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54	ANHYDROUS COSMETIC COMPOSITION COMPRISING A PRESSURE-SENSITIVE ADHESIVE SILICONE COPOLYMER, A VOLATILE SILICONE AND A PARTICULAR FLUID SILICONE								

FOR ABSTRACT SEE THE NEXT SHEET

57 ABSTRACT (NOT MORE THAN 150 WORDS)



## ANHYDROUS COSMETIC COMPOSITION COMPRISING A PRESSURE-SENSITIVE ADHESIVE SILICONE COPOLYMER, A VOLATILE SILICONE AND A PARTICULAR FLUID SILICONE

The present invention relates to an anhydrous hair treatment composition which comprises one or more copolymers based on silicone resin and on fluid silicone, one or more linear or cyclic volatile silicones, and one or more non-volatile linear polydimethylsiloxanes with a viscosity of greater than 5 cSt, the amount of copolymer being greater than 1% by weight relative to the total weight of the composition, and the composition being free of pigments or containing more than 5.5% pigments.

Coatings are thus obtained on the keratin fibres, which give the hair shampoo-remanent volume, mass and body, while at the same time maintaining the physical qualities of the keratin fibre, especially coloured coatings.



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## ANHYDROUS COSMETIC COMPOSITION COMPRISING A PRESSURE-SENSITIVE ADHESIVE SILICONE COPOLYMER, A VOLATILE SILICONE AND A PARTICULAR FLUID SILICONE

- 5 The present invention relates to a composition for treating keratin fibres, especially the hair, and also to a process for treating keratin fibres using these compositions.
- Hair is generally damaged and embrittled by the action of external atmospheric agents such as light and bad weather, and by mechanical or chemical treatments such as brushing, combing, bleaching, permanent waving and/or dyeing. As a result, the hair is often difficult to manage, and in particular is difficult to disentangle or style, and a head of hair, even a rich head of hair, has difficulty in maintaining an attractive style due to the fact that the hair lacks vigour, volume and liveliness.

This degradation of the hair is moreover increased by repetition of the permanent dyeing treatment of the hair, which consists in applying to the hair a dye precursor and an oxidizing agent.

Thus, to overcome this, it is now common practice to use styling products that allow hair to be conditioned, especially giving it body, mass or volume.

- 30 These styling products are generally cosmetic hair compositions comprising one or more polymers that have high affinity for the hair and that usually have the function of forming a film at its surface in order to modify its surface properties, especially to condition it.
  - One drawback associated with the use of these hair compositions lies in the fact that the cosmetic effects imparted by such compositions have a tendency to

disappear, especially from the very first shampoo wash. This is all the more true when one of the effects imparted is a colour effect provided by pigments.

In order to overcome this drawback, it may be envisaged to increase the remanence of the polymer deposit by directly performing a radical polymerization of certain monomers on the hair. However, the treatments thus obtained lead to degradation of the hair fibre and hair thus treated is generally difficult to disentangle.

It is moreover known practice to coat the hair with a composition comprising an electrophilic monomer of cyanoacrylate type, especially in patent application FR 2 833 489. Such a composition affords perfectly coated and non-greasy hair. However, the coating obtained requires particular operating conditions due to the reactivity of the electrophilic monomer. Moreover, the coating obtained with these electrophilic monomers becomes tacky with fatty substances such as sebum.

Particular silicone copolymers comprising a silicone resin segment and a fluid silicone segment also exist, and are more commonly known as BioPSA. These copolymers are especially described in WO 03/026 596, WO 2004/073 626, WO 2007/051 505 and WO 2007/051 506 for various cosmetic applications such as application to the hair, the nails and the skin.

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Thus, the aim of the present invention is to develop an easy-to-use process for treating keratin fibres such as the hair, which can produce coatings that are remanent with respect to shampooing and to the various attacking factors to which the hair may be subjected, especially blow-drying and perspiration, while at the same time showing better tolerance to fatty substances such as sebum. The aim of the present invention is especially to obtain easy-to-use coloured coatings, which are

resistant to external agents and which respect the integrity of keratin fibres.

This aim is achieved with the present invention, one subject of which is an anhydrous hair treatment composition which comprises one or more copolymers based on silicone resin and on fluid silicone, one or more linear or cyclic volatile silicones, and one or more non-volatile linear polydimethylsiloxanes with a 10 viscosity of greater than 5 cSt, the amount copolymer being greater than 1% by weight relative to total weight of the composition, composition being free of pigments.

15 subject of the invention is also an anhydrous composition for dyeing keratin fibres, comprising one or more copolymers based on silicone resin and on fluid linear or cyclic silicone, one or more volatile non-volatile silicones, one or more polydimethylsiloxanes with a viscosity of greater than 20 5 cSt, and a colouring pigment, the amount of copolymer being greater than 1% by weight relative to the total weight of the composition, and the amount of colouring pigments being greater than 5%.

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A subject of the invention is also a process for treating keratin fibres, for obtaining an effect that is remanent with respect to shampooing, using one or other of these compositions.

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Another subject of the invention is the use of an anhydrous composition comprising one or more copolymers based on silicone resin and on fluid silicone, with one or more colouring pigments for obtaining a coloured coating, or without pigment for obtaining a simple coating.

Coatings are thus obtained on the keratin fibres that give the hair shampoo-remanent volume, mass and body,

while at the same time maintaining the physical qualities of the keratin fibre, with, in addition, a remanent colour effect when the composition contains pigments. Such a coating is in particular resistant to the external attacking factors to which the hair may be subjected, such as blow-drying and perspiration. It furthermore affords permanent colorations without using oxidizing agents liable to degrade the hair.

10 The coating thus formed is in the form of a smooth, uniform deposit and shows excellent adhesion to the hair. Moreover, it has been found, surprisingly, that the hairs remain perfectly individualized and can be styled without any problem, and that the styling properties afforded to the fibre are shampoo-remanent.

#### Copolymer based on silicone resin and on fluid silicone

The silicone copolymer defined according to the 20 invention is derived from the reaction between a silicone resin and a fluid silicone.

Such copolymers are described, for example, in "Silicone Pressure Sensitive Adhesive", Sobieski and 25 Tangney, Handbook of Pressure Sensitive Adhesive Technology (D. Satas Ed.), Von Nostrand Reinhold, New York.

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 fluid silicone is present in a content of between 25% and 55%, the sum of the percentages of silicone resin and of fluid silicone 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 fluid silicone is present in a content of between 35% and 45%, the sum of the percentages of silicone resin and of fluid silicone being equal to 100.

Preferably, the silicone resin according to the invention is the product of condensation of groups  $SiO_2$  and of groups  $R_3(SiO)_{1/2}$  (triorganosily1) for which each group R is independently selected from methyl, ethyl, propyl and vinyl radicals and for which the ratio between the  $SiO_2$  functions and the  $R_3(SiO)_{1/2}$  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.

15 Preferably, the fluid silicone according to the invention is a diorganopolysiloxane bearing OH functions, having a viscosity of between 100 100 000 cSt at  $25\,^{\circ}\text{C}$ , for which the substituents of the diorganopolysiloxane are independently chosen 20 methyl, ethyl, propyl and vinyl radicals. diorganopolysiloxanes are preferably linear polymers. Examples of diorganopolysiloxanes may be, in a nonlimiting manner, a polydimethylsiloxane, an ethylmethyl polysiloxane, a copolymer of dimethylsiloxane and of 25 methylvinylsiloxane, and mixtures of such polymers or copolymers containing OH end groups. The preferred diorganopolysiloxane is a polydimethylsiloxane.

Examples of synthesis of such a copolymer are described, for example, in patent US 5 162 410 or in patent CA 711 756.

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

35 1. from 45% to 75% by mass of silicone resin, being the product of condensation of  $SiO_2$  and  $R_3(SiO)_{1/2}$  units for which each group R is independently selected from methyl, ethyl, propyl and vinyl radicals and for which the ratio between the  $SiO_2$ 

functions and the  $R_3(SiO)_{1/2}$  functions of the silicone resin ranges from 0.6 to 0.9;

- 2. 25% to 55% by mass of diorganopolysiloxane containing OH end functions, with a viscosity of between 100 and 100 000 cSt at 25°C. for which the substituents of diorganopolysiloxane are independently chosen from methyl, ethyl, propyl and vinyl radicals;
- 3. 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 to a temperature of between 80°C and 160°C until the adhesive nature of the resulting silicone copolymer is obtained.

- 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 different solvents with several silicone resin/fluid silicone ratios. Mention may be made especially of the grades 7-4400, 7-4500 and 7-4600. The Bio-PSA® that is particularly preferred according to the invention is the grade 7-4400.
- 30 The copolymer may be present in the composition according to the invention in a content of greater than 1% and up to 40% by weight, preferably ranging from 1.5% to 20% by weight and preferentially ranging from 1.5% to 15% by weight, relative to the total weight of the composition.

#### Volatile silicone

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In the context of the invention, the term "volatile

silicone" means a silicone that is liquid at room temperature (25°C) and at atmospheric pressure, with a vapour pressure at 25°C of greater than 0.1 mmHg, preferably between 0.1 and 300 mmHg and even more preferentially between 0.1 and 200 mmHg.

Volatile silicones that may be mentioned include linear or cyclic silicones containing from 4 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms. As volatile silicones that may be used in the invention, mention may be made especially of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, ane, octamethyltrisiloxane and decamethyltetrasiloxane, and mixtures thereof.

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

Examples that may be mentioned include the decamethylcyclopentasiloxane sold under the name DC-245 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.

This cyclic volatile silicone generally has a low viscosity, for example a viscosity of less than 5 cSt

35 Preferably, the volatile silicone is cyclic and is the decamethylcyclopentasiloxane sold under the name DC-245 by the company Dow Corning.

The volatile silicone is present in the composition

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at 25°C.

according to the invention in a content ranging from 0.1% to 99% by weight, preferably ranging from 1% to 95% by weight and preferentially ranging from 5% to 90% by weight relative to the total weight of the composition.

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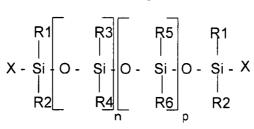
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# Non-volatile linear PDMS with a viscosity of greater than 5 cSt

- 10 The non-volatile linear polydimethylsiloxane (PDMS) with a viscosity of greater than 5 cSt is especially a silicone gum or a silicone oil with a vapour pressure of less than 0.1 mmHg at 25°C.
- The non-volatile linear PDMS with a viscosity of 15 5 cSt may be chosen polydimethylsiloxanes; alkyl dimethicones; polyphenylmethylsiloxanes such as phenyl dimethicones, phenyl trimethicones and vinyl methyl methicones; and also modified with optionally fluorinated 20 silicones aliphatic and/or aromatic groups, or with functional groups such as hydroxyl, thiol and/or amine groups.
- Preferably, the viscosity of the non-volatile linear PDMSs that are useful in the present invention is greater than 5 cSt at 25°C. According to one particular embodiment, this viscosity is between 5 cSt and 5 000 000 cSt, preferably between 100 cSt and 4 000 000 cSt and even more preferentially from 5000 to 4 000 000 cSt.

The molecular weight is generally between 500 and 800 000 g/mol, preferably from 5000 to 700 000 g/mol and even more preferentially from 50 000 to 600 000 g/mol.

This linear PDMS may be chosen especially from the silicones of formula (II):



(II)

in which:

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 $R_1$ ,  $R_2$ ,  $R_5$  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 or an aryl radical,

X is an alkyl radical containing from 1 to 6 carbon atoms, a hydroxyl radical, a vinyl radical or an amine radical,

n and p being integers chosen so as to have a compound with a viscosity of greater than 5 cSt; preferably, the sum n + p is greater than 10.

- 15 Examples that may be mentioned include the following polydimethylsiloxanes:
  - 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, and p and n are such that the molecular weight is 120 000 g/mol, such as the product sold under the name 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, and p and n are such that the molecular weight is 250 000 g/mol, for instance 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,
    - $\bullet$  the substituents  $R_1$  to  $R_6$  and X represent a methyl group, the group X represents a hydroxyl group, and n

and p are such that the molecular weight of the polymer is  $600\ 000\ \text{g/mol}$ , for instance the product sold under the name SGM  $36\ \text{by}$  the company Dow Corning,

• dimethicones of the (polydimethylsiloxane) (methylvinylsiloxane) type, such as SE63 sold by GE Bayer Silicones, and poly(dimethylsiloxane) (diphenyl) (methylvinylsiloxane) copolymers, and mixtures thereof.

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Preferably, the non-volatile linear PDMSs are oxyalkylenated.

#### **Pigments**

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According to one variant, the composition is a keratin fibre dye composition that comprises colouring pigments. Such a composition affords colouring remanent coatings, without degrading the keratin fibres.

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The term "colouring pigments" means any pigment that gives colour to keratin materials. This especially excludes white pigments such as titanium dioxide, which only make keratin materials white.

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The pigments that may be used are especially chosen from the organic and/or mineral pigments known in the art, especially those described in Kirk-Othmer's Encyclopaedia of Chemical Technology and in Ullmann's Encyclopaedia of Industrial Chemistry.

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

35 The pigments may be chosen, for example, from mineral pigments, organic pigments, lakes, pigments with special effects such as nacres or glitter flakes, and mixtures thereof.

The pigment may be a natural pigment. The term "natural pigment" means any pigment that satisfies the definition in Ullmann's encyclopaedia in the chapter on inorganic pigments. Among the mineral pigments that are useful in the present invention, mention may be made of iron oxides, chromium oxides, manganese violet, ultramarine blue, chromium hydrate and ferric blue.

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The pigment may be an organic pigment. The "organic pigment" means any pigment that satisfies the 10 definition in Ullmann's encyclopaedia in the chapter on organic pigments. The organic pigment may be chosen especially from nitroso, nitro, azo, xanthene, quinoline, anthraquinone, phthalocyanin, metal-complex, isoindolinone, isoindoline, quinacridone, perinone, 15 perylene, diketopyrrolopyrrole, thioindigo, dioxazine, triphenylmethane and quinophthalone compounds.

In particular, the white or coloured organic pigments may be chosen from carmine, carbon black, aniline 20 black, melanin, azo yellow, quinacridone, phthalocyanin blue, sorghum red, the blue pigments codified in the Color Index under the references CI 42090, 69825, 73000, 74100 and 74160, the yellow pigments codified in the Color Index under the references CI 25 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 30 red pigments codified in the Color Index under 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 35 75470. the pigments obtained and by oxidative polymerization of indole or phenolic derivatives as described in patent FR 2 679 771.

Examples that may also be mentioned include pigmentary

pastes of organic pigments, such as the product sold by the company Hoechst under the names:

- Jaune Cosmenyl IOG: Pigment Yellow 3 (CI 11710);
- Jaune Cosmenyl G: Pigment Yellow 1 (CI 11680);
- 5 Orange Cosmenyl GR: Pigment Orange 43 (CI 71105);
  - Rouge Cosmenyl R: Pigment Red 4 (CI 12085);
  - Carmine Cosmenyl FB: Pigment Red 5 (CI 12490);
  - Violet Cosmenyl RL: Pigment Violet 23 (CI 51319);
  - Bleu Cosmenyl A2R: Pigment Blue 15.1 (CI 74160);
- 10 Vert Cosmenyl GG: Pigment Green 7 (CI 74260);
  - Noir Cosmenyl R: Pigment Black 7 (CI 77266).

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 compounds especially of particles comprising a mineral core, at least one binder for ensuring the binding of the organic pigments to the core, and at least one organic pigment at least partially covering the core.

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The organic pigment may also be a lake. The term "lake" means insolubilized dyes adsorbed onto insoluble particles, the assembly thus obtained remaining insoluble during use.

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

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Among the dyes, mention may be made of cochineal carmine. Mention may also be made of the products 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 35 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 (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).

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The pigment may also be a pigment with special effects. The term "pigments with special effects" means 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 white or coloured pigments that afford a standard uniform opaque, semi-transparent or transparent shade.

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Several types of pigment with special effects exist: those with a low refractive index, such as fluorescent, photochromic or thermochromic pigments, and those with a high refractive index, such as nacres or glitter flakes.

Examples of pigments with special effects that may be mentioned include nacreous pigments such as nacreous pigments such as mica coated with titanium or with bismuth oxychloride, coloured nacreous pigments such as titanium mica with iron oxides, titanium mica especially with ferric blue or with chromium oxide, titanium mica with an organic pigment abovementioned type, and also nacreous pigments based on bismuth oxychloride. Nacreous pigments that may be mentioned include the Cellini nacres sold by Engelhard  $(mica-TiO_2-lake)$ , Prestige sold by Eckart  $(mica-TiO_2)$ , Prestige Bronze sold by Eckart (mica-Fe<sub>2</sub>O<sub>3</sub>), Colorona sold by Merck (mica-TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>).

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In addition to nacres on a mica support, multilayer pigments based on synthetic substrates such as alumina, silica, sodium calcium borosilicate or calcium aluminium borosilicate, and aluminium, may be

envisaged.

Mention may also be made of pigments interference effect that are not fixed onto substrate, for instance liquid crystals (Helicones HC Wacker), holographic interference (Geometric Pigments or Spectra f/x from Spectratek). Pigments with special effects also comprise fluorescent whether these pigments, are substances that 10 fluorescent in daylight or that produce an ultraviolet fluorescence, phosphorescent pigments, photochromic pigments, thermochromic pigments and quantum dots, sold, for example, by the company Quantum Corporation.

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Quantum dots are luminescent semiconductive nanoparticles capable of emitting, under excitation, irradiation with a wavelength of between 400 nm and 700 nm. These nanoparticles are known from 20 the literature. They may be manufactured in particular according to the processes described, for example, in US 6 225 198 or US 5 990 479, in the publications cited therein, and also in the following publications: Dabboussi B.O. et al. "(CdSe) ZnS core-shell quantum 25 dots: synthesis and characterization of a size series of highly luminescent nanocrystallites" Journal of Physical Chemistry B, vol. 101, 1997, pp. 9463-9475 and Peng, Xiaogang et al. "Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals 30 photostability and electronic accessibility", Journal of the American Chemical Society, vol. 119, No. 30, pp. 7019-7029.

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

The size of the pigments used in the cosmetic

composition according to the present invention is generally between 10 nm and 200  $\mu\text{m}$ , preferably between 20 nm and 18  $\mu\text{m}$  and more preferentially between 30 nm and 50  $\mu\text{m}$ .

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

The dispersant serves to protect the dispersed particles against agglomeration or flocculation. This 10 dispersant may be a surfactant, an oligomer, a polymer or a mixture of several thereof, bearing one or more functionalities with strong affinity for the surface of the particles to be dispersed. In particular, they can 15 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 continuous medium. In particular, 12-hydroxystearic acid esters and  $C_8$  to  $C_{20}$  fatty acid esters of polyols 20 such as glycerol or diglycerol are used, such poly(12-hydroxystearic acid) stearate 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) under the reference Dehymyls PGPH by the company 25 Henkel, or polyhydroxystearic acid such as the product sold under the reference Arlacel P100 by the company Uniqema, and mixtures thereof.

30 other dispersants that may be used in As the compositions of the invention, mention may be made of quaternary ammonium derivatives of polycondensed fatty acids, for instance Solsperse 17 000 sold by the company Avecia, and polydimethylsiloxane/oxypropylene mixtures such as those sold by the company Dow Corning 35 under the references DC2-5185 and DC2-5225 C.

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

agent.

the pigments that have been surface-treated beforehand, which are useful in the context of the 5 invention, are pigments that have totally or partially undergone a surface treatment of chemical, electronic, electrochemical, mechanochemical or mechanical nature, described an organic agent such as those especially in Cosmetics and Toiletries, February 1990, Vol. 105, pp. 53-64, before being dispersed in the 10 composition in accordance with the invention. These organic agents may be 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, 15 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 . 20 stearate or laurate; metal alkoxides; polysaccharides, for example chitosan, cellulose and derivatives thereof; polyethylene; (meth)acrylic polymers, example polymethyl methacrylates; polymers copolymers containing acrylate units; proteins; 25 alkanolamines; silicone compounds, for example polydimethylsiloxanes, alkoxysilanes, silicones, siloxysilicates; alkylsilanes and organofluorine for example perfluoroalkyl compounds, ethers; fluorosilicone compounds.

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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 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.

Preferably, the surface-treated pigments are coated 5 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.

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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.

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

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 relative to the total weight of the surfacetreated pigments.

Preferably, the surface treatments of the pigments are 30 chosen from the following treatments:

- a PEG-silicone treatment, for instance the AQ surface treatment sold by LCW;
- a chitosan treatment, for instance the CTS surface treatment sold by LCW;
- a triethoxycaprylylsilane treatment, for instance the AS surface treatment sold by LCW;
  - a methicone treatment, for instance the SI surface treatment sold by LCW;
    - a dimethicone treatment, for instance the

Covasil 3.05 surface treatment sold by LCW;

- a dimethicone/trimethyl siloxysilicate treatment, for instance the Covasil 4.05 surface treatment sold by LCW;
- 5 a lauroyllysine treatment, for instance the LL surface treatment sold by LCW;
  - a lauroyllysine dimethicone treatment, for instance the LL/SI surface treatment sold by LCW;
- a magnesium myristate treatment, for instance
   the MM surface treatment sold by LCW;
  - an aluminium dimyristate treatment, for instance the MI surface treatment sold by Miyoshi;
  - a perfluoropolymethylisopropyl ether treatment, for instance the FHC surface treatment sold by LCW;
- an isostearyl sebacate treatment, for instance the HS surface treatment sold by Miyoshi;
  - a disodium stearoyl glutamate treatment, for instance the NAI surface treatment sold by Miyoshi;
- a dimethicone/disodium stearoyl glutamate
  20 treatment, for instance the SA/NAI surface treatment
   sold by Miyoshi;
  - a perfluoroalkyl phosphate treatment, for instance the PF surface treatment sold by Daito;
- an acrylate/dimethicone copolymer and 25 perfluoroalkyl phosphate treatment, for instance the FSA treatment sold by Daito;
  - a polymethylhydrogenosiloxane/perfluoroalkyl phosphate treatment, for instance the FS01 surface treatment sold by Daito;
- a lauroyllysine/aluminium tristearate treatment,
  for instance the LL-AlSt surface treatment sold by
  Daito;
  - an octyltriethylsilane treatment, for instance the OTS surface treatment sold by Daito;
- an octyltriethylsilane/perfluoroalkyl phosphate treatment, for instance the FOTS surface treatment sold by Daito;
  - an acrylate/dimethicone copolymer treatment, for instance the ASC surface treatment sold by Daito;

- an isopropyl titanium triisostearate treatment, for instance the ITT surface treatment sold by Daito;
- a microcrystalline cellulose and carboxymethylcellulose treatment, for instance the AC surface treatment sold by Daito;
- a cellulose treatment, for instance the C2 surface treatment sold by Daito;
- an acrylate copolymer treatment, for instance the APD surface treatment sold by Daito;
- a perfluoroalkyl phosphate/isopropyl titanium triisostearate treatment, for instance the PF + ITT surface treatment sold by Daito.
- The composition in accordance with the present invention may furthermore comprise one or more surface-untreated pigments.

When it (they) are present, the amount of pigment(s) may range up to 40% and preferably up to 20%.

The composition of the invention may contain other coloured or colouring species such as hydrophilic or hydrophobic direct dyes or dye precursors.

The composition of the invention may also contain other constituents. It may especially comprise a volatile or non-volatile non-silicone organic solvent. The term "volatile" takes the same definition as that given previously for the volatile silicones.

Volatile organic solvents that may be mentioned include:

- volatile  $C_1-C_4$  alkanols such as ethanol or isopropanol;
- volatile  $C_5-C_7$  alkanes such as n-pentane, hexane, cyclopentane, 2,3-dimethylbutane, 2,2-dimethylbutane, 2-methylpentane or 3-methylpentane;
  - ullet esters of liquid  $C_1-C_{20}$  acids and of volatile  $C_1-C_8$  alcohols such as methyl acetate, n-butyl acetate,

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- ethyl acetate, propyl acetate, isopentyl acetate or ethyl 3-ethoxypropionate;
- ketones that are liquid at room temperature and volatile, such as methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone, cyclohexanone or acetone;
- volatile polyols such as propylene glycol;

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- volatile ethers such as dimethoxymethane, diethoxyethane or diethyl ether;
- 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 hydrocarbon-based oils such as volatile 15 hydrocarbon-based oils containing from 8 to 16 carbon atoms, and mixtures thereof, and especially branched  $C_8-C_{16}$  alkanes, for instance  $C_8-C_{16}$  isoalkanes (also known as isoparaffins), isododecane, isodecane and, for example, the oils sold under the trade names Isopar or Permethyl, and mixtures thereof. Mention 20 may also be made of isohexyl or isodecyl neopentanoate;
  - volatile  $C_4-C_{10}$  perfluoroalkanes such as dodecafluoropentane, tetradecafluorohexane or decafluoropentane;
  - volatile perfluorocycloalkyls such as perfluoromethylcyclopentane, 1,3-perfluorodimethylcyclohexane and perfluorodecalin, sold, respectively, under the names Flutec PC1<sup>®</sup>, Flutec PC3<sup>®</sup> and Flutec PC6<sup>®</sup> by the company F2 Chemicals, and also perfluorodimethylcyclobutane and perfluoromorpholine;
  - the volatile fluoroalkyl or heterofluoroalkyl compounds corresponding to the following formula:

$$CH_3 - (CH_2)_n [Z]_t - X - CF_3$$

35 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 0, S or NR, R being hydrogen or a radical  $-(CH_2)_n-CH_3$ 

or  $-(CF_2)_m-CF_3$ , m being 2, 3, 4 or 5.

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Among the volatile fluoroalkyl or heterofluoroalkyl compounds that may especially be mentioned are methoxynonafluorobutane sold under the name MSX  $4518^{\text{(B)}}$  and HFE-7100 $^{\text{(B)}}$  by the company 3M, and ethoxynonafluorobutane sold under the name HFE-7200 $^{\text{(B)}}$  by the company 3M.

- 10 Non-volatile organic solvents that may be mentioned include:
  - non-volatile aromatic alcohols such as benzyl alcohol or phenoxyethanol;
- esters of liquid  $C_1-C_{20}$  acids and of non-volatile  $C_1-C_{20}$  alcohols, such as isopropyl myristate;
  - ethylene carbonate, propylene carbonate or butylene carbonate;
  - non-volatile polyols such as glycerol, ethylene glycol, dipropylene glycol or butylene glycol;
- non-volatile glycol ethers, for instance diethylene glycol monomethyl ether or dipropylene glycol mono-n-butyl ether;
  - non-volatile hydrocarbon-based oils such as isohexadecane;
- non-volatile liquid  $C_{10}$ - $C_{30}$  alcohols such as oleyl alcohol; esters of liquid  $C_{10}$ - $C_{30}$  fatty alcohols such as benzoates of  $C_{10}$ - $C_{30}$  fatty alcohols and mixtures thereof; polybutene oil, isononyl isononanoate, isostearyl malate, pentaerythrityl tetraisostearate or tridecyl trimellitate;
  - $\bullet$  non-volatile perfluoro solvents such as perfluoroperhydrophenanthrene, sold under the name Flutec PC11  $^{\circledR}$  by the company F2 Chemicals.
- 35 Preferably, the organic solvent is chosen such that its boiling point is less than 200°C.

Preferably, the organic solvent is a volatile organic solvent. It is chosen, for example, from ethanol,

isopropanol, acetone and isododecane.

The organic solvent may be present in the composition according to the invention in a content ranging from 0.1% to 90% by weight, preferably ranging from 1% to 80% by weight and preferentially ranging from 5% to 70% by weight, relative to the total weight of the composition.

10 The composition of the invention may contain other particular silicone compounds other than those described previously.

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

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

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

The polymers containing a non-silicone organic backbone

grafted with monomers containing a polysiloxane, in accordance with the invention, are more preferably chosen from those described in patents US 4 693 935, US 4 728 571 and US 4 972 037 and patent applications 5 EP-A-0 412 704, EP-A-0 412 707, EP-A-0 640 105 and WO 95/00578. These are copolymers obtained by free-radical polymerization starting with ethylenically unsaturated monomers and monomers having a terminal vinyl group, or alternatively copolymers obtained by reaction of a polyolefin comprising functionalized groups and a polysiloxane macromer having a terminal function which is reactive with the said functionalized groups.

One particular family of grafted silicone polymers
which is suitable for carrying out the present
invention consists of grafted silicone polymers
comprising:

a) from 0.01% to 50% by weight of at least one polysiloxane macromer (C) of general formula (VI):

#### $X(Y)_{n}Si(R)_{3-m}Z_{m} \quad (VI)$

- b) from 0 to 98% by weight of at least one radical-polymerizable ethylenically unsaturated lipophilic monomer (A) of low lipophilic polarity;
- c) from 0 to 98% by weight of at least one 25 ethylenically unsaturated polar hydrophilic monomer (B), which is copolymerizable with the monomer(s) of the type (A);

in which:

- X denotes a vinyl group which is copolymerizable 30 with the monomers (A) and (B);
  - Y denotes a divalent bonding group;
  - R denotes hydrogen,  $C_1\text{--}C_6$  alkyl or alkoxy, or  $C_6\text{--}C_{12}$  aryl;
- Z denotes a monovalent polysiloxane unit with a number-average molecular weight of at least 500;
  - n is 0 or 1 and m is an integer ranging from 1 to 3; the percentages being calculated relative to the total weight of the monomers (A), (B) and (C).

These polymers have a number-average molecular weight ranging from 10 000 to 2 000 000 and preferably a glass transition temperature Tg or a crystal melting temperature Tm of at least  $-20^{\circ}$ C.

As examples of lipophilic monomers (A), mention may be made of acrylic or methacrylic acid esters of  $C_1$ - $C_{24}$ alcohols; styrene; polystyrene macromers; 10 acetate; vinyl propionate;  $\alpha$ -methylstyrene; butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyltoluene; acrylic or methacrylic acid esters of 1,1-dihydroperfluoroalkanols or of homologues methacrylic thereof; acrylic or acid esters  $\omega$ -hydrofluoroalkanols; acrylic or methacrylic acid 15 esters of fluoroalkylsulfonamido alcohols; acrylic or methacrylic acid esters of fluoroalkyl alcohols; acrylic or methacrylic acid esters of fluoroether alcohols; or mixtures thereof. The preferred monomers (A) are chosen from the group consisting of n-butyl 20 methacrylate, isobutyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, 2-(N-methylperfluorooctanesulfonamido)ethyl acrylate, 2-(N-butylperfluorooctanesulfonamido) ethyl acrylate and 25 heptadecafluorooctylmethylaminoethyl methacrylate, or mixtures thereof.

As examples of polar monomers (B), mention may be made acid, methacrylic acid, N,N-dimethyl-30 of acrylic dimethylaminoethyl acrylamide, methacrylate, quaternized dimethylaminoethyl methacrylate, (meth)acrylamide, N-t-butylacrylamide, maleic maleic anhydride and hemiesters thereof, hydroxyalkyl 35 (meth)acrylates, diallyldimethylammonium chloride, vinylpyrrolidone, vinyl ethers, maleimides, vinylpyridine, vinylimidazole, heterocyclic vinyl polar compounds, styrene sulfonate, allyl alcohol, vinyl alcohol and vinylcaprolactam, or mixtures thereof. The monomers (B) are preferably chosen from the group consisting of acrylic acid, N,N-dimethylacrylamide, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate and vinylpyrrolidone, and mixtures thereof.

The preferential polysiloxane macromers (C) of formula (I) are chosen from those corresponding to the general formula (VII) below:

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$$CHR^{1} = CR^{2} - C - O - (CH_{2})_{q} - (O)_{p} - Si(R^{3})_{3-m} - (-O - Si -)_{r} - R^{4}$$

$$CH_{3} - CH_{3} - CH_{$$

in which:

- R<sup>1</sup> is hydrogen or -COOH and preferably hydrogen;
- $R^2$  is hydrogen, methyl or  $-CH_2COOH$  (preferably methyl);
  - $R^3$  is  $C_1-C_6$  alkyl, alkoxy, or alkylamino,  $C_6-C_{12}$  aryl or hydroxyl (preferably methyl);
  - $R^4$  is  $C_1$ - $C_6$  alkyl, alkoxy or alkylamino,  $C_6$ - $C_{12}$  aryl or hydroxyl (preferably methyl);
- 20 q is an integer ranging from 2 to 6 (preferably 3);
  - p is 0 or 1;
  - r is an integer ranging from 5 to 700;
  - m is an integer ranging from 1 to 3 (preferably 1); preferably, p = 0.

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The polysiloxane macromers more particularly used are those of formula:

with n being a number ranging from 5 to 700.

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The copolymer with 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 the company Shin-Etsu.

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polymer with a non-silicone organic backbone grafted with monomers containing a polysiloxane may also have the following structure:

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

Other copolymers with a non-silicone organic backbone 15 grafted with monomers containing a polysiloxane may also be KP545, KP574 and KP575 sold by Shin-Etsu.

One particular embodiment of the invention consists in using a copolymer that may be obtained by radical 20 polymerization starting with the monomer mixture constituted by:

- a) 60% by weight of tert-butyl acrylate;
- b) 20% by weight of acrylic acid;
- c) 20% by weight of silicone macromer of formula:

with n being a number ranging from 5 to 700; the weight percentages being calculated relative to the total weight of the monomers.

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Another particular embodiment of the invention consists in using a copolymer that may be obtained by radical polymerization starting with the monomer mixture constituted by:

10 a) 80% by weight of tert-butyl acrylate;

b) 20% by weight of silicone macromer of formula:

with n being a number ranging from 5 to 700; the weight percentages being calculated relative to the total weight of the monomers.

Another particular family of grafted silicone polymers with a non-silicone organic backbone that is suitable for carrying out the present invention consists of grafted silicone copolymers which may be obtained by reactive extrusion-moulding of a polysiloxane macromer with a reactive terminal function on a polymer of the polyolefin type comprising reactive groups capable of reacting with the terminal function of the polysiloxane macromer to form a covalent bond for grafting the silicone onto the main chain of the polyolefin. These polymers are described, along with a process for their preparation, in patent application WO 95/00578.

The reactive polyolefins are preferably chosen from polyethylenes and polymers of ethylene-derived monomers such as propylene, styrene, alkylstyrene, butylene, butadiene, (meth)acrylates, vinyl esters or equivalents, comprising reactive functions capable of

reacting with the terminal function of the polysiloxane macromer. They are chosen more particularly from copolymers of ethylene or of ethylene derivatives and of monomers chosen from those comprising a carboxylic function such as (meth)acrylic acid; those comprising an acid anhydride function such as maleic anhydride; those comprising an acid chloride function such as (meth)acryloyl chloride; those comprising an ester function such as (meth)acryloyl chloride; those comprising an ester function such as (meth)acrylic acid esters; and those comprising an isocyanate function.

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The silicone macromers are preferably chosen from polysiloxanes comprising a functionalized group, at the end of the polysiloxane chain or close to the end of the said chain, chosen from the group consisting of alcohols, thiols, epoxy groups and primary and secondary amines, and more particularly from those corresponding to the general formula:

$$\text{T-(CH}_2)_{\text{S}}\text{-Si-[-(OSiR}^5\text{R}^6)_{\text{t}}\text{-R}^7]_{\text{y}} \qquad \text{(VIII)}$$

- in which T is chosen from the group consisting of  $NH_2$ , NHR' and an epoxy, OH, or SH function;  $R^5$ ,  $R^6$ ,  $R^7$  and R' independently denote a  $C_1$ - $C_6$  alkyl, phenyl, benzyl, or  $C_6$ - $C_{12}$  alkylphenyl or hydrogen; s is a number ranging from 2 to 100; t is a number ranging from 0 to 1000 and y is a number ranging from 1 to 3. They have a number-average molecular weight preferably ranging from 5000 to 300 000, more preferably from 8000 to 200 000 and more particularly from 9000 to 40 000.
- According to the present invention, the grafted silicone polymer(s), with a polysiloxane backbone grafted with non-silicone organic monomers, comprise a silicone main chain (or polysiloxane (≡Si-O)<sub>n</sub>) onto which is grafted, within the said chain and also optionally on at least one of its ends, at least one organic group not comprising silicone.

According to a particularly preferred embodiment of the

present invention, the silicone polymer containing a polysiloxane backbone grafted with non-silicone organic monomers which is used comprises the result of the radical copolymerization between, on the one hand, at ethylenically unsaturated least one non-silicone anionic organic monomer and/or ethylenically an unsaturated non-silicone hydrophobic organic monomer, and, on the other hand, a silicone containing in its chain at least one, and preferably several, functional 10 group(s) capable of reacting with the said ethylenic unsaturations of the said non-silicone monomers, forming a covalent bond, in particular thio functional groups.

15 According to the present invention, the said unsaturated anionic monomers ethylenically are preferably chosen, alone or as mixtures, from linear or branched, unsaturated carboxylic acids, optionally partially or totally neutralized in the form of a salt, it being possible for this or these unsaturated 20 carboxylic acid(s) to be, more particularly, acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid and crotonic acid. The suitable salts are, in particular, alkali metal salts, alkaline-earth metal salts and ammonium salts. It will likewise be noted 25 the final grafted silicone polymer, in organic group of anionic nature which comprises the result of the radical (homo)polymerization of at least one anionic monomer of unsaturated carboxylic acid type 30 can, after reaction, be post-neutralized with a base (sodium hydroxide, aqueous ammonia, etc.) in order to place it in the form of a salt.

According to the present invention, the ethylenically unsaturated hydrophobic monomers are preferably chosen, alone or as a mixture, from acrylic acid esters of alkanols and/or methacrylic acid esters of alkanols. The alkanols are preferably of  $C_1$ - $C_{18}$  and more particularly of  $C_1$ - $C_{12}$ . The preferred monomers are

chosen from the group constituted by isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isopentyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, methyl (meth)acrylate, tert-butyl (meth)acrylate, tridecyl (meth)acrylate and stearyl (meth)acrylate, or mixtures thereof.

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One family of silicone polymers containing a polysiloxane backbone grafted with non-silicone organic monomers that is particularly suitable for carrying out the present invention is constituted by silicone polymers comprising in their structure units of structure (IX ter) and units of structure (IX) and/or 15 (IX bis) below:

in which the radicals  $G_1$ , which may be identical or different, represent hydrogen, a  $C_1$ - $C_{10}$  alkyl radical or a phenyl radical; the radicals  $G_2$ , which may identical or different, represent a  $C_1$ - $C_{10}$  alkylene group;  $G_3$  represents a polymer residue resulting from the (homo)polymerization of at least one anionic containing ethylenic unsaturation; monomer represents a polymer residue resulting from (homo)polymerization of at least one hydrophobic monomer containing ethylenic unsaturation; m and n are equal to 0 or 1; a is an integer ranging from 0 to 50; b is an integer which may be between 10 and 350, c is an integer ranging from 0 to 50; with the proviso that one of the parameters a and c is other than 0.

Preferably, the unit of formula (IX) above has at least one, and even more preferentially all, of the following characteristics:

- the radicals  $G_1$  denote an alkyl radical, preferably a methyl radical;
- n is not zero, and the radicals  $G_2$  represent a divalent  $C_1$ - $C_3$  radical, preferably a propylene radical;
- $G_3$  represents a polymer radical resulting from the (homo)polymerization of at least one monomer of the ethylenically unsaturated carboxylic acid type, preferably acrylic acid and/or methacrylic acid;
- $G_4$  represents a polymer radical resulting from the (homo)polymerization of at least one monomer of the  $(C_1-C_{10})$  alkyl (meth)acrylate type, preferably isobutyl or methyl (meth)acrylate.

Examples of silicone polymers corresponding to formula (VI) are, in particular, polydimethylsiloxanes (PDMSs) 15 onto which are grafted, via a thiopropylene-type bond, secondary mixed polymer units poly(meth)acrylic acid type and of the polvalkvl (meth)acrylate type. As compounds corresponding to this 20 definition, mention may be made of dimethyl/methyl siloxane containing 3-thiopropyl groups - methyl acrylate/methyl methacrylate/methacrylic acid or Polysilicone-8 sold under the name VS80 by the company 3M.

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Other examples of silicone polymers corresponding to formula (VI) are, in particular, polydimethylsiloxanes (PDMSs) onto which are grafted, via a thiopropylenetype secondary bond, polymer units of the polyisobutyl (meth)acrylate type.

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

Preferably, the grafted silicone polymers are chosen

from the group constituted by the copolymer of polydimethylsiloxane-grafted alkyl methacrylates, copolymers of isobutyl methacrylate, of acrylic acid and of a silicone macromer, and poly dimethyl/methyl siloxane containing 3-thiopropyl groups - methyl acrylate/methyl methacrylate/methacrylic acid.

The composition of the invention may also contain a crosslinked silicone such as a crosslinked elastomeric organopolysiloxane, a high molecular weight silicone compound of three-dimensional structure, having the viscoelastic properties of a supple solid material. This elastomer is formed from high molecular weight polymer chains whose mobility is limited by a uniform network of crosslinking points. These compounds have the property of absorbing certain solvents, especially silicone solvents, and thus of thickening them, while at the same time giving the composition very good cosmetic qualities, especially in terms of spreading.

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These organopolysiloxanes may thus be in the form of dry powder, or in swollen form, in a solvent, the resulting product generally being a gel. These products may also be in dispersed form in an aqueous solution.

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

- US 5 266 321 from Kobayashi Kose,
- US 4 742 142 from Toray Silicone,
- 30 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 organopolysiloxanes particles have a number-average size ranging from 0.1 to 500 µm, preferably from 3 to 200 µm and better still from 3 to 50 µm. These particles may have any shape and

may be, for example, spherical, flat or amorphous.

The elastomeric crosslinked organopolysiloxane may be obtained via a crosslinking addition reaction of a diorganopolysiloxane containing at least one hydrogen to silicon and of a diorganopolysiloxane containing ethylenically unsaturated groups bonded to silicon, especially in the presence of a platinum catalyst; or dehydrogenation crosslinking via а 10 coupling reaction between a diorganopolysiloxane with diorganopolysiloxane hydroxyl end groups and a containing at least one hydrogen bonded to silicon, especially in the presence of an organotin compound; or crosslinking coupling reaction а diorganopolysiloxane with hydroxyl end groups and of a 15 hydrolysable organopolysilane; or via thermal crosslinking of organopolysiloxane, especially in the of organoperoxide catalyst; an crosslinking of organopolysiloxane with high-energy 20 radiation such as gamma rays, ultraviolet rays or an electron beam.

Preferably, the elastomeric crosslinked organopoly-siloxane is obtained via a crosslinking addition reaction of a diorganopolysiloxane (X) containing at least one hydrogen atom bonded to a silicon atom, and of a diorganopolysiloxane (XI) containing at least two ethylenically unsaturated groups each bonded to a different silicon atom, especially in the presence of a platinum catalyst (XII), as described, for example, in patent application EP-A-295 886.

Compound (X) is in particular an organopolysiloxane containing at least two hydrogen atoms linked to different silicon atoms in each molecule. Compound (X) may have any molecular structure, in particular a linear chain or branched chain structure or a cyclic structure. Compound (X) may have a viscosity at 25°C ranging from 1 to 50 000 centistokes, especially in

order to have good miscibility with compound (XI).

linked to silicon The organic groups atoms of compound (X) may be alkyl groups such as methyl, ethyl, propyl, butyl or octyl; substituted alkyl groups such 2-phenylethyl, 2-phenylpropyl 3,3,3-trifluoropropyl; aryl groups such as phenyl, tolyl or xylyl; substituted aryl groups such phenylethyl; and substituted monovalent hydrocarbon-10 based groups such as an epoxy group, a carboxylate ester group or a mercapto group. Compound (X) may thus be chosen from methylhydrogenopolysiloxanes containing trimethylsiloxy end groups, dimethylsiloxanemethylhydrogenosiloxane copolymers containing groups, and 15 trimethylsiloxy end dimethylsiloxanemethylhydrogenosiloxane cyclic copolymers.

Compound (XI) is advantageously a diorganopolysiloxane containing at least two lower alkenyl groups (for example of  $C_2$ - $C_4$ ); the lower alkenyl group may be chosen from vinyl, allyl and propenyl groups. These lower alkenyl groups may be located in any position of the organopolysiloxane molecule, but are preferably located at the ends of the organopolysiloxane molecule.

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The organopolysiloxane (XI) may have a branched-chain, linear-chain, cyclic or network structure, but linear-chain structure is preferred. Compound preferably has a viscosity ranging from the liquid state to the gum state. Preferably, compound (XI) has a viscosity of at least 100 centistokes at 25°C. Besides the abovementioned alkenyl groups, the other organic groups linked to the silicon atoms in compound (XI) may be alkyl groups such as methyl, ethyl, propyl, butyl or octyl; substituted alkyl groups such as 2-phenylethyl, 2-phenylpropyl or 3,3,3-trifluoropropyl; aryl groups such as phenyl, tolyl or xylyl; substituted aryl groups as phenylethyl; and substituted monovalent hydrocarbon-based groups such as an epoxy group,

carboxylate ester group or a mercapto group.

The organopolysiloxanes (XI)may be chosen methylvinylpolysiloxanes, methylvinylsiloxane-dimethyl-5 siloxane copolymers, dimethylpolysiloxanes containing dimethylvinylsiloxy end groups, dimethylsiloxanemethylphenylsiloxane copolymers containing dimethylvinylsiloxy end groups, dimethylsiloxane-diphenylsiloxane-methylvinylsiloxane copolymers containing 10 dimethylvinylsiloxy end groups, dimethylsiloxanemethylvinylsiloxane copolymers containing trimethyldimethylsiloxane-methylphenylend groups, siloxane-methylvinylsiloxane copolymers containing trimethylsiloxy end groups, methyl(3,3,3-trifluoropropyl)polysiloxane containing dimethylvinylsiloxy end 15 and dimethylsiloxane-methyl(3,3,3-trifluorogroups, copolymers containing propyl) siloxane dimethylvinylsiloxy end groups. In particular, the elastomeric organopolysiloxane may be obtained via reaction 20 dimethylpolysiloxane containing dimethylvinylsiloxy end groups and of methylhydrogenopolysiloxane containing trimethylsiloxy end groups, in the presence platinum catalyst.

- 25 Advantageously, the sum of the number of ethylenic groups per molecule of compound (XI) and of the number of hydrogen atoms linked to silicon atoms per molecule of compound (X) is at least 5.
- 30 It is advantageous for compound (X) to be added in an amount such that the molecular ratio between the total amount of hydrogen atoms linked to silicon atoms in the total of all compound (X) and amount the ethylenically unsaturated groups in compound (XI) is 35 within the range from 1.5/1 to 20/1.

Compound (XII) is the catalyst for the crosslinking reaction, and is especially chloroplatinic acid, chloroplatinic acid-olefin complexes, chloroplatinic

acid-alkenylsiloxane complexes, chloroplatinic acid-diketone complexes, platinum black or platinum on a support. The catalyst (XII) is preferably added in a proportion of from 0.1 to 1000 parts by weight and better still from 1 to 100 parts by weight, as clean platinum metal per 1000 parts by weight of the total amount of compounds (X) and (XI).

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The crosslinked organopolysiloxane obtained may be a 10 non-emulsifying compound or an emulsifying compound. "non-emulsifying" defines The term crosslinked organopolysiloxanes not containing any polyoxyalkylene "emulsifying" The term means crosslinked organopolysiloxane compounds containing at least one 15 polyoxyalkylene unit, especially polyoxyalkylene or polyoxypropylene.

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

Non-emulsifying crosslinked organopolysiloxanes are especially 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 patent application JP-A-601-194 009.

Non-emulsifying crosslinked organopolysiloxanes that may be used include 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, DC9040, DC9041, DC9509, DC9505, DC9506 and DC9045 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 containing at least two vinyl groups, which react with Si-H bonds of a polysiloxane. The emulsifying crosslinked organopolysiloxanes are especially described in patents US 5 236 986, US 5 412 004, US 5 837 793 and US 5 811 487.

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The emulsifying crosslinked organopolysiloxanes that may be used include those sold under the names KSG-21, KSG-20, KSG-30 and X-226146 by the company Shin-Etsu, and DC9010 and DC9011 by the company Dow Corning.

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The elastomeric crosslinked organopolysiloxane particles may also be in the form of a powder of elastomeric crosslinked organopolysiloxane coated with silicone resin, especially 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.

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Other elastomeric crosslinked organopolysiloxanes in powder form may be hybrid silicone powders functionalized with fluoroalkyl groups, sold especially under the name KSP-200 by the company Shin-Etsu; or hybrid silicone powders functionalized with phenyl groups, especially sold under the name KSP-300 by the company Shin-Etsu.

Other crosslinked organopolysiloxanes may be in the form of dispersions of powders in water in the presence or absence of an emulsifier, for instance the compounds BY29-119, DC2-1997, EPSX001B, EPSX002B and EPSX004A from Dow Corning.

When it is present in the composition of the invention, the polysiloxane(s) whose viscosity is greater than 100 cSt is (are) introduced in an amount generally of between 0.1% and 30% by weight, especially between 0.1% and 20% by weight and preferentially between 0.1% and 10% by weight.

The composition of the invention may also comprise a non-silicone polymer that can improve either the intrinsic properties of the composition, or the coating obtained during application to the hair, or both.

Such a polymer may be chosen from the following polymers:

- polymers that are soluble in an organic liquid medium, in particular liposoluble polymers,
  - polymers that are dispersible in an organic solvent medium, in particular polymers in the form of non-aqueous dispersions of polymer particles with a primary size of less than 1  $\mu$ m, preferably dispersions in silicone oils or hydrocarbon-based oils;
  - polymers in the form of aqueous dispersions of polymer particles with a primary size of less than 1  $\mu$ m, which are often referred to as "latices"; in this case, the composition comprises an aqueous phase;
  - water-soluble polymers; in this case, the composition comprises an aqueous phase or the polymer is applied as a pre-treatment or post-treatment to the composition according to the invention.

The polymer that may be used in the composition may be anionic, cationic, nonionic or amphoteric.

The composition may also contain fillers, which are generally substantially uncoloured compounds that are solid at room temperature and atmospheric pressure, and insoluble in the composition, even when these ingredients are brought to a temperature above room temperature.

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The fillers may be mineral or organic. The fillers may be particles of any shape, especially platelet-shaped, spherical or oblong, irrespective of their crystallographic form (for example lamellar, cubic, hexagonal or orthorhombic). Furthermore, these particles may be solid, hollow or porous, and coated or uncoated.

Among the fillers that may be used in the compositions 10 according to the invention, mention may be made especially of mineral fillers such as talc, natural or synthetic mica; kaolin; boron nitride, dioxide, precipitated calcium carbonate; magnesium 15 carbonate, magnesium hydrogen carbonate; hydroxyapatite, cerium oxide, zirconium oxide.

Advantageously, the mineral particles(s) has (have) a number-average primary size of between 0.1 and 30 µm, preferably between 0.2 and 20 20 um and even more preferentially between 0.5 and 15  $\mu m$ . For the purposes of the present invention, the term "primary particle size" means the maximum dimension that it is possible to measure between two diametrically opposite points on individual particle. The size of the organic 25 particles may be determined by transmission electron microscopy or by measuring the specific surface area via the BET method, or via laser granulometry.

30 Preferably, the mineral fillers used according to the invention are talc, boron nitride or titanium dioxide.

Among the fillers that may be used in the compositions according to the invention, mention may be made especially of organic fillers. The term "organic filler" means a polymer particle that may be derived from the polymerization of one or more monomers. The polymers constituting these organic particles may be crosslinked or non-crosslinked. The monomers used may

in particular be esters of methacrylic or acrylic acid, such as methyl acrylate and methacrylate, vinylidene chloride, acrylonitrile, or styrene and derivatives thereof.

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Advantageously, the organic particle(s) has (have) a number-average primary size of between 1 and 30  $\mu m$ , preferably between 1 and 20  $\mu m$  and even more preferentially between 1 and 15  $\mu m$ .

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organic particle(s) used in the cosmetic composition according to the invention may be chosen polyamide powders, acrylic polymer especially of polymethyl methacrylate, acrylic powders, especially of polymethyl 15 copolymer methacrylate/ethylene glycol dimethacrylate, polyallyl methacrylate/ethylene glycol dimethacrylate, of ethylene glycol dimethacrylate/lauryl methacrylate polyacrylate/alkyl or of acrylate, and polyethylene powders, 20 polystyrene powders, especially of polyethylene/acrylic acid.

Non-limiting illustrations that may particularly be mentioned as organic particles according to the invention include:

- polyamide (Nylon $^{\circledR}$ ) powders, for example those sold under the names Orgasol $^{\circledR}$  4000 and Orgasol $^{\circledR}$  2002 UD Nat Cos 204 by the company Atochem,
- acrylic polymer powders, especially of 30 polymethyl methacrylate, for instance those sold under the name Covabead<sup>®</sup> LH85 and Covabead<sup>®</sup> PMMA by the company LCW or those sold under the name Micropearl<sup>®</sup> MHB sold by the company Matsumoto,
- acrylic copolymer powders, especially of polymethyl methacrylate/ethylene glycol dimethacrylate, for instance those sold under the name Dow Corning 5640 Microsponge<sup>®</sup> Skin Oil Adsorber by the company Dow Corning, or those sold under the name Ganzpearl<sup>®</sup> GMP-0820 by the company Ganz Chemical, of polyallyl

methacrylate/ethylene glycol dimethacrylate, instance those sold under the name Polypore® L200 or Polypore® E200 sold by the company Amcol, of ethylene glycol dimethacrylate/lauryl methacrylate copolymer, for instance those sold under the name Polytrap® 6603 5 Corning, the company Dow or polyacrylate/ethylhexyl acrylate, for instance those sold under the name Techpolymer® ACX 806C by company Sekisui,

- polystyrene/divinylbenzene powders, for instance those sold under the name Techpolymer<sup>®</sup> SBX8 by the company Sekisui,

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- polyethylene powders, especially of polyethylene/acrylic acid sold under the name  ${\sf Flobeads}^{\sf B}$  by the company Sumitomo,
- acrylic polymer microspheres such as those made of the crosslinked acrylate copolymer Polytrap 6603 Adsorber $^{\circledR}$  from the company RP Scherrer,
- polyurethane powders such as the powder of the 20 copolymer of hexamethylene diisocyanate and of trimethylol hexyl lactone sold under the name Plastic Powder D-400 $^{\circledR}$  by the company Toshiki,
  - microcapsules of methyl acrylate or methacrylate polymers or copolymers, or alternatively of copolymers of vinylidene chloride and of acrylonitrile, for instance Expancel® from the company Expancel,
    - elastomeric crosslinked organopolysiloxane
       powders such as those sold under the name Trefil Powder
       E-506C by the company Dow Corning,
- of polytetrafluoroethylene, for example the product sold under the name MP 1400 by the company Dupont de Nemours.
- 35 Preferably, the organic particles used in the composition in accordance with the invention are chosen from polyamide powders and polymethyl methacrylate powders.

The compositions according to the invention may also comprise at least one oil thickener chosen from polymeric thickeners and mineral thickeners, and mixtures thereof.

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The polymeric thickener is, for example, an amorphous polymer formed by polymerization of an olefin. The olefin may especially be an elastomeric ethylenically unsaturated monomer.

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

The polymeric thickener is capable of thickening or gelling the organic phase of 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 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.

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

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/ $C_3$ - $C_4$  alkylene blocks.

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

Triblock copolymers, which are preferably hydrogenated, 10 that may be mentioned include styreneethylene/propylene-styrene copolymers, styreneethylene/butadiene-styrene copolymers, styreneisoprene-styrene copolymers styrene-butadieneand styrene copolymers. Triblock polymers are especially sold under the names Kraton® G1650, Kraton® G1652, 15 Kraton® D1101, Kraton® D1102 and Kraton® D1160 by the company Kraton Polymers.

A mixture of hydrogenated styrene-butadiene/ethylenestyrene triblock copolymer and of hydrogenated
ethylene-propylene-styrene star polymer may also be
used, such a mixture especially being in isododecane.
Such mixtures are sold, for example, by the company
Penreco under the trade names Versagel® M5960 and
Versagel® M5670.

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

The polymeric thickener may be present in a content ranging from 0.1% to 10% by weight, preferably ranging from 0.5% to 8% by weight and more preferentially ranging from 1% to 5% by weight relative to the total weight of the composition.

The composition may also comprise at least one mineral oil-thickening agent such as an organophilic clay or

fumed silicas.

Organophilic clays are clays modified with chemical compounds that make the clay able to swell in oily media.

Clays are products that are already well known per se, which are described, for example, in the publication "Minéralogie des argiles [Mineralogy of clays],

S. Caillère, S. Hénin, 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.

25 Clays that are cosmetically compatible and acceptable with keratin materials such as the skin are preferably used.

The organophilic clay may be chosen from 30 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, alkyl aryl sulfonates 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; stearalkonium 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 oxhydric flame, producing a finely divided silica. This process makes it possible especially to obtain hydrophilic silicas having a large number of silanol groups at their surface. Such hydrophilic silicas are sold, for example, under the names Aerosil 130<sup>®</sup>, Aerosil 200<sup>®</sup>, Aerosil 255<sup>®</sup>, Aerosil 300<sup>®</sup> and Aerosil 380<sup>®</sup> by the company Degussa, and Cab-O-Sil HS-5<sup>®</sup>, Cab-O-Sil EH-5<sup>®</sup>, Cab-O-Sil LM-130<sup>®</sup>, Cab-O-Sil MS-55<sup>®</sup> and Cab-O-Sil M-5<sup>®</sup> by the company Cabot.

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It is possible to chemically modify the surface of the 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:

- trimethylsiloxyl 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 sold, for example, under the references Aerosil R812® by the company Degussa and Cab-O-Sil

TS-530® by the company Cabot;

- dimethylsilyloxyl or polydimethylsiloxane groups, which are obtained especially 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 sold, for example, under the references Aerosil R972® and Aerosil R974® by the company Degussa and Cab-O-Sil TS-610® and 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.

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

The mineral oil-thickening agent may be present in the composition in a content ranging from 0.1% to 8% by weight, preferably in a content ranging from 0.2% to 6% by weight and preferentially ranging from 0.5% to 4% by weight relative to the total weight of the composition.

25 The compositions in accordance with the invention may also contain at least one agent usually used in cosmetics, chosen, for example, from reducing agents, fatty substances, plasticizers, softeners, antifoams, moisturizers, UV-screening agents, mineral colloids, 30 solubilizers, peptizers, fragrances, proteins, vitamins, propellants, oxyethylenated oxyethylenated waxes, paraffins, C10-C30 fatty acids such as stearic acid or lauric acid, and C10-C30 fatty amides such as lauric diethanolamide.

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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.

Needless to say, a person skilled in the art will take care to select this or these optional additives(s) such that the advantageous properties intrinsically associated with the formation of the coating in accordance with the invention are not, or are not substantially, adversely affected.

The composition according to the invention may be in any form that is suitable for application to the hair, especially in the form of a cream, a mousse, a stick, a dispersion of vesicles, especially of ionic or nonionic lipids, a two-phase or multiphase lotion, an aerosol spray, for example lacquers, a powder or a paste.

15 The composition according to the invention is an anhydrous composition, i.e. a composition containing less than 2% by weight of water, or even less than 0.3% water, in particular free of water, the water present resulting solely from the residual water provided by the mixed ingredients.

The composition described above may be used on dry or wet hair. The additives described previously, when they are present, may be applied to the hair simultaneously with the composition of the invention or separately. The composition may be rinsed out or left in. It is also possible subsequently to wash the hair, this washing not being obligatory.

30 EXAMPLES

#### Examples:

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	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
$\alpha, \omega$ -Dihydroxylated polydi- methylsiloxane/cyclopenta- dimethylsiloxane mixture (14.7/85.3) sold under the	20 g	-				

name DC1501 Fluid (*)						
Linear silicone DC200 Fluid 500 000 cSt (*)	-	-	-	_	-	3 g
BioPSA 7-4400 (*)	10 g	-	10 g	10 g	10 g	10 g
BioPSA 7-4500 (*)	-	10 g	-	-	-	-
Isododecane	-	_	30 g	-	_	-
Volatile linear silicone DC200 Fluid 1 cSt(*)	-	-	-	qs 100 g	-	-
Ethanol	-	-	-	_	20 g	-
Volatile cyclic silicone DC245 Fluid (*)	qs 100 g	qs 100 g	qs 100 g	_	qs 100 g	<b>q</b> s 100 g

(\*) sold by Dow Corning

0.3 g of the composition is applied to a 1-g lock of clean, wet hair of tone depth 4. After a leave-on time of 15 minutes, the lock is dried with a hairdryer for 2 minutes. A lock whose hairs are individualized and coated is obtained. This coating is shampoo-remanent.

	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11	Ex 12
$\alpha,\omega$ -Dihydroxylated polydi-methylsiloxane/cyclopenta-dimethylsiloxane mixture (14.7/85.3) sold under the name DC1501 Fluid (*)	20 g	20 g	20 g	20 g	20 g	-
Linear silicone DC200 Fluid 500 000 cSt (*)	-	-	-	-	-	3 g
BioPSA 7-4400 (*)	10 g	-	10 g	10 g	10 g	10 g
BioPSA 7-4500 (*)	-	10 g	-	_	-	-
Mica nacre coated with brown iron oxide, sold by Eckart under the name Prestige Bronze	10 g	10 g	10 g	10 g	10 g	10 g

Isododecane	_	_	30 g	-		30 g
Volatile linear silicone DC200 Fluid 1 cSt(*)	_	-	-	qs 100 g	· <del>-</del>	_
Ethanol	_	_	-	-	20 g	_
Volatile cyclic silicone	qs	qs	qs	_	qs	qs
DC245 Fluid (*)	100 g	100 g	100 g		100 g	100 g

(\*) sold by Dow Corning

0.8 g of the composition is applied to a 1 g lock of clean, wet hair. After a leave-on time of 15 minutes, the lock is dried with a hairdryer for 2 minutes. A coloured lock whose hairs are individualized and whose colour is shampoo-remanent is obtained.

## Examples with organic and mineral pigments:

Ex 13 Ex 14 Ex 15 Ex 16 Ex 17 Ex 1.8  $\alpha, \omega$ -Dihydroxylated polydimethylsiloxane/cyclopenta-20 g 20 g 20 g 20 g dimethylsiloxane mixture (14.7/85.3) sold under the name DC1501 Fluid (\*) Linear silicone DC200 Fluid 3 g 3 g 500 000 cSt (\*) BioPSA 7-4400 (\*) 10 g 10 g 10 g 10 g 10 g 10 g Red iron oxide sold by Sun 10 g 10 g 10 g under the name Sunpuro Disperse Red 122, CI 73915 sold by Sun under the name 10 g 10 g 10 g Sunfast Magenta 122 Isododecane 30 g 30 g 30 g 30 g qs Volatile cyclic qs qs qs qs qs silicone DC245 Fluid (\*) 100 g 100 g 100 g 100 g 100 g 100 g

## (\*) sold by Dow Corning

0.8 g of the composition is applied to a 1-g lock of clean, wet hair. After a leave-on time of 15 minutes, the lock is dried with a hairdryer for 2 minutes. A coloured lock whose hairs are individualized and whose colour is shampoo-remanent is obtained.

# Examples with thickened formulations:

Τ	U

	Ex 19	Ex 20	Ex 21	Ex 22	Ex 23	Ex 24
α,ω-Dihydroxylated polydi- methylsiloxane/cyclopenta- dimethylsiloxane mixture (14.7/85.3) sold under the name DC1501 Fluid (*)	20 g	20 g	20 g	20 g	-	-
Linear silicone DC200 Fluid 500 000 cSt (*)	-	-	-	-	3 g	3 g
BioPSA 7-4400 (*)	10 g					
Mica nacre coated with brown iron oxide, sold by Eckart under the name Prestige Bronze	-	10 g	-	10 g	-	10 g
Isododecane	_	<u>-</u>	30 g	30 g	30 g	30 g
Smectite at 10% in isododecane, sold by Elementis under the name Bentone Gel ISD v	25 g					
Volatile cyclic silicone DC245 Fluid (*)	qs 100 g					

(\*) sold by Dow Corning

For Examples 19, 21 and 23:

0.3 g of the composition is applied to a 1-g lock of clean, wet hair of tone depth 4. After a leave-on time of 15 minutes, the lock is dried with a hairdryer for 2

minutes. A lock whose hairs are individualized and coated is obtained. This coating is shampoo-remanent.

For Examples 20, 22 and 24:

5 0.8 g of the composition is applied to a 1 g lock of clean, wet hair. After a leave-on time of 15 minutes, the lock is dried with a hairdryer for 2 minutes. A coloured lock whose hairs are individualized and whose colour is shampoo-remanent is obtained.

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## Comparative examples

The following compositions 25, 25Bis, 26 and 26bis were prepared. Examples 25 and 26 were prepared with an amount of BioPSA higher than 1 % whereas the examples 25bis and 26bis were prepared with 1% of BioPSA.

	Comp 25	Comp. 25bis	Comp. 26	Comp 26bis
CYCLOPENTASILOXANE (and) DIMETHICONOL sold by DOW CORNING under the name DC 1501 FLUID	20	20	20	20
BioPSA 7-4400 (*)	10	1	10	1
Mica nacre coated with brown iron oxide, sold by Eckart under the name Prestige Bronze	10	10	•	-
Isododécane	-	·	30	30
Smectite at 10% in isododecane, sold by Elementis under the name Bentone Gel ISD v	25	25	25	25
Volatile cyclic silicone DC245 Fluid (*)	Qsp 100	Qsp 100	Qsp 100	Qsp 100

(\*) sold by Dow Corning

Each composition was applied on locks (1g) having of tone depth of 4 (corresponding to a clear chestnut color). For the examples 25 and 25bis, the amount of the composition applied on the locks was 0.8 g. For the examples 26 and 26bis, the amount of the composition applied on the locks was 0.3 g.

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The locks were then washed with a shampoo (ultra doux

camomille from Garnier).

For the locks treated with the compositions 25 and 25bis, the color was evaluated in the L\*a\*b\* system, 5 before and after the shampoo step by using a spectrocolorimeter Minolta CM-3600d, illuminant D65.

According to this system, L\* indicates the lightness. The lowest is the value of L\*, the most intense is the color of the hair. The chromaticity coordinates are expressed by the parameters a\* and b\*, a\* indicating the axis of red/green shades and b\* the axis of yellow/blue shades.

15  $\Delta$ E, which is the color variation between a colored lock and a colored lock after 1 shampoo, is obtained from the following formula:

$$\Delta E = \sqrt{(L^* - L_o^*)^2 + (a^* - a_o^*)^2 + (b^* - b_o^*)^2}$$

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wherein L\* indicates lightness and a\* and b\* are the chromaticity coordinates of the colored locks after 1 shampoo whereas L0\* indicates the lightness and a0\* and b0\* are the chromaticity of the colored locks before shampoo. The lowest is the value of  $\Delta E$ , the most resistant to shampoo is the color of the hair.

The obtained results are reported in the table below:

		L*	a*	b*	ΔΕ
Ex 25	Before shampoo	41.99	12.27	18.83	•
Ex 25	After shampoo	40.39	10.16	16.48	3.5
Ex 25bis	Before shampoo	38.26	11.11	17.33	-
Ex 25bis	After shampoo	21.9	4.31	5.9	21

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These results show that when the BioPSA is used in an amount higher than 1 %, the obtained color exhibits a better resistance to shampoo.

For the locks 26 and 26bis, the evaluation was conducted qualitatively. By touching the locks 26 after and before, it can be felt that after the shampoo the presence of a coating on the hair with a higher body.

5 With the lock 26bis, after shampoo, the coating is no more present. The touching is very near of the one of natural hair before treating with the composition 26 bis.



### CLAIMS

- Anhydrous hair treatment composition which comprises one or more copolymers based on silicone resin and on fluid silicone, one or more linear or cyclic volatile silicones, and one or more non-volatile linear polydimethylsiloxanes with a viscosity of greater than 5 cSt, the amount of copolymer being greater than 1% by weight relative to the total weight of the composition, and the composition being free of pigments.
- 2. Anhydrous composition for dyeing hair, comprising one or more copolymers based on silicone resin and on fluid silicone, one or more linear or cyclic volatile silicones, one or more non-volatile linear polydimethylsiloxanes with a viscosity of greater than 5 cSt at 25°C, and a colouring pigment, the amount of copolymer being greater than 1% by weight relative to the total weight of the composition, and the amount of colouring pigments being greater than 5%.
- 3. Composition according to Claim 1 or 2, in which the copolymer comprises the silicone resin in a content.

  25 of between 40% and 70% and the fluid silicone in a content of between 30% and 60%, the sum of the percentages of silicone resin and of fluid silicone being equal to 100.
- 4. Composition according to Claims 1 to 3, in which the silicone resin is present in a content of between 55% and 65% and the fluid silicone is present in a content of between 35% and 45%.
- 35 5. Composition according to any one of the preceding claims, in which the copolymer is present in a content of greater than 1% and up to 40% by weight, relative to the total weight of the composition.
  - 6. Composition according to Claim 5, in which the

copolymer is present in a content ranging from 1.5% to 20% by weight, relative to the total weight of the composition.

- 5 7. Composition according to Claim 1, in which the cyclic silicone is chosen from octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane, and mixtures thereof.
- 10 8. Composition according to Claim 7, in which the cyclic silicone is decamethylcyclopentasiloxane.
- 9. Composition according to any one of the preceding claims, in which the non-volatile linear polydimethyl15 siloxane is chosen from polydimethylsiloxanes; alkyl dimethicones; polyphenylmethylsiloxanes; and also silicones modified with optionally fluorinated aliphatic and/or aromatic groups, or with functional groups such as hydroxyl, thiol and/or amine groups.
- 10. Composition according to Claim 9, in which the polyphenylmethylsiloxanes are as phenyl dimethicones, phenyl trimethicones and vinyl methyl methicones.

- 25 11. Composition according to Claim 9 or 10, in which the polydimethylsiloxane has a viscosity of between 100 cSt and 4 000 000 cSt at  $25^{\circ}$ C.
- 12. Composition according to any one of Claims 2 to 30 11, in which the pigment is a natural pigment or a nacre.
- 13. Composition according to any one of Claims 2 to 12, in which the amount of pigment is not more than 35 40%.
  - 14. Composition according to Claim 13, in which the amount of pigment is not more than 20%.

- 15. Composition according to any one of the preceding claims, also comprising a non-silicone additional solvent.
- 5 16. Composition according to Claim 15, in which the non-silicone additional solvent is a hydrocarbon or an alcohol.
- 17. Composition according to any one of the preceding claims, also comprising a thickener.
  - 18. Composition according to Claim 17, in which the thickener is organomodified clay.
- 19. Process for treating keratin fibres, which comprises the application of a composition as defined in any one of the preceding claims, optionally followed, after a leave-in time, by rinsing and/or washing.

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20. Use of an anhydrous composition comprising one or more copolymers based on silicone resin and on fluid silicone and one or more colouring pigments, for obtaining a coloured coating on the hair.

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- 21. Use according to Claims 19 to 20, in which the composition also comprises a non-volatile linear PDMS.
- 22. Use of a composition according to Claim 1 for 30 treating the hair.
  - 23. Anhydrous hair composition substantially as herein described and exemplified in any one of Examples 1 to

Dated this 11th of July 2008

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