eckart under the name Prestige Soft Bronze	8 g
Poly(isobornyl methacrylate-isobornyl co-acrylate-isobutyl co-acrylate-co-acrylic acid at 50% in isododecane as prepared in the above example	8 g
MQ-T propyl resin (30:70) at 30% in isododecane as prepared in the above example	16.6 g
Ethanol	5 g
Isododecane	Qs 100 g

0.6 g of composition D is applied on a 1g hair tress of tone height 4, clean and wet. After waiting 2 minutes, the tress is dried with a hair dryer at a temperature of 80°C for 2 minutes. A coloured tress is obtained, with the hair well separated. When the tress is wetted again it is very hydrophobic in water and it dries very quickly at room temperature. Moreover, the shaping produced by brushing stands up well to conditions of high humidity. These effects resist shampooing.

10

Example 5

The following compositions are prepared:

Composition 1	
Poly(isobornyl methacrylate-isobornyl co-acrylate-isobutyl co-acrylate-co-acrylic acid at 50% in isododecane as prepared in the above example	16 g
MQ-T propyl resin (30:70) at 30% in isododecane as prepared in the above example	28 g
Isododecane	Qs 100 g

Composition 2	
Ammonium lauryl sulphate in aqueous solution at 77%	41 g
Alkyl (C ₈ /C ₁₆) polyglucoside (1,4) in aqueous solution at 53% marketed under the name Plantacare 818 UP by the company Cognis	7.5 g
Water	Qs 100 g

10 g of composition 1 is added to 90g of composition 2, and the mixture is stirred. 1 g of the mixture is then applied on a wet 2.5 g tress. After waiting 5 minutes, the tress is then rinsed. The tress obtained dries much more quickly during brushing than a tress that was treated with 1 g of composition 2. Moreover, the shaping produced by brushing stands up better to conditions of high humidity.

The supramolecular polymer used in the above examples is synthesized as follows.

106.1 g of polymer GI2000 marketed by the company NISSO, in the presence of 22 mg of catalyst, dibutyltin dilaurate, is heated at 80°C, under vacuum for 2 hours. The temperature of the mixture is lowered to 20°C, under argon, followed by addition of 10 mL of isododecane. 19.3 g of isophorone diisocyanate is added. The mixture is stirred for 16 hours at 20°C, under controlled atmosphere, then it is heated to 120°C, followed by addition of 25 mL of propylene carbonate. 12 g of 6-methyl isocytosine is added. This gives a homogeneous white suspension. This suspension is heated to 140°C and is stirred

at this temperature for 6 hours. The reaction is monitored by infrared spectroscopy, until the peak characteristic of the isocyanates (2250 cm^{-1}) disappears completely. The mixture is then brought back to 30°C , and 400 mL of heptane, 200 mL of THF and 50 mL of ethanol are added to the mixture, prior to filtration on Celite. Stripping with isododecane allows polymer 1e to be obtained at 20% of dry extract. The polymer is characterized by GPC ($M_n = 7000$ with an Ip of 2.05).

The poly(isobornyl acrylate/isobornyl methacrylate/isobutyl acrylate/acrylic acid) copolymer used in the examples is synthesized according to the following procedure.

300 g of isododecane is put in a 1-litre reactor, then the temperature is raised, going from room temperature (25°C) to 90°C in 1 hour.

Then the following are added, at 90°C and in 1 hour: 105 g of isobornyl methacrylate (manufactured by Arkema), 105 g of isobornyl acrylate (manufactured by Arkema) and 1.8 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox® 141 from Akzo Nobel).

The mixture is held at 90°C for 1.5 h.

Then the following are introduced into the preceding mixture, still at 90°C and in 30 minutes: 75 g of isobutyl acrylate (manufactured by Fluka), 15 g of acrylic acid and 1.2 g of 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane.

The mixture is held at 90°C for 3 hours, then the whole is cooled.

A solution is obtained with 50% of active substance in polymer in isododecane.

A polymer is obtained comprising a first rigid block of poly(isobornyl acrylate/isobornyl methacrylate) having a T_g of 110°C , a second flexible block of poly(isobutyl acrylate/acrylic acid) having a T_g of -9°C and an intermediate block which is an isobornyl acrylate/isobornyl methacrylate/isobutyl acrylate/acrylic acid random polymer.

The siloxane resin was synthesized according to the following procedure:

The following resins are used:

Resin MQ = a resin MQ of formula $M_{0.43}Q_{0.57}$ and with $M_n = 3230$ dissolved in xylene at 70.8 wt.% solids. Resin MQ was manufactured according to the techniques described by Daudt in patent US 2 676 182.

5 Propyl resin T = a propyl silsesquioxane resin at 74.8 wt.% in toluene. The propyl silsesquioxane resin was obtained by hydrolysis of propyl trichlorosilane.

Preparation of resins MQT^{Pr}

10 A resin MQ, a propyl resin T, xylene and 1M KOH in water in the proportions shown in Table 1 are put in a three-necked flask equipped with a stirrer, a temperature probe and a Dean-Stark trap equipped with a condenser at the top. The Dean-Stark trap is pre-filled with xylene to ensure maintaining a
15 solids level of 50% in the reactor. The mixture in the reactor is maintained at a reflux temperature (between 100 and 140°C) for at least 3 hours. Any water forming in the reaction mixture is removed continuously if necessary and trapped as an azeotrope in the Dean-Stark apparatus. After 3 hours of
20 reflux, the water is removed from the apparatus and heating continues for a further 30 minutes. After cooling the mixture, an excess of acetic acid is added to neutralize the KOH in the mixture. The mixture is then filtered to remove the salts that formed, by passing through a filter under pressure. Solvent
25 exchange is carried out by heating the mixture in a rotary evaporator under vacuum. After removing most of the xylene, decamethylcyclopentasiloxane - or isododecane - is added while continuing to remove any residual aromatic solvent. The structures of the resultant siloxane resins are characterized
30 by ²⁹Si NMR spectroscopy and CPG and the results are summarized in Table 1 below.

Table 1

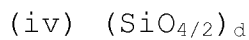
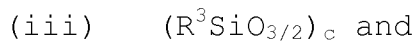
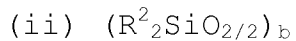
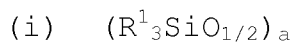
Weight ratio of MQ/T ^{Pr} resins added	resin MQ, wt.%	propyl resin T, wt.%	xylene, wt.%	1M KOH, wt.%	acetic acid, wt.%
(30:70)	20.9	48.8	29.2	0.9	0.2

CLAIMS

1. Composition for treating keratin fibres comprising

• one or more ethylenic block copolymers, containing at least one first block having a glass transition temperature (T_g) greater than or equal to 40°C and being derived wholly or partly from one or more first monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature greater than or equal to 40°C, and at least one second block having a glass transition temperature less than or equal to 20°C and being derived wholly or partly from one or more second monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature less than or equal to 20°C, said first block and said second block being joined together by a random intermediate segment comprising at least one of said first monomers constituting the first block and at least one of said second monomers constituting the second block, and said block copolymer having a polydispersity index I greater than 2,

• a siloxane resin comprising the units:



with

R¹, R² and R³ representing independently an alkyl group having from 1 to 8 carbon atoms, an aryl group, a carbinol group or an amino group,

a being between 0.05 and 0.5,

b being between zero and 0.3,

c being greater than zero,

d being between 0.05 and 0.6,

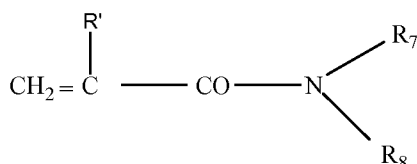
a + b + c + d = 1,

and more than 40 mol.% of the groups R³ of the siloxane resin are propyl groups, and

• one or more volatile solvents, the weight ratio of the volatile solvent to the ethylenic block copolymer being greater than 2.

2. Composition according to Claim 1, characterized in that the ethylenic block copolymer comprises a first block obtained from the first monomer(s), which are such that the homopolymer prepared from these monomers has a glass transition temperature greater than or equal to 40°C, and are selected from:

- the methacrylates of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_4$ in which R_4 represents an unsubstituted, linear or branched alkyl group, containing from 1 to 4 carbon atoms, a C_4 to C_{12} cycloalkyl group,
- the acrylates of formula $\text{CH}_2=\text{CH}-\text{COOR}_5$ in which R_5 represents a C_4 to C_{12} cycloalkyl group,
- the (meth)acrylamides of formula:



where R_7 and R_8 , which may be identical or different, each represent a hydrogen atom or a linear or branched C_1 to C_{12} alkyl group, or R_7 represents H and R_8 represents a 1,1-dimethyl-3-oxobutyl group,

and R' denotes H or methyl;

and in that said second monomer(s), which are such that the homopolymer prepared from these monomers has a glass transition temperature less than or equal to 20°C, are selected from:

- the acrylates of formula $\text{CH}_2=\text{CHCOOR}_9$, R_9 representing an unsubstituted, linear or branched C_1 to C_{12} alkyl group, with the exception of the tert-butyl group, in which optionally one or more heteroatoms selected from O, N, S are intercalated,
- the methacrylates of formula $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOR}_{10}$, R_{10} representing an unsubstituted linear or branched C_6 to C_{12} alkyl group, in which optionally one or more heteroatoms selected from O, N and S are intercalated;
- the vinyl esters of formula $\text{R}_{11}-\text{CO}-\text{O}-\text{CH}=\text{CH}_2$ where R_{11} represents a linear or branched C_4 to C_{12} alkyl group;
- the ethers of vinyl alcohol and of C_4 to C_{12} alcohol,

- the C₄ to C₁₂ N-alkyl acrylamides, such as N-octylacrylamide,
- and mixtures thereof.

3. Composition according to Claim 1 or 2, characterized in that said block copolymer is such that said first block is obtained from at least one acrylate monomer of formula CH₂=CH-COOR₅ in which R₅ represents a C₄ to C₁₂ cycloalkyl group and from at least one methacrylate monomer of formula CH₂=C(CH₃)-COOR₄ in which R₄ represents a C₄ to C₁₂ cycloalkyl group, and said second block is obtained from at least one second monomer with glass transition temperature less than or equal to 20°C and from an acrylic acid monomer.

4. Composition according to Claim 3, characterized in that R₅ and R₄ represent, independently or simultaneously, an isobornyl group.

5. Composition according to any one of the preceding claims, in which the ethylenic block polymer comprises a second block obtained from acrylic acid and from isobutyl acrylate and a first block obtained from isobornyl acrylate and from isobornyl methacrylate.

6. Composition according to any one of the preceding claims, characterized in that said ethylenic block copolymer comprises from 50 to 80 wt.% of isobornyl methacrylate/acrylate, from 10 to 30 wt.% of isobutyl acrylate and from 2 to 10 wt.% of acrylic acid.

7. Composition according to any one of the preceding claims, in which the volatile solvent(s) is(are) selected from water, ethanol, isopropanol, acetone, volatile alkanes, in particular isododecane, decamethylcyclopentasiloxane, octamethyltrisiloxane and decamethyltetrasiloxane and mixtures thereof.

8. Composition according to any one of the preceding claims, in which the siloxane resin comprises the units

- (i) (R¹₃SiO_{1/2})_a
- (ii) (R²₂SiO_{2/2})_b
- (iii) (R³₃SiO_{3/2})_c and
- (iv) (SiO_{4/2})_d

with

R^1 , R^2 and R^3 representing independently an alkyl or hydroxyalkyl group having from 1 to 8 carbon atoms, an aryl group or an amino group, R^1 preferably being a methyl group and R^3 preferably being a propyl group,

5 a being between 0.05 and 0.5,

b being between zero and 0.3,

c being greater than zero,

d being between 0.05 and 0.6,

$a + b + c + d = 1$,

10 and more than 40 mol.% of the groups R^3 of the siloxane resin are propyl groups.

9. Composition according to any one of the preceding claims in which the siloxane resin is obtained by a method comprising the reaction between:

15 A) a resin MQ comprising at least 80 mol.% of units $(R^1_3SiO_{1/2})_a$ and $(SiO_{4/2})_d$

R^1 representing a methyl group,

a and d being greater than zero,

the ratio a/d being between 0.5 and 1.5;

20 and

B) a propyl resin T comprising at least 80 mol.% of units $(R^3SiO_{3/2})_c$,

R^3 representing a propyl group,

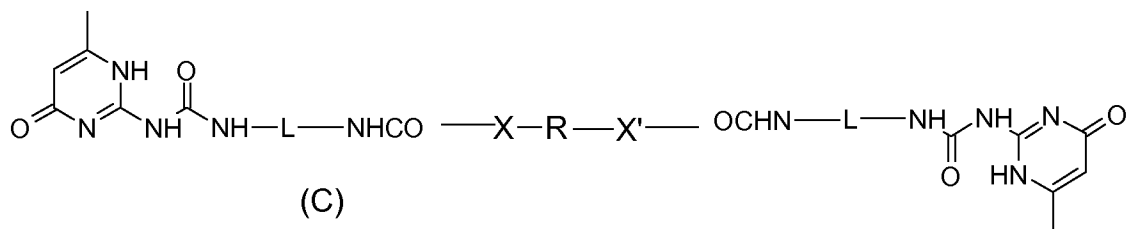
c being greater than zero,

25 where the mass ratio A/B is between 95:5 and 15:85, preferably the mass ratio A/B is 30:70.

10. Composition according to any one of the preceding claims, additionally comprising a hydrophobic film-forming polymer.

30 **11.** Composition according to any one of the preceding claims, additionally comprising a polyalkene-based supramolecular polymer.

12. Composition according to any one of the preceding claims, in which the supramolecular polymer of the invention
35 is of formula C:



with

X and X', which may be identical or different, selected from O, S, NH, or NR_a, R_a representing a C₁-C₆ alkyl group;

R representing a homo- or copolymer derived from one or more
5 mono- or polyunsaturated C₂-C₁₀ alkenes;

and L denoting a group: phenylene; 1,4-nitrophenyl; 1,2-
ethylene; 1,6-hexylene; 1,4-butylene; 1,6-(2,4,4-
trimethylhexylene); 1,4-(4-methylpentylene); 1,5-(5-
methylhexylene); 1,6-(6-methylheptylene); 1,5-(2,2,5-
10 trimethylhexylene); 1,7-(3,7-dimethyloctylene); -isophorone-;
4,4'-methylene biscyclohexylene; tolylene; 2-methyl-1,3-
phenylene; 4-methyl-1,3-phenylene; 4,4-biphenylenemethylene.

13. Composition according to any one of the preceding claims
comprising one or more additional silicone compounds selected
15 from the polysiloxanes having a viscosity greater than 100
cSt, preferably selected from the silicone oils, even more
particularly selected from the oils of the
polydimethylsiloxane type.

14. Composition according to any one of the claims
20 comprising one or more pigments.

15. Composition according to any one of the preceding
claims, additionally comprising one or more surfactants
selected from the anionic surfactants, the non-ionic
surfactants and the cationic surfactants, preferably an
25 anionic surfactant selected from the alkylsulphates, the
alkylethersulphates and mixtures thereof or a cationic
surfactant selected from the salts of primary, secondary or
tertiary fatty amines, optionally polyoxyalkylenated; the
quaternary ammonium salts such as the chlorides or the
30 bromides of tetraalkylammonium, of
alkylamidoalkyltrialkylammonium, of trialkylbenzylammonium, of
trialkylhydroxyalkylammonium or of alkylpyridinium; the
derivatives of imidazoline and mixtures thereof.

16. Method for treating keratin fibres comprising the application of a composition as defined in any one of Claims 1 to 17 on the keratin fibres, optionally followed by drying at a temperature above 40°C.