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(71) Applicant (*for all designated States except US*): **L'OREAL** [FR/FR]; 14, rue Royale, F-75008 Paris (FR).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **BRUN, Gaëlle** [FR/FR]; 2 rue Plichon, F-75011 Paris (FR).

(74) Agent: **WATTREMEZ, Catherine**; L'Oreal, D.I.P.I., 25-29 Quai Aulagnier, F-92665 Asnieres-Sur-Seine Cedex (FR).

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(54) Title: HAIR DYEING PROCESS USING PRESSURE-SENSITIVE ADHESIVE SILICONES WITH A PRETREATMENT STEP

(57) Abstract: The subject of the present invention is a process for dyeing keratin fibres, comprising the following steps: a) a first composition comprising one or more silicone or non-silicone, amino polymers is applied, b) a second cosmetic composition comprising one or more pressure-sensitive adhesive silicones, one or more volatile solvents and one or more pigments is applied. Coatings which make it possible to obtain persistent coloured coatings on hair are thus obtained on the keratin fibres.



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HAIR DYEING PROCESS USING PRESSURE - SENSITIVE ADHESIVE SILICONES WITH A PRETREATMENT STEP

The subject of the present invention is a process for dyeing human keratin fibres, comprising two steps, one of which involves a composition comprising in particular a pressure-sensitive adhesive silicone.

It is known practice to provide coatings on the hair comprising pigments, these pigments thus being used as a mixture with film-forming polymers such as particular silicone copolymers based on silicone resin and fluid silicone, more commonly known as BioPSA. These copolymers are in particular described in patent applications WO 03/026596, WO 2004/073626, WO 2007/051505 and WO 2007/051506 for various cosmetic applications such as application to the hair, the nails and the skin.

Compositions using these polymers are described, moreover, in European patent application EP 2 095 810, the subject of which is a composition comprising one or more copolymers based on silicone resin and fluid silicone, one or more volatile solvents, and one or more silicone resins having at least one trifunctional unit of formula $(\text{CH}_3)_2\text{SiO}_{3/2}$ (T unit).

Mention may also be made of European application EP 2 016 933, which relates, *inter alia*, to the use of anhydrous compositions for treating hair comprising one or more copolymers based on silicone resin and fluid silicone, one or more linear or cyclic volatile silicones and, optionally, pigments, advantageously in the presence of one or more non-volatile linear polydimethylsiloxanes.

It is also possible to obtain coloured coatings of fibres by involving pigments combined with mixtures based on silicone resin and fluid silicone.

These combinations of copolymers or of polymer blends with pigments make it possible to obtain a colouring which is visible, regardless of the initial colour of the hair, without requiring prior bleaching thereof, and chromatic, in particular when the pigments used are pearlescent agents. This colouring is not yet sufficiently resistant to shampooing.

In addition, in the previous cases, it has however been possible to note that the effect obtained varies according to the state of sensitization of the hair treated.

It is important to be able to further improve the persistence of the coating effects provided by such copolymers, independently of the state of the fibres treated.

Thus, one of the aims of the present invention is to develop coloured coatings which exhibit further improved resistance to shampooing and which produce satisfactory results regardless of the type of hair treated.

This aim and others are achieved with the present invention, the subject of which is a process for dyeing keratin fibres, comprising the following steps:

a) a first composition comprising one or more silicone or non-silicone, amino

polymers is applied,

- b) a second cosmetic composition comprising one or more pressure-sensitive adhesive silicones, one or more volatile solvents and one or more pigments is applied.

5 Thus, the invention makes it possible to increase the resistance of the coatings to shampooing.

The present invention also makes it possible to improve the cosmetic properties of the coating, in particular the feel of the hair thus coated. The hair is therefore softer and more manageable and the hairs are well separated.

10 Brushing of the locks during application is also facilitated.

It should also be noted that the composition retains the physical qualities of the keratin fibres, since it makes it possible to obtain persistent, strong and/or chromatic colourings, without the use of oxidizing agents capable of degrading said fibres.

15 In what follows, unless otherwise indicated, the limits of the ranges indicated are included in the invention.

The first step of the process therefore consists in using a first composition comprising a silicone or non-silicone, amino polymer.

Amino polymer

20 Preferably, the amino polymer of the first composition does not comprise a quaternized group.

Non-silicone amino polymer

When the amino polymer used is a non-silicone polymer, it is advantageously chosen from polylysine (for example Polysine 25% solution, sold by the company
25 Chisso), polyethyleneimines (for example Lupasol P sold by the company BASF), and copolymers of polyvinylamine and of n-vinylformamide (for example Catiofast VFH sold by the company BASF), or mixtures thereof.

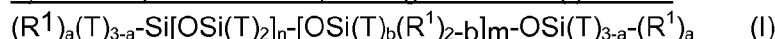
Amino silicones

When the amino polymer used is a silicone polymer, it is advantageously chosen
30 from amino silicones comprising one or more intrachain amine functions.

For the purpose of the invention, the term "intrachain amine function" is intended to mean that said amine function is linked to a silicon atom by means of a hydrocarbon-based group optionally interrupted with an oxygen atom; said silicon atom not being at one of the ends of the polymer chain. The amine function may be a
35 primary, secondary or tertiary amine function. In other words, the amino silicones of the composition according to the invention have one or more amino groups located in the main chain or on the pendant links of the polymer.

In particular, the amino silicone(s) present in the composition according to the invention is (are) chosen from the following compounds:

a) the compounds corresponding to formula (I) below:



in which:

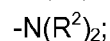
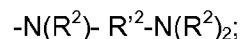
T, which may be identical or different, represent a hydrogen atom, or a phenyl, hydroxyl or C₁-C₈ alkyl radical, and preferably methyl, or C₁-C₁₅ alkoxy radical,

a denotes the number 0 or an integer from 1 to 3,

b denotes 0 or 1, and in particular 1,

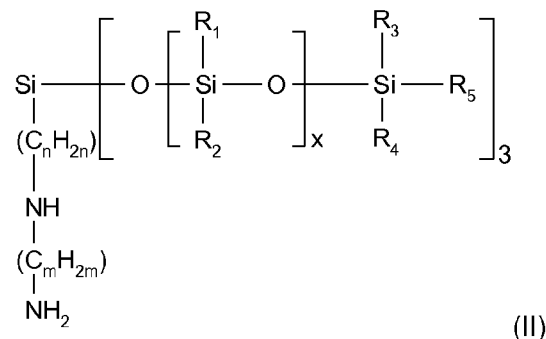
m and n are numbers such that the sum (n + m) can range especially from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and especially from 49 to 149, and m possibly denoting a number from 1 to 2000 and especially from 1 to 10;

R¹, which may be identical or different, represent a monovalent radical of formula -C_qH_{2q}L in which q is a number from 2 to 8 and L is an amino group chosen from the following groups:



in which R² can denote a hydrogen atom, a phenyl, a benzyl or a saturated monovalent hydrocarbon-based radical, for example a C₁-C₂₀ alkyl radical, and R'² can denote a C₂-C₁₀ alkyl group;

b) the amino silicones of the formula (II):



in which:

- R₁, R₂, R₃ and R₄, which may be identical or different, denote a C₁-C₄ alkyl radical or a phenyl group,

- R₅ denotes a C₁-C₄ alkyl radical or a hydroxyl group,

- n is an integer ranging from 1 to 5,

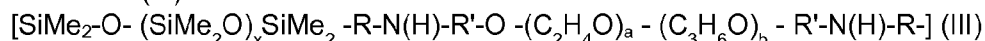
- m is an integer ranging from 1 to 5,

and in which x ranges from 2 to 500, preferably from 5 to 100;

c) polyoxyalkylenated amino silicones of (AB)_n type

A being a polysiloxane block and B being a polyoxyalkylene block, comprising at least one amine group.

In particular, mention may be made of the compounds consisting of repeating units of formula (III):



in which:

- a is an integer greater than or equal to 1, preferably between 5 and 200 and even more particularly between 5 and 100,

- b is an integer between 0 and 200, preferably between 4 and 200 and even more particularly between 5 and 100,

- R, which may be identical or different, represent a divalent organic group which is bonded to the adjacent silicon atom via a carbon-silicon bond and to a nitrogen atom,

- R', which may be identical or different, represent a divalent organic group which is bonded to the adjacent oxygen atom via a carbon-oxygen bond and to a nitrogen atom;

the number of repeating units and x being such that the weight-average molecular weight of the silicone is preferably between 5000 and 1 000 000 and even more particularly between 10 000 and 200 000.

According to one variant, the compounds of formula (III) are such that R represents a C₂-C₁₂ hydrocarbon-based radical optionally comprising one or more heteroatoms such as oxygen. More particularly, R denotes an ethylene, linear or branched propylene, linear or branched butylene or -CH₂CH₂CH₂OCH(OH)CH₂- radical.

Moreover, R' is a C₂-C₁₂ hydrocarbon-based radical optionally comprising one or more heteroatoms such as oxygen. More particularly, R' denotes a divalent alkylene radical, for instance ethylene, linear or branched propylene or linear or branched butylene.

In one variant of the invention, the siloxane blocks preferably represent between 50 and 95 mol% relative to the total weight of the silicone, and more particularly between 70 and 85 mol%. The level of amine is generally between 0.02 and 0.5 meq/g of copolymer in a solution at 30% in dipropylene glycol, and more particularly between 0.05 and 0.2.

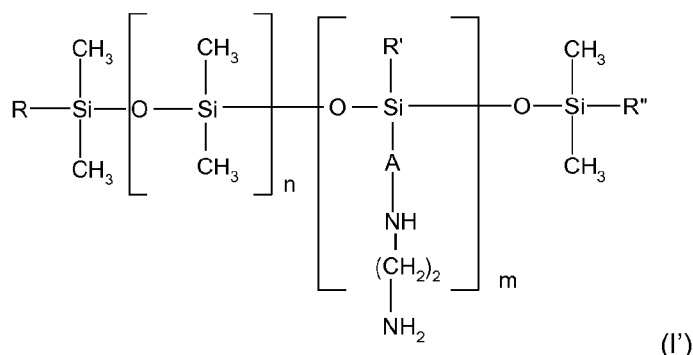
These block copolymers are prepared, *inter alia*, by means of processes known to those skilled in the art, for example by reacting a silicone α,ω -diepoxide or dichloro silicone with an α,ω -diaminopolyoxyalkylene.

Among the compounds of formula (III), mention may be made of the product
5 Silsoft A-843 sold by the company Momentive Performance Materials.

Other polyoxyalkylenated amino silicones of (AB)_n type are, for example, the products AP 8201 and CE 8401 Emulsion sold by the company Dow Corning, and also the compounds Silsoft A+, Silsoft A-553 and Silsoft A-858 sold by the company Momentive Performance Materials.

10 Advantageously, the amino silicone(s) is (are) chosen from the silicones of formula (I), in particular the silicones of formula (I) in which R¹ represents a monovalent radical of formula -C_qH_{2q}L in which q is a number from 2 to 8 and L is an amino group chosen from the groups -N(R²)-R²-N(R²)₂ and -N(R²)₂; R², R² and q being as defined above.

15 More particularly, the composition according to the invention comprises one or more amino silicones chosen from the silicones having the following formulae:

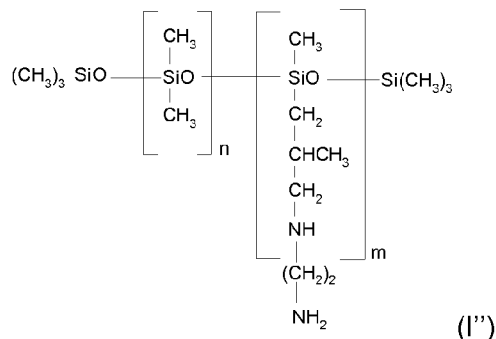


in which R, R' and R'', which may be identical or different, denote a C₁-C₄ alkyl radical, preferably CH₃; a C₁-C₁₅ alkoxy radical; or OH; A represents a linear or branched
20 C₃-C₈, preferably C₃-C₆, alkylene radical; m and n are integers which depend on the molecular weight and the sum of which is between 1 and 2000.

An example of an amino silicone according to the invention of formula (I) is in particular the product sold under the name AP 6088, from the company Dow Corning.

Other compounds of formula (I), and more particularly of formula (I'), are, for
25 example, the products DC 2-8822A and DC 2-8040, in which the alkoxy group contains from 11 to 15 carbon atoms, sold by the company Dow Corning, and the products AP-8468 and DC 949, sold by the company Dow Corning.

By way of other examples of amino silicones of this type, mention may be made of those corresponding to formula (I'') below:



in which n and m have the meanings indicated in formula (I) or (I').

The amino silicone sold under the name DC 2-8566, by the company Dow Corning, is an example thereof.

- 5 The composition may also comprise, as amino silicone, compounds known under the name Wacker Belsil ADM LOG 1 sold by the company Wacker; and DC 2-8299 cationic Emulsion, from Dow Corning, which corresponds to a silicone of polydimethylsiloxane type comprising aminoethyl iminopropyl groups, and comprising a methoxy and/or hydroxyl function and alpha,omega-silanols in a cationic aqueous emulsion, for example at 60%.
- 10 Mention may also be made of the amino silicones known under the name Polysilicone-9 or Elastomer OS from the company Kao, corresponding to a polymer having a PDMS main chain and pendant oxazoline units.

- 15 The silicone or non-silicone, amino polymers of the composition used in the first step can be present in a content ranging from 0.1% to 20% by weight, relative to the total weight of the composition, preferably ranging from 0.2% to 15% by weight, and more preferably ranging from 0.5% to 10% by weight.

Water content

- 20 The composition of the first step is preferably an aqueous composition. In particular, the water content is then between 5% and 99.9% by weight relative to the weight of this composition. Preferably, the water content of this composition ranges from 50% to 97% by weight, relative to the weight of the composition.

- 25 As indicated previously, the composition used during the second step comprises one or more pressure-sensitive adhesive silicones, one or more volatile solvents and one or more pigments.

Pressure-sensitive adhesive silicones

- 30 According to a first variant of the invention, the pressure-sensitive adhesive silicone(s) of the composition used in step b) is (are) copolymers based on silicone resin and on silicone of dimethiconol type.

According to a second variant of the invention, the pressure-sensitive adhesive

silicone(s) of the composition used in step b) comprise(s) a mixture of one or more silicones of dimethiconol type and of one or more silicone resins of MQ type.

Copolymer based on silicone resin and on silicone of dimethiconol type

5 The silicone copolymer of the invention is derived from the reaction between a silicone resin and a silicone of dimethiconol type.

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

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

Preferably, the silicone resin according to the invention is the product of condensation of SiO_2 groups and of $\text{R}_3(\text{SiO})_{1/2}$ (triorganosilyl) groups for which each R group is independently selected from methyl, ethyl, propyl and vinyl radicals and for
20 which the ratio between the SiO_2 functions and the $\text{R}_3(\text{SiO})_{1/2}$ functions of the silicone resin ranges from 0.6 to 0.9. Triorganosilyl groups that may be used to form the silicone resin may be trimethylsilyl, triethylsilyl, methylmethylpropylsilyl or dimethylvinylsilyl groups, and mixtures thereof. The trimethylsilyl group is preferred in the context of the invention.

25 Preferably, the silicone of dimethiconol type according to the invention is a diorganopolysiloxane comprising OH end functions, having a viscosity of between 100 and 100 000 cSt at 25°C, for which the substituents of the diorganopolysiloxane are independently chosen from methyl, ethyl, propyl or vinyl radicals. The diorganopolysiloxanes are preferably linear polymers. Examples of
30 diorganopolysiloxane may be, without limitation, a polydimethylsiloxane, an ethylmethylpolysiloxane, a copolymer of dimethylsiloxane and methylvinylsiloxane, and mixtures of such polymers or copolymers having OH ends. The preferred diorganopolysiloxane is a polydimethylsiloxane.

Examples of synthesis of such a copolymer are, for example, described in patent
35 US 5 162 410 or in patent CA 711756.

The copolymers according to the present invention may therefore be prepared by heating the following mixture:

- from 45% to 75% by mass of silicone resin, being the product of condensation of SiO_2 and $\text{R}_3(\text{SiO})_{1/2}$ units, for which each R group is independently selected from methyl, ethyl, propyl or vinyl radicals and for which the ratio between the SiO_2 functions and the $\text{R}_3(\text{SiO})_{1/2}$ functions of the silicone resin ranges from 0.6 to 0.9;

5 - from 25% to 55% by mass of diorganopolysiloxane comprising OH end functions, with a viscosity of between 100 and 100 000 cSt at 25°C, for which the substituents of the diorganopolysiloxane are independently chosen from methyl, ethyl, propyl or vinyl radicals;

10 - from 0.001% to 5% of a suitable catalyst, which is preferably an organic aliphatic amine compound preferably chosen from primary amines, secondary amines, tertiary amines, carboxylic acid salts of the amines mentioned above and quaternary ammonium salts.

The mixture is heated at a temperature of between 80°C and 160°C until the adhesive nature of the resulting silicone copolymer is obtained.

15 The copolymers that are preferred according to the invention are sold by Dow Corning under the reference Bio-PSA®, these Bio-PSA® copolymers possibly being in two forms, standard or amine-compatible, and being provided in various solvents with several silicone resin/fluid silicone ratios. Mention may in particular be made of the grades 7-4400, 7-4500 and 7-4600. The Bio-PSA® that is particularly preferred
20 according to the invention is the grade 7-4400.

Mixture based on silicone resin and on dimethiconol silicone

The pressure-sensitive adhesive silicone(s) can be chosen from mixtures of one or more silicone resins of MQ type and of one or more silicones of dimethiconol type.

25 What has been indicated in the context of the definition of the silicone resins and of the silicones of dimethiconol type which are part of the synthesis of the copolymers remains valid in the present case, and reference may be made thereto, regardless of whether this concerns the nature of the silicones or the respective proportions thereof, which are, in this case, expressed relative to the weight of the mixture of the silicone resin and of the silicone of dimethiconol type.

30 This mixture of silicone of dimethiconol type and of silicone resin can be in the form of a dispersion in a volatile solvent or in the form of an emulsion in water, and is for example described in international application WO 03/028677.

Commercial compounds corresponding to such mixtures are DC 7355 (E207484), DC Q2-7735 (E207500), DC Q2-7406 (E207501) and DC Q2-7566
35 (E207502), these being forms as a dispersion in organic solvents. A commercial compound as a dispersion in water is DC 5-7300.

Amount

The composition used in the second step of the process according to the invention advantageously has a content of pressure-sensitive adhesive silicone(s) ranging from 0.2% to 60% by weight, relative to the weight of the composition. Preferably, this content ranges from 1% to 30% by weight, relative to the weight of the composition.

More specifically, when the pressure-sensitive adhesive silicone(s) is (are) copolymer(s) as described above, this or these copolymer(s) may in particular be present in the composition according to the invention in a content of greater than 1% and up to 40% by weight, relative to the total weight of the composition, preferably ranging from 1.5% to 20% by weight, and preferentially ranging from 1.5% to 15% by weight.

When the pressure-sensitive adhesive silicone(s) is (are) mixtures of MQ resin and of dimethiconol, the MQ resin is advantageously present in the composition in a content ranging from 0.1% to 30% by weight, relative to the total weight of the composition, preferably ranging from 0.2% to 20% by weight, and more preferentially ranging from 0.5% to 15% by weight, and the silicone of dimethiconol type is present in the composition in a content ranging from 0.1% to 30% by weight, relative to the total weight of the composition, preferably ranging from 0.2% to 20% by weight, and more preferentially ranging from 0.5% to 15% by weight.

Volatile solvent

The composition used in the second step of the process according to the invention comprises one or more volatile solvents.

In the context of the invention, the term "volatile solvent" means a compound that is liquid at ambient temperature (20°C) and at atmospheric pressure (760 mmHg), with a vapour pressure at 20°C of greater than 0.1 mmHg, preferably between 0.1 and 300 mmHg, and even more preferentially between 0.5 and 200 mmHg.

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

Volatile non-silicone organic solvents that may be mentioned include:

- volatile C₁-C₄ alkanols such as ethanol or isopropanol;
- volatile C₅-C₆ alkanes such as n-pentane, hexane, cyclopentane, 2,3-dimethylbutane, 2,2-dimethylbutane, 2-methylpentane or 3-methylpentane;
- C₇-C₁₄ linear alkanes such as n-undecane or n-tridecane;
- linear esters of liquid C₁-C₂₀ acids and of volatile C₁-C₈ alcohols, such as methyl acetate, n-butyl acetate, ethyl acetate, propyl acetate or ethyl 3-ethoxypropionate;
- ketones that are liquid at ambient temperature and volatile, such as methyl

ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone or acetone;

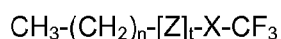
- volatile polyols such as propylene glycol;
- volatile ethers such as dimethoxymethane, diethoxyethane or diethyl ether;
- 5 - volatile glycol ethers such as 2-butoxyethanol, butyl diglycol, diethylene glycol monomethyl ether, propylene glycol n-butyl ether or propylene glycol monomethyl ether acetate;

- volatile branched hydrocarbon-based oils containing from 8 to 16 carbon atoms, and mixtures thereof, and in particular branched C₈-C₁₆ alkanes, for instance C₈-C₁₆ isoalkanes (also known as isoparaffins), isododecane, isodecane and, for example, the oils sold under the trade names Isopar or Permethyl, and mixtures thereof, esters such as isohexyl or isodecyl neopentanoate; isopentyl acetate;

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

15 - 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, and also perfluorodimethylcyclobutane and perfluoromorpholine;

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



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

Among the volatile fluoroalkyl or heterofluoroalkyl compounds, mention may in particular be made of the methoxynonafluorobutane sold under the name MSX 4518® and HFE-7100® by the company 3M, and the ethoxynonafluorobutane sold under the name HFE-7200® by the company 3M.

30 Preferably, the solvent is chosen such that its boiling point is less than 200°C.

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

35 Volatile silicone solvents that may be mentioned include low-viscosity silicone compounds chosen from linear or cyclic silicones containing from 2 to 7 carbon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms, for example octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane,

heptamethylethyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane, and mixtures thereof. According to one particular embodiment, the silicone compound is chosen from cyclopentadimethylsiloxane and dodecamethylcyclohexasiloxane.

5 This volatile silicone generally has a low viscosity, for example a viscosity of less than 10 cSt at 25°C.

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

By way of example, mention may be made of the decamethylcyclopentasiloxane
10 sold under the name DC-245 by the company Dow Corning, the dodecamethylcyclohexasiloxane sold under the name DC-246 by the company Dow Corning, the octamethyltrisiloxane sold under the name DC-200 Fluid 1 cSt by the company Dow Corning, and the decamethyltetrasiloxane sold under the name DC-200 Fluid 1.5 cSt by the company Dow Corning.

15 According to one particular embodiment of the invention, the volatile solvent(s) is (are) chosen from water, ethanol, isopropanol, acetone, isododecane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, octamethyltrisiloxane and decamethyltetrasiloxane, and mixtures thereof.

The volatile solvent(s) may be present in the composition that is of use in the
20 process of the invention in a content ranging from 0.1% to 95% by weight, relative to the total weight of the composition, preferably ranging from 1% to 90% by weight, and more preferentially ranging from 5% to 90% by weight.

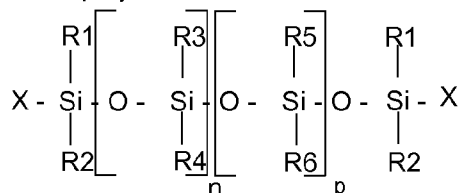
Additional silicone compounds

25 The compositions of the second step and/or of the first step of the process of the invention may comprise other cosmetic additives. In particular, the compositions may contain additional silicone compounds different from the volatile silicones, from the amino silicone, from the MQ resin and from the silicone of dimethiconol type.

According to one particular embodiment, these compositions may comprise one
30 or more polysiloxanes having a viscosity of greater than 100 cSt, preferentially greater than 300 cSt. The viscosity of these polysiloxanes can be measured according to standard ASTM D-445. Such polysiloxanes may be silicone oils, gums or resins or crosslinked silicones.

By way of polysiloxanes having a viscosity of greater than 100 cSt, mention may
35 in particular be made of polydimethylsiloxanes; alkyl dimethicones; polyphenylmethylsiloxanes such as phenyl dimethicones, phenyl trimethicones and vinylmethyl methicones; and also silicones modified with aliphatic and/or aromatic groups, which are optionally fluorinated, or with functional groups such as thiol groups.

Such polysiloxanes can be chosen from the silicones of formula (I):



(I)

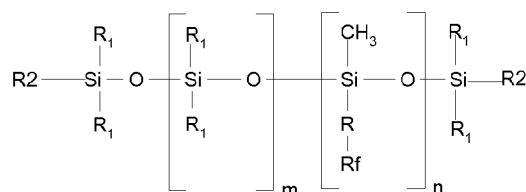
in which:

5 R_1 , R_2 , R_5 and R_6 are, together or separately, an alkyl radical containing 1 to 6 carbon atoms, R_3 and R_4 are, together or separately, an alkyl radical containing from 1 to 6 carbon atoms, a vinyl radical, an aryl radical, an aminoalkyl radical containing from 1 to 6 carbon atoms, which is optionally substituted, or a thioalkyl radical containing from 1 to 6 carbon atoms, X is an alkyl radical containing from 1 to 6 carbon atoms, a vinyl radical, an aminoalkyl radical containing from 1 to 6 carbon atoms, which is optionally substituted, or a thioalkyl radical containing from 1 to 6 carbon atoms, n and p being integers chosen so as to obtain a viscosity of greater than 300 cSt.

By way of example, mention may be made of the following polydimethylsiloxanes:

- 15 • the substituents R_1 to R_6 and X represent a methyl group, such as the product sold under the name Baysilicone TP 3898 by the company General Electric, and the product sold under the name AK 500 000 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 the product sold under the name
- 20 Dow Corning 200 Fluid 60 000 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 the product sold under the name Mirasil DM 500 000 by the company Rhodia and the product sold under the name Dow Corning 200 Fluid 500 000 cSt by the company Dow Corning,
- 25 • dimethicones of the (polydimethylsiloxane)(methylvinylsiloxane) type, such as SE63 sold by GE Bayer Silicones, poly(dimethylsiloxane)(diphenyl)(methylvinylsiloxane) copolymers, and mixtures thereof.

When the polysiloxane comprises a fluoro group, the copolymers having the following structure may be chosen:



in which:

R represents a linear or branched, divalent alkyl group containing 1 to 6 carbon atoms, preferably a methyl, ethyl, propyl or butyl divalent group, R_f represents a fluoroalkyl radical, in particular a perfluoroalkyl radical, containing 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 or a phenyl radical, R₂ represents R₁ or R_f,

m is chosen from 0 to 500, preferably from 0 to 200, and n is chosen from 1 to 1000, preferably from 1 to 500.

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

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

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

The polysiloxane may be a resin other than an MQ resin. The term "resin" is intended to mean a crosslinked or noncrosslinked three-dimensional structure. By way of example of a polysiloxane resin, mention may be made of silsesquioxanes and siloxysilicates.

The nomenclature of silicone resins is known as "MDTQ", the resin being described as a function of the various siloxane monomeric units that it comprises, each of the letters "MDTQ" characterizing a type of unit.

The letter M represents the monofunctional unit of formula (CH₃)₃SiO_{1/2}, the silicon atom being linked to a single oxygen atom in the polymer comprising this unit.

The letter D signifies a difunctional (CH₃)₂SiO_{2/2} unit in which the silicon atom is linked to two oxygen atoms.

The letter T represents a trifunctional unit of formula (CH₃)SiO_{3/2}.

In the M, D and T units 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-based (in particular alkyl) radical containing from 2 to 10 carbon atoms or a phenyl group or alternatively a hydroxyl group.

Finally, the letter Q signifies a tetrafunctional SiO_{4/2} unit in which the silicon atom is linked to four hydrogen atoms, themselves linked to the rest of the polymer.

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

By way of example of these silicone resins, mention may be made of:

- polysilsesquioxanes of formula $(\text{CH}_3\text{SiO}_{3/2})_x$ (T units) in which at least one of the methyl radicals can be substituted with a group R as defined above. Preferably, the number x of T units of the silsesquioxane is less than or equal to 500, it is more preferably 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;

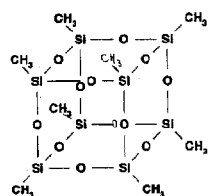
- polymethylsilsesquioxanes which are polysilsesquioxanes in which none of the methyl radicals are substituted with another group. Such polymethylsilsesquioxanes are described in document US 5 246 694, the content of which is incorporated by way of reference;

- polypropylsilsesquioxanes, for which the methyl radicals are replaced with propyl radicals. These compounds, and also the synthesis thereof, are in particular described in patent application WO 2005/075567;

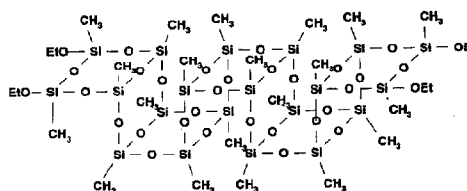
- polyphenylsilsesquioxanes, for which the methyl radicals are replaced with phenyl radicals. These compounds, and also the synthesis thereof, are in particular described in patent application US 2004/0180011.

By way of examples of commercially available polymethylsilsesquioxane resins, mention may be made of those which are marketed:

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



Cage



Ladder

- by the company Shin-Etsu under the references KR-220L, which are composed of T units of formula $\text{CH}_3\text{SiO}_{3/2}$ and have SiOH (silanol) terminal groups, under the reference KR-242A, which comprise 98% of T units and 2% of dimethyl units D and

have SiOH terminal groups, or else under the reference KR-251, comprising 88% of T units and 12% of dimethyl units D and having SiOH terminal groups.

By way of examples of commercially available polypropylsilsesquioxane resins, mention may be made of those which are marketed:

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

By way of examples of commercially available polyphenylsilsesquioxane resins, mention may be made of those which are marketed:

- 10 - by the company Dow Corning under the reference Dow Corning 217 Flake Resin, which is a silanol-terminated polyphenylsilsesquioxane;
 - by the company Wacker under the reference Belsil SPR 45 VP.

As siloxysilicate resins, mention may be made of 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
15 by the company Wacker. Mention may also be made of the trimethylsiloxysilicate resins marketed in a solvent such as cyclomethicone, sold under the name KF-7312J by the company Shin-Etsu, and DC 749 and DC 593 by the company Dow Corning.

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

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

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

The composition of the invention may also contain a crosslinked silicone such as
30 a crosslinked elastomeric organopolysiloxane, which is a high-molecular-weight silicone compound having a three-dimensional structure, with the viscoelastic properties of a flexible solid material. These organopolysiloxanes may thus be in powdered dry form, or in swollen form, in a solvent, the resulting product generally being a gel. These products may also be in a form dispersed in an aqueous solvent.

35 The synthesis of these organopolysiloxanes is described in the following patents:

- US 5 266 321 from Kobayashi Kose,
- US 4 742 142 from Toray Silicone,
- US 5 654 362 from Dow Corning Corp,

- patent application FR 2 864 784.

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

The crosslinked organopolysiloxane obtained may be a non-emulsifying compound or an emulsifying compound. The term "non-emulsifying" defines crosslinked organopolysiloxanes which do not contain polyoxyalkylene units. The term "emulsifying" signifies crosslinked organopolysiloxane compounds having at least one polyoxyalkylene, in particular polyoxyethylene or polyoxypropylene, unit.

The crosslinked organopolysiloxane particles may be conveyed in the form of a gel constituted of a crosslinked organopolysiloxane included in at least one hydrocarbon-based oil and/or one silicone oil. In these gels, the organopolysiloxane particles are commonly non-spherical particles. The crosslinked organopolysiloxane particles may also be in the form of a powder, in particular in the form of a spherical powder.

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

As non-emulsifying crosslinked organopolysiloxanes, use may be made of 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 and USG-103 by the company Shin-Etsu, DC 9040, DC 9041, DC 9509, DC 9505, DC 9506 and DC 9045 by the company Dow Corning, Gransil by the company Grant Industries, and SFE 839 by the company General Electric.

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

As emulsifying crosslinked organopolysiloxanes, use may be made of those marketed under the names KSG-21, KSG-20 and KSG-30 by the company Shin Etsu, and DC 9010 and DC 9011 by the company Dow Corning.

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

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

Preferably, the crosslinked organopolysiloxane is non-emulsifying.

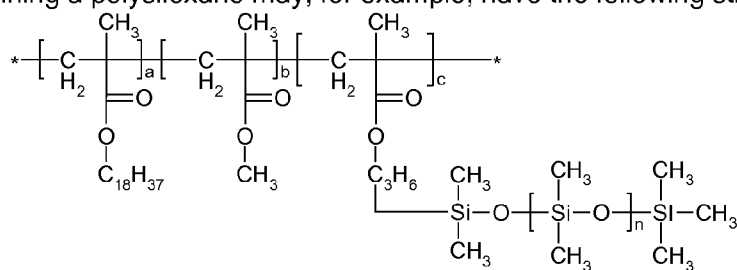
The composition of the invention may also contain a grafted silicone polymer. In the context of the invention, the term "grafted silicone polymer" is intended to mean a polymer comprising a polysiloxane portion and a portion constituted of a non-silicone organic chain, one of the two portions constituting the main chain of the polymer, the other being grafted onto said main chain.

The grafted silicone polymers used in the cosmetic composition according to the invention are preferably chosen from the group constituted of polymers having a non-silicone organic backbone grafted with monomers containing a polysiloxane, polymers having a polysiloxane backbone grafted with non-silicone organic monomers, and mixtures thereof.

The non-silicone organic monomers constituting the main chain of the grafted silicone polymer may be chosen from free-radical-polymerizable, ethylenically unsaturated monomers, polycondensation-polymerizable monomers, such as those forming polyamides, polyesters or polyurethanes, and ring-opening monomers such as those of the oxazoline or caprolactone type.

The polymers having a non-silicone organic backbone grafted with monomers containing a polysiloxane, in accordance with the invention, can be chosen 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 free-radical polymerization starting from ethylenically unsaturated monomers and silicone macromers having a terminal vinyl group, or else copolymers obtained by reaction of a polyolefin comprising functionalized groups and of a polysiloxane macromer having a terminal function that is reactive with said functionalized groups.

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



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

Other copolymers having a non-silicone organic backbone grafted with monomers containing a polysiloxane may also be KP545, KP574 and KP575 sold by

Shin Etsu.

As a grafted silicone compound, mention may also be made of the isobutyl methacrylate/bis(hydroxypropyl) dimethicone acrylate copolymer sold by Grant Industries under the name Granacrysil BMAS.

5 According to the present invention, the grafted silicone polymer(s), having a polysiloxane backbone grafted with non-silicone organic monomers, comprise(s) a main chain of silicone (or polysiloxane ($\text{=Si-O-})_n$) onto which is grafted, within said chain and also, optionally, at at least one of its ends, at least one organic group which does not comprise silicone.

10 Examples of silicone polymers corresponding to the definition are, in particular, polydimethylsiloxanes (PDMSs) onto which are grafted, by means of a thiopropylene-type connecting chain, mixed polymer units of the poly(meth)acrylic acid type and of the poly(alkyl (meth)acrylate) type. As a compound corresponding to this definition, mention may be made of polydimethylsiloxane or polymethylsiloxane comprising
15 methyl 3-(propylthio)acrylate/methyl methacrylate/methacrylic acid groups, or Polysilicone-8 marketed under the name VS80 by the company 3M.

Other examples of silicone polymers are in particular polydimethylsiloxanes (PDMSs) onto which are grafted, by means of a thiopropylene-type connecting chain, polymer units of the poly(isobutyl (meth)acrylate) type.

20 Preferably, the number-average molecular mass of the silicone polymers having a polysiloxane backbone grafted with non-silicone organic monomers, of the invention, ranges from 10 000 to 1 000 000 approximately, and even more preferably from 10 000 to 100 000 approximately.

25 Preferably, the grafted silicone polymers are chosen from the group constituted of polydimethylsiloxane-grafted alkyl methacrylate copolymer, isobutyl methacrylate/acrylic acid/silicone macromer copolymers and polydimethylsiloxane or polymethylsiloxane comprising methyl 3-(propylthio)acrylate/methyl methacrylate/methacrylic acid groups.

30 The preferred silicone compounds are silicone oils, in particular those described in formula (I), and silicone resins.

When they are present in the composition(s) of the first and/or of the second step of the process according to the invention, the amount of additional silicone compounds is between 0.1% and 30% by weight, preferably between 0.1% and 20% by weight, and even more preferentially between 0.1% and 10% by weight, relative to the total
35 weight of the composition.

Pigments

In addition, the composition of the second step comprises one or more pigments.

By pigment is meant all of the pigments which provide colour to keratin 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%.

5 The pigments which may be used are chosen in particular from organic pigments and/or mineral pigments that are known in the art, particularly those described in Kirk-Othmer's encyclopaedia of chemical technology and Ullmann's encyclopaedia of industrial chemistry.

These pigments may be in the form of powder or pigmentary paste. They may be coated or uncoated.

10 The pigments may, for example, be chosen from mineral pigments, organic pigments, lakes, special-effect pigments such as pearlescent agents, metallic pigments or glitter, and mixtures thereof.

The pigment may be a mineral pigment. A mineral pigment is any pigment which satisfies the definition in Ullmann's encyclopaedia in the chapter on inorganic
15 pigments. The mineral pigments useful in the present invention include iron oxides or chromium oxides, manganese violet, ultramarine blue, chromium hydrate and Prussian blue, and titanium dioxide.

The pigment may be a metallic particle consisting of a pure metal or of an alloy of metals comprising more than 80% metals.

20 The metal particle that is of use in the composition of the invention is advantageously in the form of "platelets". The term "platelets" denotes particles of which the ratio of the largest dimension to the smallest dimension, called aspect ratio, is greater than or equal to 5.

The term "dimensions" denotes the dimensions given by the statistical particle
25 size distribution to half the population, termed D50. The metallic particle in particular has an aspect ratio of greater than or equal to 8, and especially greater than or equal to 10, and for example greater than or equal to 15.

The metallic particle may be chosen from silver, aluminium, iron, chromium, nickel, molybdenum, gold, copper, zinc, tin, magnesium, steel, bronze, titanium and
30 alloys of these metals. The metallic particle is preferably chosen from copper, zinc, aluminium, titanium, silver, gold and alloys of these metals. Use is more preferentially made of a metallic particle chosen from aluminium (advantageously having an aluminium content of greater than or equal to 99%), copper (advantageously having a copper content of greater than or equal to 95%), and bronze (preferably having a
35 copper content ranging from 70% to 95% and a zinc content ranging from 5% to 30%).

The metallic particles have, for example, according to their largest dimension, an average size of less than or equal to 25 µm, in particular less than or equal to 10 µm.

The term "average size" denotes the dimension given by the statistical particle size distribution to half the population, termed D50.

Said particles generally have a thickness of less than or equal to 1 μm , especially less than or equal to 0.7 μm , in particular less than or equal to 0.5 μm .

5 As metal particles that can be used in the composition according to the invention, mention may be made of aluminium particles, such as those sold under the names Starbrite 2100 EAC® by the company Siberline and Metalure® by the company Eckart. Mention may also be made of bronze powders such as those sold under the names Premior Super 8000 by the company Wolstenholme and under the names Rothoflex,
10 Lithoflex and Standard by the company Eckart, with, for example, the references Standart Bronze Powder Offset 3000 Super Pale Gold (D50 3-5 μm) and Lithoflex XA 40-03 Rich Pale Gold (D50 3-5 μm). Mention may also be made of particles of metal alloy, for instance silica-coated bronze powders sold under the name Visionaire Honey (size 5-50 μm) and under the name Visionaire Amber (size 5-50 μm) by the company
15 Eckart and also those sold under the name Dorolan 08/0 Pale Gold (D50 7-9 μm), the SiO₂-coated aluminium powder sold under the reference Visionaire Silver Sea (size 5-50 μm) and the SiO₂-coated copper powders sold under the reference Visionaire Cinnamon (size 5-50 μm) and under the reference Visionaire Lava (size 5-50 μm) by the company Eckart, and also those sold under the name Dorolan 10/0 Copper (D50
20 9-11 μm).

The pigment may be an organic pigment. By organic pigment is meant any pigment that satisfies the definition in Ullmann's encyclopaedia in the chapter on organic pigments. The organic pigment may in particular be chosen from nitroso, nitro, azo, xanthene, quinoline, anthraquinone, phthalocyanine, isoindolinone, isoindoline,
25 quinacridone, perinone, perylene, diketopyrrolopyrrole, thioindigo, dioxazine, triphenylmethane and quinophthalone compounds.

In particular, the organic pigments may be chosen from carmine, carbon black, aniline black, azo yellow, quinacridone, phthalocyanine blue, sorghum red, the blue pigments codified in the Color Index under the references CI 42090, 69800, 69825,
30 73000, 74100 and 74160, the yellow pigments codified in the Color Index under the references CI 11680, 11710, 15985, 19140, 20040, 21100, 21108, 47000 and 47005, the green pigments codified in the Color Index under the references CI 61565, 61570 and 74260, the orange pigments codified in the Color Index under the references CI 11725, 15510, 45370 and 71105, the red pigments codified in the Color Index under
35 the references CI 12085, 12120, 12370, 12420, 12490, 14700, 15525, 15580, 15620, 15630, 15800, 15850, 15865, 15880, 17200, 26100, 45380, 45410, 58000, 73360, 73915 and 75470, and the pigments obtained by oxidative polymerization of indole or phenol derivatives, such as described in patent FR 2 679 771.

The pigments in accordance with the invention may also be in the form of composite pigments, as described in patent EP 1 184 426. These composite pigments may be composed in particular of particles comprising an inorganic core, at least one binder providing attachment of the organic pigments to the core, and at least one
5 organic pigment which at least partially covers the core.

The organic pigment may also be a lake. By lake is meant dyes adsorbed onto insoluble particles, the assembly thus obtained remaining insoluble during use.

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

Among the dyes, mention may be made of cochineal carmine. Mention may also be made of the dyes known under 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 45 430), D&C Red 4 (CI 15 510), D&C Red 33 (CI 17 200), D&C Yellow 5
15 (CI 19 140), D&C Yellow 6 (CI 15 985), D&C Green (CI 61 570), D&C Yellow 1 O (CI 77 002), D&C Green 3 (CI 42 053), D&C Blue 1 (CI 42 090).

An example of a lake that may be mentioned is the product known under the following name: D&C Red 7 (CI 15 850:1).

The pigment may also be a special-effect pigment. By special-effect pigments
20 are meant pigments that generally create a non-uniform coloured appearance (characterized by a certain shade, a certain vivacity and a certain lightness) that changes as a function of the conditions of observation (light, temperature, observation angles, etc.). They thus contrast with coloured pigments that afford a conventional uniform opaque, semi-transparent or transparent shade.

Several types of special-effect pigments exist: those with a low refractive index, such as fluorescent, photochromic or thermochromic pigments, and those with a higher refractive index, such as pearlescent agents or flakes.

Examples of special-effect pigments include pearlescent pigments such as mica coated with titanium dioxide, or with bismuth oxychloride, coloured pearlescent
30 pigments such as mica coated with titanium dioxide and iron oxides, mica coated with iron oxide, mica coated with titanium dioxide and especially with Prussian blue or chromium oxide, mica coated with titanium dioxide and an organic pigment as defined above, and also pearlescent pigments based on bismuth oxychloride. These pigments may also be mica particles superposed on their surface with at least two successive
35 layers of metal oxides and/or organic colorants.

The pearlescent agents may more particularly possess a yellow, pink, red, bronze, orange, brown, gold and/or copper glint or colour.

By way of illustration of pearlescent agents that can be used in the context of the

present invention, mention may in particular be made of pearlescent agents of gold colour sold in particular by Engelhard under the name Gold 222C (Cloisonne), Sparkle Gold (Timica), Gold 4504 (Chromalite) and Monarch Gold 233X (Cloisonne); bronze pearlescent agents sold in particular by Merck under the names Bronze Fine (17384) (Colorona) and Bronze (17353) (Colorona), by Eckart under the name Prestige Bronze and Prestige Soft Bronze, and by Engelhard under the name Super Bronze (Cloisonne); orange pearlescent agents sold in particular by Engelhard under the names Orange 363C (Cloisonne) and Orange MCR 101 (Cosmica) and by Merck under the names Passion Orange (Colorona) and Matte Orange (17449) (Microna); brown-coloured pearlescent agents sold in particular by Engelhard under the names Nu Antique Copper 340XB (Cloisonne) and Brown CL4509 (Chromalite); pearlescent agents with a copper glint sold in particular by Engelhard under the name Copper 340A (Timica) and by Eckart under the name Prestige Copper and Prestige Soft Copper; pearlescent agents with a red glint sold in particular by Merck under the name Sienna Fine (17386) (Colorona); pearlescent agents with a yellow glint sold in particular by Engelhard under the name Yellow (4502) (Chromalite); red-coloured pearlescent agents with a gold glint sold in particular by Engelhard under the name Sunstone G012 (Gemtone); black pearlescent agents with a gold glint sold in particular by Engelhard under the name Nu Antique Bronze 240 AB (Timica); blue pearlescent agents sold in particular by Merck under the name Matte Blue (17433) (Microna) or Dark Blue (117324) (Colorona); white pearlescent agents with a silvery glint sold in particular by Merck under the name Xirona Silver; and golden green pinkish orangey pearlescent agents sold in particular by Merck under the name Indian Summer (Xirona), and their mixtures.

In addition to pearlescent agents on a mica support, it is also possible to envisage multi-layer pigments based on synthetic substrates such as alumina, silica, calcium sodium borosilicate or calcium aluminium borosilicate, and aluminium.

Mention may also be made of pigments with an interference effect that are not fixed onto a substrate, for instance liquid crystals (Helicones HC from Wacker), holographic interference flakes (Geometric Pigments or Spectra f/x from Spectratek). Special-effect pigments further comprise fluorescent pigments, whether these are substances that are fluorescent in daylight or that produce an ultraviolet fluorescence, phosphorescent pigments, photochromic pigments, thermochromic pigments and quantum dots, sold, for example, by Quantum Dots Corporation.

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

The 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 preferentially between 30 nm and 50 μm .

The pigments may be dispersed in the product by means of a dispersant.

5 The dispersant serves to protect the dispersed particles against their agglomeration or flocculation. This dispersant may be a surfactant, an oligomer, a polymer or a mixture of two or more thereof, bearing one or more functionalities with strong affinity for the surface of the particles to be dispersed. In particular, they can physically or chemically attach to the surface of the pigments. These dispersants also contain at least one functional group that is compatible with or soluble in the
10 continuous medium. In particular, esters of 12-hydroxystearic acid in particular and of C8 to C20 fatty acid and of polyols such as glycerol or diglycerol are used, such as the stearate of poly(12-hydroxystearic acid) with a molecular weight of about 750 g/mol, such as the product sold under the name Solsperse 21 000 by the company Avecia, polyglyceryl-2 dipolyhydroxystearate (CTFA name) sold under the reference Dehymyls
15 PGPH by the company Henkel, or poly-hydroxystearic acid such as the product sold under the reference Arlacel P100 by the company Uniqema, and mixtures thereof.

Mention may be made, as other dispersants that can be used in the compositions used in the invention, of the quaternary ammonium derivatives of polycondensed fatty acids, such as Solsperse 17 000 sold by Avecia, and
20 polydimethylsiloxane/ oxypropylene mixtures, such as those sold by Dow Corning under the references DC2-5185 and DC2-5225 C.

The pigments used according to the invention may be surface-treated with an organic agent.

Thus, the pigments that have been surface-treated beforehand, which are useful
25 in the context of the invention, are pigments that have totally or partially undergone a surface treatment of chemical, electronic, electrochemical, mechanochemical or mechanical nature, with an organic agent such as those described especially in Cosmetics and Toiletries, February 1990, Vol. 105, pp. 53-64, before being dispersed in the composition in accordance with the invention. These organic agents may be
30 chosen, for example, from amino acids; waxes, for example carnauba wax and beeswax; fatty acids, fatty alcohols and derivatives thereof, such as stearic acid, hydroxystearic acid, stearyl alcohol, hydroxystearyl alcohol and lauric acid and derivatives thereof; anionic surfactants; lecithins; sodium, potassium, magnesium, iron, titanium, zinc or aluminium salts of fatty acids, for example aluminium stearate or
35 laurate; metal alkoxides; polysaccharides, for example chitosan, cellulose and derivatives thereof; polyethylene; (meth)acrylic polymers, for example polymethyl methacrylates; polymers and copolymers containing acrylate units; proteins; alkanolamines; silicone compounds, for example silicones, polydimethylsiloxanes,

alkoxysilanes, alkylsilanes and siloxysilicates; organofluorine compounds, for example perfluoroalkyl ethers; fluorosilicone compounds.

The surface-treated pigments that are useful in the cosmetic composition according to the invention may also have been treated with a mixture of these
5 compounds and/or may have undergone several surface treatments.

The surface-treated pigments that are useful in the context of the present invention may be prepared according to surface-treatment techniques that are well known to those skilled in the art, or may be commercially available in the required form.

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

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

15 The surface treatment may thus be performed, 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 especially described in patent US 4 578 266.

An organic agent covalently bonded to the pigments will preferably be used.

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

The amount of pigments is generally between 0.1% and 40% by weight, preferably 0.5% and 20% by weight of the total weight of the composition containing
25 them (second composition).

Thickeners

The compositions used in the process according to the invention may comprise one or more thickeners chosen from polymeric thickeners and inorganic thickeners,
30 and mixtures thereof.

The thickener may be inorganic or organic, and polymeric or non-polymeric. The thickener may be chosen to thicken an aqueous phase or a fatty phase of the composition, as appropriate.

The term "thickener" means a compound which modifies the rheology of the medium into which it is incorporated by increasing by at least 100 cps the viscosity of
35 the medium at 25°C and at a shear rate of 1 s⁻¹. This viscosity may be measured using a cone/plate viscometer (Haake R600 rheometer or the like).

The aqueous-medium thickener may be chosen from:

- hydrophilic clays,
 - hydrophilic fumed silica,
 - water-soluble cellulose-based thickeners, such as hydroxyethylcellulose, methylcellulose or hydroxypropylcellulose. Among these, mention may in particular be made of the gums sold under the name Cellosize QP 4400 H by the company Amerchol,
 - nonionic guar gums comprising C₁-C₆ hydroxyalkyl groups. By way of example, mention may be made of hydroxymethyl, hydroxypropyl and hydroxybutyl groups. Such guar gums are in particular sold under the trade names Jaguar HP8, Jaguar HP60, Jaguar HP120 and Jaguar HP105 by the company Meyhall or under the name Galactasol 40H4FD2 by the company Aqualon,
 - carrageenans,
 - locust bean gum, scleroglucan gum, gellan gum, rhamsan gum or karaya gum,
 - alginates, maltodextrins, starch and derivatives thereof, and hyaluronic acid and salts thereof,
 - polyglyceryl (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 Bozepol C by the company Hoechst, Sepigel 305 by the company Seppic by the company Allied Colloid, or,
 - the crosslinked methacryloyloxyethyltrimethylammonium chloride homopolymers sold under the name Salcare SC95 by the company Allied Colloid,
 - associative polymers, and in particular associative polyurethanes.
- Such thickeners are especially described in patent application EP-A-1 400 234, the content of which is incorporated by way of reference.
- The oily-medium thickener may be chosen from:
- organophilic clays;
 - hydrophobic fumed silicas;
 - alkyl guar gums (with a C₁-C₆ alkyl group), such as those described in EPA708 114;
 - oil-gelling polymers, for instance triblock polymers or star polymers resulting from the polymerization or copolymerization of at least one monomer containing an ethylenic group, for instance the polymers sold under the name Kraton;
 - polymers with a weight-average molecular mass of less than 100 000, comprising a) a polymeric backbone containing hydrocarbon-based repeating units containing at least one heteroatom, and optionally b) at least one pendant fatty chain and/or at least one terminal fatty chain, which are optionally functionalized, containing

from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, as described in applications WO-A-02/056847 and WO-A-02/47619, the content of which is incorporated by way of reference; in particular, polyamide resins (especially comprising alkyl groups containing from 12 to 22 carbon atoms) such as those
5 described in US-A-5783657, the content of which is incorporated by way of reference;

- the silicone-based polyamide resins as described in application EP-A-1266647 and in the French patent application filed under No. 0 216 039, the content of which is incorporated by way of reference.

Such thickeners are especially described in patent application EP-A-1 400 234,
10 the content of which is incorporated by way of reference.

The thickener may be an organic gelling agent, i.e. an agent comprising at least one organic compound. The organogelling agents may be chosen from those described in application WO-A-03/105788, the content of which is incorporated by way of reference.

15 More specifically, the polymeric thickener present in the composition according to the invention is an amorphous polymer formed by polymerization of an olefin. The olefin may especially be an elastomeric ethylenically unsaturated monomer.

Examples of olefins that may be mentioned include ethylenic carbide monomers especially containing one or two ethylenic unsaturations, containing from 2 to 5 carbon
20 atoms, such as ethylene, propylene, butadiene or isoprene.

The polymeric thickener is capable of thickening or gelling the composition. The term "amorphous polymer" means a polymer that does not have a crystalline form. The polymeric thickener may also be film-forming.

The polymeric thickener may especially be a diblock, triblock, multiblock, radial
25 or star copolymer, or mixtures thereof.

Such polymeric thickeners are described in patent application US-A-2002/005 562 and in patent US-A-5 221 534.

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

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

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

Diblock copolymers, preferably hydrogenated, that may be mentioned include
35 styrene-ethylene/propylene copolymers and styrene-ethylene/butadiene copolymers. The diblock polymers are especially sold under the name Kraton® G1701E by the company Kraton Polymers.

Triblock copolymers, which are preferably hydrogenated, that may be mentioned

include styrene-ethylene/propylene-styrene copolymers, styrene-ethylene/butadiene-styrene copolymers, styrene-isoprene-styrene copolymers and styrene-butadiene-styrene copolymers. Triblock polymers are especially sold under the names Kraton® G1650, Kraton® G1652, Kraton® D1101, Kraton® D1102 and Kraton® D1160 by the company Kraton Polymers.

Use may also be made of a mixture of styrene-butylene/ethylene-styrene triblock hydrogenated copolymer and of ethylene-propylene-styrene hydrogenated star polymer, such a mixture being in particular in isododecane. Such mixtures are sold, for example, 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, organophilic clays are clays modified with chemical compounds that make the clay able to swell.

Clays are products that are already well known per se, which are described, for example, in the publication *Mineralogie des argiles* [Mineralogy of clays], S. Caillere, S. Henin, M. Rautureau, 2nd Edition 1982, Masson, the teaching of which is included herein by way of reference.

Clays are silicates containing a cation that may be chosen from calcium, magnesium, aluminium, sodium, potassium and lithium cations, and mixtures thereof.

Examples of such products that may be mentioned include clays of the smectite family such as montmorillonites, hectorites, bentonites, beidellites and saponites, and also of the vermiculite, stevensite and chlorite families.

These clays may be of natural or synthetic origin. Clays that are cosmetically compatible and acceptable with keratin materials are preferably used.

The organophilic clay may be chosen from montmorillonite, bentonite, hectorite, attapulgite and sepiolite, and mixtures thereof. The clay is preferably a bentonite or a hectorite.

These clays may be modified with a chemical compound chosen from quaternary amines, tertiary amines, amine acetates, imidazolines, amine soaps, fatty sulfates, alkylarylsulfonates and amine oxides, and mixtures thereof.

Organophilic clays that may be mentioned include quaternium-18 bentonites such as those sold under the names Bentone 3, Bentone 38 and Bentone 38V by the company Rheox, Tixogel VP by the company United Catalyst, Claytone 34, Claytone 40 and Claytone XL by the company Southern Clay; stearylquaternium bentonites such as those sold under the names Bentone 27 by the company Rheox, Tixogel LG by the company United Catalyst and Claytone AF and Claytone APA by the company

Southern Clay; quaternium-18/benzalkonium bentonites such as those sold under the names Claytone HT and Claytone PS by the company Southern Clay.

The fumed silicas may be obtained by high-temperature hydrolysis of a volatile silicon compound in an oxyhydric flame, producing a finely divided silica. This process makes it possible in particular to obtain hydrophilic silicas which have a large number of silanol groups at their surface. Such hydrophilic silicas are sold, for example, under the names Aerosil 130®, Aerosil 200®, Aerosil 255®, Aerosil 300® and Aerosil 380® by the company Degussa, and Cab-O-Sil HS5®, Cab-O-Sil EH5®, Cab-O-Sil LM-130®, Cab-O-Sil MS55® and Cab-O-Sil M-5® by the company Cabot.

It is possible to chemically modify the surface of said silica, via a chemical reaction generating a reduction in the number of silanol groups. It is especially possible to substitute silanol groups with hydrophobic groups: a hydrophobic silica is then obtained.

The hydrophobic groups may be:

- trimethylsiloxy groups, which are obtained especially by treating fumed silica in the presence of hexamethyldisilazane. Silicas thus treated are known as "Silica silylate" according to the CTFA (6th edition, 1995). They are, for example, sold under the references Aerosil R812® by the company Degussa, and Cab-O-Sil TS-530® by the company Cabot.

- dimethylsilyloxy or polydimethylsiloxane groups, which are especially obtained by treating fumed silica in the presence of polydimethylsiloxane or dimethyldichlorosilane. Silicas thus treated are known as "Silica dimethyl silylate" according to the CTFA (6th edition, 1995). They are, for example, sold under the references Aerosil R972®, Aerosil R974® by the company Degussa, and Cab-O-Sil TS-610®, "Cab-O-Sil TS-720® by the company Cabot.

The fumed silica preferably has a particle size that may be nanometric to micrometric, for example ranging from about 5 to 200 nm.

An organomodified bentonite or hectorite is preferably used as inorganic thickener.

The thickener(s) may be present in the composition(s) of the first and/or of the second step in a total content ranging from 0.1% to 10% by weight, relative to the total weight of the composition, preferably ranging from 0.5% to 7% by weight, and more preferentially ranging from 0.5% to 5% by weight.

Additives

The compositions used in the second step of the process in accordance with the invention may also comprise one or more agents normally used in the cosmetics industry, chosen, for example, from anionic, amphoteric or zwitterionic surfactants,

anionic, cationic, non-ionic, amphoteric or zwitterionic polymers, or mixtures thereof; reducing agents, fatty substances, plasticizers, softeners, antifoams, moisturizing agents, UV-screening agents, mineral colloids, peptizing agents, solubilizing agents, fragrances, proteins, vitamins, propellants, oxyethylenated or non-oxyethylenated
5 waxes, paraffins, C₁₀-C₃₀ fatty acids such as stearic acid or lauric acid, C₁₀-C₃₀ fatty amides such as lauric diethanolamide; sequestrants; dispersants; ceramides; preservatives; opacifiers, conditioning agents, and in particular cationic polymers or surfactants.

10 The above additives are generally present in an amount for each of them of between 0.01% and 20% by weight, relative to the weight of the composition of the second step.

Of course, those skilled in the art will take care to select this or these optional additive(s) in such a way that the advantageous properties intrinsically associated with the formation of the coating in accordance with the invention are not, or are not
15 substantially, impaired.

The compositions used in the process according to the invention may in particular be in the form of a suspension, a dispersion, a solution, a gel, an emulsion, in particular an oil-in-water (O/W) or water-in-oil (W/O) emulsion or a multiple emulsion (W/O/W or polyol/O/W or O/W/O), in the form of a cream, a mousse, a stick, a
20 dispersion of vesicles, in particular of ionic or non-ionic lipids, a two-phase or multi-phase lotion, a spray, a powder or a paste.

The composition used in the context of the second step of the process may be an anhydrous composition, i.e. a composition containing less than 2% by weight of water, or even less than 0.5% of water, in particular free of water, the water not being
25 added during the preparation of the composition, but corresponding to the residual water introduced by the ingredients mixed together. The composition may also be in the form of a lacquer.

Application process

30 As indicated previously, the treatment process according to the invention consists in applying, to keratin fibres, a first composition, which is preferably aqueous, as described and comprising one or more silicone or non-silicone, amino polymers.

It should be noted that the process according to the invention can be carried out on any type of light or dark natural hair or on hair that has undergone a cosmetic
35 treatment such as a permanent wave, dyeing, bleaching or hair straightening.

In addition, the preferably aqueous composition of the first step can be used on dry or wet hair. The pretreatment cosmetic composition is preferably applied to clean hair.

In accordance with a first variant of the invention, the composition of the first step is left in place and the keratin fibres are optionally dried or left to dry.

According to another variant, optionally after a leave-in time, the fibres are rinsed with water and optionally dried.

5 Preferably, the leave-in time between the application of the composition of the first step of the process according to the invention and the application of the cosmetic composition of the second step can be between a few seconds and 60 minutes, preferably between 30 seconds and 15 minutes, and even more preferentially between 1 minute and 5 minutes.

10 The composition of the first step is preferably rinsed out with water.

Next, in a second step, the cosmetic composition comprising one or more pressure-sensitive adhesive silicones, one or more volatile solvents and one or more pigments, described above, is applied.

15 The composition of the second step can be used on dry or wet hair, and preferably on dry hair.

The additives described above, when they are present, can be applied to the hair simultaneously with the compositions of the process of the invention, or separately.

The second composition can optionally be rinsed out. It is also possible to subsequently wash the hair, this washing not being obligatory.

20 It is also possible to use an application process with heating for this second step. According to this particular embodiment, the application to the hair is carried out, for example, using a comb, a fine brush, a coarse brush or the fingers.

25 The application of the composition of the second step is then followed by drying at a temperature above 40°C. According to one particular embodiment, this temperature is greater than 45°C. According to another particular embodiment, this temperature is greater than 45°C and less than 220°C.

The drying may be carried out immediately after the application or after a leave-in time that may range from 1 minute to 30 minutes.

30 Preferably, the hair is dried, in addition to supplying heat, with a flow of air. This flow of air during drying makes it possible to improve the individualization of the coating.

During drying, a mechanical action may be carried out on the locks of hair, such as combing, brushing or by running the fingers through the hair.

35 The drying step of the process of the invention may be carried out with a hood, a hairdryer, a smoothing iron, etc.

When the drying step is carried out with a hood or a hairdryer, the drying temperature is between 40 and 110°C, preferably between 50 and 90°C.

When the drying step is carried out with a smoothing iron, the drying temperature

is between 110 and 220°C, preferably between 140 and 200°C.

Once the drying is complete, a final rinse or shampoo wash may optionally be carried out.

The invention will be illustrated more fully using the following non-limiting
5 examples.

EXAMPLES

The contents indicated are in grams of product as it is per 100 g of composition.

10 Example 1:

The following compositions are prepared:

Composition 1:

Composition	1
Trimethylsiloxy-terminated polydimethylsiloxane comprising aminoethyl and aminoisobutyl groups, sold by Dow Corning under the reference DC 2-8566	5 g
Water	Qs 100 g

Compositions 2:

Composition	2	2'
Silicone resin/fluid silicone copolymer diluted to 40% in isododecane, sold under the name BioPSA 7-4405 by Dow Corning	17.5 g	17.5 g
Alpha,omega-dihydroxylated PDMS gum of very high molecular weight proposed under the name SGM 36 by Dow Corning	1.5 g	1.5 g
Mica pearlescent agent coated with brown iron oxide, sold by Eckart under the name Prestige Soft Bronze	5 g	-
Silica-coated bronze powder sold under the name Dorolan 10/0 Pale Gold by Eckart	-	5 g
Isododecane	Qs 100 g	Qs 100 g

15 0.6 g of composition 1 is applied to a lock of 1 g of clean, wet permanent-waved hair.

After a leave-in time of 5 minutes, the lock is rinsed and dried. 0.6 g of composition 2 or 2' is then applied to the dry lock.

After a leave-in time of 2 minutes, the lock is dried with a hairdryer at a
20 temperature of 80°C for 2 minutes.

A coloured lock of which the hairs are individualized and the colour of which is

shampoo-fast is obtained.

When only composition 2 or 2' is applied without the pretreatment, the shampoo-fastness of the colour is markedly inferior.

5 **Example 2:**

The following compositions are prepared:

Compositions 3:

Composition	3	3'
Dispersion of MQ resin and dimethiconol gum sold by Dow Corning under the name DC Q2-7406 Adhesive	15.5 g	15.5 g
Polydimethylsiloxane sold by Dow Corning under the name Silicone Fluid 500.000 CS	1.5 g	1.5 g
Mica pearlescent agent coated with brown iron oxide, sold by Eckart under the name Prestige Soft Bronze	5 g	-
Silica-coated bronze powder sold under the name Dorolan 10/0 Pale Gold by Eckart	-	5 g
Isododecane	Qs 100 g	Qs 100 g

0.6 g of composition 1 is applied to a lock of 1 g of clean, wet permanent-waved hair.

10 After a leave-in time of 5 minutes, the lock is rinsed and dried. 0.6 g of composition 3 or 3' is then applied to the dry lock.

After a leave-in time of 2 minutes, the lock is dried with a hairdryer at a temperature of 80°C for 2 minutes.

15 A coloured lock of which the hairs are individualized and the colour of which is shampoo-fast is obtained.

When only composition 3 or 3' is applied without the pretreatment, the shampoo-fastness of the colour is markedly inferior.

Example 3:

20 The following compositions are prepared:

Composition 4:

Composition	4
Polyvinylamine/n-vinylformamide at 20% in an aqueous solution, sold by BASF under the reference Catiofast VFH	25 g
Water	Qs 100 g

0.6 g of composition 4 is applied to a lock of 1 g of clean, wet permanent-waved hair.

After a leave-in time of 5 minutes, the lock is rinsed and dried. 0.6 g of

composition 2 or 2' is then applied to the dry lock.

After a leave-in time of 2 minutes, the lock is dried with a hairdryer at a temperature of 80°C for 2 minutes.

5 A coloured lock of which the hairs are individualized and the colour of which is shampoo-fast is obtained.

When only composition 2 or 2' is applied without the pretreatment, the shampoo-fastness of the colour is markedly inferior.

Example 4:

10 The following compositions are prepared:

Composition 5:

Composition	5
Trimethylsiloxy-terminated polydimethylsiloxane comprising aminoethyl and aminoisobutyl groups, sold by Dow Corning under the reference DC 2-8566	5 g
Myristyl/cetyl/stearyl myristate/palmitate/stearate mixture (Crodamol MS PA from Croda)	0.7 g
Cetylstearyl alcohol	3.5 g
Hydroxyethylcellulose (MW 1 300 000) (Natrosol 250HHR from Aqualon)	0.2 g
Behenyltrimethylammonium chloride at 80% in an isopropanol/water mixture (Genamin KDMP from Clariant)	2 g
Ester of vitamin F and of glucose	0.01 g
Non-pregelatinized potato starch acetate (Perfectamyl AC from Avebe)	1 g
Fragrance, preservatives	qs
Water	Qs 100 g

Composition 6:

Composition	6
Silicone resin/fluid silicone copolymer diluted to 40% in isododecane, sold under the name BioPSA 7-4405 by Dow Corning	17.5 g
Alpha,omega-dihydroxyl PDMS gum of very high molecular weight, proposed under the name SGM 36 by Dow Corning	1.5 g
Mica pearlescent agent coated with brown iron oxide, sold by Eckart under the name Prestige Soft Bronze	5 g
Polymethylsilsesquioxane sold under the name Wacker Belsil PMS MK Powder by the company Wacker	3 g
Disteardimonium hectorite (10%) and propylene carbonate (3%) in	15 g

isododecane, sold by Elementis under the name Bentone Gel ISD V	
Mixture of n-undecane/n-tridecane in a 70/30 ratio	30 g
Isododecane	Qs 100 g

0.6 g of composition 5 is applied to a lock of 1 g of clean, wet permanent-waved hair.

After a leave-in time of 5 minutes, the lock is rinsed and dried. 0.6 g of composition 6 is then applied to the dry lock.

- 5 After a leave-in time of 2 minutes, the lock is dried with a hairdryer at a temperature of 80°C for 2 minutes.

A coloured lock of which the hairs are individualized and the colour of which is shampoo-fast is obtained.

CLAIMS

1. Process for dyeing keratin fibres, comprising the following steps:

- 5 a) a first composition comprising one or more silicone or non-silicone, amino polymers is applied,
- b) a second cosmetic composition comprising one or more pressure-sensitive adhesive silicones, one or more volatile solvents and one or more pigments is applied.

10 2. Process according to the preceding claim, in which the first composition is aqueous.

3. Process according to either one of the preceding claims, in which the amino polymer does not comprise a quaternized group.

15 4. Process according to any one of the preceding claims, in which the amino polymer is a non-silicone polymer chosen from polylysine, polyethyleneimines, and copolymers of polyvinylamine and of n-vinylformamide.

5. Process according to any one of Claims 1 to 3, in which the amino polymer is a silicone polymer comprising more particularly at least one intrachain amine function, and preferably chosen from:

a) the compounds corresponding to formula (I) below:

20 $(R^1)_a(T)_{3-a}-Si[OSi(T)_2]_n-[OSi(T)_b(R^1)_{2-b}]_m-OSi(T)_{3-a}(R^1)_a \quad (I)$

in which:

T, which may be identical or different, represent a hydrogen atom, or a phenyl, hydroxyl or C₁-C₈ alkyl radical, and preferably methyl, or a C₁-C₁₅ alkoxy radical,

a denotes the number 0 or an integer from 1 to 3,

25 b denotes 0 or 1, and in particular 1,

m and n are numbers such that the sum (n + m) can range especially from 1 to 2000 and in particular from 50 to 150, n possibly denoting a number from 0 to 1999 and especially from 49 to 149, and m possibly denoting a number from 1 to 2000 and especially from 1 to 10;

30 R¹, which may be identical or different, represent a monovalent radical of formula -C_qH_{2q}L in which q is a number from 2 to 8 and L is an amino group chosen from the following groups:

-N(R²)-R²-N(R²)₂;

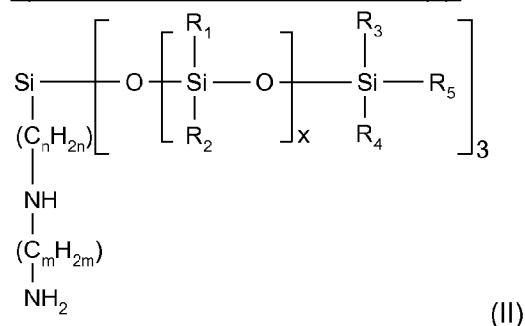
-N(R²)₂;

35 in which

R² can denote a hydrogen atom, a phenyl, a benzyl or a monovalent saturated hydrocarbon-based radical, for example a C₁-C₂₀ alkyl radical,

and R² can denote a C₂-C₁₀ alkyl group;

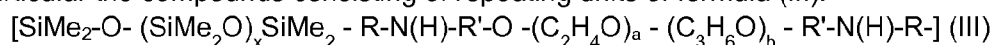
b) the amino silicones of formula (II):



in which:

- R₁, R₂, R₃ and R₄, which may be identical or different, denote a C₁-C₄ alkyl radical or a phenyl group,
- R₅ denotes a C₁-C₄ alkyl radical or a hydroxyl group,
- n is an integer ranging from 1 to 5,
- m is an integer ranging from 1 to 5,
- and in which x ranges from 2 to 500, preferably from 5 to 100;

c) the polyoxyalkylenated amino silicones of (AB)_n type, A being a polysiloxane block and B being a polyoxyalkylene block, comprising at least one amine group, and in particular the compounds consisting of repeating units of formula (III):

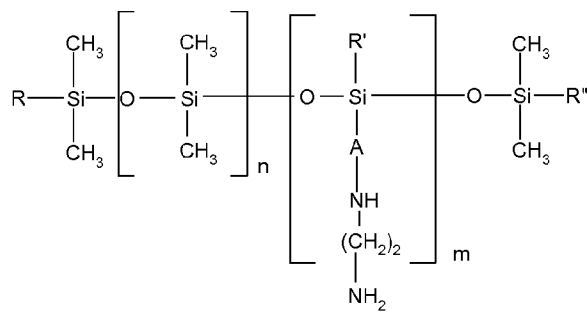


in which:

- a is an integer greater than or equal to 1, preferably between 5 and 200 and even more particularly between 5 and 100,
- b is an integer between 0 and 200, preferably between 4 and 200 and even more particularly between 5 and 100,
- R, which may be identical or different, represent a divalent organic group which is bonded to the adjacent silicon atom via a carbon-silicon bond and to a nitrogen atom,
- R', which may be identical or different, represent a divalent organic group which is bonded to the adjacent oxygen atom via a carbon-oxygen bond and to a nitrogen atom;
- the number of repeating units and x being such that the weight-average molecular weight of the silicone is preferably between 5000 and 1 000 000.

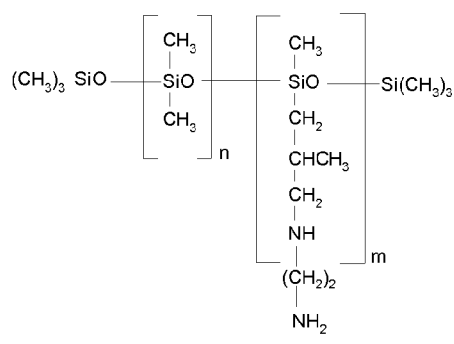
6. Process according to the preceding claim, in which the amino silicone(s) is (are) chosen from the silicones of formula (I).

7. Process according to any one of the preceding claims, in which the amino silicone(s) is (are) chosen from the silicones having the following formulae:



in which R, R' and R'', which may be identical or different, denote a C₁-C₄ alkyl radical, preferably CH₃; a C₁-C₁₅ alkoxy radical; or OH; A represents a linear or branched C₃-C₈, preferably C₃-C₆, alkylene radical; m and n are integers which depend on the molecular weight and the sum of which is between 1 and 2000.

8. Process according to the preceding claim, in which the amino silicone of formula (I') is the amino silicone corresponding to formula (I'') below:



in which n and m have the meanings indicated in formula (I) or (I').

9. Process according to any one of the preceding claims, in which the pressure-sensitive adhesive silicone(s) of the composition used in step b) are copolymers based on silicone resin and on silicone of dimethiconol type.

10. Process according to the preceding claim, in which the copolymer(s) comprise(s) a silicone resin in a content of between 45% and 75% and the silicone of dimethiconol type in a content of between 25% and 55%, with the sum of the percentages of silicone resin and of silicone of dimethiconol type being equal to 100.

11. Process according to any one of the preceding claims, in which the pressure-sensitive adhesive silicone(s) of the composition used in step b) comprise a mixture of one or more silicones of dimethiconol type and of one or more silicone resins of MQ type.

12. Process according to the preceding claim, in which the mixture of silicone resin of MQ type and silicone of dimethiconol type comprises the silicone resin in a content of between 45% and 75% and the dimethiconol silicone in a content of between 25% and 55%, with the sum of the percentages of silicone resin and of dimethiconol silicone being equal to 100.

13. Process according to any one of the preceding claims, in which the amount of pressure-sensitive adhesive silicones of the composition used in step b) ranges from 0.2% to 60% by weight, preferably from 1% to 30% by weight, relative to the total weight of the composition.

5 **14.** Process according to any one of the preceding claims, in which the volatile solvent(s) is (are) chosen from water, non-silicone organic solvents and silicone organic solvents.

10 **15.** Process according to any one of the preceding claims, in which the volatile solvent(s) present in the composition used in step b) is (are) chosen from water, ethanol, isopropanol, acetone, isododecane, decamethylcyclopentasiloxane, octamethyltrisiloxane, decamethyltetrasiloxane and dodecamethylcyclhexasiloxane, or mixtures thereof.

15 **16.** Process according to any one of the preceding claims, in which the composition used in step b) comprises one or more pigments chosen from pearlescent agents.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/055487

A. CLASSIFICATION OF SUBJECT MATTER INV. A61K8/84 A61K8/88 A61K8/898 A61Q5/06 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) A61K A61Q		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	EP 1 543 820 A1 (PROCTER & GAMBLE [US]) 22 June 2005 (2005-06-22) the whole document -----	1
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 29 April 2011	Date of mailing of the international search report 12/05/2011	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Yon, Jean-Michel	

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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