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(54) **NON-TRANSFER COSMETIC COMPOSITION COMPRISING A DISPERSION OF A GRAFTED ETHYLENE POLYMER**

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(57) **ABSTRACT**

The invention provides a cosmetic lipcare and/or lip makeup composition comprising at least one cosmetically acceptable organic liquid medium and a dispersion of a grafted ethylenic polymer, the said polymer being such that, when dispersed in sufficient amount in the composition, the composition is able to form a deposit having a transfer of less than or equal to 35%.

NON-TRANSFER COSMETIC COMPOSITION COMPRISING A DISPERSION OF A GRAFTED ETHYLENE POLYMER

[0001] The present invention relates to a cosmetic lipcare and/or lip makeup composition comprising a dispersion of a grafted ethylenic polymer in a liquid fatty phase, intended for application to lips.

[0002] The composition according to the invention may be a makeup composition or a care composition, preferably a makeup composition.

[0003] Lipstick compositions are commonly employed to provide an aesthetic colour to the lips. These makeup products generally include fatty phases such as waxes and oils, pigments and/or fillers, and, optionally, additives such as cosmetic or dermatological actives.

[0004] These compositions, when applied to the lips, exhibit the drawback of transferring: that is, of at least partly depositing, leaving marks on certain substrates with which they may be brought into contact, and in particular a glass, cup, cigarette, item of clothing or the skin. One consequence is a mediocre persistence of the applied film, necessitating regular renewal of application of the lipstick composition.

[0005] "No-transfer" lip makeup compositions are therefore sought which have the advantage of forming a deposit which does not undergo at least partial deposition on the substrates with which they are brought into contact (glass, clothing, cigarette, fabrics).

[0006] In order to limit the transfer of cosmetic compositions it is known to employ volatile oils, in particular in amounts greater than 40% by weight. When present in large amount, these volatile oils make the makeup product, in particular the lipstick, uncomfortable for the user: the makeup deposit confers a sensation of drying and of tautening.

[0007] Likewise known are products in the form of two separate compositions to be applied one over the other to the lips to give a no-transfer makeup. For example, the Lipfinity product from Max Factor, as described in patent application WO 97/17057, is a product comprising two compositions to be applied successively: the base composition contains a silicone resin and volatile oils, and the surface (or topcoat) composition contains a sucrose ester. However, applying two compositions to make themselves up may be prohibitive for certain users.

[0008] It is an object of the present invention to provide a new formulation pathway for a cosmetic composition, in particular a lip makeup composition, which allows a deposit having good non-transfer properties to be obtained, in particular without the use of a substantial proportion of volatile oils, the said deposit being obtainable with this single composition.

[0009] It is another object of the invention to provide a cosmetic composition, in particular a lip makeup composition, which allows a comfortable deposit to be obtained on the lips.

[0010] The inventors have found that it is possible to obtain such a composition using a dispersion of a specific grafted polymer in a liquid fatty phase. The composition allows a deposit to be obtained, in particular a lip makeup, which exhibits good non-transfer properties. Moreover, the deposit obtained on the lips does not give rise to a sensation of drying or tautening for the user: the deposit is therefore comfortable.

[0011] More specifically, therefore, the present invention has as its object a cosmetic composition comprising a polymer dispersion as described below, the composition being in particular as defined below.

[0012] The invention firstly provides a cosmetic lipcare and/or lip makeup composition comprising a dispersion, in a liquid fatty phase, of particles, preferably solid particles, of a grafted ethylenic polymer, the said polymer being such that, when dispersed in sufficient amount in the composition, the latter is able to form advantageously a deposit having a transfer of less than or equal to 35%.

[0013] With further advantage, the composition according to the invention is able to form a deposit having a transfer of less than or equal to 30%, preferably less than or equal to 25%, preferably less than or equal to 20%, preferably less than or equal to 15%, preferably less than or equal to 10%, preferably less than or equal to 5%. The invention also provides a cosmetic method of making up or non-therapeutically caring for the lips, comprising the application to the lips of a composition as defined above.

[0014] The invention additionally provides for the use of a composition as defined above to give a non-transfer deposit, in particular non-transfer makeup on the lips.

[0015] The invention further provides for the use of a grafted ethylenic polymer, dispersed in a liquid fatty phase, in a cosmetic composition to give a non-transfer deposit, in particular non-transfer makeup on lips.

[0016] The invention additionally provides for the use, in a cosmetic composition, of a sufficient amount of a dispersion, in a liquid fatty phase, of a grafted ethylenic polymer to give a deposit on the lips that has a transfer of less than or equal to 35%.

[0017] The transfer of the deposit obtained with the composition according to the invention is determined according to the protocol described below.

[0018] A substrate (a rectangle of 40 mm×70 mm with a thickness of 3 mm) made of polyethylene foam that is adhesive on one of the faces, having a density of 33 kg/m^3 (sold under the name RE40X70EP3 from Joint Technique Lyonnais Ind.), is preheated on a hotplate which is maintained at a temperature of 40° C. so that the surface of the substrate is maintained at a temperature of 33° C.±1° C.

[0019] With the substrate left on the hotplate, the composition is applied over the entire non-adhesive surface of the substrate, by spreading it with the aid of a fine brush to give a deposit of the composition of approximately 15 μm, and is then left to dry for 30 minutes.

[0020] After drying, the support is bonded via its adhesive face to an anvil which has a diameter of 20 mm and is equipped with a screw pitch. The substrate/deposit assembly is then cut by means of a punch with a diameter of 18 mm. The anvil is subsequently screwed onto a press (Statif Manuel Imada SV-2 from Someco) which is equipped with a dynamometer (Imada DPS-20 from Someco).

[0021] White photocopier paper, 80 g/m^2, is placed on the bed of the press and then the substrate/deposit assembly is pressed on the paper at a pressure of 2.5 kg for 30 seconds. After the substrate/deposit assembly has been removed, some of the deposit has undergone transfer to the paper. The colour of the deposit transferred to the paper is then measured by means of a Minolta CR300 colorimeter, the colour being characterized by the colorimetric parameters L*, a* and b*. The colorimetric parameters L^*_0, a^*_0 and b^*_0 of the colour of the uncoated paper used are measured.

[0022] A determination is then made of the colour difference ΔE1 between the colour of the transferred deposit relative to the colour of the uncoated paper, in accordance with the following relationship:

$$\Delta E1=\sqrt{(L^*-L_0^*)^{2+}(a^*-a_0^*)^2+(b^*-b_0^*)^2}$$

[0023] Furthermore, a total transfer reference is prepared by applying the composition directly to paper identical to that used before, at ambient temperature (25° C.), the composition being spread by means of a fine brush to give a deposit of the composition of approximately 15 μm, and then left to dry for 30 minutes at ambient temperature (25° C.). After the deposit has dried, the colorimetric parameters L*', a*' and b*' of the colour of the deposit placed on the paper are measured directly, corresponding to the total transfer reference colour. The colorimetric parameters $L^{*\prime}_0$, $a^{*\prime}_0$ and $b^{*\prime}_0$ of the colour of the uncoated paper used are measured.

[0024] A determination is then made of the colour difference ΔE2 between the total transfer reference colour relative to the colour of the uncoated paper, in accordance with the following relationship:

$$\Delta E2=\sqrt{(L^{*\prime}-L_0^{*\prime})^{2+}(a^{*\prime}-a_0^{*\prime})^2+(b^{*\prime}-b^{*\prime})^2}$$

[0025] The transfer of the composition, expressed as a percentage, is equal to the following ratio:

$$100\times\Delta E1/\Delta E2$$

[0026] The measurement is carried out on 4 substrates in succession and the transfer value corresponds to the average of the 4 measurements obtained with the 4 substrates.

[0027] The composition according to the invention comprises a dispersion of particles, preferably solid particles, of a grafted ethylenic polymer in a liquid fatty phase.

[0028] The term "ethylenic" polymer means a polymer obtained by polymerization of ethylenically unsaturated monomers.

[0029] The dispersion of grafted ethylenic polymer is especially free of stabilizing polymer different from the said grafted polymer, such as those described in EP 749 747 and the particles of grafted ethylenic polymer are therefore not surface-stabilized with such additional stabilizing polymers. The grafted polymer is therefore dispersed in the liquid fatty phase in the absence of additional surface stabilizer for the particles.

[0030] The term "grafted" polymer means a polymer having a skeleton comprising at least one side chain that is pendent or located at the end of a chain, and preferably pendent.

[0031] Advantageously, the grafted ethylenic polymer comprises an ethylenic skeleton which is insoluble in the said liquid fatty phase, and side chains which are attached covalently to the said skeleton and are soluble in the said fatty phase.

[0032] The grafted ethylenic polymer is especially a non-crosslinked polymer. In particular, the polymer is obtained by polymerization of monomers comprising only one polymerizable group.

[0033] Preferably, the grafted ethylenic polymer is a film-forming polymer.

[0034] The term "film-forming" polymer means a polymer capable of forming, by itself or in the presence of an auxiliary film-forming agent, a film which is continuous, in particular to the touch and/or to the naked eye, and which is adherent to a substrate, in particular to keratin materials.

[0035] According to one embodiment of the invention, the grafted ethylenic polymer is a grafted acrylic polymer.

[0036] The grafted ethylenic polymer is especially obtainable by free-radical polymerization in an organic polymerization medium:

> **[0037]** of at least one ethylenic monomer, in particular of at least one acrylic monomer and optionally of at least one additional non-acrylic vinyl monomer, to form the said insoluble skeleton; and
>
> **[0038]** of at least one macromonomer containing a polymerizable end group to form the side chains, the said macromonomer having a weight-average molecular mass of greater than or equal to 200 and the proportion of the polymerized macromonomer representing from 0.05% to 20% by weight of the polymer.

[0039] The medium in which the grafted polymer is supplied for its formulation, called organic liquid dispersion medium, may be identical to the polymerization medium.

[0040] However, the polymerization medium may be totally or partially replaced with another organic liquid medium. This other organic liquid medium may be added, after polymerization, to the polymerization medium. The said polymerization medium is then totally or partially evaporated.

[0041] The liquid fatty phase of the cosmetic composition may contain the organic polymerization medium.

[0042] The liquid fatty phase may contain liquid organic compounds other than those present in the dispersion medium. These other compounds are chosen such that the grafted polymer remains in the dispersed state in the liquid fatty phase.

[0043] The organic liquid dispersion medium is present in the liquid fatty phase of the composition according to the invention owing to the introduction into the composition of the dispersion of grafted polymer obtained.

[0044] The liquid fatty phase:

[0045] The liquid fatty phase comprises, preferably predominantly, one or more liquid organic compounds (or oils) as defined below.

[0046] In particular, the liquid fatty phase is a non-aqueous liquid organic phase that is immiscible with water at room temperature (25° C.).

[0047] The term “liquid organic compound” means a non-aqueous compound that is in liquid form at room temperature (25° C.) and therefore flows under its own weight.

[0048] The term “silicone compound” means a compound containing at least one silicon atom.

[0049] The composition according to the invention advantageously contains a volatile oil as described below.

[0050] The term “volatile oil” means an oil capable of evaporating from the skin or the lips in less than one hour, especially having a vapour pressure, at room temperature and atmospheric pressure, ranging from 10^{-3} to 300 mmHg (0.13 Pa to 40 000 Pa).

[0051] The volatile oil may be silicone-based or non-silicone-based. It may be selected especially from octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, isododecane, isodecane and isohexadecane, and mixtures thereof.

[0052] The volatile oil is advantageously present in an amount ranging from 1% to 70% by weight, relative to the total weight of the composition, preferably ranging from 5% to 50% by weight and preferentially ranging from 10% to 35% by weight.

[0053] The liquid fatty phase may contain a non-volatile oil as described below. The non-volatile oil is advantageously present in an amount ranging from 1% to 80% by weight, relative to the total weight of the composition, preferably ranging from 5% to 60% by weight and preferentially ranging from 10% to 50% by weight.

[0054] Among the liquid organic compounds or oils that may be present in the liquid fatty phase, mention may be made of liquid organic compounds, especially silicone-based or non-silicone-based, having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 $(MPa)^{1/2}$, preferably 17 $(MPa)^{1/2}$. When the liquid organic compounds are chosen from monoalcohols, their total solubility parameter according to the Hansen solubility space may be greater than 17 $(MPa)^{1/2}$ while remaining less than or equal to 20 $(MPa)^{1/2}$.

[0055] The total solubility parameter 6 according to the Hansen solubility space is defined in the article “Solubility parameter values” by Eric A. Grulke in the work “Polymer Handbook”, 3rd Edition, Chapter VII, p. 519-559, by the relationship:

$$\delta=(\delta_D^2+\delta_P^2+\delta_H^2)^{1/2}$$

in which

[0056] δ_D characterizes the London dispersion forces arising from the formation of dipoles induced during molecular impacts,

[0057] δ_P characterizes the Debye interaction forces between permanent dipoles, and

[0058] δ_H characterizes the forces of specific interactions (such as hydrogen bonds, acid/base, donor/acceptor, etc.).

[0059] The definition of solvents in the solubility space according to Hansen is described in the article by C. M. Hansen: “The three-dimensional solubility parameters”, J. Paint Technol. 39, 105 (1967).

[0060] Among the liquid organic compounds, especially silicone-based or non-silicone-based, having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 $(MPa)^{1/2}$, preferably less than or equal to 17 $(MPa)^{1/2}$, mention may be made of liquid fatty substances, especially oils, which may be chosen from natural or synthetic, carbon-based, hydrocarbon-based, fluoro and silicone oils, which are optionally branched, alone or as a mixture.

[0061] Among these oils, mention may be made of plant oils formed from fatty acid esters and from polyols, in particular triglycerides, such as sunflower oil, sesame oil or rapeseed oil, or esters derived from acids or alcohols containing a long chain (i.e. a chain containing from 6 to 20 carbon atoms), in particular the esters of formula RCOOR' in which R represents a higher fatty acid residue containing from 7 to 19 carbon atoms and R' represents a hydrocarbon-based chain containing from 3 to 20 carbon atoms, such as palmitates, adipates and benzoates, in particular diisopropyl adipate.

[0062] Mention may also be made of linear, branched and/or cyclic alkanes which may be volatile, and in particular liquid paraffin, liquid petroleum jelly or hydrogenated polyisobutylene, isododecane or “Isopars”, volatile isoparaffins. Mention may also be made of esters, ethers and ketones.

[0063] Mention may also be made of silicone oils such as polydimethylsiloxanes and polymethylphenylsiloxanes, optionally substituted with aliphatic and/or aromatic groups, which are optionally fluorinated, or with functional groups such as hydroxyl, thiol and/or amine groups, and volatile silicone oils, which are especially cyclic.

[0064] In particular, mention may be made of volatile and/or non-volatile, optionally branched silicone oils.

[0065] As volatile silicone oils that may be used in the invention, mention may be made of linear or cyclic silicones containing from 2 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms. Mention may be made in particular of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, and mixtures thereof.

[0066] As the non-volatile silicone oils that may be mentioned are non-volatile polydialkylsiloxanes, such as non-volatile polydimethylsiloxanes (PDMS); polydimethylsiloxanes comprising alkyl, alkoxy or phenyl groups, which are pendent or at the end of a silicone chain, these groups containing from 2 to 24 carbon atoms; phenyl silicones, for instance phenyl trimethicones, phenyl dimethicones, phenyl trimethylsiloxy diphenylsiloxanes, diphenyl dimethicones, diphenyl methyldiphenyltrisiloxanes and polymethylphenylsiloxanes; polysiloxanes modified with fatty acids (especially of C_8-C_{20}), fatty alcohols (especially of C_8-C_{20}) or polyoxyalkylenes (especially polyoxyethylene and/or polyoxypropylene); amino polysiloxanes; polysiloxanes containing hydroxyl groups; fluoro polysiloxanes comprising a fluorinated group that is pendent or at the end of a silicone chain, containing from 1 to 12 carbon atoms, all or some of the hydrogen atoms of which are replaced with fluorine atoms; and mixtures thereof.

[0067] As non-silicone-based liquid organic compounds with a total solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa) $^{1/2}$, mention may be made in particular of:

[0068] linear, branched or cyclic esters containing at least 6 carbon atoms, especially 6 to 30 carbon atoms;

[0069] ethers containing at least 6 carbon atoms, especially 6 to 30 carbon atoms; and

[0070] ketones containing at least 6 carbon atoms, especially 6 to 30 carbon atoms.

[0071] The liquid monoalcohols having a total solubility parameter according to the Hansen solubility space of less than or equal to 20 (MPa)$^{1/2}$ that may be mentioned include aliphatic fatty liquid monoalcohols containing from 6 to 30 carbon atoms, the hydrocarbon-based chain not comprising a substitution group. Monoalcohols according to the invention that may be mentioned include oleyl alcohol, octyldodecanol, decanol and linoleyl alcohol.

[0072] Non-Silicone-Based Medium

[0073] According to a first embodiment of the invention, the liquid fatty phase may be a non-silicone-based liquid fatty phase.

[0074] The term "non-silicone-based liquid fatty phase" means a fatty phase comprising one or more non-silicone-based liquid organic compound(s) or oil(s), such as those mentioned above, the said non-silicone-based compounds being predominantly present in the liquid fatty phase, i.e. to at least 50% by weight, especially from 50% to 100% by weight, preferably from 60% to 100% by weight (for example from 60% to 99% by weight), or alternatively from 65% to 100% by weight (for example from 65% to 95% by weight), relative to the total weight of the liquid fatty phase.

[0075] The non-silicone-based liquid organic compounds may especially be chosen from: non-silicone-based liquid organic compounds having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)$^{1/2}$, preferably less than or equal to 17 (MPa)^{12}. When the liquid organic compounds are chosen from monoalcohols, their total solubility parameter according to the Hansen solubility space may be greater than 17 (MPa)$^{1/2}$ while remaining less than or equal to 20 (MPa)$^{1/2}$,

[0076] The said non-silicone-based liquid fatty phase may thus optionally comprise silicone-based liquid organic compounds or oils, such as those mentioned previously, which may be present in an amount of less than 50% by weight, especially ranging from 0.1% to 40% by weight, or even ranging from 1% to 35% by weight, or alternatively ranging from 5% to 30% by weight, relative to the total weight of the liquid fatty phase.

[0077] According to one particular embodiment of the invention, the non-silicone-based liquid fatty phase does not contain silicone-based liquid organic compounds or oils.

[0078] When the liquid fatty phase is a non-silicone-based liquid fatty phase, the macromonomers present in the grafted polymer are advantageously carbon-based macromonomers as described below.

[0079] In particular, when the liquid fatty phase is a non-silicone-based liquid fatty phase, the grafted polymer present in the composition is advantageously a non-silicone-based grafted polymer.

[0080] The term "non-silicone-based grafted polymer" means a grafted polymer predominantly containing a carbon-based macromonomer and optionally containing not more than 7% by weight and preferably not more than 5% by weight of silicone macromonomer, or even being free of silicone macromonomer.

[0081] Silicone-Based Medium

[0082] According to a second embodiment of the invention, the liquid fatty phase may be a silicone-based liquid fatty phase.

[0083] The term "silicone-based liquid fatty phase" means a fatty phase comprising one or more silicone-based liquid organic compound(s) or silicone oil(s) such as those described previously, the said silicone compounds being predominantly present in the liquid fatty phase, i.e. to at least 50% by weight, especially from 50% to 100% by weight, preferably from 60% to 100% by weight (for example from 60% to 99% by weight), or else from 65% to 100% by weight (for example from 65% to 95% by weight), relative to the total weight of the liquid fatty phase.

[0084] The silicone-based liquid organic compounds may especially be chosen from liquid organic compounds which are silicone-based and have an overall solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)$^{1/2}$, preferably less than or equal to 17 (MPa)$^{1/2}$.

[0085] The said silicone-based liquid fatty phase may thus optionally comprise non-silicone-based liquid organic compounds or oils, as described previously, which may be present in an amount of less than 50% by weight, especially ranging from 0.1% to 40% by weight, or even ranging from 1% to 35% by weight, or else ranging from 5% to 30% by weight, relative to the total weight of the liquid fatty phase.

[0086] According to one particular embodiment of the invention, the silicone-based liquid fatty phase does not contain any non-silicone-based liquid organic compounds.

[0087] When the liquid fatty phase is a silicone-based liquid fatty phase, the macromonomers present in the grafted polymer are advantageously silicone-based macromonomers as described below.

[0088] In particular, when the liquid fatty phase is a silicone-based liquid fatty phase, the grafted polymer present in the composition is advantageously a silicone-based grafted polymer.

[0089] The term "silicone-based grafted polymer" means a grafted polymer predominantly containing a silicone-based macromonomer and optionally containing up to 7% by weight and preferably up to 5% by weight of carbon-based macromonomer, or even being free of carbon-based macromonomer.

[0090] The Grafted Polymer

[0091] The choice of monomers constituting the skeleton of the polymer, of the macromonomers, the molecular weight of the polymer, and the proportion of the monomers and macromonomers may be made as a function of the liquid organic dispersion medium so as advantageously to obtain a dispersion of particles of grafted polymers, in particular a stable dispersion, this choice possibly being made by a person skilled in the art.

[0092] The term "stable dispersion" means a dispersion that is not liable to form a solid deposit or to undergo liquid/solid phase separation, especially after centrifugation, for example, at 4000 rpm for 15 minutes.

[0093] The grafted ethylenic polymer forming the particles in dispersion thus comprises a skeleton that is insoluble in the said fatty phase and a portion that is soluble in the said fatty phase.

[0094] The grafted ethylenic polymer may be a random polymer.

[0095] According to the invention, the term "grafted ethylenic polymer" means a polymer that may be obtained by free-radical polymerization:

[0096] of one or more ethylenic monomer(s);

[0097] with one or more macromonomer(s), in an organic polymerization medium.

[0098] According to the invention, the term "grafted acrylic polymer" means a polymer that may be obtained by free-radical polymerization:

[0099] of at least one acrylic monomer, and optionally of at least one additional non-acrylic vinyl monomer; and

[0100] of at least one macromonomer, in an organic polymerization medium.

[0101] Advantageously, the acrylic monomers represent from 50% to 100% by weight, preferably from 55% to 100% by weight (especially from 55% to 95% by weight) and preferentially from 60% to 100% by weight (especially from 60% to 90% by weight) of the mixture of acrylic monomers+optional non-acrylic vinyl monomers.

[0102] Preferably, the acrylic monomers are chosen from monomers whose homopolymer is insoluble in the dispersion medium under consideration, i.e. the homopolymer is in solid (or non-dissolved) form at a concentration of greater than or equal to 5% by weight at ambient temperature (20° C.) in the said dispersion medium.

[0103] Macromonomers:

[0104] According to the invention, the expression "macromonomer containing a polymerizable end group" means any polymer comprising on only one of its ends a polymerizable end group capable of reacting during the polymerization reaction with acrylic monomers and optionally the additional non-acrylic vinyl monomers constituting the skeleton. The macromonomer makes it possible to form the side chains of the grafted acrylic polymer. The polymerizable group of the macromonomer may advantageously be an ethylenically unsaturated group capable of free-radical polymerization with the monomers constituting the skeleton.

[0105] The term "carbon-based macromonomer" means a non-silicone-based macromonomer and especially an oligomeric macromonomer obtained by polymerization of ethylenically unsaturated non-silicone-based monomer(s), and mainly by polymerization of acrylic and/or non-acrylic vinyl monomers.

[0106] The term "silicone-based macromonomer" means an organopolysiloxane macromonomer and in particular a polydimethylsiloxane macromonomer.

[0107] Preferably, the macromonomer is chosen from macromonomers whose homopolymer is soluble in the dispersion medium under consideration, i.e. fully dissolved at a concentration of greater than or equal to 5% by weight and at room temperature in the said dispersion medium.

[0108] Thus, the grafted acrylic polymer comprises a skeleton (or main chain) consisting of a sequence of acrylic units resulting from the polymerization especially of one or more acrylic monomers and of side chains (or grafts) derived from the reaction of the macromonomers, the said side chains being covalently bonded to the said main chain.

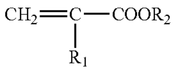
[0109] The skeleton (or main chain) is insoluble in the dispersion medium under consideration, whereas the side chains (or grafts) are soluble in the said dispersion medium.

[0110] The monomers:

[0111] In the present patent application, the term "acrylic monomer" means monomers chosen from (meth)acrylic acid, (meth)acrylic acid esters (also known as (meth)acrylates), and (meth)acrylic acid amides (also known as (meth)acrylamides).

[0112] As acrylic monomers that may be used to constitute the insoluble skeleton of the polymer, mention may be made, alone or as a mixture, of the following monomers, and also the salts thereof:

[0113] (i) the (meth)acrylates of formula:



$$CH_2=C(R_1)-COOR_2$$

in which:

[0114] R_1 denotes a hydrogen atom or a methyl group;

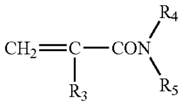
[0115] R_2 represents a group chosen from:

[0116] a linear or branched alkyl group containing from 1 to 6 carbon atoms, the said group possibly comprising in its chain one or more heteroatoms chosen from O, N and S; and/or possibly comprising one or more substituents chosen from —OH, halogen atoms (F, Cl, Br or I) and —NR'R" with R' and R", which may be identical or different, chosen from linear or branched C_1-C_4 alkyls; and/or possibly being substituted with at least one polyoxyalkylene group, in particular with C_2-C_4 alkylene, especially polyoxyethylene and/or polyoxypropylene, the said polyoxyalkylene group consisting of the repetition of 5 to 30 oxyalkylene units;

[0117] a cyclic alkyl group containing from 3 to 6 carbon atoms, the said group possibly comprising in its chain one or more heteroatoms chosen from O, N and S, and/or possibly comprising one or more substituents chosen from OH and halogen atoms (F, Cl, Br or I).

[0118] Examples of R_2 that may be mentioned include the methyl, ethyl, propyl, butyl, isobutyl, methoxyethyl, ethoxyethyl, methoxypolyoxyethylene (350 OE), trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, dimethylaminoethyl, diethylaminoethyl or dimethylaminopropyl group;

[0119] (ii) the (meth)acrylamides of formula:



$$CH_2{=}C(R_3){-}CON(R_4)(R_5)$$

in which:

[0120] R_3 denotes a hydrogen atom or a methyl group;

[0121] R_4 and R_5, which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing from 1 to 6 carbon atoms, which may comprise one or more substituents chosen from —OH, halogen atoms (F, Cl, Br or I) and —NR'R" with R' and R", which may be identical or different, chosen from linear or branched C_1-C_4 alkyls; or

[0122] R_4 represents a hydrogen atom and R_5 represents a 1,1-dimethyl-3-oxobutyl group.

[0123] As examples of alkyl groups that can constitute R_4 and R_5, mention may be made of n-butyl, t-butyl, n-propyl, dimethylaminoethyl, diethylaminoethyl and dimethylaminopropyl;

[0124] (iii) the (meth)acrylic monomers comprising at least one carboxylic acid, phosphoric acid or sulphonic acid function, such as acrylic acid, methacrylic acid or acrylamidopropanesulphonic acid.

[0125] Among these acrylic monomers, those that may be mentioned most particularly are methyl, ethyl, propyl, butyl and isobutyl (meth)acrylates; methoxyethyl or ethoxyethyl (meth)acrylates; trifluoroethyl methacrylate; dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl acrylate; dimethylaminopropylmethacrylamide; methacrylic acid; and the salts thereof; and mixtures thereof.

[0126] Preferably, the acrylic monomers are selected from methyl acrylate, methoxyethyl acrylate, methyl methacrylate, 2-hydroxyethyl methacrylate, methacrylic acid and dimethylaminoethyl methacrylate, and mixtures thereof.

[0127] According to one embodiment, the grafted acrylic polymer is obtainable by free-radical polymerization of one or more acrylic monomers and of one or more additional non-acrylic vinyl monomers, and of the said macromonomer.

[0128] Among the additional non-acrylic vinyl monomers that may be mentioned are:

[0129] vinyl esters of formula:

$$R_6{-}COO{-}CH{=}CH_2$$

in which R_6 represents a linear or branched alkyl group containing from 1 to 6 carbon atoms, or a cyclic alkyl group containing from 3 to 6 carbon atoms and/or an aromatic group, for example of benzene, anthracene or naphthalene type;

[0130] non-acrylic vinyl monomers comprising at least one carboxylic acid, phosphoric acid or sulphonic acid function, such as crotonic acid, maleic anhydride, itaconic acid, fumaric acid, maleic acid, styrenesulphonic acid, vinylbenzoic acid or vinylphosphoric acid, and the salts thereof;

[0131] non-acrylic vinyl monomers comprising at least one tertiary amine function, such as 2-vinylpyridine or 4-vinylpyridine;

[0132] and mixtures thereof.

[0133] The acrylic monomer preferably represents from 50% to 100% by weight, preferably from 60% to 100% by weight, preferentially from 70% to 100% by weight of the mixture of acrylic monomer and of optional non-acrylic vinyl monomer.

[0134] Advantageously, the acrylic monomers present in the grafted polymer comprise at least (meth)acrylic acid and at least one monomer selected from the (meth)acrylates and (meth)acrylamides described previously in sections (i) and (ii). Preferably, the acrylic monomers comprise at least (meth)acrylic acid and at least one monomer selected from C_1-C_3 alkyl (meth)acrylates. (Meth)acrylic acid may be present in a content of at least 5% by weight (especially ranging from 5% to 80% by weight), preferably of at least 10% by weight (especially ranging from 10% to 70% by weight), and preferentially of at least 15% by weight (especially ranging from 15% to 60% by weight), relative to the total weight of the polymer.

[0135] Among the salts that may be mentioned are those obtained by neutralization of acid groups with mineral bases such as sodium hydroxide, potassium hydroxide or ammonium hydroxide, or organic bases such as alkanolamines, for instance monoethanolamine, diethanolamine, triethanolamine or 2-methyl-2-amino-1-propanol.

[0136] Mention may also be made of the salts formed by neutralization of tertiary amine units, for example using a mineral or organic acid. Among the mineral acids that may be mentioned are sulphuric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid and boric acid. Among the organic acids that may be mentioned are acids comprising one or more carboxylic, sulphonic or phosphonic groups. They may be linear, branched or cyclic aliphatic acids, or alternatively aromatic acids. These acids may also comprise one or more heteroatoms chosen from O and N, for example in the form of hydroxyl groups. Acetic acid or propionic acid, terephthalic acid, and citric acid and tartaric acid may especially be mentioned.

[0137] According to one embodiment of the invention, the grafted acrylic polymer does not contain any additional non-acrylic vinyl monomers as described above. In this embodiment, the insoluble skeleton of the grafted ethylenic polymer is formed solely from acrylic monomers as described previously.

[0138] It is understood that these non-polymerized acrylic monomers may be soluble in the dispersion medium under consideration, but the polymer formed with these monomers is insoluble in the dispersion medium.

[0139] According to one particular embodiment of the invention, the grafted ethylenic polymer may be obtained by free-radical polymerization in an organic polymerization medium:

[0140] of a main acrylic monomer chosen from C_1-C_3 alkyl (meth)acrylates, alone or as a mixture, and optionally of one or more additional acrylic monomers chosen from acrylic acid, methacrylic acid and alkyl(meth)acrylates of formula (I) defined below, and salts thereof, to form the said insoluble skeleton; and

[0141] of at least one silicone-based macromonomer comprising a polymerizable end group, as defined previously.

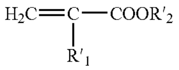
[0142] Main acrylic monomers that may be used include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-propyl acrylate, n'-propyl methacrylate, isopropyl acrylate and isopropyl methacrylate, and mixtures thereof.

[0143] Methyl acrylate, methyl methacrylate and ethyl methacrylate are most particularly preferred.

[0144] The additional acrylic monomers may be chosen from:

[0145] (meth)acrylic acid and its salts,

[0146] the (meth)acrylates of formula (I), and salts thereof:



$$H_2C{=}C(R'_1){-}COOR'_2 \qquad (I)$$

in which:

[0147] R_{11} denotes a hydrogen atom or a methyl group;

[0148] R_{12} represents

[0149] a linear or branched alkyl group containing from 1 to 6 carbon atoms, the said group comprising in its chain one or more oxygen atoms and/or comprising one or more substituents chosen from

[0150] —OH, halogen atoms (F, Cl, Br or I) and —NR'R", with R' and R", which may be identical or different, being chosen from linear or branched C_1-C_3 alkyls;

[0151] a cyclic alkyl group containing from 3 to 6 carbon atoms, the said group possibly comprising in its chain one or more oxygen atoms and/or possibly comprising one or more substituents chosen from OH and halogen atoms (F, Cl, Br or I);

[0152] and mixtures thereof.

[0153] Examples of R'_2 that may be mentioned include the methoxyethyl, ethoxyethyl, trifluoroethyl; 2-hydroxyethyl, 2-hydroxypropyl, dimethylaminoethyl, diethylaminoethyl and dimethylaminopropyl groups.

[0154] Among these additional acrylic monomers, mention may be made most particularly of (meth)acrylic acid, methoxyethyl or ethoxyethyl (meth)acrylates; trifluoroethyl methacrylate; dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate and 2-hydroxyethyl acrylate, the salts thereof, and mixtures thereof.

[0155] Acrylic acid and methacrylic acid are most particularly preferred.

[0156] The macromonomers comprise at one of the ends of the chain a polymerizable end group capable of reacting during the polymerization with the acrylic monomers and optionally the additional vinyl monomers, to form the side chains of the grafted ethylenic polymer. The said polymerizable end group may in particular be a vinyl or (meth)acrylate (or (meth)acryloyloxy) group, and preferably a (meth-)acrylate group.

[0157] The macromonomers are preferably chosen from macromonomers whose homopolymer has a glass transition temperature (Tg) of less than or equal to 25° C., especially ranging from −100° C. to 25° C. and preferably ranging from −80° C. to 0° C.

[0158] The macromonomers have a weight-average molecular mass of greater than or equal to 200, preferably greater than or equal to 300, preferentially greater than or equal to 500, and more preferentially greater than 600.

[0159] Preferably, the macromonomers have a weight-average molecular mass (Mw) ranging from 300 to 100 000, preferably ranging from 500 to 50 000, preferentially ranging from 800 to 20 000, more preferentially ranging from 800 to 10 000, and more preferentially still ranging from 800 to 6000.

[0160] In the present patent application, the weight-average (Mw) and number-average (Mn) molar masses are determined by liquid gel permeation chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

[0161] Carbon-based macromonomers that may in particular be mentioned include:

[0162] (i) linear or branched alkyl acrylate or methacrylate C_8-C_{22} homopolymers and copolymers having a polymerizable end group selected from vinyl or (meth)acrylate groups, among which mention may be made in particular of: poly(2-ethylhexyl acrylate) macromonomers with a mono(meth)acrylate end group; poly(dodecyl acrylate) or poly(dodecyl methacrylate) macromonomers with a mono(meth)acrylate end group; poly(stearyl acrylate) or poly(stearyl methacrylate) macromonomers with a mono(meth)acrylate end group.

[0163] Such macromonomers are described in particular in the patents EP 895 467 and EP 96 459, and in the article by Gillman K. F., Polymer Letters, Vol 5, page 477-481 (1967).

[0164] Mention may be made in particular of macromonomers based on poly(2-ethylhexyl acrylate) or poly(dodecyl acrylate) with a mono(meth)acrylate end group;

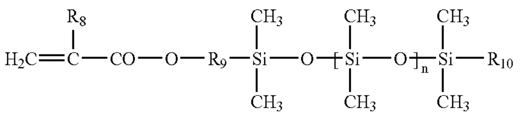
[0165] (ii) polyolefins having an ethylenically unsaturated end group, in particular containing a (meth)acrylate end group. Examples of such polyolefins that may be mentioned in particular include the following macromonomers, it being understood that they have a (meth)acrylate end group: polyethylene macromonomers, polypropylene macromonomers, macromonomers of polyethylene/polypropylene copolymer, macromonomers of polyethylene/polybutylene copolymer, polyisobutylene macromonomers; polybutadiene macromonomers; polyisoprene macromonomers; polybutadiene macromonomers; poly(ethylene/butylene)-polyisoprene macromonomers.

[0166] Such macromonomers are described in particular in U.S. Pat. No. 5,625,005, which mentions ethylene/butylene and ethylene/propylene macromonomers containing a (meth)acrylate reactive end group.

[0167] Mention may be made in particular of the poly(ethylene/butylene) methacrylate such as that sold under the name Kraton Liquid L-1253 by Kraton Polymers.

[0168] Silicone-based macromonomers that may be mentioned in particular include polydimethylsiloxanes containing mono(meth)acrylate end groups, and especially those of formula (II) below:

(II)



$$H_2C{=}\overset{R_8}{C}-CO-O-R_9-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-R_{10}$$

in which R_8 denotes a hydrogen atom or a methyl group; R_9 denotes a divalent hydrocarbon-based group containing from 1 to 10 carbon atoms and optionally contains one or two ether bonds —O—; R_{10} denotes an alkyl group containing from 1 to 10 carbon atoms and especially from 2 to 8 carbon atoms; n denotes an integer ranging from 1 to 300, preferably ranging from 3 to 200 and preferentially ranging from 5 to 100.

[0169] Silicone-based macromonomers that may be used include monomethacryloyloxypropyl polydimethylsiloxanes such as those sold under the name PS560-K6 by the company United Chemical Technologies Inc. (UCT) or under the name MCR-M17 by the company Gelest Inc.

[0170] Preferably, the polymerized macromonomer (constituting the side chains of the grafted polymer) represents from 0.05% to 20% by weight of the total weight of the polymer, preferably from 0.1% to 15% by weight, preferentially from 0.2% to 10% by weight and more preferentially from 0.3% to 8% by weight.

[0171] As particularly preferred grafted ethylenic polymer dispersed in a non-silicone-based liquid fatty phase, it is possible to use those obtained by polymerization:

[0172] of methyl acrylate and of a polyethylene/polybutylene macromonomer containing a methacrylate end group (especially Kraton L-1253), in particular in a solvent chosen from isododecane, isononyl isononanoate, octyldodecanol, diisostearyl malate or a C_{12}-C_{15} alkyl benzoate (such as Finsolv TN);

[0173] of methoxyethyl acrylate and of a polyethylene/polybutylene macromonomer containing a methacrylate end group (especially Kraton L-1253), in particular in isododecane;

[0174] of methyl acrylate/methyl methacrylate monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group (especially Kraton L-1253), in particular in isododecane;

[0175] of methyl acrylate/acrylic acid monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group (especially Kraton L-1253), in particular in isododecane;

[0176] of methyl acrylate/dimethylaminoethyl methacrylate monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group (especially Kraton L-1253), in particular in isododecane;

[0177] of methyl acrylate/2-hydroxyethyl methacrylate monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group (especially Kraton L-1253), in particular in isododecane.

[0178] As particularly preferred grafted acrylic polymer dispersed in a silicone-based liquid fatty phase, it is possible to use those obtained by polymerization:

[0179] of methyl acrylate and of the monomethacryloyloxypropyl polydimethylsiloxane macromonomer with a weight-average molecular weight ranging from 800 to 6000, in particular in decamethylcyclopentasiloxane or phenyl trimethicone;

[0180] of methyl acrylate, acrylic acid and the monomethacryloxypropyl polydimethylsiloxane macromonomer with a weight-average molecular weight ranging from 800 to 6000, in particular in decamethylcyclopentasiloxane or phenyl trimethicone.

[0181] The weight-average molecular mass (Mw) of the grafted polymer is preferably between 10 000 and 300 000, especially between 20 000 and 200 000 and better still between 25 000 and 150 000.

[0182] By virtue of the abovementioned characteristics, in a given organic dispersion medium, the polymers have the capacity of folding over on themselves, thus forming particles of substantially spherical shape, the periphery of these particles having the deployed side chains, which ensure the stability of these particles. Such particles resulting from the characteristics of the grafted polymer have the particular feature of not aggregating in the said medium and thus of being self-stabilized and of forming a particularly stable polymer particle dispersion.

[0183] In particular, the grafted ethylenic polymers of the dispersion are capable of forming nanometre-sized particles, with a mean size ranging from 10 to 400 nm and preferably from 20 to 200 nm.

[0184] As a result of this very small size, the grafted polymer particles in dispersion are particularly stable and therefore have little susceptibility to form agglomerates.

[0185] The dispersion of grafted polymer may thus be a dispersion that is stable and does not form sediments when it is placed at room temperature (25° C.) for an extended period (for example 24 hours).

[0186] Preferably, the dispersion of grafted polymer particles has a solids content (or dry extract) of polymer of from 40% to 70% by weight of solids and especially from 45% to 65% by weight.

[0187] The dispersion of grafted polymer particles may be prepared by a process comprising a free-radical copolymerization step, in an organic polymerization medium, of one or more acrylic monomers as defined above with one or more macromonomers as defined above.

[0188] As mentioned previously, the liquid organic dispersion medium may be identical to or different from the polymerization medium.

[0189] The copolymerization may be performed conventionally in the presence of a polymerization initiator. The polymerization initiators may be free-radical initiators. In general, such a polymerization initiator may be chosen from organic peroxide compounds such as dilauroyl peroxide, dibenzoyl peroxide or tert-butyl peroxy-2-ethylhexanoate; diazo compounds such as azobisisobutyronitrile or azobisdimethylvaleronitrile.

[0190] The reaction may also be initiated using photoinitiators or with radiation such as UV or neutrons, or with plasma.

[0191] In general, to perform this process, at least a portion of the organic polymerization medium, a portion of the additional acrylic and/or vinyl monomers, which will constitute the insoluble skeleton after polymerization, all of the macromonomer (which will constitute the side chains of the polymer) and a portion of the polymerization initiator are introduced into a reactor whose size is suitable for the amount of polymer to be prepared. At this stage of introduction, the reaction medium forms a relatively homogeneous medium.

[0192] The reaction medium is then stirred and heated up to a temperature to obtain polymerization of the monomers and macromonomers. After a certain time, the initially homogeneous and clear medium leads to a dispersion of milky appearance. A mixture consisting of the remaining portion of monomers and of the polymerization initiator is then added. After an adequate time during which the mixture is heated with stirring, the medium stabilizes in the form of a milky dispersion, the dispersion comprising polymer particles stabilized in the medium in which they have been created, the said stabilization being due to the presence, in the polymer, of side chains that are soluble in the said dispersion medium.

[0193] The polymer dispersion may be present in a proportion of from 3% to 95% by weight in the composition, in particular from 4% to 90% by weight, or even from 20% to 70% by weight.

[0194] The grafted polymer may be present in the composition according to the invention in an amount in terms of solids content (or active substance) ranging from 1% to 66.5% by weight relative to the total weight of the composition, preferably ranging from 6% to 45% and more preferably ranging from 8% to 40% by weight.

[0195] The present examples illustrate the preparation of polymers in accordance with the invention and capable of forming a dispersion of particles in an organic medium under consideration.

[0196] In these examples, following preparation of the said dispersion, determinations are made of the weight-average (Mw) and number-average (Mn) molar masses of the polymer, the glass transition temperature of the polymer, the solids content (or dry extract) of the dispersion, and the size of the polymer particles.

[0197] The weight-average (Mw) and number-average (Mn) molar masses are determined by liquid gel-permeation chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

[0198] The glass transition temperature (Tg) is measured in accordance with standard ASTM D3418-97, by differential enthalpy analysis (DSC "Differential Scanning Calorimetry") on a calorimeter, over a temperature range of between −100° C. and +150° C. at a heating rate of 10° C./min in 150 μl aluminium crucibles.

[0199] The crucibles are prepared as follows: 1001 μl of the dispersion obtained are introduced into a 150 μl aluminium crucible and the solvent is allowed to evaporate over 24 hours at ambient temperature and at 50% relative humidity. The operation is repeated and the crucible is then introduced into the Mettler DSC30 calorimeter.

[0200] The solids content (or dry extract), in other words the amount of non-volatile matter, may be measured in a variety of ways: mention may be made, for example, of the methods involving oven drying or the methods involving drying by exposure to infrared radiation.

[0201] The solids content is preferably measured by heating the sample with infrared rays with a wavelength of from 2 μm to 3.5 μm. The substances present in the composition that have a high vapour pressure evaporate under the effect of this radiation. Measuring the weight loss from the sample allows the dry extract of the composition to be determined. These measurements are performed by means of a commercial infrared desiccator LP16 from Mettler. This technique is fully described in the documentation for the instrument supplied by Mettler.

[0202] The measurement protocol is as follows: approximately 1 g of the composition is spread onto a metal cup. After this cup has been introduced into the desiccator, it is subjected to a setpoint temperature of 120° C. for an hour. The wet mass of the sample, corresponding to the initial mass, and the dry mass of the sample, corresponding to the mass after radiation exposure, are measured by means of a precision balance. The solids content is calculated as follows:

$$\text{Dry extract}=100\times(\text{dry mass}/\text{wet mass}).$$

[0203] The particle sizes may be measured by a variety of techniques: mention may be made, in particular, of light scattering techniques (dynamic and static), Coulter counter methods, sedimentation rate measurements (related to the size via Stokes' law) and microscopy. These techniques allow a particle diameter and, in certain cases, a particle size distribution to be measured.

[0204] The sizes and size distributions of the particles in the compositions according to the invention are preferably measured by static light scattering using a commercial granulometer of type MasterSizer 2000 from Malvern. The data are processed on the basis of the Mie scattering theory. This theory, which is exact for isotropic particles, makes it possible to determine an "effective" particle diameter in the case of non-spherical particles. This theory is described in particular in the work by Van de Hulst, H. C., "Light Scattering by Small Particles," Chapters 9 and 10, Wiley, New York, 1957.

[0205] The composition is characterized by its “effective” mean diameter by volume D[4.3], which is defined as follows:

$$D\,[4.3] = \frac{\sum_i V_i \cdot d_i}{\sum_i V_i}$$

in which V_i represents the volume of particles with an effective diameter d_i. This parameter is described in particular in the technical documentation accompanying the granulometer.

[0206] The measurements are carried out at 25° C. on a dilute particle dispersion obtained from the composition as follows: 1) dilution by a factor of 100 with water, 2) homogenization of the solution, 3) standing of the solution for 18 hours, 4) recovery of the whitish uniform supernatant.

EXAMPLE 1

Polymer Obtained by Polymerizing Methyl Acrylate and the Macromonomer Corresponding to a Polyethylene/Polybutylene Copolymer Containing Methacrylate End Groups (Kraton L-1253).

[0207] A reactor is charged with 2 kg of heptane, 2 kg of isododecane, 2.8 kg of methyl acrylate and 1.2 kg of a macromonomer of the type constituting a polyethylene/polybutylene copolymer containing methacrylate end groups (Kraton L-1253) and 320 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S).

[0208] The reaction mixture is stirred and heated at ambient temperature to 90° C. over 1 hour. After 15 minutes at 90° C., a change is observed in the appearance of the reaction medium, which passes from transparent to milky in appearance. Heating with stirring is maintained for a further 15 minutes, and then a mixture consisting of 16 kg of methyl acrylate and 200 g of Trigonox 12S is added dropwise over 1 hour.

[0209] Heating takes place subsequently at 90° C. for 4 hours and then the heptane is distilled from the reaction medium. At the end of this distillation operation, a stable dispersion is obtained of particles of polymer thus prepared in isododecane.

[0210] The grafted polymer contains 6% by weight of macromonomer relative to the weight of the polymer.

[0211] The characteristics of the polymer and of the particles formed by the said polymer are as follows:

[0212] Weight-average molecular mass Mw=119 900

[0213] Number-average molecular mass Mn=16 300

[0214] Polydispersity index (Mw/Mn)=7.37

[0215] Glass transition: 10° C. by Mettler DSC;

[0216] Dry extract: 52.4% in isododecane, carried out by thermobalance;

[0217] Particle size: 46 nm with a polydispersity of 0.05, performed on a Malvern Autosizer Lo-C at 25° C.

[0218] The stability of the resulting dispersion is demonstrated by implementing the following stability protocol: a haemolysis tube is charged with 8 ml of the dispersion prepared and is centrifuged at 4000 rpm for 15 minutes with the aid of a Jouan C100-S5 centrifuge. After 15 minutes it is found that there is no phase separation, thereby demonstrating that the dispersion is stable.

EXAMPLE 2

Polymer Obtained by Polymerizing Methyl Acrylate, Acrylic Acid and the Macromonomer Corresponding to a Polyethylene/Polybutylene Copolymer (Kraton L-1253).

[0219] A 1 litre reactor is charged with 200 g of heptane, 200 g of isododecane, 14 g of methyl acrylate, 10 g of acrylic acid and 16 g of a macromonomer of the type constituting a polyethylene/polybutylene copolymer containing methacrylate end groups (Kraton L-1253) and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S).

[0220] The reaction mixture is stirred and heated at ambient temperature to 90° C. over 1 hour. After 15 minutes at 90° C., a change is observed in the appearance of the reaction medium, which passes from transparent to milky in appearance. Heating with stirring is maintained for a further 15 minutes, and then a mixture consisting of 130 g of methyl acrylate, 30 g of acrylic acid and 2 g of Trigonox 12S is added dropwise over 1 hour.

[0221] Heating takes place subsequently at 90° C. for 4 hours and then the heptane is distilled from the reaction medium. At the end of this distillation operation, a stable dispersion is obtained of particles of polymer thus prepared in isododecane.

[0222] The characteristics of the polymer and of the particles formed by the said polymer are as follows:

[0223] Weight-average molecular mass Mw=175 294

[0224] Number-average molecular mass Mn=28 265

[0225] Polydispersity index (Mw/Mn)=6.2

[0226] Dry extract: 54.9% in isododecane;

[0227] Particle size: 85 nm with a polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25° C.

[0228] The grafted polymer contains 8% by weight of macromonomer relative to the weight of the polymer.

[0229] The stability of the resulting dispersion is demonstrated by implementing the following stability protocol: a haemolysis tube is charged with 8 ml of the dispersion prepared and is centrifuged at 4000 rpm for 15 minutes with the aid of a Jouan C100-S5 centrifuge. After 15 minutes it is found that there is no phase separation, thereby demonstrating that the dispersion is stable.

EXAMPLE 3

Polymer Obtained by Polymerizing Methyl Acrylate, Acrylic Acid and the Monomethacryloyloxypropyl Polydimethylsiloxane Macromonomer

[0230] The macromonomer has a weight-average molecular weight of 5000 and is sold under the name MCR-M17 by Gelest Inc.

[0231] A 1 litre reactor is charged with 200 g of heptane, 200 g of decamethylcyclopentasiloxane, 26 g of methyl acrylate, 14 g of monomethacryloyloxypropyl polydimethylsiloxane MCR-M17 and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S).

[0232] The reaction mixture is stirred and heated to 90° C. over 1 hour. After 15 minutes at 90° C., a change is observed in the appearance of the reaction medium, which passes from transparent to milky in appearance. Heating with stirring is maintained for a further 15 minutes, and then a mixture consisting of 120 g of methyl acrylate, 40 g of acrylic acid and 2 g of Trigonox 21S is added dropwise over 1 hour. Heating takes place subsequently at 90° C. for 4 hours and then the heptane is distilled from the reaction medium.

[0233] At the end of this distillation operation, a stable dispersion is obtained of particles of polymer thus prepared in decamethylcyclopentasiloxane.

[0234] The grafted polymer contains 7% by weight of macromonomer (and therefore of side chains soluble in D5) relative to the weight of the polymer.

[0235] The characteristics of the polymer and of the particles formed by the said polymer are as follows:

[0236] Dry extract: 50% in decamethylcyclopentasiloxane, performed by thermobalance

[0237] Glass transition: 12° C. by Mettler DSC

[0238] Particle size: 170 nm with a polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25° C.

EXAMPLE 4

Polymer Obtained by Polymerizing Methyl Acrylate, Acrylic Acid and the Macromonomer Corresponding to a Polyethylene/Polybutylene Copolymer Containing Methacrylate End Groups (Kraton L-1253).

[0239] A 1 litre reactor is charged with 200 g of heptane, 200 g of isododecane, 28 g of methyl acrylate, 12 g of a macromonomer of the type constituting a polyethylene/polybutylene copolymer containing methacrylate end groups (Kraton L-1253) and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S).

[0240] The reaction mixture is stirred and heated at ambient temperature to 90° C. over 1 hour. After 15 minutes at 90° C., a change is observed in the appearance of the reaction medium, which passes from transparent to milky in appearance. Heating with stirring is maintained for a further 15 minutes, and then a mixture consisting of 150 g of methyl acrylate, 10 g of acrylic acid and 2 g of Trigonox 12S is added dropwise over 1 hour.

[0241] Heating takes place subsequently at 90° C. for 4 hours and then the heptane is distilled from the reaction medium. At the end of this distillation operation, a stable dispersion is obtained of particles of polymer thus prepared in isododecane.

[0242] The grafted polymer contains 6% by weight of macromonomer relative to the weight of the polymer.

[0243] The characteristics of the polymer and of the particles formed by the said polymer are as follows:

[0244] Weight-average molecular mass Mw=143 639

[0245] Number-average molecular mass Mn=23 965

[0246] Polydispersity index (Mw/Mn)=5.99

[0247] Theoretical dry extract: 51.3% in isododecane

[0248] Particle size: 48 nm with a polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25° C.

[0249] After the stability protocol has been implemented in accordance with Example 1, it is found that the resulting dispersion is stable.

[0250] The composition according to the invention may also comprise at least fatty substances that are solid at ambient temperature, selected in particular from waxes, pasty fatty substances, gums and mixtures thereof. These fatty substances may be of animal, plant, mineral or synthetic origin.

[0251] By pasty fatty substance is meant a lipophilic fatty compound comprising at a temperature of 23° C. a liquid fraction and a solid fraction.

[0252] The said pasty compound preferably has a hardness at 20° C. ranging from 0.001 to 0.5 MPa, preferably from 0.002 to 0.4 MPa.

[0253] The hardness is measured according to a method involving penetration of a probe into a sample of compound, and in particular by means of a texture analyser (for example the TA-XT2i from Rhéo) which is equipped with a stainless steel cylinder 2 mm in diameter. The hardness measurement is performed at 20° C. in the centre of 5 samples. The cylinder is introduced into each sample at a pre-speed of 1 mm/s and then at a measuring speed of 0.1 mm/s, the depth of penetration being 0.3 mm. The value found for the hardness is that of the maximum peak.

[0254] The liquid fraction of the pasty compound measured at 23° C. represents preferably 9% to 97% by weight of the compound. This fraction that is liquid at 23° C. represents preferably between 15% and 85%, more preferably between 40% and 85% by weight. The liquid fraction by weight of the pasty compound at 23° C. is equal to the ratio of the enthalpy of fusion consumed at 23° C. to the enthalpy of fusion of the pasty compound.

[0255] The enthalpy of fusion of the pasty compound is the enthalpy consumed by the compound in passing from the solid state to the liquid state. The pasty compound is said to be in the solid state when the entirety of its mass is in solid crystalline form. The pasty compound is said to be in the liquid state when the entirety of its mass is in liquid form.

[0256] The enthalpy of fusion of the pasty compound is equal to the area under the curve of the thermogram obtained by means of a differential scanning calorimeter (DSC), such as the calorimeter sold under the name MDSC 2920 by TA Instrument, with a temperature rise of 5 or 10° C. per minute, according to standard ISO 11357-3:1999. The enthalpy of fusion of the pasty compound is the amount of energy required to cause the compound to pass from the solid state to the liquid state. It is expressed in J/g.

[0257] The enthalpy of fusion consumed at 23° C. is the amount of energy absorbed by the sample in passing from the solid state to the state in which it exists at 23° C., composed of a liquid fraction and a solid fraction.

[0258] The liquid fraction of the pasty compound measured at 32° C. represents preferably from 30% to 100% by weight of the compound, preferably from 80% to 100%, more preferably from 90% to 100% by weight of the compound. When the liquid fraction of the pasty compound measured at 32° C. is 100%, the temperature of the end of the melting range of the pasty compound is less than or equal to 32° C.

[0259] The liquid fraction of the pasty compound measured at 32° C. is equal to the ratio of the enthalpy of fusion consumed at 32° C. to the enthalpy of fusion of the pasty compound. The enthalpy of fusion consumed at 32° C. is calculated in the same way as for the enthalpy of fusion consumed at 23° C.

[0260] A wax for the purposes of the present invention is understood to mean a lipophilic compound which is solid at ambient temperature (25° C.) and exhibits a reversible solid/liquid state change, having a melting point of greater than or equal to 30° C. and possibly as high as 120° C.

[0261] The melting point of the wax can be measured by means of a differential scanning calorimeter (DSC), an example being the calorimeter sold under the name DSC 30 by the company Mettler.

[0262] The waxes may be hydrocarbon, fluoro and/or silicone waxes and may be of plant, mineral, animal and/or synthetic origin. In particular the waxes have a melting point greater than or equal to 30° C. and better still greater than 45° C.

[0263] As a wax which can be used in the composition of the invention mention may be made of beeswax, carnauba wax or candelilla wax, paraffin, microcrystalline waxes, ceresin or ozokerite; synthetic waxes such as polyethylene or Fischer-Tropsch waxes; and silicone waxes such as alkyl or alkoxy dimethicones having from 16 to 45 carbon atoms.

[0264] The gums are generally high-molecular-weight polydimethylsiloxanes (PDMS) or cellulose gums or polysaccharides, and the pasty substances are generally hydrocarbon compounds such as lanolins and derivatives thereof or else PDMSs.

[0265] The nature and amount of the solid substances depend on the desired textures and mechanical properties. As a guide, the composition may contain from 0.1% to 50% by weight of waxes, relative to the total weight of the composition, and better still from 1% to 30% by weight.

[0266] The composition may therefore include water or a mixture of water and hydrophilic organic solvent(s) such as alcohols, and especially linear or branched lower monoalcohols having from 2 to 5 carbon atoms, such as ethanol, isopropanol or n-propanol, and polyols, such as glycerol, diglycerol, propylene glycol, sorbitol, pentylene glycol, and polyethylene glycols, or else C_2 ethers and C_2-C_4 aldehydes which are hydrophilic.

[0267] The water or the mixture of water and hydrophilic organic solvents may be present in the composition according to the invention in an amount ranging from 0.1% to 99% by weight, relative to the total weight of the composition, and preferably from 1% to 80%, and more preferably from 10% to 80% by weight.

[0268] The composition according to the invention may further comprise one or more colorants selected from water-soluble dyes and pulverulent colorants such as pigments, nacres and mixtures thereof. The colorants may be present in the composition in an amount ranging from 0.01% to 50% by weight, relative to the weight of the composition, preferably from 0.01% to 30% by weight.

[0269] One of the subjects of the invention is a lipcare and/or lip makeup composition comprising a dispersion of particles of a grafted ethylenic polymer in a liquid fatty phase and at least one pulverulent colorant selected in particular from pigments, nacres or other filler having an optical effect, and mixtures thereof. The Applicant has found, in effect, that pulverulent materials, especially pigments, disperse readily in the dispersion of particles of grafted ethylenic polymer as described above, without employing substantial amounts of dispersant or even without adding any dispersant at all.

[0270] By pigments are meant particles of any form, white or coloured, organic or inorganic, which are insoluble in the physiological medium and are intended for colouring the composition.

[0271] By nacres are meant particles of any form which are iridescent and, in particular, are produced by certain molluscs in their shell or else are synthesized.

[0272] The pigments may be white or coloured, organic and/or inorganic. Among inorganic pigments mention may be made of titanium dioxide, optionally with surface treatment, zirconium oxide or cerium oxide, and also zinc oxide, iron oxide (black, yellow or red) or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, and metal powders such as aluminium powder and copper powder.

[0273] Among organic pigments mention may be made of carbon black, D & C-type pigments, and lakes based on cochineal carmine, barium, strontium, calcium or aluminium.

[0274] Mention may also be made of effect pigments, such as particles comprising an organic or inorganic, natural or synthetic substrate, for example glass, acrylic resins, polyester, polyurethane, polyethylene terephthalate, ceramics or aluminas, the said substrate being covered or not covered with metallic substances such as aluminium, gold, silver, platinum, copper, bronze, or with metal oxides such as titanium dioxide, iron oxide, chromium oxide and mixtures thereof.

[0275] The nacreous pigments may be selected from white nacreous pigments such as titanium-coated mica, or bismuth oxychloride, coloured nacreous pigments such as titanium mica coated with iron oxides, titanium mica coated with, in particular, ferric blue or chromium oxide, titanium mica covered with an organic pigment of the aforementioned type, and nacreous pigments based on bismuth oxychloride. It is also possible to use interference pigments, especially liquid-crystal or multilayer pigments.

[0276] The water-soluble dyes are, for example, beetroot juice and methylene blue.

[0277] The composition according to the invention may comprise at least one filler, in particular in an amount ranging from 0.01% to 50% by weight, relative to the total weight of the composition, preferably ranging from 0.01% to 30% by weight. By fillers are meant particles of any shape, colourless or white, inorganic or synthetic, which are insoluble in the medium of the composition irrespective of the temperature at which the composition is manufactured. These fillers serve in particular to modify the rheology or texture of the composition.

[0278] The fillers may be organic or inorganic and of any shape, platelet-like, spherical or oblong, whatever the crystallographic form (for example sheet, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide (Nylon®) powders (orgasol® from Atochem), poly-β-alanine power and polyethylene powder, powders of tetrafluoroethylene (Teflon®)) polymers, lauroyllysine, starch, boron nitride, polymeric hollow microspheres such as those of polyvinylidene chloride/acrylonitrile such as Expancel® (Nobel Industries), acrylic acid copolymers (Polytrap® from the Dow Corning company) and silicone resin microbeads (Tospearls® from Toshiba, for example), particles of elastomeric polyorganosiloxanes, precipitated calcium carbonate, magnesium carbonate and hydrogencarbonate, hydroxyapatite, hollow silica microspheres (Silica Beads® from Maprecos), ceramic or glass microcapsules, and metal soaps derived from organic carboxylic acids having from 8 to 22 carbon atoms, preferably from 12 to 18 carbon atoms, for example zinc stearate, magnesium stearate or lithium stearate, zinc laurate and magnesium myristate.

[0279] The pigments, nacres or solid fillers may be dispersed in the liquid fatty phase of the composition in the presence of a dispersant.

[0280] The purpose of the dispersant is to protect the dispersed particles against agglomeration or flocculation. This dispersant may be a surfactant, an oligomer, a polymer or a mixture of two or more thereof, carrying one or more functionalities having a high affinity for the surface of the particles to be dispersed. In particular, they may become physically or chemically attached to the surface of the pigments. These dispersants additionally exhibit at least one functional group which is compatible with or soluble in the continuous medium. Use is made in particular of the esters of 12-hydroxystearic acid, in particular, and of a C_8 to C_{20} fatty acid and a polyol such as glycerol, diglycerol, such as poly(12-hydroxystearic) acid stearate with a molecular weight of approximately 750 g/mol, such as that sold under the name Solsperse 21 000 by Avecia, polyglyceryl-2 dipolyhydroxystearate (CTFA name) sold under the reference Dehymyls PGPH by Henkel, or else polyhydroxystearic acid such as that sold under the reference Arlacel P100 by Uniqema, and mixtures thereof.

[0281] As other dispersants which can be used in the composition of the invention, mention may be made of quaternary ammonium derivatives of polycondensed fatty acids, such as Solsperse 17 000, sold by Avecia, and of mixtures of polydimethylsiloxane/oxypropylene such as those sold by Dow Corning under the references DC2-5185 and DC2-5225 C.

[0282] Polydihydroxystearic acid and the esters of 12-hydroxystearic acid are preferably intended for a hydrocarbon-based or fluorine-based medium, whereas mixtures of dimethylsiloxane oxyethylene/oxypropylene are preferably intended for a silicone-based medium.

[0283] The pigments, nacres or fillers may be introduced into the composition in the form of a particulate paste comprising the particles, a liquid medium and the dispersant. The liquid medium of the particulate paste is advantageously one of the oils whose use is desired in the composition forming part of the liquid fatty phase.

[0284] The composition according to the invention may additionally comprise ingredients commonly used in cosmetology, such as vitamins, trace elements, softeners, sequestrants, perfumes, alkalifying or acidifying agents, preservatives, sunscreens, surfactants, antioxidants or mixtures thereof.

[0285] It will be appreciated that the skilled person will take care to select this or these optional additional compounds, and/or their amount, in such a way that the advantageous properties of the corresponding composition according to the invention are not, or not substantially, adversely affected by the addition envisaged.

[0286] The composition according to the invention may be in the form in particular of a suspension, dispersion, solution, gel, emulsion, especially an oil-in-water (O/W) or water-in-oil (W/O) or multiple (W/O/W or polyol/O/W or O/W/O) emulsion, in the form of a cream, paste, mousse, a dispersion of vesicles, especially of ionic or nonionic lipids, or in the form of a two-phase or multiphase lotion. The composition may be anhydrous; for example, it may comprise an anhydrous stick or paste.

[0287] By "anhydrous" is meant a composition which may contain less than 5% of water, better still less than 3% of water, and more preferably 1% of water relative to the total weight of the composition.

[0288] The skilled person will be able to select the appropriate presentation form, and also the method of preparing it, on the basis of his or her general knowledge, taking into account, first, the nature of the constituents used, particularly their solubility in the vehicle, and, secondly, the application intended for the composition.

[0289] According to another aspect the invention also pertains to a cosmetic assembly comprising:

[0290] i) a container delimiting at least one compartment, the said container being closed by a closing member; and

[0291] ii) a composition disposed within the said compartment, the composition being in accordance with the invention.

[0292] The container may be in any suitable form. It may in particular be in the form of a bottle, tube, jar, case, box, sachet or carton.

[0293] The closing member may be in the form of a removable stopper, a lid, a cap, a tear-off strip or a capsule, particularly of the type comprising a body attached to the container and a cover cap articulated on the body. It may also be in the form of a member for selectively closing the container, especially a pump, a valve or a flap.

[0294] The container may be combined with an applicator. The applicator may be in the form of a fine brush, as described for example in patent FR 2 722 380. The applicator may be in the form of a block of foam or of elastomer, a felt or a spatula. The applicator may be free (a tuft or sponge) or may be securely attached to a rod carried by the closing member, as described for example in patent U.S. Pat. No. 5,492,426. The applicator may be securely attached to the container, as described, for example, by patent FR 2 761 959.

[0295] The product may be contained directly in the container or indirectly. By way of example, the product may be disposed on an impregnated support, especially in the form of a wipe or a pad, and may be disposed (individually or in plurality) in a carton or in a sachet. A support of this kind incorporating the product is described for example in patent application WO 01/03538.

[0296] The closing member may be coupled to the container by screwing. Alternatively the coupling between the closing member and the container is accomplished other than by screwing, in particular via a bayonet mechanism, by snap fastening, gripping, welding, adhesive bonding, or magnetic attraction. By "snap fastening" is meant, in particular, any system involving the crossing of a bead or cord of material by elastic deformation of a portion, in particular of the closing member, followed by return to the elastically unconstrained position of the said portion after the crossing of the bead or cord.

[0297] The container may be at least partly made of thermoplastic material. Examples of thermoplastic materials that may be mentioned include polypropylene and polyethylene.

[0298] Alternatively the container is made of non-thermoplastic material, in particular of glass or of metal (or alloy).

[0299] The container may have rigid walls or deformable walls, in the form in particular of a tube or a tubular bottle.

[0300] The container may comprise means intended for distributing or facilitating the distribution of the composition. By way of example, the container may have deformable walls so as to allow the composition to exit in response to a positive pressure within the container, this positive pressure being caused by elastic (or non-elastic) squeezing of the walls of the container. Alternatively, and particularly when the product is in the form of a stick, the product may be driven out by a piston mechanism. Still in the case of a stick, the container may comprise a mechanism, in particular a rack mechanism, or a mechanism with a threaded rod, or with a helical groove, and may be capable of moving a stick in the direction of the said opening. A mechanism of this kind is described for example in patent FR 2 806 273 or in patent FR 2 775 566. A mechanism of this kind for a liquid product is described in patent FR 2 727 609.

[0301] The container may be composed of a carton with a base delimiting at least one housing containing the composition and a cover which is articulated, in particular, on the base and is able to cover the said base at least partly. A carton of this kind is described for example in patent application WO 03/013423 or in patent FR 2 791 042.

[0302] The container may be equipped with a drainer arranged in the region of the opening of the container. A drainer of this kind allows the applicator to be wiped and, where appropriate, allows the rod to which it may be securely attached to be wiped. A drainer of this kind is described for example in patent FR 2 792 618.

[0303] The content of the patents or patent applications cited above is incorporated by reference into the present application.

[0304] The invention is illustrated in greater detail by the examples described below.

EXAMPLE 5

Lipstick

[0305]

Ingredients, INCI name	% by mass
Octyldodecanol	11.75
VP-eicosene copolymer (Antaron V 220, ISP)	15
Polyethylene (Polywax 500, Bareco)	13
Pigments	10.25
Polymer of Example 1	50

[0306] In a melting pot, the waxes, the oily phase and the pigments in the form of a millbase are introduced into the oily phase containing the PVP-eicosene. The mixture is melted at 100° C. with Rayneri stirring. When the preparation is liquid, the whole is left at 100° C. for 40 minutes. Then the volatile ingredients, or ingredients containing volatile solvents, are introduced. The pot is covered in order to limit evaporation, and the mixture is left with stirring for 10 minutes. The formula is then cast at 42° C. before being placed in a freezer. Demoulding is carried out when the mould temperature is approximately 4° C.

[0307] The transfer of this formula was measured in accordance with the protocol described above. It is equal to 1.85±0.1.

EXAMPLE 6

Lipstick

[0308] In a melting pot, with Rayneri stirring, the waxes, pigment pastes and sucrose ester are introduced, the temperature is stabilized at 105° C., the mixture is turned for 30 minutes, and then the nacres are added, followed by the polymer dispersion and the perfume, after which the mixture is turned for 10 minutes and then cast in a mould at 42° C. The mould is placed in a freezer and demoulding is carried out when the mould is at approximately 4° C.;

Ingredients	% by mass
Pigments	8.20
Hydrogenated polyisobutene (Parleam)	5.18
Polyhydroxystearic acid (Octacare DSPOL300, Avecia)	0.21
C30–C50 alcohols (Performacol 550 Alcohol, New Phase Technologies)	2

-continued

Ingredients	% by mass
Polyethylene (Polywax 500, Bareco)	10
Sucrose acetate isobutyrate (Eastman SAIB Special, Eastman Chemical)	5
Polymer of Example 1	68.82
Perfume	qs

[0309] The transfer, measured according to the protocol described above, is 1.2.

EXAMPLE 7

Lipstick

[0310]

Pigments	8.20
Hydrogenated polyisobutene (Parleam)	5.18
Polyhydroxystearic acid (Octacare DSPOL300, Avecia)	0.21
C30-C50 alcohols (Performacol 550 Alcohol, New Phase Technologies)	2
Polyethylene (Polywax 500, Bareco)	10
Sucrose acetate isobutyrate (Eastman SAIB Special, Eastman Chemical)	5
Polymer of Example 4	68.82
Perfume	qs

1. Cosmetic lipcare and/or lip makeup composition comprising a dispersion, in a liquid fatty phase, of particles of a grafted ethylenic polymer, the said polymer being such that, when dispersed in sufficient amount in the composition, the latter is able to form a deposit having a transfer of less than or equal to 35%.

2. Composition according to claim 1, characterized in that it is able to form a deposit having a transfer of less than or equal to 30%, preferably less than or equal to 25%, preferably less than or equal to 20%, preferably less than or equal to 15%, preferably less than or equal to 10%, preferably less than or equal to 5%.

3. Composition according to either of the preceding claims, characterized in that the grafted ethylenic polymer comprises an ethylenic skeleton which is insoluble in the said liquid fatty phase and side chains which are attached covalently to the said skeleton and are soluble in the said liquid fatty phase.

4. Composition according to one of the preceding claims, characterized in that the ethylenic polymer is dispersed in the absence of additional stabilizer at the surface of the particles.

5. Composition according to one of the preceding claims, characterized in that the ethylenic polymer is a grafted acrylic polymer.

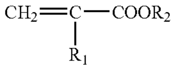
6. Composition according to claims **3** and **5**, characterized in that the grafted ethylenic polymer in dispersion is a grafted acrylic polymer obtainable by free-radical polymerization in an organic polymerization medium:

of at least one acrylic monomer, and optionally of at least one additional non-acrylic vinyl monomer, to form the said insoluble skeleton; and

of at least one macromonomer containing a polymerizable end group to form the side chains, the said macromonomer having a weight-average molecular mass of greater than or equal to 200 and the amount of polymerized macromonomer representing from 0.05% to 20% by weight of the polymer.

7. Composition according to claim 6, characterized in that the acrylic monomer is selected, alone or in a mixture, from the following monomers, and also the salts thereof:

(i) the (meth)acrylates of formula:



$$CH_2=C(R_1)-COOR_2$$

in which:

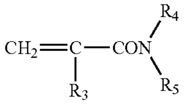
R_1 denotes a hydrogen atom or a methyl group;

R_2 represents a group chosen from:

a linear or branched alkyl group containing from 1 to 6 carbon atoms, the said group possibly comprising in its chain one or more heteroatoms chosen from O, N and S; and/or possibly comprising one or more substituents chosen from —OH, halogen atoms (F, Cl, Br or I) and —NR'R" with R' and R", which may be identical or different, chosen from linear or branched C_1-C_4 alkyls; and/or possibly being substituted with at least one polyoxyalkylene group, especially polyoxyethylene and/or polyoxypropylene, the said polyoxyalkylene group consisting of the repetition of 5 to 30 oxyalkylene units;

a cyclic alkyl group containing from 3 to 6 carbon atoms, the said group possibly comprising in its chain one or more heteroatoms chosen from O, N and S, and/or possibly comprising one or more substituents chosen from OH and halogen atoms (F, Cl, Br or I);

(ii) the (meth)acrylamides of formula:



$$CH_2=C(R_3)-CON(R_4)(R_5)$$

in which:

R_3 denotes a hydrogen atom or a methyl group;

R_4 and R_5, which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing from 1 to 6 carbon atoms, which may comprise one or more substituents chosen from —OH, halogen atoms (F, Cl, Br or I) and —NR'R" with R' and R", which may be identical or different, chosen from linear or branched C_1-C_4 alkyls; or

R_4 represents a hydrogen atom and R_5 represents a 1,1-dimethyl-3-oxobutyl group;

(iii) the (meth)acrylic monomers comprising at least one carboxylic acid, phosphoric acid or sulphonic acid function, such as acrylic acid, methacrylic acid or acrylamidopropanesulphonic acid.

8. Composition according to claim 7, characterized in that the acrylic monomer is selected from methyl, ethyl, propyl, butyl and isobutyl (meth)acrylates; methoxyethyl or ethoxyethyl (meth)acrylates; trifluoroethyl methacrylate; dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate; dimethylaminopropylmethacrylamide; methacrylic acid; and the salts thereof.

9. Composition according to claim 7, characterized in that the acrylic monomer is selected from methyl acrylate, methoxyethyl acrylate, methyl methacrylate, 2-hydroxyethyl methacrylate, methacrylic acid and dimethylaminoethyl methacrylate, and mixtures thereof.

10. Composition according to claim 7, characterized in that the acrylic monomer is acrylic acid.

11. Composition according to any one of claims 7 to 10, characterized in that the grafted polymer comprises (meth)acrylic acid.

12. Composition according to any one of claims 7 to 11, characterized in that the acrylic monomers comprise at least (meth)acrylic acid and at least one monomer selected from the (meth)acrylates and (meth)acrylamides described in sections (i) and (ii) in claim 8.

13. Composition according to any one of claims 7 to 12, characterized in that the acrylic monomers comprise at least (meth)acrylic acid and at least one monomer selected from C_1-C_3 alkyl (meth)acrylates.

14. Composition according to any one of the preceding claims, characterized in that the (meth)acrylic acid is present in an amount of at least 5% by weight, relative to the total weight of the polymer, in particular ranging from 5% to 80% by weight, preferably at least 10% by weight, in particular ranging from 10% by weight to 70% by weight, preferentially at least 15% by weight, in particular ranging from 15% to 60% by weight.

15. Composition according to claim 6 or one of its dependent claims, characterized in that the grafted acrylic polymer does not contain any additional non-acrylic vinyl monomer.

16. Composition according to claim 6, or one of its dependent claims, characterized in that the grafted acrylic polymer is obtainable by free-radical polymerization of one or more acrylic monomers and one or more additional non-acrylic vinyl monomers, and of the said macromonomer.

17. Composition according to claim 16, characterized in that the additional non-acrylic vinyl monomers are selected from:

vinyl esters of formula:

R_6—COO—CH=CH_2

in which R_6 represents a linear or branched alkyl group containing from 1 to 6 carbon atoms, or a cyclic alkyl group containing from 3 to 6 carbon atoms and/or an aromatic group, for example of benzene, anthracene or naphthalene type;

non-acrylic vinyl monomers comprising at least one carboxylic acid, phosphoric acid or sulphonic acid function, such as crotonic acid, maleic anhydride, itaconic acid, fumaric acid, maleic acid, styrenesulphonic acid, vinylbenzoic acid or vinylphosphoric acid, and the salts thereof;

non-acrylic vinyl monomers comprising at least one tertiary amine function, such as 2-vinylpyridine or 4-vinylpyridine;

and mixtures thereof.

18. Composition according to claim 6 or one of its dependent claims, characterized in that the acrylic monomer represents from 50% to 100% by weight, preferably from 60% to 100% by weight, preferentially from 70% to 100% by weight of the mixture of acrylic monomer and of optional non-acrylic vinyl monomer.

19. Composition according to claim 6 or one of its dependent claims, characterized in that the macromonomer comprises at one of the ends of the chain a polymerizable end group selected from a vinyl group or a (meth)acrylate group, and preferably a (meth)acrylate group.

20. Composition according to claim 6 or one of its dependent claims, characterized in that the weight-average molecular mass of the macromonomer is greater than or equal to 300, preferentially greater than or equal to 500, and more preferentially greater than 600.

21. Composition according to the preceding claim, characterized in that the macromonomer has a weight-average molecular mass (Mw) ranging from 300 to 100 000, preferably ranging from 500 to 50 000, preferentially ranging from 800 to 20 000, more preferentially ranging from 800 to 10 000, and more preferentially still ranging from 800 to 6000.

22. Composition according to claim 6 or one of its dependent claims, characterized in that the polymerized macromonomer represents from 0.1% to 15% by weight of the total weight of the polymer, preferably from 0.2% to 10% by weight, and preferentially from 0.3% to 8% by weight.

23. Composition according to one of the preceding claims, characterized in that the liquid fatty phase comprises a liquid organic compound selected from liquid organic compounds having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 $(MPa)^{1/2}$, preferably less than or equal to 17 $(MPa)^{1/2}$.

24. Composition according to one of claims 1 to 22, characterized in that the liquid fatty phase comprises a liquid organic compound selected from monoalcohols having a total solubility parameter according to the Hansen solubility space of less than or equal to 20 $(MPa)^{1/2}$.

25. Composition according to any one of the preceding claims, characterized in that it comprises a volatile oil.

26. Composition according to the preceding claim, characterized in that it comprises a volatile oil selected from octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, isododecane, isodecane and isohexadecane and mixtures thereof.

27. Composition according to claim 25 or 26, characterized in that the volatile oil is present in an amount ranging from 1% to 70% by weight, relative to the total weight of the composition, preferably ranging from 5% to 50% by weight and preferentially ranging from 10% to 35% by weight.

28. Composition according to one of the preceding claims, characterized in that the liquid fatty phase is a non-silicone-based liquid fatty phase.

29. Composition according to the preceding claim, characterized in that the non-silicone-based liquid fatty phase is composed of at least 50% by weight of at least one non-silicone-based organic liquid compound selected from:

non-silicone-based organic liquid compounds having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 $(MPa)^{1/2}$;

liquid monoalcohols having a total solubility parameter according to the Hansen solubility space of less than or equal to 20 $(MPa)^{1/2}$; and

mixtures thereof.

30. Composition according to either of claims **28** and **29**, characterized in that the non-silicone-based liquid fatty phase contains less than 50% by weight of silicone-based liquid organic compounds having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 $(MPa)^{1/2}$.

31. Composition according to one of claims 28 to 30, characterized in that the non-silicone-based liquid fatty phase does not contain silicone-based liquid organic compounds.

32. Composition according to one of claims 6 to 31, characterized in that the macromonomer is a carbon-based macromonomer.

33. Composition according to the preceding claim, characterized in that the carbon-based macromonomer is selected from:

(i) linear or branched C_8-C_{22} alkyl acrylate or methacrylate homopolymers and copolymers having a polymerizable end group selected from vinyl or (meth)acrylate groups;

(ii) polyolefins having a polymerizable ethylenically unsaturated end group.

34. Composition according to claim 33, characterized in that the carbon-based macromonomer is selected from:

(i) poly(2-ethylhexyl acrylate) macromonomers with a mono(meth)acrylate end group; poly(dodecyl acrylate) macromonomers with a mono(meth)acrylate end group; poly(dodecyl methacrylate) macromonomers; poly(stearyl acrylate) macromonomers with a mono(meth)acrylate end group; poly(stearyl methacrylate) macromonomers with a mono(meth)acrylate end group;

(ii) polyethylene macromonomers, polypropylene macromonomers, macromonomers of polyethylene/polypropylene copolymer, macromonomers of polyethylene/polybutylene copolymer, polyisobutylene macromonomers, polybutadiene macromonomers, polyisoprene macromonomers, polybutadiene macromonomers, poly(ethylene/butylene)-polyisoprene macromonomers, these macromonomers having a (meth)acrylate end group.

35. Composition according to claim 34, characterized in that the carbon-based macromonomer is selected from:

(i) poly(2-ethylhexyl acrylate) macromonomers with a mono(meth)acrylate end group, poly(dodecyl acrylate) macromonomers with a mono(meth)acrylate end group;

(ii) poly(ethylene/butylene) methacrylate.

36. Composition according to claim 35, characterized in that the grafted polymer is selected from the polymers obtained by polymerization:

of methyl acrylate and of a polyethylene/polybutylene macromonomer containing a methacrylate end group, in particular in a solvent chosen from isododecane, isononyl isononanoate, octyldodecanol, diisostearyl malate and a C_{12}-C_{15} alkyl benzoate;

of methoxyethyl acrylate and of a polyethylene/polybutylene macromonomer containing a methacrylate end group, in particular in isododecane;

of methyl acrylate/methyl methacrylate monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group, in particular in isododecane;

of methyl acrylate/acrylic acid monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group, in particular in isododecane;

of methyl acrylate/dimethylaminoethyl methacrylate monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group, in particular in isododecane;

of methyl acrylate/2-hydroxyethyl methacrylate monomers and of a polyethylene/polybutylene macromonomer containing a methacrylate end group, in particular in isododecane.

37. Composition according to any one of claims 28 to 36, characterized in that the grafted polymer is a non-silicone-based grafted polymer.

38. Composition according to the preceding claim, characterized in that the non-silicone-based grafted polymer contains predominantly a carbon-based macromonomer and optionally contains not more than 7% by weight of silicone-based macromonomer.

39. Composition according to claim 37 or 38, characterized in that the non-silicone-based grafted polymer is free of silicone-based macromonomer.

40. Composition according to one of claims 1 to 27, characterized in that the liquid fatty phase is a silicone-based liquid fatty phase.

41. Composition according to claim 40, characterized in that the silicone-based liquid fatty phase is composed of at least 50% by weight of at least one silicone-based organic liquid compound selected from silicone-based organic liquid compounds having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 $(MPa)^{1/2}$.

42. Composition according to either of claims **40** and **41**, characterized in that the silicone-based organic liquid compound comprises a volatile silicone oil.

43. Composition according to claim 42, characterized in that the volatile silicone oil is selected from octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane and mixtures thereof.

44. Composition according to one of claims **30** and **41** to **43**, characterized in that the silicone-based organic liquid compound comprises a non-volatile silicone oil.

45. Composition according to the preceding claim, characterized in that the non-volatile silicone oil is selected from non-volatile polydialkylsiloxanes; polydimethylsiloxanes comprising alkyl, alkoxy or phenyl groups, which are pendent or at the end of a silicone chain, these groups containing from 2 to 24 carbon atoms; phenyl silicones; polysiloxanes modified with fatty acids (especially of C_8-C_{20}), fatty alcohols (especially of C_8-C_{20}) or polyoxyalkylenes (especially polyoxyethylene and/or polyoxypropylene); amino polysiloxanes; polysiloxanes containing hydroxyl groups; fluoro polysiloxanes comprising a fluorinated group that is pendent or at the end of a silicone chain, containing from 1 to 12 carbon atoms, all or some of the hydrogen atoms of which are replaced with fluorine atoms; and mixtures thereof.

46. Composition according to one of the preceding claims, characterized in that the liquid fatty phase contains less than 50% by weight of non-silicone-based liquid organic compounds.

47. Composition according to claim 29 or 46, characterized in that the non-silicone-based organic liquid compound having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 $(MPa)^{1/2}$ is selected from carbon-based oils, hydrocarbon-based oils and fluoro oils, alone or in a mixture; linear, branched and/or cyclic alkanes, optionally volatile; esters, and especially linear, branched or cyclic esters having at least 6 carbon atoms; ketones, and especially ketones having at least 6 carbon atoms; ethers, and especially ethers having at least 6 carbon atoms.

48. Composition according to claim 29, characterized in that the monoalcohols having a total solubility parameter according to the Hansen solubility space of less than or equal to 20 $(MPa)^{1/2}$ are selected from aliphatic fatty monoalcohols having 6 to 30 carbon atoms, the hydrocarbon chain containing no substitution group, and especially oleyl alcohol, octyldodecanol, decanol and linoleyl alcohol.

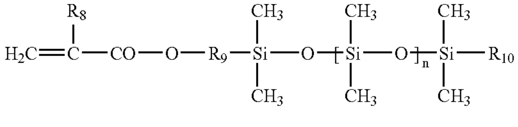
49. Composition according to claims 40 to 45, characterized in that the liquid fatty phase contains no non-silicone-based liquid organic compounds.

50. Composition according to one of claims **6** and **40** to **48**, characterized in that the macromonomer is a silicone-based macromonomer.

51. Composition according to claim 50, characterized in that the silicone-based macromonomer is an organopolysiloxane macromonomer, preferably a polydimethylsiloxane macromonomer.

52. Composition according to claim 50 or 51, characterized in that the silicone-based macromonomer is selected from the macromonomers of formula (II) below:

(II)



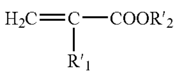
$$H_2C=\overset{R_8}{C}-CO-O-R_9-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-R_{10}$$

in which R_8 denotes a hydrogen atom or a methyl group; R_9 denotes a divalent hydrocarbon group having from 1 to 10 carbon atoms and optionally contains one or two ether bonds —O—; R_{10} denotes an alkyl group having from 1 to 10 carbon atoms, in particular from 2 to 8 carbon atoms; n denotes an integer ranging from 1 to 300, preferably ranging from 3 to 200 and preferentially ranging from 5 to 100.

53. Composition according to claim 5 and either of claims 50 to 51, characterized in that the grafted acrylic polymer is obtainable by free-radical polymerization in the polymerization medium:

of a main acrylic monomer selected from C_1-C_3 alkyl (meth)acrylates, alone or in a mixture, and optionally one or more additional acrylic monomers selected from acrylic acid, methacrylic acid and alkyl (meth)acrylates of formula (I):

(I)



$$H_2C=\underset{R'_1}{C}-COOR'_2$$

in which:

R_{11} denotes a hydrogen atom or a methyl group;

R_{12} represents

a linear or branched alkyl group containing from 1 to 6 carbon atoms, the said group containing in its chain one or more oxygen atoms and/or containing one or more substituents selected from —OH, halogen atoms (F, Cl, Br, I) and —NR'R", where R' and R", which are identical or different, are selected from C_1-C_3 linear or branched alkyls;

a cyclic alkyl group containing from 3 to 6 carbon atoms, it being possible for the said group to contain in its chain one or more oxygen atoms and/or to contain one or more substituents selected from OH and halogen atoms (F, Cl, Br, I);

and salts thereof, to form the said insoluble skeleton;

and of a silicone-based macromonomer.

54. Composition according to the preceding claim, characterized in that R_{12} denotes a group selected from methoxyethyl, ethoxyethyl, trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, dimethylaminoethyl, diethylaminoethyl and dimethylaminopropyl groups.

55. Composition according to claim 50 or 51, characterized in that the main acrylic monomer is selected from methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate and mixtures thereof.

56. Composition according to claim 50, characterized in that the main acrylic monomer is selected from methyl acrylate, methyl methacrylate, ethyl acrylate and mixtures thereof.

57. Composition according to one of claims 50 to 53, characterized in that the additional acrylic monomer is selected from (meth)acrylic acid, methoxyethyl (meth)acrylate, ethoxyethyl (meth)acrylate, trifluoroethyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate and salts thereof.

58. Composition according to the preceding claim, characterized in that the additional acrylic monomer is selected from acrylic acid and methacrylic acid.

59. Composition according to claim 49, characterized in that the macromonomer is selected from polydimethylsiloxanes containing a mono(meth)acrylate end group, and especially monomethacryloyloxypropyl polydimethylsiloxanes.

60. Composition according to one of claims **5** and **37** to **56**, characterized in that the grafted acrylic polymer is selected from the polymers obtained by polymerization:

of methyl acrylate and a monomethacryloyloxypropyl polydimethylsiloxane macromonomer having a weight-average molecular weight ranging from 800 to 6000, in particular in decamethylcyclopentasiloxane or phenyl trimethicone;

of methyl acrylate, acrylic acid and a monomethacryloyloxypropyl polydimethylsiloxane macromonomer having a weight-average molecular weight ranging from 800 to 6000, in particular in decamethylcyclopentasiloxane or phenyl trimethicone.

61. Composition according to any one of claims 40 to 60, characterized in that the grafted polymer is a silicone-based grafted polymer.

62. Composition according to the preceding claim, characterized in that the silicone-based grafted polymer contains predominantly a silicone-based macromonomer and optionally contains not more than 7% by weight of carbon-based macromonomer.

63. Composition according to claim 61 or 62, characterized in that the silicone-based grafted polymer is free of carbon-based macromonomer.

64. Composition according to one of the preceding claims, characterized in that the grafted ethylenic polymer has a weight-average molecular mass (Mw) of between 10 000 and 300 000, especially between 20 000 and 200 000, more preferably between 25 000 and 150 000.

65. Composition according to one of the preceding claims, characterized in that the particles of grafted ethylenic polymer have an average size ranging from 10 to 400 nm, preferably ranging from 20 to 200 nm.

66. Composition according to one of the preceding claims, characterized in that the grafted ethylenic polymer is a film-forming polymer.

67. Lipcare and/or lip makeup composition comprising a dispersion of particles of a grafted ethylenic polymer in a liquid fatty phase and at least one pulverulent colorant selected in particular from pigments, nacres or other fillers having an optical effect and mixtures thereof.

68. Composition according to the preceding claim, characterized in that it comprises a dispersion of particles of a grafted ethylenic polymer in a liquid fatty phase as defined according to one of claims 3 to 60.

69. Composition according to any one of the preceding claims, characterized in that the grafted ethylenic polymer is present in the composition in an amount, in terms of solids content, ranging from 1% to 66.5% by weight relative to the total weight of the composition, preferably ranging from 6% to 45% and better still ranging from 8% to 40% by weight.

70. Composition according to any one of the preceding claims, characterized in that it contains from 0.1% to 50% by weight of waxes, relative to the total weight of the composition, and preferably from 1% to 30% by weight.

71. Composition according to any one of the preceding claims, characterized in that it comprises a cosmetic ingredient selected from vitamins, trace elements, softeners, sequestrants, perfumes, alkalifying or acidifying agents, preservatives, surfactants, sunscreens, antioxidants and mixtures thereof.

72. Cosmetic composition according to any one of the preceding claims, characterized in that it is in the form of a paste or stick.

73. Cosmetic composition according to any one of the preceding claims, characterized in that it is in anhydrous form.

74. Cosmetic assembly comprising:

a) a container delimiting at least one compartment, the said container being closed by a closing member; and

b) a composition disposed within the said compartment, the composition being in accordance with any one of the preceding claims.

75. Cosmetic assembly according to claim 74, characterized in that the container is formed, at least in part, of at least one thermoplastic material.

76. Cosmetic assembly according to claim 74, characterized in that the container is formed, at least in part, of at least one non-thermoplastic material, in particular of glass or of metal.

77. Assembly according to any one of claims 74 to 76, characterized in that, with the container in its closed position, the closing member is screwed onto the container.

78. Assembly according to any one of claims 74 to 77, characterized in that, with the container in its closed position, the closing member is coupled to the container other than by screwing, in particular by snap fastening, adhesive bonding or welding.

79. Cosmetic method of making up or non-therapeutically caring for the lips, comprising the application to the lips of a composition according to any one of claims 1 to 73.

80. Use of a composition according to any one of claims 1 to 73 to give a non-transfer deposit, in particular a non-transfer makeup deposit on the lips.

81. Use of a sufficient amount of a dispersion, in a liquid fatty phase, of a grafted ethylenic polymer in a cosmetic composition to give a deposit on the lips that has a transfer of less than or equal to 35%.

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