(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau

(43) International Publication Date
22 June 2017 (22.06.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/102359 Al

(51) International Patent Classification:
A61K 8/29 (2006.01) ***A61Q 1/02*** (2006.01)
A61K 8/36 (2006.01)

(21) International Application Number:
PCT/EP20 16/07945 1

(22) International Filing Date:
1 December 2016 (01 .12.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1562601 17 December 201 5 (17. 12.2015) FR
1562607 17 December 201 5 (17. 12.2015) FR

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(81) Designated States *(unless otherwise indicated, for every kind cf national protection available):* AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

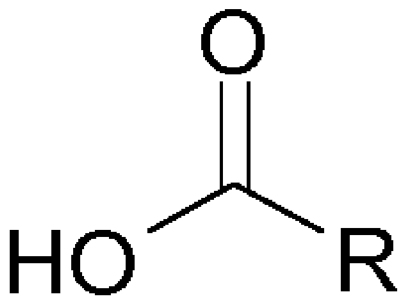
(84) Designated States *(unless otherwise indicated, for every kind cf regional protection available):* ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration cf the time limit for amending the claims and to be republished in the event cf receipt cf amendments (Rule 48.2(h))*

(54) Title: COMPOSITION OF GEL/GEL TYPE BASED ON HYDROPHOBIC COATED PIGMENTS AND A LIQUID FATTY ACID AND/OR A GLYCOL COMPOUND



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(57) Abstract: The present invention relates to a composition for coating keratin materials, more particularly for making up and/or caring for keratin materials, containing: - at least one aqueous phase gelled with at least one hydrophilic gelling agent selected from synthetic polymeric gelling agents, mixed silicates, fumed silicas, and mixtures thereof; and - at least one oily phase gelled with at least one lipophilic gelling agent; said phases forming therein a macroscopically homogeneous mixture and said composition also comprising: - at least one hydrophobic-coated pigment; and - at least one liquid fatty acid of formula (1) below: in which R is chosen from: a) a saturated, branched C14-C22, preferably Cis, alkyl group, or b) an alkyl group comprising at least one linear or branched C_{14}-C_{22}, preferably C_{18}, double bond; and/or - at least one glycol compound of formula (2) below: CH_3- $[CH_2CH_2]$m-[COO]„ — CH_2-CH(OH)-CH $_2$0 H in which: - m is between 2 and 4 - n is equal to 0 or 1; said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2); said gelled aqueous phase comprising at least one synthetic polymeric gelling agent and said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2).

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Composition of gel/gel type based on hydrophobic coated pigments and a liquid fatty acid and/or a glycol compound

The present invention is directed towards proposing for the field of caring for and/or making up keratin materials, especially the skin and/or the lips, and in particular the skin and keratin fibres, especially the eyebrows, a novel galenical form that is most particularly advantageous with regard to its technical performance and the sensations it affords the user during its application thereto, in particular to the skin.

The term "keratin materials" especially means the skin, the lips, the eyebrows and/or the eyelashes, in particular the skin and/or the eyebrows, and preferably the skin.

Cosmetic compositions, for example foundations, are commonly used to give the skin an aesthetic colour, but also to hide and/or unify imperfections of the skin relief such as wrinkles and/or fine lines and/or scars. In this regard, many solid or fluid, anhydrous or non-anhydrous formulations have been developed to date.

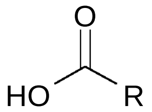
Multi-phase compositions exist at the present time, which are advantageous as regards the makeup properties they impart, especially a matt effect and coverage, and persistence of the makeup.

"Gel-gel" compositions have already been proposed in the cosmetics field and are particularly advantageous as alternatives to emulsions, which have a tendency to give a substantial greasy and tacky sensation, lack of freshness and lack of lightness for the textures obtained. Formulations of this type combine a gelled aqueous phase with a gelled oily phase. Thus, gel/gel formulations are described in Almeida et al., Pharmaceutical Development and Technology, 2008, 13:487, tables 1 and 2, page 488; WO 99/65455; BRPI 0405758-9; WO 99/62497; JP 2005-1 12834 and WO 2008/081 175, FR 2 984 736, FR 3 002 444, FR 3 004 343, WO 14/1 28 680, WO201 4/1 28679 and WO 14/1 28 678. However, these formulations are not entirely satisfactory. Specifically, the use of particular materials such as hydrophobic-treated pigments in high contents in the fatty phase of compositions of gel/gel type has a tendency to increase the viscosity of said fatty phase. A substantial difference in viscosity between the gel of the aqueous phase and the gel of the fatty phase has a tendency to lead to compositions of gel/gel type that are macroscopically non-homogeneous: the highly concentrated pigmented oily gel disperses in macro-domains which are then visible to the naked eye and gives the product an unaesthetic appearance as a lack of smoothness and/or lack of gloss. These macroscopic heterogeneities may lead to degradation of the sensory perception on application (i.e.: freshness, lightness, emollience, comfort, coverage of imperfections) and also to a loss of stability of the composition over time.

There thus remains a need to find novel formulations of the gel-gel type which give good makeup properties such as a matt effect, good coverage, good sensory properties such as freshness and lightness on application and also good persistence over time without the drawbacks mentioned previously as macroscopic heterogeneities .

The Applicant has discovered, surprisingly, that this objective can be achieved with a composition, especially comprising a physiologically acceptable medium, especially for coating keratin materials, more particularly for making up and/or caring for keratin materials, such as the skin, containing:

- at least one aqueous phase gelled with at least one hydrophilic gelling agent selected from synthetic polymeric gelling agents, mixed silicates, fumed silicas, and mixtures thereof ; and
- at least one oily phase gelled with at least one lipophilic gelling agent; said phases forming therein a macroscopically homogeneous mixture and said composition also comprising:
- at least one hydrophobic-coated pigment; and
- at least one liquid fatty acid of formula (1) below:



in which R is chosen from:

a) a saturated, branched CM-C22, preferably C18, alkyl group, or

b) an alkyl group comprising at least one linear or branched CM-C22, preferably C18, double bond ; and/or

- at least one glycol compound of formula (1) below:

$$CH_3\text{-}[CH_2CH_2]_m\text{-}[COO]_n\text{-}CH_2\text{-}CH(OH)CH_2OH \qquad (1)$$

in which:

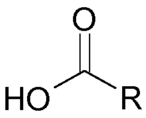
- m is between 2 and 4
- n is equal to 0 or 1 ;

said gelled aqueous phase comprising at least one synthetic polymeric gelling agent and said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2).

This discovery forms the basis of the invention.

Thus, according to one of its aspects, the present invention relates to a composition, especially comprising a physiologically acceptable medium, especially for coating keratin materials, more particularly for making up and/or caring for keratin materials, such as the skin, containing:

- at least one aqueous phase gelled with at least one hydrophilic gelling agent selected from synthetic polymeric gelling agents, mixed silicates, fumed silicas, and mixtures thereof ; and
- at least one oily phase gelled with at least one lipophilic gelling agent; said phases forming therein a macroscopically homogeneous mixture and said composition also comprising:
- at least one hydrophobic-coated pigment; and
- at least one liquid fatty acid of formula (1) below:



(1)

in which R is chosen from:

a) a saturated, branched **CM-C22,** preferably C18, alkyl group, or

b) an alkyl group comprising at least one linear or branched **CM-C22,** preferably C18, double bond; and/or

- at least one glycol compound of formula (2) below:

$$CH_3\text{-} [CH_2CH_2]_m\text{-} [COO]_n\text{-} CH_2\text{-}CH(OH)CH_2OH$$

(2)

in which:

- m is between 2 and 4
- n is equal to 0 or 1; said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2) ; said gelled aqueous phase comprising at least one synthetic polymeric gelling agent and said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2).

The invention also relates to a process for coating keratin materials, more particularly for making up and/or caring for keratin materials, such as the skin, characterized in that it comprises the application to the keratin materials of a composition as defined previously.

Definitions

In the context of the present invention, the term "keratin material" means especially the skin (body, face, area around the eyes), the lips, the eyelashes and the eyebrows. More particularly, the term "keratin material" means the skin.

The term "physiologically acceptable" means compatible with the skin and/or its integuments, which has a pleasant colour, odour and feel, and which does not cause any unacceptable discomfort (stinging, tautness or redness) liable to discourage the consumer from using this composition.

The term "liquid fatty acid of formula (1)" means any compound of formula (1) that is in liquid form at room temperature (25°C) and atmospheric pressure (10^5 Pa).

GEL-GEL

To begin with, it is important to note that a composition according to the invention of gel-gel type is different from an emulsion.

An emulsion is generally constituted by an oily liquid phase and an aqueous liquid phase. It is a dispersion of droplets of one of the two liquid phases in the other. The size of the droplets forming the dispersed phase of the emulsion is typically about a micrometre (0.1 to 100 μm). Furthermore, an emulsion requires the presence of a surfactant or of an emulsifier to ensure its stability over time.

In contrast, a composition according to the invention consists of a macroscopically homogeneous mixture of two immiscible gelled phases. These two phases both have a gel-type texture. This texture is especially reflected visually by a consistent and/or creamy appearance.

The term *"macroscopically homogeneous mixture"* means a mixture in which each of the gelled phases cannot be individualized by the naked eye.

More precisely, in a composition according to the invention, the gelled aqueous phase and the gelled oily phase interpenetrate and thus form a stable, consistent product. This consistency is achieved by mixing interpenetrated macrodomains. These interpenetrated macrodomains are not measurable objects. Thus, by microscope, the composition according to the invention is very different from an emulsion. A composition according to the invention cannot be characterized either as having a *"sense",* i.e. an O/W or W/O sense.

Thus, a composition according to the invention has a consistency of gel type. The stability of the composition is long-lasting without surfactant. Consequently, a composition, especially a cosmetic composition, according to the invention does not require any surfactant or silicone emulsifier to ensure its stability over time.

It is known practice from the prior art to observe the intrinsic nature of a mixture of aqueous and oily gels in a composition of gel-gel type, for example, by introducing a dyestuff either into the aqueous gelled phase or into the lipophilic gelled phase, before the formation of the composition of gel-gel type. During visual inspection, in a composition of gel-gel type, the dyestuff appears uniformly dispersed, even if the dye is present solely in the gelled aqueous phase or in the gelled oily phase. Specifically, if two different dyes of different colours are introduced, respectively, into the oily phase and into the aqueous phase, before formation of the composition of gel-gel type, the two colours may be observed as being uniformly dispersed throughout the composition of gel-gel type. This is different from an emulsion in which, if a dye, which is soluble in water or soluble in oil, is introduced, respectively, into the aqueous and oily phases, before forming the emulsion, the colour of the dye present will only be observed in the outer phase (Remington: The Science and Practice of Pharmacy, 19th Edition (1995), Chapter 21, page 282).

It is also known practice to distinguish a composition of gel-gel type from an emulsion by performing a "drop test". This test consists in demonstrating the bi-continuous nature of a composition of gel-gel type. Specifically, as mentioned previously, the consistency of a composition is obtained by means of the interpenetration of the aqueous and oily gelled domains. Consequently, the bi-continuous nature of a composition of gel-gel type may be demonstrated by means of a simple test with, respectively, hydrophilic and hydrophobic solvents. This test consists in depositing, firstly, one drop of a hydrophilic solvent on a first sample of the test composition, and, secondly, one drop of a hydrophobic solvent on a second sample of the same test composition, and in analysing the behaviour of the two drops of solvents. In the case of an O/W emulsion, the drop of hydrophilic solvent diffuses into the sample and the drop of hydrophobic solvent remains at the surface of the sample. In the case of a W/O emulsion, the drop of hydrophilic solvent remains at the surface of the sample and the drop of hydrophobic solvent diffuses throughout the sample. Finally, in the case of a composition of gel-gel type (bi-continuous system), the hydrophilic and hydrophobic drops diffuse throughout the sample.

In the case of the present invention, the test that will be preferred for distinguishing a composition of gel-gel type from an emulsion is a dilution test. Specifically, in a composition of gel-gel type, the aqueous and oily gelled domains interpenetrate and form a consistent and stable composition, in which the behaviour in water and in oil is different from the behaviour of an emulsion. Consequently, the behaviour during dilution of a composition of gel-gel type (bi-continuous system) may be compared to that of an emulsion.

More specifically, the dilution test consists in placing 40 g of product and 160 g of dilution solvent (water or oil) in a 500 ml_ plastic beaker. The dilution is performed with controlled stirring to avoid any emulsification. In particular, this is performed using a planetary mixer: Speed Mixer TM DAC400FVZ®. The speed of the mixer is set at 1500 rpm for 4 minutes. Finally, observation of the resulting sample is performed using a light microscope at a magnification of * 100 (*1 0*1 0). It may be noted that oils such as Parleam® and Xiameter PMX-200 Silicone Fluid 5CS® sold by Dow Corning are suitable as dilution solvent, in the same respect as one of the oils contained in the composition.

In the case of a composition of gel-gel type (bi-continuous system), when it is diluted in oil or in water, a heterogeneous appearance is always observed. When a composition of gel-gel type (bi-continuous system) is diluted in water, pieces of oily gel in suspension are observed, and when a composition of gel-gel type (bi-continuous system) is diluted in oil, pieces of aqueous gel in suspension are observed.

In contrast, during dilution, emulsions have a different behaviour. When an O/W emulsion is diluted in an aqueous solvent, it gradually reduces without having a heterogeneous and lumpy appearance. This same O/W emulsion, on dilution with oil, has a heterogeneous appearance (pieces of O/W emulsion suspended in the oil). When a W/O emulsion is diluted with an aqueous solvent, it has a heterogeneous appearance (pieces of W/O emulsion suspended in the water). This same W/O emulsion, when diluted in oil, gradually reduces without having a heterogeneous and lumpy appearance.

According to the present invention, the aqueous gelled phase and the oily gelled phase forming a composition according to the invention are present therein in a weight ratio ranging from 95/5 to 5/95. More preferentially, the aqueous phase and the oily phase are present in a weight ratio ranging from 30/70 to 80/20.

The ratio between the two gelled phases is adjusted according to the desired cosmetic properties.

Thus, in the case of a makeup composition, in particular for the face, it will be advantageous to favour an aqueous gelled phase/oily gelled phase weight ratio of greater than 1, especially ranging from 60/40 to 90/10, preferably ranging from 60/40 to 80/20, preferentially from 60/40 to 70/30 and even more preferentially to favour an aqueous gelled phase/oily gelled phase weight ratio of 60/40 or 70/30.

These preferred ratios are particularly advantageous for obtaining fresh and light compositions.

Advantageously, a composition according to the invention may thus be in the form of a creamy gel with a minimum stress below which it does not flow unless it has been subjected to an external mechanical stress.

As emerges from the text hereinbelow, a composition according to the invention may have a minimum threshold stress of 1.5 Pa and in particular greater than 10 Pa.
It may also advantageously have a stiffness modulus G* at least equal to 400 Pa and preferably greater than 1000 Pa.

According to an advantageous embodiment variant, the gelled phases under consideration to form a composition according to the invention may have, respectively, a threshold stress of greater than 1.5 Pa and preferably greater than 10 Pa.

Characterization of the threshold stresses is performed by oscillating rheology measurements. Methodology is proposed in the illustrative chapter of the present text.

In general, the corresponding measurements are taken at 25°C using a Haake® RS600 imposed-stress rheometer equipped with a plate-plate measuring body (60 mm diameter) fitted with an anti-evaporation device (bell jar). For each measurement, the sample is placed delicately in position and the measurements start 5 minutes after placing the sample in the jaws (2 mm). The test composition is then subjected to a stress ramp from 10^{-2} to 10^3 Pa at a set frequency of 1 Hz.

A composition according to the invention may also have a certain elasticity. This elasticity may be characterized by a stiffness modulus G* which, under this minimum stress threshold, may be at least equal to 400 Pa and preferably greater than 1000 Pa. The value G* of a composition may be obtained by subjecting the composition under consideration to a stress ramp from 10^{-2} to 10^3 Pa at a set frequency of 1 Hz.

HYDROPHILIC GELLING AGENT

For the purposes of the present invention, the term "hydrophilic gelling agent" means a compound that is capable of gelling the aqueous phase of the compositions according to the invention.

The gelling agent is hydrophilic and is thus present in the aqueous phase of the composition.

The gelling agent may be water-soluble or water-dispersible.

As stated above, the aqueous phase of a composition according to the invention is gelled with at least one hydrophilic gelling agent.

The hydrophilic gelling agent may be chosen from synthetic polymeric gelling agents, polymeric gelling agents that are natural or of natural origin, mixed silicates and fumed silicas, and mixtures thereof.

Preferably, the hydrophilic gelling agent may be chosen from synthetic polymeric gelling agents.

I. Polymeric gelling agents that are natural or of natural origin

The polymeric hydrophilic gelling agents that are suitable for use in the invention may be natural or of natural origin.

For the purposes of the invention, the term "of natural origin" is intended to denote polymeric gelling agents obtained by modification of natural polymeric gelling agents.

These gelling agents may be particulate or non-particulate.

More specifically, these gelling agents fall within the category of polysaccharides.

In general, polysaccharides may be divided into several categories.

Thus, the polysaccharides that are suitable for use in the invention may be homopolysacchandes such as fructans, glucans, galactans and mannans or heteropolysaccharides such as hemicellulose.

Similarly, they may be linear polysaccharides such as pullulan or branched polysaccharides such as gum arabic and amylopectin, or mixed polysaccharides such as starch.

More particularly, the polysaccharides that are suitable for use in the invention may be distinguished according to whether or not they are starchy.

LA. Starchy polysaccharides

As representatives of this category, mention may be made most particularly of native starches, modified starches and particulate starches.

Native starches

The starches that may be used in the present invention are more particularly macromolecules in the form of polymers consisting of elementary moieties which are anhydroglucose units (dextrose), linked via a(1 ,4) bonds of chemical formula $(C6HioO_5)n$. The number of these moieties and their assembly make it possible to distinguish amylose, a molecule formed from about 600 to 1000 linearly linked glucose units, and amylopectin, a polymer branched approximately every 25 glucose residues (a(1 ,6) bond). The total chain may include between 10 000 and 100 000 glucose residues.

Starch is described in particular in Kirk-Othmer's Encyclopaedia of Chemical Technology, 3rd edition, volume 21, pages 492-507, Wiley Interscience, 1983.

The relative proportions of amylose and of amylopectin, and their degree of polymerization, vary as a function of the botanical origin of the starches. On average, a sample of native starch consists of about 25% amylose and 75% amylopectin.

Occasionally, phytoglycogen is present (between 0 and 20% of the starch), which is an analogue of amylopectin but branched every 10 to 15 glucose residues.

Starch may be in the form of semicrystalline granules: amylopectin is organized in leaflets, amylose forms a less well organized amorphous zone between the various leaflets.

Amylose is organized in a straight helix with six glucoses per turn. It dissociates into assimilable glucose under the action of enzymes, amylases, all the more easily when it is in amylopectin form. Specifically, the helical formation does not promote the accessibility of starch to the enzymes.

Starches are generally in the form of a white powder, which is insoluble in cold water, whose elemental particle size ranges from 3 to 100 microns.

By treating it with hot water, starch paste is obtained. It is exploited in industry for its thickening and gelling properties.

The botanical origin of the starch molecules used in the present invention may be cereals or tubers. Thus, the starches are chosen, for example, from corn starch, rice starch, tapioca starch, cassava starch, barley starch, potato starch, wheat starch, sorghum starch and pea starch.

The native starches are represented, for example, by the products sold under the names C*Amilogel™, Cargill Gel™, C* Gel™, Cargill Gum™, DryGel™ and

C*Pharm Gel^{TM} by the company Cargill, under the name Corn Starch by the company Roquette, and under the name Tapioca Pure by the company National Starch.

Modified starches

The modified starches used in the composition of the invention may be modified via one or more of the following reactions: pregelatinization, degradation (acid hydrolysis, oxidation, dextrinization), substitution (esterification, etherification), crosslinking (esterification), bleaching.

More particularly, these reactions can be carried out in the following way:
- pregelatinization by splitting the starch granules (for example drying and cooking in a drying drum);
- acid hydrolysis giving rise to very rapid retrogradation on cooling;
- oxidation with strong oxidizing agents (alkaline medium, in the presence of sodium hypochlorite NaOCl for example) leading to the depolymerization of the starch molecule and to the introduction of carboxyl groups into the starch molecule (mainly oxidation of the hydroxyl group at Ce);
- dextrinization in acid medium at high temperature (hydrolysis followed by repolymerization);
- crosslinking with functional agents capable of reacting with the hydroxyl groups of the starch molecules, which will thus bond together (for example with glyceryl and/or phosphate groups);
- esterification in alkaline medium for the grafting of functional groups, especially C1-C6 acyl (acetyl), C1-C6 hydroxyalkyl (hydroxyethyl or hydroxypropyl), carboxymethyl or octenylsuccinic.

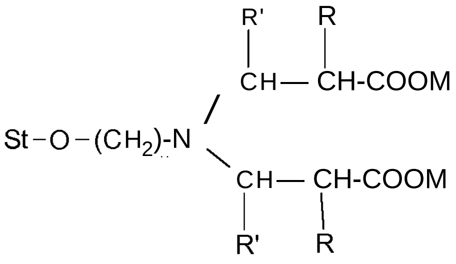
Monostarch phosphates (of the type St-O-PO-(OX)2), distarch phosphates (of the type St-O-PO-(OX)-O-St) or even tristarch phosphates (of the type St-O-PO-(O-St)$_2$) or mixtures thereof may especially be obtained by crosslinking with phosphorus compounds.

X especially denotes alkali metals (for example sodium or potassium), alkaline-earth metals (for example calcium or magnesium), ammonium salts, amine salts, for instance those of monoethanolamine, diethanolamine, triethanolamine, 3-amino-1 ,2-propanediol, or ammonium salts derived from basic amino acids such as lysine, arginine, sarcosine, ornithine or citrulline.

The phosphorus compounds can, for example, be sodium tripolyphosphate, sodium orthophosphate, phosphorus oxychloride or sodium trimetaphosphate.

According to the invention, it is also possible to use amphoteric starches, these amphoteric starches containing one or more anionic groups and one or more cationic groups. The anionic and cationic groups may be linked to the same reactive site of the starch molecule or to different reactive sites; they are preferably linked to the same reactive site. The anionic groups may be of carboxylic, phosphate or sulfate type, preferably carboxylic. The cationic groups can be of primary, secondary, tertiary or quaternary amine type.

The amphoteric starches are in particular chosen from the compounds having the following formulae:



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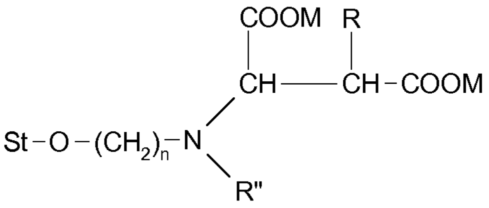

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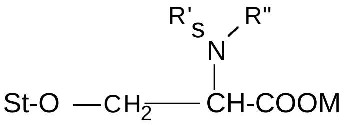
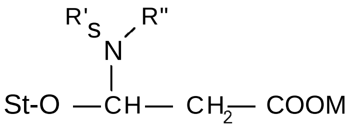


(III)

$\text{St-O}-CH_2-\overset{\overset{R'_s\quad R''}{N}}{CH}-COOM$



(IV)

$\text{St-O}-\overset{\overset{R'_s\quad R''}{N}}{CH}-CH_2-COOM$

in which:
- St-O represents a starch molecule;
- R, which may be identical or different, represents a hydrogen atom or a methyl radical;
- R', which may be identical or different, represents a hydrogen atom, a methyl radical or a -COOH group;
- n is an integer equal to 2 or 3;
- M, which may be identical or different, denotes a hydrogen atom, an alkali metal or alkaline-earth metal such as Na, K, Li or NH_4, a quaternary ammonium or an organic amine;
- R" represents a hydrogen atom or an alkyl radical containing from 1 to 18 carbon atoms.

These compounds are especially described in patents US 5 455 340 and US 4 017 460.

The starch molecules may be derived from any plant source of starch, especially such as corn, potato, oat, rice, tapioca, sorghum, barley or wheat. It is also possible to use the hydrolysates of the starches mentioned above.

The modified starches are represented, for example, by the products sold under the names C*Tex-Instant® (pregelatinized adipate), C*StabiTex-Instant® (pregelatinized phosphate), C*PolarTex-Instant (pregelatinized hydroxypropyl), C*Set (acid hydrolysis, oxidation), C*size (oxidation), C*BatterCrisp® (oxidation), C*DrySet® (dextrinization), C*TexTM (acetyl distarch adipate), C*PolarTexTM® (hydroxypropyl distarch phosphate), C* StabiTexTM® (distarch phosphate, acetyl distarch phosphate) by the company Cargill, by distarch phosphates or compounds rich in distarch phosphate such as the product sold under the references Prejel VA-70-T AGGL® (gelatinized hydroxypropyl cassava distarch phosphate) or Prejel TK1® (gelatinized cassava distarch phosphate) or Prejel 200® (gelatinized acetyl cassava distarch phosphate) by the company Avebe or Structure Zea® from National Starch (gelatinized corn distarch phosphate).

As examples of oxidized starches, use will be made especially of those sold under the name C*size® from the company Cargill.

The native or modified starches described above may be advantageously used in a proportion of from 0.1 % to 8% by weight of solids and preferably at about 1% by weight, relative to the total weight of the aqueous phase.

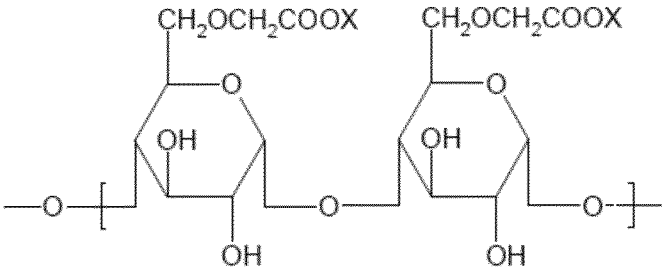
Particulate starches

Particulate starches that may be mentioned in particular include:
- starches grafted with an acrylic polymer (homopolymer or copolymer) and especially with sodium polyacrylate, for instance those sold under the names Sanfresh ST100MC® by the company Sanyo Chemical Industries or Makimousse 25®, Makimousse 12® by the company Daito Kasei (INCI name: Sodium polyacrylate starch),
- hydrolyzed starches grafted with an acrylic polymer (homopolymer or copolymer), and especially acryloacrylamide/sodium acrylate copolymer, for instance those sold under the names Water Lock A-240®, A-1 80®, B-204®, D-223®, A-1 00®, C-200® and D-223® by the company Grain Processing (INCI name: Starch/acrylamide/sodium acrylate copolymer);
- polymers based on starch, gum and cellulose derivative, such as the product containing starch and sodium carboxymethylcellulose, for instance the product sold under the name Lysorb 220® by the company Lysac.

Mention may be made most particularly of Ci-C_4 carboxyalkyl starches, also referred to hereinbelow as carboxyalkyl starch. These compounds are obtained by grafting carboxyalkyl groups onto one or more alcohol functions of starch, especially by reaction of starch and of sodium monochloroacetate in alkaline medium.

The carboxyalkyl groups are generally attached via an ether function, more particularly to carbon 1. The degree of substitution with carboxyalkyl units of the Ci-C_4 carboxyalkyl starch preferably ranges from 0.1 to 1 and more particularly from 0.1 5 to 0.5. The degree of substitution is defined according to the present invention as being the mean number of hydroxyl groups substituted with an ester or ether group per monosaccharide unit of the polysaccharide.

The carboxyalkyl starches are advantageously used in the form of salts and especially of salts of alkali metals or alkaline-earth metals such as Na, K, Li, NH_4, or salts of a quaternary ammonium or of an organic amine such as monoethanolamine, diethanolamine or triethanolamine. The **(Ci-C_4)** carboxyalkyl starches are advantageously, in the context of the present invention, carboxymethyl starches. The carboxymethyl starches preferably comprise units having the following formula:



in which X, optionally covalently bonded to the carboxylic unit, denotes a hydrogen atom, an alkali metal or alkaline-earth metal such as Na, K, Li, NH_4, a quaternary ammonium or an organic amine, for instance monoethanolamine, diethanolamine or triethanolamine.

Preferably, X denotes a cation Na^+. The carboxyalkyl starches that may be used according to the present invention are preferably non-pregelatinized carboxyalkyl starches. The carboxyalkyl starches that may be used according to the present invention are preferably partially or totally crosslinked carboxyalkyl starches.

In general, a crosslinked carboxyalkyl starch has, in contrast with a non-crosslinked carboxyalkyl starch, an increased, controllable viscosity of increased stability. The crosslinking thus makes it possible to reduce the syneresis phenomena and to increase the resistance of the gel to shear effects.

The carboxyalkyl starches under consideration according to the invention are more particularly potato carboxyalkyl starches. Thus, the carboxyalkyl starches that may be used according to the present invention are preferably sodium salts of carboxyalkyl starches, in particular a sodium salt of potato carboxymethyl starch, sold especially under the name Primojel® by the company DMV International or Glycolys® and Glycolys® LV by the company Roquette.

According to a particular mode, use will be made of the potato carboxymethyl starches sold especially under the name Glycolys® by the company Roquette. As stated previously, the **Ci-C_4** carboxyalkyl starch particles are present in the compositions according to the invention in a swollen and non-split form. This swelling may be characterized by a swelling power Q which may advantageously be between 10 and 30 ml/g and preferably between 15 and 25 ml (volume of adsorbed liquid)/g of dry particulate material.

Thus, the size of the swollen carboxyalkyl starch particles used according to the present invention generally ranges from 25 to 300 μιτι. For example, the gel Primojel® containing 10% by weight of potato carboxyalkyl starch and sodium salt in water contains more than 80% of swollen particles of this starch with a diameter of greater than 50 microns and more particularly greater than 100 microns.

According to a preferred embodiment variant of the invention, these particles are used for the preparation of the compositions according to the invention, in this swollen particulate state. To do so, these particles are advantageously used in the form of an aqueous gel either prepared beforehand or already commercially available. The gels under consideration according to the invention are advantageously translucent.

For example, a carboxymethyl starch gel such as Primojel® which is at a concentration of 10% by weight may be adjusted to the required concentration before being used for preparing the expected composition.

Such a particulate starch may be used in a proportion of from 0.1 % to 5% by weight of solids relative to the total weight of the aqueous phase, preferably from 0.5% to 2.5% by weight and in particular in a proportion of about 1.5% by weight, relative to the total weight of the aqueous phase.

According to one embodiment variant, the hydrophilic gelling agent is non-starchy.

1.B. Non-starchy polysaccharides

In general, the non-starchy polysaccharides may be chosen from polysaccharides produced by microorganisms; polysaccharides isolated from algae, and higher plant polysaccharides, such as homogeneous polysaccharides, in particular celluloses and derivatives thereof or fructosans, heterogeneous polysaccharides such as gum arabics, galactomannans, glucomannans and pectins, and derivatives thereof; and mixtures thereof.

In particular, the polysaccharides may be chosen from fructans, gellans, glucans, amylose, amylopectin, glycogen, pullulan, dextrans, celluloses and derivatives thereof, in particular methylcelluloses, hydroxyalkylcelluloses, ethylhydroxyethylcelluloses and carboxymethylcelluloses, mannans, xylans, lignins, arabans, galactans, galacturonans, alginate-based compounds, chitin, chitosans, glucuronoxylans, arabinoxylans, xyloglucans, glucomannans, pectic acids and pectins, arabinogalactans, carrageenans, agars, glycosaminoglucans, gum arabics, tragacanth gums, ghatti gums, karaya gums, locust bean gums, galactomannans such as guar gums and nonionic derivatives thereof, in particular hydroxypropyl guar, and ionic derivatives thereof, biopolysaccharide gums of microbial origin, in particular scleroglucan or xanthan gums, mucopolysaccharides, and in particular chondroitin sulfates, and mixtures thereof.

These polysaccharides may be chemically modified, especially with urea or urethane groups or by hydrolysis, oxidation, esterification, etherification, sulfation, phosphatation, amination, amidation or alkylation reaction, or by several of these modifications.

The derivatives obtained may be anionic, cationic, amphoteric or nonionic.

Advantageously, the polysaccharides may be chosen from carrageenans, in particular kappa carrageenan, gellan gum, agar-agar, xanthan gum, alginate-based compounds, in particular sodium alginate, scleroglucan gum, guar gum, inulin and pullulan, and mixtures thereof.

In general, the compounds of this type that may be used in the present invention are chosen from those described especially in Kirk-Othmer's *Encyclopedia of Chemical Technology,* Third Edition, 1982, volume 3, pp. 896-900, and volume 15, pp. 439-458, in *Polymers in Nature* by E.A. MacGregor and C.T. Greenwood, published by John Wiley & Sons, Chapter 6, pp. 240-328, 1980, in the book by Robert L. Davidson entitled *Handbook of Water-Soluble Gums and Resins* published by McGraw Hill Book Company (1980) and in *Industrial Gums - Polysaccharides and their Derivatives,* edited by Roy L. Whistler, Second Edition, published by Academic Press Inc.

Such a gelling agent may be used in a proportion of from 0.1 % to 8% by weight of solids relative to the total weight of the aqueous phase, especially from 0.1 % to 6% by weight, preferably from 0.5% to 2.5% by weight and in particular in a proportion of about 1%, or alternatively in a proportion of about 1.5% by weight, relative to the total weight of the aqueous phase.

More precisely, these polysaccharides that are suitable for use in the invention may be distinguished according to whether they are derived from microorganisms, from algae or from higher plants, and are detailed below.

Polysaccharides produced by microorganisms

Xanthan

Xanthan is a heteropolysaccharide produced on an industrial scale by the aerobic fermentation of the bacterium *Xanthomonas campestris.* Its structure consists of a main chain of β(1,4)-linked β-D-glucoses, similar to cellulose. One glucose molecule in two bears a trisaccharide side chain composed of an a-D-mannose, a β-D-glucuronic acid and a terminal β-D-mannose. The internal mannose residue is generally acetylated on carbon 6. About 30% of the terminal mannose residues bear a pyruvate group linked in chelated form between carbons 4 and 6. The charged pyruvic acids and glucuronic acids are ionizable, and are thus responsible for the anionic nature of xanthan (negative charge down to a pH equal to 1). The content of pyruvate and acetate residues varies according to the bacterial strain, the fermentation process, the conditions after fermentation and the purification steps. These groups may be neutralized in commercial products with Na^+, K^+ or

Ca^{2+} ions (Satia company, 1986). The neutralized form may be converted into the acid form by ion exchange or by dialysis of an acidic solution.

Xanthan gums have a molecular weight of between 1 000 000 and 50 000 000 and a viscosity of between 0.6 and 1.65 Pa.s for an aqueous composition containing 1% of xanthan gum (measured at 25°C on a Brookfield viscometer of LVT type at 60 rpm).

Xanthan gums are represented, for example, by the products sold under the names Rhodicare® by the company Rhodia Chimie, under the name Satiaxane™ by the company Cargill Texturizing Solutions (for the food, cosmetic and pharmaceutical industries), under the name Novaxan™ by the company ADM, and under the names Kelzan® and Keltrol® by the company CP-Kelco.

Pullulan

Pullulan is a polysaccharide consisting of maltotriose units, known under the name a(1 ,4)-a(1 ,6)-glucan. Three glucose units in maltotriose are connected via an a(1 ,4) glycoside bond, whereas the consecutive maltotriose units are connected to each other via an a(1 ,6) glycoside bond.

Pullulan is produced, for example, under the reference Pullulan PF 20 by the group Hayashibara in Japan.

Dextran and dextran sulfate

Dextran is a neutral polysaccharide not bearing any charged groups, which is biologically inert, prepared by fermentation of beet sugar containing solely hydroxyl groups.

It is possible to obtain dextran fractions of different molecular weights from native dextran by hydrolysis and purification. Dextran may in particular be in the form of dextran sulfate.

Dextran is represented, for example, by the products sold under the name Dextran® or Dextran T® by the company Pharmacosmos, or under the name Dextran 40 Powder® or Dextran 70 Powder® by the company Meito Sangyo Co. Dextran sulfate is sold by the company PK Chemical A/S under the name Dextran sulphate.

SuccinoQlycan

Succinoglycan is an extracellular polymer of high molecular weight produced by bacterial fermentation, consisting of octasaccharide repeating units (repetition of 8 sugars). Succinoglycans are sold, for example, under the name Rheozan® by the company Rhodia.

Scleroglucan

Scleroglucan is a nonionic branched homopolysaccharide consisting of β-D-glucan units. The molecules consist of a linear main chain formed from D-glucose units linked via β(1,3) bonds and of which one in three is linked to a side D-glucose unit via a β(1,6) bond.

A more complete description of scleroglucans and of their preparation may be found in patent US 3 301 848.

Scleroglucan is sold, for example, under the name Amigel® by the company Alban Muller, or under the name Actigum™ CS by the company Cargill.

Gellan gum

Gellan gum is an anionic linear heteropolyoside based on oligoside units composed of 4 saccharides (tetra-oside). D-Glucose, L-rhamnose and D-glucuronic acid in 2:1:1 proportions are present in gellan gum in the form of monomer elements.

It is sold, for example, under the name Kelcogel CG LA® by the company CP Kelco.

Polysaccharides isolated from algae

Galactans

The polysaccharide according to the invention may be a galactan chosen especially from agar and carrageenans.

Carrageenans are anionic polysaccharides constituting the cell walls of various red algae (Rhodophyceae) belonging to the Gigartinacae, Hypneaceae, Furcellariaceae and Polyideaceae families. They are generally obtained by hot aqueous extraction from natural strains of said algae. These linear polymers, formed by disaccharide units, are composed of two D-galactopyranose units linked alternately by a(1,3) and β(1,4) bonds. They are highly sulfated polysaccharides (20-50%) and the a-D-galactopyranosyl residues may be in 3,6-anhydro form. Depending on the number and position of sulfate-ester groups on the repeating disaccharide of the molecule, several types of carrageenans are distinguished, namely: kappa-carrageenans, which bear one sulfate-ester group, iota-carrageenans, which bear two sulfate-ester groups, and lambda-carrageenans, which bear three sulfate-ester groups.

Carrageenans are composed essentially of potassium, sodium, magnesium, triethanolamine and/or calcium salts of polysaccharide sulfate esters.

Carrageenans are sold especially by the company SEPPIC under the name Solagum®, by the company Gelymar under the names Carragel®, Carralact® and Carrasol®, by the company Cargill, under the names Satiagel™ and Satiagum™, and by the company CP-Kelco under the names Genulacta®, Genugel® and Genuvisco®.

Galactans of agar type are galactose polysaccharides contained in the cell wall of some of these species of red algae (rhodophyceae). They are formed from a polymer group whose base backbone is a β(1,3) D-galactopyranose and a(1,4) L 3-6 anhydrogalactose chain, these units repeating regularly and alternately. The differences within the agar family are due to the presence or absence of solvated methyl or carboxyethyl groups. These hybrid structures are generally present in variable percentage, depending on the species of algae and the harvest season.

Agar-agar is a mixture of polysaccharides (agarose and agaropectin) of high molecular mass, between 40 000 and 300 000 $g.mol^{-1}$. It is obtained by manufacturing algal extraction liquors, generally by autoclaving, and by treating these liquors which comprise about 2% of agar-agar, so as to extract the latter.

Agar is produced, for example, by the group B&V Agar Producers under the names Gold Agar,® Agarite® and Grand Agar® by the company Hispanagar, and under the names Agar-Agar®, QSA® (Quick Soluble Agar), and Puragar® by the company Setexam.

Furcellaran

Furcellaran is obtained commercially from red algae *Furcellaria fasztigiata.* Furcellaran is produced, for example, by the company Est-Agar.

Alqinate-based compound

For the purposes of the invention, the term *"alginate-based compound'* means alginic acid, alginic acid derivatives and salts of alginic acid (alginates) or of said derivatives.

Preferably, the alginate-based compound is water-soluble.

Alginic acid, a natural substance resulting from brown algae or certain bacteria, is a polyuronic acid composed of 2 uronic acids linked by 1,4-glycosidic bonds: β-D-mannuronic (M) acid and a-L-glucuronic (G) acid.

Alginic acid is capable of forming water-soluble salts (alginates) with alkali metals such as sodium, potassium or lithium, substituted cations of lower amines and of ammonium such as methylamine, ethanolamine, diethanolamine or triethanolamine. These alginates are water-soluble in aqueous medium at a pH equal to 4, but dissociate into alginic acid at a pH below 4.

This (these) alginate-based compound(s) are capable of crosslinking in the presence of at least one crosslinking agent, by fornnation of ionic bonds between said alginate-based compound(s) and said crosslinking agent(s). The fornnation of multiple crosslinking between several molecules of said alginate-based compound(s) leads to the formation of a water-insoluble gel.

Use is preferably made of alginate-based compounds that have a weight-average molecular mass ranging from 10 000 to 1 000 000, preferably from 15 000 to 500 000 and better still from 20 000 to 250 000.

According to a preferred embodiment, the alginate-based compound is alginic acid and/or a salt thereof.

Advantageously, the alginate-based compound is an alginate salt, and preferably sodium alginate.

The alginate-based compound may be chemically modified, especially with urea or urethane groups or by hydrolysis, oxidation, esterification, etherification, sulfatation, phosphatation, amination, amidation or alkylation reaction, or by several of these modifications.

The derivatives obtained may be anionic, cationic, amphoteric or nonionic.

The alginate-based compounds that are suitable for use in the invention may be represented, for example, by the products sold under the names Kelcosol®, Satialgine™, Cecalgum™ or Algogel™ by the company Cargill Products, under the name Protanal™ by the company FMC Biopolymer, under the name Grindsted® Alginate by the company Danisco, under the name Kimica Algin® by the company Kimica, and under the names Manucol® and Manugel® by the company ISP.

Polysaccharides of higher plants

This category of polysaccharides may be divided into homogeneous polysaccharides (only one saccharide species) and heterogeneous polysaccharides composed of several types of saccharides.

a) Homogeneous polysaccharides and derivatives thereof

The polysaccharide according to the invention may be chosen from celluloses and derivatives or fructosans.

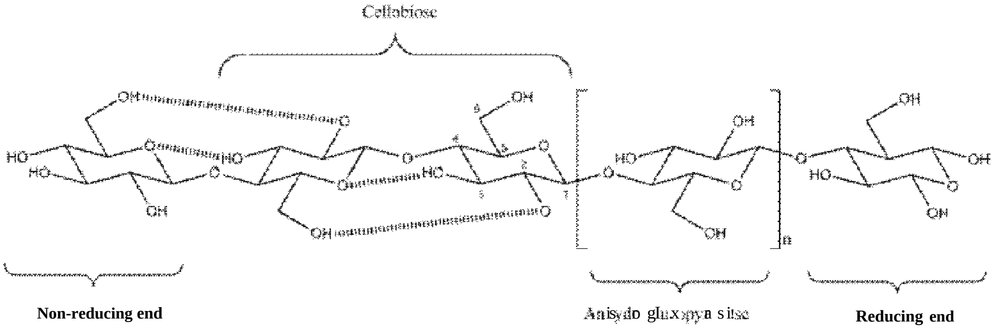
Cellulose and derivatives

The polysaccharide according to the invention may also be a cellulose or a derivative thereof, especially cellulose ethers or esters (e.g.: methylcellulose, carboxymethylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxymethylpropylcellulose, cellulose acetate, cellulose nitrate, nitrocellulose).

The invention may also contain a cellulose-based associative polymer. According to the invention, the term "cellulose-based compound" means any polysaccharide compound bearing in its structure linear sequences of anhydroglucopyranose residues (AGU) linked together via β(1,4) bonds. The repeating unit is the cellobiose dimer. The AGUs are in chair conformation and bear 3 hydroxyl functions: 2 secondary alcohols (in position 2 and 3) and a primary alcohol (in position 6). The polymers thus formed combine together via intermolecular bonds of hydrogen bond type, thus giving the cellulose a fibrillar structure (about 1500 molecules per fibre).

The degree of polymerization differs enormously depending on the origin of the cellulose; its value may range from a few hundred to several tens of thousands.

Cellulose has the following chemical formula:



The hydroxyl groups of cellulose may react partially or totally with various chemical reagents to give cellulose derivatives having intrinsic properties. The cellulose derivatives may be anionic, cationic, amphoteric or nonionic. Among these derivatives, cellulose ethers, cellulose esters and cellulose ester ethers are distinguished.

Among the nonionic cellulose ethers, mention may be made of alkylcelluloses such as methylcelluloses and ethylcelluloses; hydroxyalkylcelluloses such as hydroxymethylcelluloses, hydroxyethylcelluloses and hydroxypropylcelluloses; and mixed hydroxy-alkylalkylcelluloses such as hydroxypropylmethylcelluloses, hydroxyethylmethylcelluloses, hydroxyethylethylcelluloses and hydroxybutylmethylcelluloses.

Among the anionic cellulose ethers, mention may be made of carboxyalkyl celluloses and salts thereof. By way of example, mention may be made of carboxymethylcelluloses, carboxymethylmethylcelluloses and carboxymethylhydroxyethylcelluloses and sodium salts thereof.

Among the cationic cellulose ethers, mention may be made of crosslinked or non-crosslinked, quaternized hydroxyethylcelluloses.

The quaternizing agent may in particular be glycidyltrimethylammonium chloride or a fatty amine such as laurylamine or stearylamine. Another cationic cellulose ether that may be mentioned is hydroxyethylcellulosehydroxypropyltrimethylammonium.

The quaternized cellulose derivatives are, in particular:
- quaternized celluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyi or alkylaryl groups comprising at least 8 carbon atoms, or mixtures thereof,
- quaternized hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyi or alkylaryl groups comprising at least 8 carbon atoms, or mixtures thereof.

The alkyl radicals borne by the above quaternized celluloses or hydroxyethylcelluloses preferably contain from 8 to 30 carbon atoms. The aryl radicals preferably denote phenyl, benzyl, naphthyl or anthryl groups.

Examples of quaternized alkylhydroxyethylcelluloses containing C8-C30 fatty chains that may be indicated include the products Quatrisoft LM 200®, Quatrisoft LM-X 529-1 8-A®, Quatrisoft LM-X 529-1 8B® (C12 alkyl) and Quatrisoft LM-X 529-8® (C18 alkyl) sold by the company Amerchol and the products Crodacel QM®, Crodacel QL® (C12 alkyl) and Crodacel QS® (C18 alkyl) sold by the company Croda.

Among the cellulose derivatives, mention may also be made of:
- celluloses modified with groups comprising at least one
fatty chain, for instance hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl groups, especially of C8-C22, arylalkyi and alkylaryl groups, such as Natrosol Plus Grade 330 CS® (C16 alkyls) sold by the company Aqualon, and
- celluloses modified with polyalkylene glycol alkylphenyl ether groups, such as the product Amercell Polymer HM-1 500® (nonylphenyl polyethylene glycol (15) ether) sold by the company Amerchol.

Among the cellulose esters are mineral esters of cellulose (cellulose nitrates, sulfates, phosphates, etc.), organic cellulose esters (cellulose monoacetates, triacetates, amidopropionates, acetatebutyrates, acetatepropionates and acetatetrimellitates, etc.), and mixed organic/mineral esters of cellulose, such as cellulose acetatebutyrate sulfates and cellulose acetatepropionate sulfates. Among the cellulose ester ethers, mention may be made of hydroxypropylmethylcellulose phthalates and ethylcellulose sulfates.

The cellulose-based compounds of the invention may be chosen from unsubstituted celluloses and substituted celluloses.

The celluloses and derivatives are represented, for example, by the products sold under the names Avicel® (microcrystalline cellulose, MCC) by the company FMC Biopolymers, under the name Cekol® (carboxymethylcellulose) by the company Noviant (CP-Kelco), under the name Akucell AF (sodium carboxymethylcellulose) by the company Akzo Nobel, under the name Methocel™ (cellulose ethers) and EthocelTM® (ethylcellulose) by the company Dow, and under the names Aqualon® (carboxymethylcellulose and sodium carboxymethylcellulose), Benecel® (methylcellulose), BlanoseTM (carboxymethylcellulose), Culminal® (methylcellulose, hydroxypropylmethylcellulose), Klucel® (hydroxypropylcellulose), Polysurf® (cetylhydroxyethylcellulose) and Natrosol® CS (hydroxyethylcellulose) by the company Hercules Aqualon.

Fructosans

The polysaccharide according to the invention may especially be a fructosan chosen from inulin and derivatives thereof (especially dicarboxy and carboxymethyl inulins).

Fructans or fructosans are oligosaccharides or polysaccharides comprising a sequence of anhydrofructose units optionally combined with several saccharide residues other than fructose. Fructans may be linear or branched. Fructans may be products obtained directly from a plant or microbial source or alternatively products whose chain length has been modified (increased or decreased) by fractionation, synthesis or hydrolysis, in particular enzymatic. Fructans generally have a degree of polymerization from 2 to about 1000 and preferably from 2 to about 60.

Three groups of fructans are distinguished. The first group corresponds to products whose fructose units are for the most part linked via $\beta(2,1)$ bonds. These are essentially linear fructans such as inulins.

The second group also corresponds to linear fructoses, but the fructose units are essentially linked via $\beta(2,6)$ bonds. These products are levans.

The third group corresponds to mixed fructans, i.e. containing $\beta(2,6)$ and $\beta(2,1)$ sequences. These are essentially branched fructans, such as graminans.

The preferred fructans in the compositions according to the invention are inulins. Inulin may be obtained, for example, from chicory, dahlia or Jerusalem artichoke, preferably from chicory.

In particular, the polysaccharide, especially the inulin, has a degree of polymerization from 2 to about 1000 and preferably from 2 to about 60, and a degree of substitution of less than 2 on the basis of one fructose unit.

The inulin used for this invention is represented, for example, by the products sold under the name BeneoTM inulin® by the company Orafti, and under the name Frutafit® by the company Sensus.

b) Heterogeneous polysaccharides and derivatives thereof

The polysaccharides that may be used according to the invention may be gums, for instance cassia gum, karaya gum, konjac gum, gum tragacanth, tara gum, acacia gum or gum arabic.

Gum arabic

Gum arabic is a highly branched acidic polysaccharide which is in the form of mixtures of potassium, magnesium and calcium salts. The monomer elements of the free acid (arabic acid) are D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid.

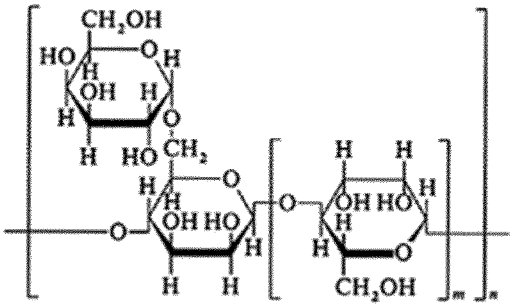
Galactomannans (guar, locust bean, fenugreek, tara gum) and derivatives (guar phosphate, hydroxypropyl guar, etc.)

Galactomannans are nonionic polyosides extracted from the endosperm of leguminous seeds, of which they constitute the storage carbohydrate.

Galactomannans are macromolecules consisting of a main chain of β(1,4) linked D-mannopyranose units, bearing side branches consisting of a single D-galactopyranose unit a(1,6) linked to the main chain. The various galactomannans differ, firstly, by the proportion of a-D-galactopyranose units present in the polymer, and secondly by significant differences in terms of distribution of galactose units along the mannose chain.

The mannose/galactose (M/G) ratio is about 2 for guar gum, 3 for tara gum and 4 for locust bean gum.

Galactomannans have the following chemical structure:



m « 3: Locust beam pan
$m = 1$: Guar gum
$m = 2$: T«ra gum

Guar

Guar gum is characterized by a mannose/galactose ratio of the order of 2/1. The galactose group is regularly distributed along the mannose chain.

The guar gums that may be used according to the invention may be nonionic, cationic or anionic. According to the invention, use may be made of chemically modified or unmodified nonionic guar gums.

The unmodified nonionic guar gums are, for example, the products sold under the names Vidogum GH®, Vidogum G® and Vidocrem® by the company Unipektin and under the name Jaguar® by the company Rhodia, under the name Meypro® Guar by the company Danisco, under the name Viscogum™ by the company Cargill, and under the name Supercol® guar gum by the company Aqualon.

The hydrolysed nonionic guar gums that may be used according to the invention are represented, for example, by the products sold under the name Meyprodor® by the company Danisco.

The modified nonionic guar gums that may be used according to the invention are preferably modified with C_1-C_6 hydroxyalkyi groups, among which mention may be made, for example, of hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl groups.

Such nonionic guar gums optionally modified with hydroxyalkyi groups are sold, for example, under the trade names Jaguar HP60®, Jaguar HP 105® and Jaguar HP 120® (hydroxypropyl guar) by the company Rhodia or under the name N-Hance® HP (hydroxypropyl guar) by the company Aqualon.

The cationic galactomannan gums preferably have a cationic charge density of less than or equal to 1.5 meq./g, more particularly between 0.1 and 1 meq./g. The charge density may be determined by the Kjeldahl method. It generally corresponds to a pH of the order of 3 to 9.

In general, for the purposes of the present invention, the term *"cationic galactomannan gum"* means any galactomannan gum containing cationic groups and/or groups that can be ionized into cationic groups.

The preferred cationic groups are chosen from those comprising primary, secondary, tertiary and/or quaternary amine groups.

The cationic galactomannan gums used generally have a weight-average molecular mass of between 500 and 5×10^6 approximately and preferably between 10^3 and 3×10^6 approximately.

The cationic galactomannan gums that may be used according to the present invention are, for example, gums comprising tri(C_i-C_4)alkylammonium cationic groups. Preferably, 2% to 30% by number of the hydroxyl functions of these guar gums bear trialkylammonium cationic groups.

Mention may very particularly be made, among these trialkylammonium groups, of the trimethylammonium and triethylammonium groups.

Even more preferentially, these groups represent from 5% to 20% by weight relative to the total weight of the modified galactomannan gum.

According to the invention, the cationic galactomannan gum is preferably a guar gum comprising hydroxypropyltrimethylammonium groups, i.e. a guar gum modified, for example, with 2,3-epoxypropyltrimethylammonium chloride.

These galactomannan gums, in particular guar gums modified with cationic groups are products already known per se and are, for example, described in patents US 3 589 578 and US 4 031 307. Such products are moreover sold especially under the trade names Jaguar EXCEL®, Jaguar C13 S®, Jaguar C 15®, Jaguar C 17® and Jaguar C162 (Guar Hydroxypropyltrimonium Chloride) by the company Rhodia, under the name Amilan® Guar (Guar Hydroxypropyltrimonium Chloride) by the company Degussa, and under the name N-Hance® 3000 (Guar Hydroxypropyltrimonium Chloride) by the company Aqualon.

The anionic guar gums that may be used according to the invention are polymers comprising groups derived from carboxylic, sulfonic, sulfenic, phosphoric, phosphonic or pyruvic acid. The anionic group is preferably a carboxylic acid group. The anionic group may also be in the form of an acid salt, especially a sodium, calcium, lithium or potassium salt.

The anionic guar gums that may be used according to the invention are preferentially carboxymethyl guar derivatives (carboxymethyl guar or carboxymethyl hydroxypropyl guar).

Locust bean

Locust bean gum is extracted from the seeds of the locust bean tree *(Ceratonia siliqua).*

The unmodified locust bean gum that may be used in this invention is sold, for example, under the name Viscogum™ by the company Cargill, under the name Vidogum L by the company Unipektin and under the name Grinsted® LBG by the company Danisco.

The chemically modified locust bean gums that may be used in this invention may be represented, for example, by the cationic locust beans sold under the name Catinal CLB® (locust bean hydroxypropyltrimonium chloride) by the company Toho.

Tara gum

The tara gum that may be used in the context of this invention is sold, for example, under the name Vidogum SP® by the company Unipektin.

Glucomannans (konjac gum)

Glucomannan is a polysaccharide of high molecular weight (500 000 < Mglucomannan < 2 000 000) composed of D-mannose and D-glucose units with a branch every 50 or 60 units approximately. It is found in wood, but is also the main constituent of konjac gum. Konjac *(Amorphophallus konjac)* is a plant of the Araceae family.

The products that may be used according to the invention are sold, for example, under the names Propol® and Rheolex® by the company Shimizu.

LM and HM pectins, and derivatives

Pectins are linear polymers of a-D-galacturonic acid (at least 65%) linked in positions 1 and 4 with a certain proportion of carboxylic groups esterified with a methanol group. About 20% of the sugars constituting the pectin molecule are neutral sugars (L-rhamnose, D-glucose, D-galactose, L-arabinose, D-xylose). L-Rhamnose residues are found in all pectins, incorporated into the main chain in positions 1,2.
Uronic acid molecules bear carboxyl functions. This function gives pectins the capacity for exchanging ions, when they are in COO^- form. Divalent ions (in particular calcium) have the capacity of forming ionic bridges between two carboxyl groups of two different pectin molecules.

In the natural state, a certain proportion of the carboxylic groups are esterified with a methanol group. The natural degree of esterification of a pectin may range between 70% (apple, lemon) and 10% (strawberry) depending on the source used. Using pectins with a high degree of esterification, it is possible to hydrolyse the $-COOCH_3$ groups so as to obtain weakly esterified pectins. Depending on the proportion of methylated or non-methylated monomers, the chain is thus more or less acidic. HM (high-methoxy) pectins are thus defined as having a degree of esterification of greater than 50%, and LM (low-methoxy) pectins are defined as having a degree of esterification of less than 50%.

In the case of amidated pectins, the -OCH3 group is substituted with an $-NH_2$ group.

Pectins are especially sold by the company Cargill under the name Unipectine™, by the company CP-Kelco under the name Genu, and by Danisco under the name Grinsted Pectin®.

Other polysaccharides

Among the other polysaccharides that may be used according to the invention, mention may also be made of chitin (poly-N-acetyl-D-glucosamine, β(1,4)-2-acetamido-2-deoxy-D-glucose), chitosan and derivatives (chitosan-beta-glycerophosphate, carboxymethylchitin, etc.) such as those sold by the company France-Chitine; glycosaminoglycans (GAG) such as hyaluronic acid, chondroitin sulfate, dermatan sulfate, keratan sulfate, and preferably hyaluronic acid; xylans (or arabinoxylans) and derivatives.

Arabinoxylans are polymers of xylose and arabinose, all grouped under the name *pentosans.*

Xylans consist of a main chain of β(1,4) linked D-xylose units and on which are found three substituents (Rouau & Thibault, 1987): acid units, a-L-arabinofuranose units, side chains which may contain arabinose, xylose, galactose and glucuronic acid.

According to this variant, the polysaccharide is preferably hyaluronic acid, or a salt thereof such as the sodium salt (sodium hyaluronate).

II. Synthetic polymeric gelling agents

For the purposes of the invention, the term "synthetic" means that the polymer is neither naturally existing nor a derivative of a polymer of natural origin.

The synthetic polymeric hydrophilic gelling agent under consideration according to the invention may or may not be particulate.

For the purposes of the invention, the term "particulate" means that the polymer is in the form of particles, preferably spherical particles.

As emerges from the text hereinbelow, the polymeric hydrophilic gelling agent is advantageously chosen from crosslinked acrylic homopolymers or copolymers; associative polymers, in particular associative polymers of polyurethane type; polyacrylamides and crosslinked and/or neutralized 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers; modified or unmodified carboxyvinyl polymers, and mixtures thereof, especially as defined below.

II.A. Particulate synthetic polymeric gelling agents

They are preferably chosen from crosslinked polymers.

They may especially be crosslinked acrylic homopolymers or copolymers, which are preferably partially neutralized or neutralized, and which are in particulate form.

According to one embodiment, the particulate gelling agent according to the present invention is chosen from crosslinked sodium polyacrylates. Preferably, it has in the dry or non-hydrated state a mean size of less than or equal to 100 μιτι and preferably less than or equal to 50 μιτι. The mean size of the particles corresponds to the mass-average diameter (D50) measured by laser particle size analysis or another equivalent method known to those skilled in the art.

Thus, preferably, the particulate gelling agent according to the present invention is chosen from crosslinked sodium polyacrylates, preferably in the form of particles with a mean size (or mean diameter) of less than or equal to 100 microns, more preferably in the form of spherical particles.

As examples of crosslinked sodium polyacrylates, mention may be made of those sold under the brand names Octacare X100®, X110® and RM100® by the company Avecia, those sold under the names Flocare GB300® and Flosorb 500® by the company SNF, those sold under the names Luquasorb 1003®, Luquasorb 1010®, Luquasorb 1280® and Luquasorb 1110® by the company BASF, those sold under the names Water Lock G400® and G430® (INCI name: Acrylamide/Sodium acrylate copolymer) by the company Grain Processing.

Mention may also be made of crosslinked polyacrylate microspheres, for instance those sold under the name Aquakeep® 10 SH NF by the company Sumitomo Seika.

Such gelling agents may be used in a proportion of from 0.1 % to 5% by weight of solids relative to the total weight of the aqueous phase, especially from 0.5% to 2% by weight and in particular in a proportion of about from 0.8% to 1.7% by weight, relative to the total weight of the aqueous phase.

II.B. Non-particulate synthetic polymeric gelling agents

This family of gelling agents may be detailed under the following subfamilies:
1. Associative polymers,
2. Polyacrylamides and crosslinked and/or neutralized 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers, and
3. Modified or unmodified carboxyvinyl polymers.

II.B.1 Associative polymers

For the purposes of the present invention, the term *"associative polymer"* means any amphiphilic polymer comprising in its structure at least one fatty chain and at least one hydrophilic portion. The associative polymers in accordance with the present invention may be anionic, cationic, nonionic or amphoteric.

Associative anionic polymers

Among the associative anionic polymers that may be mentioned are those comprising at least one hydrophilic unit, and at least one fatty-chain allyl ether unit, more particularly those whose hydrophilic unit is formed by an unsaturated ethylenic anionic monomer, more particularly by a vinylcarboxylic acid and most particularly by an acrylic acid or a methacrylic acid or mixtures thereof, and whose fatty-chain allyl ether unit corresponds to the monomer of formula (I) below:

$$CH_2 = C(R')CH_2 O B_n R \quad (I)$$

in which R' denotes H or CH_3, B denotes an ethylenoxy radical, n is zero or denotes an integer ranging from 1 to 100, R denotes a hydrocarbon-based radical chosen from alkyl, arylalkyl, aryl, alkylaryl and cycloalkyl radicals, containing from 8 to 30 carbon atoms, preferably 10 to 24 carbon atoms and even more particularly from 12 to 18 carbon atoms.

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

Among the associative anionic polymers that may also be mentioned are maleic anhydride/C3o-C38 a-olefin/alkyl maleate terpolymers, such as the product (maleic anhydride/C3o-C38 a-olefin/isopropyl maleate copolymer) sold under the name Performa V 1608 by the company Newphase Technologies.

Among the associative anionic polymers, mention may be made, according to a preferred embodiment, of copolymers comprising among their monomers an α,β-monoethylenically unsaturated carboxylic acid and an ester of an α,β-monoethylenically unsaturated carboxylic acid and of an oxyalkylenated fatty alcohol.

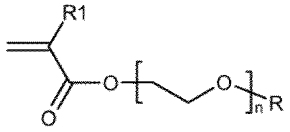
Preferentially, these compounds also comprise as monomer an ester of an α,β-monoethylenically unsaturated carboxylic acid and of a Ci-C$_4$ alcohol.

Examples of compounds of this type that may be mentioned include Aculyn 22® sold by the company Rohm & Haas, which is a methacrylic acid/ethyl acrylate/oxyalkylenated stearyl methacrylate (comprising 20 EO units) terpolymer or Aculyn 28® (methacrylic acid/ethyl acrylate/oxyethylenated behenyl methacrylate (25 EO) terpolymer).

Associative anionic polymers that may also be mentioned include anionic polymers comprising at least one hydrophilic unit of olefinic unsaturated carboxylic acid type, and at least one hydrophobic unit exclusively of (Cio-C3o)alkyl ester of unsaturated carboxylic acid type. Examples that may be mentioned include the anionic polymers described and prepared according to patents US 3 915 921 and US 4 509 949.

Associative anionic polymers that may also be mentioned include anionic terpolymers.

The anionic terpolymer used according to the invention is a linear or branched and/or crosslinked terpolymer, of at least one monomer (1) bearing an acid function in free form, which is partially or totally salified with a nonionic monomer (2) chosen from N,N-dimethylacrylamide and 2-hydroxyethyl acrylate and at least one polyoxyethylenated alkyl acrylate monomer (3) of formula (I) below:



(I)

in which R1 represents a hydrogen atom, R represents a linear or branched C2-C8 alkyl radical and n represents a number ranging from 1 to 10.

The term *"branched polymer"* denotes a non-linear polymer which bears pendent chains so as to obtain, when this polymer is dissolved in water, a high degree of entanglement leading to very high viscosities, at a low speed gradient.

The term *"crosslinked polymer"* denotes a non-linear polymer which is in the form of a three-dimensional network that is insoluble in water but swellable in water, leading to the production of a chemical gel.

The acid function of the monomer (1) is especially a sulfonic acid or phosphonic acid function, said functions being in free or partially or totally salified form.

The monomer (1) may be chosen from styrenesulfonic acid, ethylsulfonic acid and 2-methyl-2-[(1-oxo-2-propenyl]amino]-1-propanesulfonic acid (also known as acryloyldimethyl taurate), in free or partially or totally salified form. It is present in the anionic terpolymer preferably in molar proportions of between 5 mol% and 95 mol% and more particularly between 10 mol% and 90 mol%. The monomer (1) will more particularly be 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propanesulfonic acid in free or partially or totally salified form.

The acid function in partially or totally salified form will preferably be an alkali metal salt such as a sodium or potassium salt, an ammonium salt, an amino alcohol salt such as a monoethanolamine salt, or an amino acid salt such as a lysine salt.

The monomer (2) is preferably present in the anionic terpolymer in molar proportions of between 4.9 mol% and 90 mol%, more particularly between 9.5 mol% and 85 mol% and even more particularly between 19.5 mol% and 75 mol%.

In formula (I), examples of linear **Cs-Ci6** alkyl radicals that may be mentioned include octyl, decyl, undecyl, tridecyl, tetradecyl, pentadecyl and hexadecyl.

In formula (I), examples of branched **Cs-Ci6** alkyl radicals that may be mentioned include 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, 4-methylpentyl, 5-methylhexyl, 6-methylheptyl, 15-methylpentadecyl, 16-methylheptadecyl and 2-hexyloctyl.

According to a particular form of the invention, in formula (I), R denotes a C12-C16 alkyl radical.

According to a particular form of the invention, in formula (I), n ranges from 3 to 5.

Tetraethoxylated lauryl acrylate will more particularly be used as monomer of formula (I).

The monomer (3) of formula (I) is preferably present in the anionic terpolymer in molar proportions ranging from 0.1 mol% to 10 mol% and more particularly from 0.5 mol% to 5 mol%.

According to a particular mode of the invention, the anionic terpolymer is crosslinked and/or branched with a diethylenic or polyethylenic compound in the proportion expressed relative to the total amount of monomers used, from 0.005 mol% to 1 mol%, preferably from 0.01 mol% to 0.5 mol% and more particularly from 0.01 mol% to 0.25 mol%.

The crosslinking agent and/or branching agent is preferably chosen from ethylene glycol dimethacrylate, diallyloxyacetic acid or a salt thereof, such as sodium diallyloxyacetate, tetraallyloxyethane, ethylene glycol diacrylate, diallylurea, triallylamine, trimethylolpropane triacrylate and methylenebis(acrylamide), or mixtures thereof.

The anionic terpolymer may contain additives such as complexing agents, transfer agents or chain-limiting agents.

Use will be made more particularly of an anionic terpolymer of 2-methyl-2-[(1 -oxo-2-propenyl)amino]-1 -propanesulfonic acid partially or totally salified in the form of the ammonium salt, N,N-dimethylacrylamide and tetraethoxylated lauryl acrylate crosslinked with trimethylolpropane triacrylate, of INCI name Polyacrylate Crosspolymer-6, such as the product sold under the trade name Sepimax Zen® by the company SEPPIC.

Cationic associative polymers

Cationic associative polymers that may be mentioned include polyacrylates bearing amine side groups.

The polyacrylates bearing quaternized or non-quaternized amine side groups contain, for example, hydrophobic groups of the type such as Steareth-20 (polyoxyethylenated (20) stearyl alcohol).

Examples of polyacrylates bearing amino side chains that may be mentioned are the polymers 8781-121B or 9492-103 from the company National Starch.

Nonionic associative polymers

The nonionic associative polymers may be chosen from:
- copolymers of vinylpyrrolidone and of fatty-chain hydrophobic monomers;
- copolymers of C_1-C_6 alkyl methacrylates or acrylates and of amphiphilic monomers comprising at least one fatty chain;
- copolymers of hydrophilic methacrylates or acrylates and of hydrophobic monomers comprising at least one fatty chain, for instance the polyethylene glycol methacrylate/lauryl methacrylate copolymer;
- associative polyurethanes.

Associative polyurethanes are nonionic block copolymers comprising in the chain both hydrophilic blocks usually of polyoxyethylene nature (referred to as polyether polyurethanes), and hydrophobic blocks that may be aliphatic sequences alone and/or cycloaliphatic and/or aromatic sequences.

In particular, these polymers comprise at least two hydrocarbon-based lipophilic chains containing from 6 to 30 carbon atoms, separated by a hydrophilic block, the hydrocarbon-based chains possibly being pendent chains or chains at the end of the hydrophilic block. In particular, it is possible for one or more pendent chains to be envisaged. In addition, the polymer may comprise a hydrocarbon-based chain at one end or at both ends of a hydrophilic block.

Associative polyurethanes may be block polymers, in triblock or multiblock form. The hydrophobic blocks may thus be at each end of the chain (for example: triblock copolymer containing a hydrophilic central block) or distributed both at the ends and in the chain (for example: multiblock copolymer). These polymers may also be graft polymers or star polymers. Preferably, the associative polyurethanes are triblock copolymers in which the hydrophilic block is a polyoxyethylene chain comprising from 50 to 1000 oxyethylene groups. In general, associative polyurethanes comprise a urethane bond between the hydrophilic blocks, whence arises the name.

According to one preferred embodiment, a nonionic associative polymer of polyurethane type is used as gelling agent.

As examples of nonionic fatty-chain polyurethane polyethers that may be used in the invention, it is also possible to use Rheolate® FX 1100 (Steareth-1 00/PEG 136/HDI (hexamethyl diisocyanate) copolymer), Rheolate® 205 containing a urea function, sold by the company Elementis, or Rheolate® 208, 204 or 212, and also Acrysol® RM 184 or Acrysol® RM 2020.

Mention may also be made of the product Elfacos® T210 containing a C_{12}-C_{14} alkyl chain, and the product Elfacos® T21 2 containing a C_{16-18} alkyl chain (PPG-14 Palmeth-60 Hexyl Dicarbamate), from Akzo.

The product DW 1206B® from Rohm & Haas containing a C_{20} alkyl chain and a urethane bond, sold at a solids content of 20% in water, may also be used.

Use may also be made of solutions or dispersions of these polymers, especially in water or in aqueous/alcoholic medium. Examples of such polymers that may be mentioned are Rheolate® 255, Rheolate® 278 and Rheolate® 244 sold by the company Elementis. The products DW 1206F and DW 1206J sold by the company Rohm & Haas may also be used.

The associative polyurethanes that may be used according to the invention are in particular those described in the article by G. Fonnum, J. Bakke and Fk. Hansen, Colloid Polym. Sci., 271 , 380-389 (1993).

Even more particularly, according to the invention, use may also be made of an associative polyurethane that may be obtained by polycondensation of at least three compounds comprising (i) at least one polyethylene glycol comprising from 150 to 180 mol of ethylene oxide, (ii) stearyl alcohol or decyl alcohol, and (iii) at least one diisocyanate.

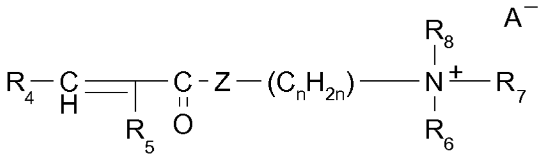
Such polyurethane polyethers are sold in particular by the company Rohm & Haas under the names Aculyn® 46 and Aculyn® 44. Aculyn® 46 is a polycondensate of polyethylene glycol containing 150 or 180 mol of ethylene oxide, of stearyl alcohol and of methylenebis(4-cyclohexyl isocyanate) (SMDI), at 15% by weight in a matrix of maltodextrin (4%) and water (81 %), and Aculyn® 44 is a polycondensate of polyethylene glycol containing 150 or 180 mol of ethylene oxide, of decyl alcohol and of methylenebis(4-cyclohexyl isocyanate) (SMDI), at 35% by weight in a mixture of propylene glycol (39%) and water (26%).

Use may also be made of solutions or dispersions of these polymers, especially in water or in aqueous/alcoholic medium. Examples of such polymers that may be mentioned include SER AD FX1010®, SER AD FX1035® and SER AD 107® from the company Elementis, and Rheolate® 255, Rheolate® 278 and Rheolate® 244 sold by the company Elementis. Use may also be made of the products Aculyn® 44, Aculyn® 46, DW 1206F® and DW 1206J®, and also Acrysol® RM 184 from the company Rohm & Haas, or alternatively Borchigel LW 44® from the company Borchers, and mixtures thereof.

Amphoteric associative polymers

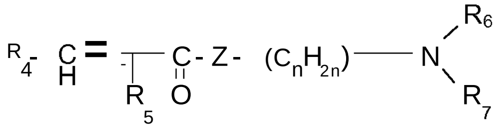
Among the associative amphoteric polymers of the invention, mention may be made of crosslinked or non-crosslinked, branched or unbranched amphoteric polymers, which may be obtained by copolymerization:

1) of at least one monomer of formula (IVa) or (IVb):



$$R_4-\underset{H}{C}=\underset{R_5}{C}-\underset{\overset{\|}{O}}{C}-Z-(C_nH_{2n})-\overset{R_8}{\underset{R_6}{N^+}}-R_7 \quad A^-$$

(IVa)



$$R_4-\underset{H}{C}=\underset{R_5}{C}-\underset{\overset{\|}{O}}{C}-Z-(C_nH_{2n})-N\begin{matrix}R_6\\R_7\end{matrix}$$

(IVb)

in which R_4 and R_5, which may be identical or different, represent a hydrogen atom or a methyl radical,

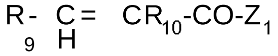
R6, R7 and Rs, which may be identical or different, represent a linear or branched alkyl radical containing from 1 to 30 carbon atoms;

Z represents an NH group or an oxygen atom;

n is an integer from 2 to 5;

A^- is an anion derived from an organic or mineral acid, such as a methosulfate anion or a halide such as chloride or bromide;

2) of at least one monomer of formula (V):

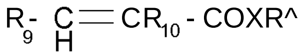


$$R_9-\underset{H}{C}=CR_{10}-CO-Z_1 \qquad (V)$$

in which R_9 and Rio, which may be identical or different, represent a hydrogen atom or a methyl radical;

Z_1 represents a group OH or a group NHC(CH$_3$)2CH$_2$SO3H;

3) of at least one monomer of formula (VI):



$$R_9-\underset{H}{C}=CR_{10}-COXR^\wedge \qquad (VI)$$

in which R_9 and Rio, which may be identical or different, represent a hydrogen atom or a methyl radical, X denotes an oxygen or nitrogen atom and Rn denotes a linear or branched alkyl radical containing from 1 to 30 carbon atoms;

4) optionally at least one crosslinking or branching agent; at least one of the monomers of formula (IVa), (IVb) or (VI) comprising at least one fatty chain containing from 8 to 30 carbon atoms and said compounds of the monomers of formulae (IVa), (IVb), (V) and (VI) possibly being quaternized, for example with a Ci-C$_4$ alkyl halide or a Ci-C$_4$ dialkyl sulfate.

The monomers of formulae (IVa) and (IVb) of the present invention are preferably chosen from the group consisting of:

- dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate,
- diethylaminoethyl methacrylate, diethylaminoethyl acrylate,
- dimethylaminopropyl methacrylate, dimethylaminopropyl acrylate,
- dimethylaminopropylmethacrylamide, dimethylaminopropylacrylamide,

which are optionally quaternized, for example with a Ci-C$_4$ alkyl halide or a Ci-C$_4$ dialkyl sulfate.

More particularly, the monomer of formula (IVa) is chosen from acrylamidopropyltrimethylammonium chloride and methacrylamidopropyltrimethylammonium chloride.

The compounds of formula (V) of the present invention are preferably chosen from the group formed by acrylic acid, methacrylic acid, crotonic acid, 2-methylcrotonic acid, 2-acrylamido-2-methylpropanesulfonic acid and 2-methacrylamido-2-methylpropanesulfonic acid. More particularly, the monomer of formula (V) is acrylic acid.

The monomers of formula (VI) of the present invention are preferably chosen from the group formed by C12-C22 and more particularly C16-C18 alkyl acrylates or methacrylates.

The crosslinking or branching agent is preferably chosen from N,N'-methylenebisacrylamide, triallylmethylammonium chloride, allyl methacrylate, n-methylolacrylamide, polyethylene glycol dimethacrylates, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate and allyl sucrose.

The polymers according to the invention may also contain other monomers such as nonionic monomers and in particular Ci-C$_4$ alkyl acrylates or methacrylates.

The ratio of the number of cationic charges/anionic charges in these amphoteric polymers is preferably equal to about 1.

The weight-average molecular weights of the associative amphoteric polymers represents a weight-average molecular mass of greater than 500, preferably ranging from 10 000 to 10 000 000 and even more preferentially from 100 000 to 8 000 000.

Preferably, the associative amphoteric polymers of the invention contain from 1 mol% to 99 mol%, more preferentially from 20 mol% to 95 mol% and even more preferentially from 25 mol% to 75 mol% of compound(s) of formula (IVa) or (IVb). They also preferably contain from 1 mol% to 80 mol%, more preferentially from 5 mol% to 80 mol% and even more preferentially from 25 mol% to 75 mol% of compound(s) of formula (V). The content of compound(s) of formula (VI) is preferably from 0.1 mol% to 70 mol%, more preferentially from 1 mol% to 50 mol% and even more preferentially from 1 mol% to 10 mol%. The crosslinking or branching agent, when it is present, is preferably from 0.0001 mol% to 1 mol% and even more preferentially from 0.0001 mol% to 0.1 mol%.

Preferably, the mole ratio between the compound(s) of formula (IVa) or (IVb) and the compound(s) of formula (V) ranges from 20/80 to 95/5 and more preferentially from 25/75 to 75/25.

The associative amphoteric polymers according to the invention are described, for example, in patent application WO 98/44012.

The amphoteric polymers that are particularly preferred according to the invention are chosen from acrylic acid/acrylamidopropyltrimethylammonium chloride/stearyl methacrylate copolymers.

According to a preferred embodiment, the associative polymer is chosen from nonionic associative polymers and more particularly from associative polyurethanes, such as Steareth-100/PEG-136/HDI Copolymer sold under the name Rheolate FX 1100® by Elementis.

Such an associative polymer is advantageously used in a proportion of from 0.1 % to 8% by weight of solids and preferably from 0.5% to 4% by weight, relative to the total weight of the aqueous phase.

II.B.2 Polyacrylamides and 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers

The polymers used that are suitable as aqueous gelling agent for the invention may be crosslinked or non-crosslinked homopolymers or copolymers comprising at least the 2-acrylamidomethylpropanesulfonic acid (AMPS®) monomer, in a form partially or totally neutralized with a mineral base other than aqueous ammonia, such as sodium hydroxide or potassium hydroxide.

They are preferably totally or almost totally neutralized, i.e. at least 90% neutralized.

These AMPS® polymers according to the invention may be crosslinked or non-crosslinked.

When the polymers are crosslinked, the crosslinking agents may be chosen from the polyolefinically unsaturated compounds commonly used for crosslinking polymers obtained by radical polymerization.

Examples of crosslinking agents that may be mentioned include divinylbenzene, diallyl ether, dipropylene glycol diallyl ether, polyglycol diallyl ethers, triethylene glycol divinyl ether, hydroquinone diallyl ether, ethylene glycol or tetraethylene glycol di(meth)acrylate, trimethylolpropane triacrylate, methylenebisacrylamide, methylenebismethacrylamide, triallylamine, triallyl cyanurate, diallyl maleate, tetraallylethylenediamine, tetraallyloxyethane, trimethylolpropane diallyl ether, allyl (meth)acrylate, allylic ethers of alcohols of the sugar series, or other allyl or vinyl ethers of polyfunctional alcohols, and also the allylic esters of phosphoric and/or vinylphosphonic acid derivatives, or mixtures of these compounds.

According to one preferred embodiment of the invention, the crosslinking agent is chosen from methylenebisacrylamide, allyl methacrylate and trimethylolpropane triacrylate (TMPTA). The degree of crosslinking generally ranges from 0.01 mol% to 10 mol% and more particularly from 0.2 mol% to 2 mol% relative to the polymer.

The AMPS® polymers that are suitable for use in the invention are water-soluble or water-dispersible. In this case, they are:
- either "homopolymers" comprising only AMPS® monomers and, if they are crosslinked, one or more crosslinking agents such as those defined above;
- or copolymers obtained from AMPS® and from one or more hydrophilic or hydrophobic ethylenically unsaturated monomers and, if they are crosslinked, one or more crosslinking agents such as those defined above. When said copolymers comprise hydrophobic ethylenically unsaturated monomers, these monomers do not comprise a fatty chain and are preferably present in small amounts.

For the purpose of the present invention, the term *"fatty chain"* means any hydrocarbon-based chain comprising at least 7 carbon atoms.

The term *"water-soluble or water-dispersible"* means polymers which, when introduced into an aqueous phase at 25°C, at a mass concentration equal to 1%, make it possible to obtain a macroscopically homogeneous and transparent solution, i.e. a solution with a maximum light transmittance value, at a wavelength equal to 500 nm, through a sample 1 cm thick, of at least 60% and preferably of at least 70%.

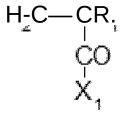
The *"homopolymers "* according to the invention are preferably crosslinked and neutralized, and they may be obtained according to the preparation process comprising the following steps:

(a) the monomer such as AMPS in free form is dispersed or dissolved in a solution of tert-butanol or of water and tert-butanol;
(b) the monomer solution or dispersion obtained in (a) is neutralized with one or more mineral or organic bases, preferably aqueous ammonia NH_3, in an amount making it possible to obtain a degree of neutralization of the sulfonic acid functions of the polymer ranging from 90% to 100%;
(c) the crosslinking monomer(s) are added to the solution or dispersion obtained in (b);
(d) a standard free-radical polymerization is performed in the presence of free-radical initiators at a temperature ranging from 10 to 150°C; the polymer precipitates in the tert-butanol-based solution or dispersion.

The water-soluble or water-dispersible AMPS® copolymers according to the invention contain water-soluble ethylenically unsaturated monomers, hydrophobic monomers, or mixtures thereof.

The water-soluble comonomers may be ionic or nonionic.

Among the ionic water-soluble comonomers, examples that may be mentioned include the following compounds, and salts thereof:
- (meth)acrylic acid,
- styrenesulfonic acid,
- vinylsulfonic acid and (meth)allylsulfonic acid,
- vinylphosphonic acid,
- maleic acid,
- itaconic acid,
- crotonic acid,
- water-soluble vinyl monomers of formula (A) below:

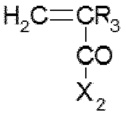


$$H_2C{=}CR_1(CO{-}X_1) \quad (A)$$

in which:
- Ri is chosen from H, $-CH_3$, -C2H5 and -C3H7,
- Xi is chosen from:
- alkyl oxides of type -OR2 where R_2 is a linear or branched, saturated or unsaturated hydrocarbon-based radical containing from 1 to 6 carbon atoms, substituted with at least one sulfonic (-SO3$^-$) and/or sulfate (-SO$_4^-$) and/or phosphate
(-PO4H2-) group.

Among the nonionic water-soluble comonomers, examples that may be mentioned include:
- (meth)acrylamide,
- N-vinylacetamide and N-methyl-N-vinylacetamide,
- N-vinylformamide and N-methyl-N-vinylformamide,
- maleic anhydride,
- vinylamine,

- N-vinyllactams comprising a cyclic alkyl group containing from 4 to 9 carbon atoms, such as N-vinylpyrrolidone, N-butyrolactam and N-vinylcaprolactam,
- vinyl alcohol of formula $CH_2=CHOH$,
- water-soluble vinyl monomers of formula (B) below:

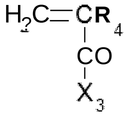


$$H_2C=C(R_3)-CO-X_2 \quad (B)$$

in which:
- R_3 is chosen from H, $-CH_3$, $-C_2H_5$ and $-C_3H_7$,
- X_2 is chosen from alkyl oxides of the type $-OR_4$ where R_4 is a linear or branched, saturated or unsaturated hydrocarbon-based radical containing from 1 to 6 carbon atoms, optionally substituted with a halogen (iodine, bromine, chlorine or fluorine) atom; a hydroxyl (-OH) group; ether.

Mention is made, for example, of glycidyl (meth)acrylate, hydroxyethyl methacrylate, and (meth)acrylates of ethylene glycol, of diethylene glycol or of polyalkylene glycol.

Among the hydrophobic co-monomers without a fatty chain, mention may be made, for example, of:
- styrene and derivatives thereof, such as 4-butylstyrene, a-methylstyrene and vinyltoluene;
- vinyl acetate of formula $CH_2=CH-OCOCH_3$;
- vinyl ethers of formula $CH_2=CHOR$ in which R is a linear or branched, saturated or unsaturated hydrocarbon-based radical containing from 1 to 6 carbons;
- acrylonitrile;
- caprolactone;
- vinyl chloride and vinylidene chloride;
- silicone derivatives, which, after polymerization, result in silicone polymers such as methacryloxypropyltris(trimethylsiloxy)silane and silicone methacrylamides;
- hydrophobic vinyl monomers of formula (C) below:



$$H_2C=C(R_4)-CO-X_3 \quad (C)$$

in which:
- R_4 is chosen from H, $-CH_3$, $-C_2H_5$ and $-C_3H_7$;
- X_3 is chosen from:
- alkyl oxides of the type $-OR_5$ where R_5 is a linear or branched, saturated or unsaturated hydrocarbon-based radical containing from 1 to 6 carbon atoms.

Mention is made, for example, of methyl methacrylate, ethyl methacrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate, cyclohexyl acrylate, isobornyl acrylate and 2-ethylhexyl acrylate.

The water-soluble or water-dispersible AMPS® polymers of the invention preferably have a molar mass ranging from 50 000 to 10 000 000 g/mol, preferably from 80 000 to 8 000 000 g/mol, and even more preferably from 100 000 to 7 000 000 g/mol.

As water-soluble or water-dispersible AMPS® homopolymers suitable for use in the invention, mention may be made, for example, of crosslinked or non-crosslinked polymers of sodium acrylamido-2-methylpropanesulfonate, such as that used in the commercial product Simulgel 800 (CTFA name: Sodium Polyacryloyldimethyl Taurate), crosslinked ammonium acrylamido-2-methylpropanesulfonate polymers (INCI name: Ammonium Polyacryldimethyltauramide) such as those described in patent EP 0 815 928 B1 and such as the product sold under the trade name Hostacerin AMPS® by the company Clariant.

As water-soluble or water-dispersible AMPS copolymers in accordance with the invention, examples that may be mentioned include:

- crosslinked acrylamide/sodium acrylamido-2-methylpropanesulfonate copolymers, such as that used in the commercial product Sepigel 305® (CTFA name: Polyacrylamide**/Ci3-Ci**$_4$ Isoparaffin/ Laureth-7) or that used in the commercial product sold under the name Simulgel 600® (CTFA name: Acrylamide/Sodium acryloyldimethyltaurate/lsohexadecane/Polysorbate-80) by the company SEPPIC;
- copolymers of AMPS® and of vinylpyrrolidone or vinylformamide, such as that used in the commercial product sold under the name Aristoflex AVC® by the company Clariant (CTFA name: Ammonium Acryloyldimethyltaurate/VP copolymer) but neutralized with sodium hydroxide or potassium hydroxide;
- copolymers of AMPS® and of sodium acrylate, for instance the AMPS®/sodium acrylate copolymer, such as that used in the commercial product sold under the name Simulgel EG® by the company SEPPIC or under the trade name Sepinov EM® (CTFA name: Hydroxyethyl acrylate/Sodium acryloyldimethyltaurate copolymer);
- copolymers of AMPS® and of hydroxyethyl acrylate, for instance the AMPS®/hydroxyethyl acrylate copolymer, such as that used in the commercial product sold under the name Simulgel NS® by the company SEPPIC (CTFA name: Hydroxyethyl acrylate/sodium acryloyldimethyltaurate copolymer (and) squalane (and) polysorbate 60), or such as the product sold under the name Sodium acrylamido-2-methylpropanesulfonate/hydroxyethyl acrylate copolymer, such as the commercial product Sepinov EMT 10® (INCI name: Hydroxyethyl acrylate/Sodium acryloyldimethyltaurate copolymer).

As preferred water-soluble or water-dispersible AMPS® copolymers in accordance with the invention, mention may be made of copolymers of AMPS® and of hydroxyethyl acrylate.

In general, an aqueous phase according to the invention may comprise from 0.1 % to 8% by weight, preferably from 0.2% to 5% by weight and more preferentially from 0.7% to 5% by weight of solids of polyacrylamide(s) and/or of crosslinked and/or neutralized 2-acrylamido-2-methylpropanesulfonic acid polymer(s) and copolymer(s) relative to its total weight.

II.B.3 Modified or unmodified carboxyvinyl polymers

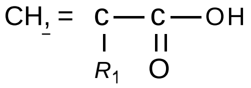
The modified or unmodified carboxyvinyl polymers may be copolymers derived from the polymerization of at least one monomer (a) chosen from α,β-ethylenically unsaturated carboxylic acids or esters thereof, with at least one ethylenically unsaturated monomer (b) comprising a hydrophobic group.

The term *"copolymers"* means both copolymers obtained from two types of monomer and those obtained from more than two types of monomer, such as terpolymers obtained from three types of monomer.

Their chemical structure more particularly comprises at least one hydrophilic unit and at least one hydrophobic unit. The term "hydrophobic group or unit" means a radical with a saturated or unsaturated, linear or branched hydrocarbon-based chain, comprising at least 8 carbon atoms, preferably from 10 to 30 carbon atoms, in particular from 12 to 30 carbon atoms and more preferentially from 18 to 30 carbon atoms.

Preferably, these copolymers are chosen from copolymers derived from the polymerization:

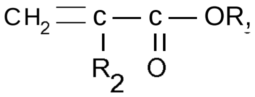
- of at least one monomer of formula (1) below:



$$CH_2=C(R_1)-C(=O)-OH \quad (1)$$

in which R_1 denotes H or CH_3 or $C2H_5$, i.e. acrylic acid, methacrylic acid or ethacrylic acid monomers, and

- of at least one monomer of unsaturated carboxylic acid (Cio-C3o)alkyl ester type corresponding to the monomer of formula (2) below:



$$CH_2=C(R_2)-C(=O)-OR_3 \quad (2)$$

in which R_2 denotes H or CH_3 or $C2H_5$ (i.e. acrylate, methacrylate or ethacrylate units) and preferably H (acrylate units) or CH_3 (methacrylate units), R3 denoting a C10-C30 and preferably C12-C22 alkyl radical.

The unsaturated carboxylic acid (Cio-C3o)alkyl esters are preferably chosen from lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate and dodecyl acrylate, and the corresponding methacrylates, such as lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate, and mixtures thereof.

According to a preferred embodiment, these polymers are crosslinked.

Among the copolymers of this type that will be used more particularly are polymers derived from the polymerization of a monomer mixture comprising:

- essentially acrylic acid,
- an ester of formula (2) described above in which R_2 denotes H or CH_3, R_3 denoting an alkyl radical containing from 12 to 22 carbon atoms, and

- a crosslinking agent, which is a well-known copolymerizable unsaturated polyethylenic monomer, for instance diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide.

Among the copolymers of this type, use will more particularly be made of those consisting of from 95% to 60% by weight of acrylic acid (hydrophilic unit), 4% to 40% by weight of C_{10}-C_{30} alkyl acrylate (hydrophobic unit) and 0 to 6% by weight of crosslinking polymerizable monomer, or alternatively those consisting of from 98% to 96% by weight of acrylic acid (hydrophilic unit), 1% to 4% by weight of C_{10}-C_{30} alkyl acrylate (hydrophobic unit) and 0.1 % to 0.6% by weight of crosslinking polymerizable monomer such as those described previously.

Among the abovementioned polymers, the ones that are most particularly preferred according to the present invention are acrylate/Cio-C3o-alkyl acrylate copolymers (INCI name: Acrylates/C_{10-30} Alkyl acrylate Crosspolymer) such as the products sold by the company Lubrizol under the trade names Pemulen TR-1®, Pemulen TR-2®, Carbopol 1382®, Carbopol EDT 2020® and Carbopol Ultrez 20® Polymer, and even more preferentially Pemulen TR-2®.

Among the modified or unmodified carboxyvinyl polymers, mention may also be made of sodium polyacrylates such as those sold under the name Cosmedia SP® containing 90% solids and 10% water, or Cosmedia SPL® as an inverse emulsion containing about 60% solids, an oil (hydrogenated polydecene) and a surfactant (PPG-5 Laureth-5), both sold by the company Cognis.

Mention may also be made of partially neutralized sodium polyacrylates that are in the form of an inverse emulsion comprising at least one polar oil, for example the product sold under the name Luvigel® EM by the company BASF.

The modified or unmodified carboxyvinyl polymers may also be chosen from crosslinked (meth)acrylic acid homopolymers.

For the purposes of the present patent application, the term *"(meth)acrylic"* means *"acrylic or methacrylic"*.

Examples that may be mentioned include the products sold by Lubrizol under the names Carbopol 910, 934, 940, 941, 934 P, 980, 981, 2984, 5984 and Carbopol Ultrez 10 Polymer, or by 3V-Sigma under the name Synthalen® K, Synthalen® L or Synthalen® M.

Among the modified or unmodified carboxyvinyl polymers, mention may be made in particular of Carbopol® (INCI name: carbomer) and Pemulen® (CTFA name: Acrylates/C_{10-30} alkyl acrylate crosspolymer) sold by the company Lubrizol.

The modified or unmodified carboxyvinyl polymers may be present in a proportion of from 0.1 % to 5% by weight of solids relative to the weight of the aqueous phase, in particular from 0.3% to 1% by weight and preferably from 0.4% to 1% by weight, relative to the weight of the aqueous phase.

Advantageously, a composition according to the invention comprises a synthetic polymeric hydrophilic gelling agent chosen from 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers.

According to a preferred variant, the synthetic polymeric hydrophilic gelling agent is a crosslinked sodium polyacrylate or, preferably, a copolymer of 2-acrylamido-2-methylpropanesulfonic acid and of hydroxyethyl acrylate.

According to another preferred variant, the synthetic polymeric hydrophilic gelling agent is at least one ammonium 2-acrylamido-2-methylpropanesulfonate polymer.

III. Other hydrophilic gelling agents

These gelling agents are more particularly chosen from mixed silicates and fumed silicas.

III.A. Mixed silicate

For the purposes of the present invention, the term "mixed silicate" means all silicates of natural or synthetic origin containing several (two or more) types of cations chosen from alkali metals (for example Na, Li, K) or alkaline-earth metals (for example Be, Mg, Ca), transition metals and aluminium.

According to a particular embodiment, the mixed silicate(s) are in the form of solid particles containing at least 10% by weight of at least one silicate relative to the total weight of the particles. In the rest of the present description, these particles are referred to as *"silicate particles".*

Preferably, the silicate particles contain less than 1% by weight of aluminium relative to the total weight of the particles. Even more preferably, they contain from 0 to 1% by weight of aluminium relative to the total weight of the particles.

Preferably, the silicate particles contain at least 50% by weight of silicate and better still at least 70% by weight relative to the total weight of the particles. Particles containing at least 90% by weight of silicates, relative to the total weight of the particles, are particularly preferred.

In particular, it is an alkali metal or alkaline-earth metal, aluminium or iron silicate or mixture of silicates.

Preferably, it is sodium, magnesium and/or lithium silicate.

To ensure good cosmetic properties, these silicates are generally in a finely divided form, and in particular in the form of particles with a mean size ranging from 2 nm to 1 μιτι (from 2 to 1000 nm), preferably from 5 to 600 nm and even more preferentially from 20 to 250 nm.

The silicate particles may have any form, for example the form of spheres, flakes, needles, platelets, discs, leaflets, or totally random forms. Preferably, the silicate particles are in the form of discs or leaflets.

Thus, the term *"mean size"* of the particles means the numerical mean size of the largest dimension (length) that it is possible to measure between two diametrically opposite points on an individual particle. The size may be determined, for example, by transmission electron microscopy or by measuring the specific surface area via the BET method or with a laser particle size analyser.

When the particles are in the form of discs or leaflets, they generally have a thickness ranging from about 0.5 to 5 nm.

The silicate particles may consist of an alloy with metal or metalloid oxides, obtained, for example, by thermal melting of the various constituents thereof. When the particles also comprise such a metal or metalloid oxide, this oxide is preferably chosen from silicon, boron or aluminium oxide.

According to a particular embodiment of the invention, the silicates are phyllosilicates, namely silicates having a structure in which the SiO_4 tetrahedra are organized in leaflets between which the metal cations are enclosed.

The mixed silicates that are suitable for use in the invention may be chosen, for example, from montmorillonites, hectorites, bentonites, beidellite and saponites. According to a preferred embodiment of the invention, the mixed silicates used are more particularly chosen from hectorites and bentonites, and better still from laponites.

A family of silicates that is particularly preferred in the compositions of the present invention is thus the laponite family. Laponites are sodium magnesium silicates also possibly containing lithium, which have a layer structure similar to that of montmorillonites. Laponite is the synthetic form of the natural mineral known as *hectorite.* The synthetic origin of this family of silicates is of considerable advantage over the natural form, since it allows good control the composition of the product. In addition, laponites have the advantage of having a particle size that is much smaller than that of the natural minerals hectorite and bentonite.

Laponites that may especially be mentioned include the products sold under the following names: Laponite® XLS, Laponite® XLG, Laponite® RD, Laponite® RDS, Laponite® XL21 (these products are sodium magnesium silicates and sodium lithium magnesium silicates) by the company Rockwood Additives Limited.

Such gelling agents may be used in a proportion of from 0.1 % to 8% by weight of solids relative to the total weight of the aqueous phase, especially from 0.1 % to 5% by weight and in particular from 0.5% to 3% by weight, relative to the total weight of the aqueous phase.

<u>III.B. Hydrophilic fumed silica</u>

The fumed silicas according to the present invention are hydrophilic.

The hydrophilic fumed silicas are obtained by pyrolysis of silicon tetrachloride ($SiCl_4$) in a continuous flame at 1000°C in the presence of hydrogen and oxygen. Among the fumed silicas of hydrophilic nature that may be used according to the present invention, mention may especially be made of those sold by the company Degussa or Evonik Degussa under the trade names Aerosil® 90, 130, 150, 200, 300 and 380 or alternatively by the company Cabot under the name Carbosil H5®.

Such gelling agents may be used in a proportion of from 0.1 % to 10% by weight of solids relative to the total weight of the aqueous phase, especially from 0.1 % to 5% by weight and in particular from 0.5% to 3% by weight, relative to the total weight of the aqueous phase.

LIPOPHILIC GELLING AGENT

For the purposes of the present invention, the term *"lipophilic gelling agent"* means a compound that is capable of gelling the oily phase of the compositions according to the invention.

The gelling agent is lipophilic and is thus present in the oily phase of the composition.

The gelling agent is liposoluble or lipodispersible.

As emerges from the text hereinbelow, the lipophilic gelling agent is advantageously chosen from particulate gelling agents, organopolysiloxane elastomers, semi-crystalline polymers, dextrin esters and polymers containing hydrogen bonding, and mixtures thereof.

I. Particulate gelling agents

The particulate gelling agent used in the composition according to the invention is in the form of particles, preferably spherical particles.

As representative lipophilic particulate gelling agents that are suitable for use in the invention, mention may be made most particularly of polar and apolar waxes, modified clays, and silicas such as fumed silicas and hydrophobic silica aerogels.

Waxes

The term "wax" under consideration in the context of the present invention generally means a lipophilic compound that is solid at room temperature (25°C), with a solid/liquid reversible change of state, having a melting point of greater than or equal to 30°C, which may be up to 200°C and in particular up to 120°C.

Within the context of the invention, the melting point corresponds to the temperature of the most endothermic peak observed in thermal analysis (DSC) as described in the standard ISO 11357-3: 1999. The melting point of the wax may be measured using a differential scanning calorimeter (DSC), for example the calorimeter sold under the name *MDSC 2920* by the company TA Instruments.

The measuring protocol is as follows:

A sample of 5 mg of wax placed in a crucible is subjected to a first temperature rise ranging from -20°C to 100°C, at a heating rate of 10°C/minute, it is then cooled from 100°C to -20°C at a cooling rate of 10°C/minute and is finally subjected to a second temperature rise ranging from -20°C to 100°C at a heating rate of 5°C/minute. During the second temperature rise, the variation in the difference in power absorbed by the empty crucible and by the crucible containing the sample of wax is measured as a function of the temperature. The melting point of the compound is the temperature value corresponding to the top of the peak of the curve representing the variation in the difference in power absorbed as a function of the temperature.

The waxes that may be used in the compositions according to the invention are chosen from waxes that are solid at room temperature, of animal, plant, mineral or synthetic origin, and mixtures thereof.

The waxes, for the purposes of the invention, may be those generally used in the cosmetic or dermatological fields. They may in particular be polar or apolar, and hydrocarbon-based, silicone and/or fluoro waxes, optionally comprising ester or hydroxyl functions. They may also be of natural or synthetic origin.

a) Apolar waxes

For the purposes of the present invention, the term "apolar wax" means a wax whose solubility parameter at 25°C as defined below, δ_a, is equal to 0 $(J/cm^3)^{½}$.

The definition of the solubility parameters in the Hansen three-dimensional solubility space are described in the article by CM. Hansen: *The three-dimensional solubility parameters,* J. Paint Technol. 39, 105 (1967).

According to this Hansen space:

- δ_D characterizes the London dispersion forces derived from the formation of dipoles induced during molecular impacts;
- δ_p characterizes the Debye interaction forces between permanent dipoles and also the Keesom interaction forces between induced dipoles and permanent dipoles;
- δ_h characterizes the specific interaction forces (such as hydrogen bonding, acid/base, donor/acceptor, etc.); and
- δ_a is determined by the equation: $\delta_a = (\delta_p^2 + \delta_h^2)^{½}$.

The parameters δ_p, δ_h, δ_D and δ_a are expressed in $(J/cm^3)^{½}$.

The solubility parameters are calculated with the HSPiP v4.1 software.

The apolar waxes are in particular hydrocarbon-based waxes formed solely from carbon and hydrogen atoms, and free of heteroatoms such as N, O, Si and P.

The apolar waxes are chosen from microcrystalline waxes, paraffin waxes, ozokerite and polyethylene waxes, and mixtures thereof.

An ozokerite that may be mentioned is Ozokerite Wax SP 1020 P®.

As microcrystalline waxes that may be used, mention may be made of Multiwax W 445® sold by the company Sonneborn, and Microwax HW® and Base Wax 30540® sold by the company Paramelt, and Cerewax® No. 3 sold by the company Baerlocher.

As microwaxes that may be used in the compositions according to the invention as apolar wax, mention may be made especially of polyethylene microwaxes such as those sold under the names Micropoly 200®, 220®, 220L® and 250S® by the company Micro Powders.

Polyethylene waxes that may be mentioned include Performalene 500-L Polyethylene® and Performalene 400 Polyethylene® sold by New Phase Technologies, and Asensa® SC 211 sold by the company Honeywell.

b) Polar wax

For the purposes of the present invention, the term "*polar* wax" means a wax whose solubility parameter at 25°C, δa, is other than 0 $(J/cm^3)^{1/2}$.
In particular, the term "*polar* wax" means a wax whose chemical structure is formed essentially from, or even constituted by, carbon and hydrogen atoms, and comprising at least one highly electronegative heteroatom such as an oxygen, nitrogen, silicon or phosphorus atom.

The polar waxes may in particular be hydrocarbon-based, fluoro or silicone waxes.

Preferentially, the polar waxes may be hydrocarbon-based waxes.

The term "*hydrocarbon-based* wax" means a wax formed essentially from, or even constituted by, carbon and hydrogen atoms, and optionally oxygen and nitrogen atoms, and that does not contain any silicon or fluorine atoms. It may contain alcohol, ester, ether, carboxylic acid, amine and/or amide groups.

According to the invention, the term "*ester* wax" means a wax comprising at least one ester function. According to the invention, the term "*alcohol* wax" means a wax comprising at least one alcohol function, i.e. comprising at least one free hydroxyl (OH) group.

The following may especially be used as ester wax:

- ester waxes such as those chosen from:

i) waxes of formula R1COOR2 in which R_1 and R2 represent linear, branched or cyclic aliphatic chains in which the number of atoms ranges from 10 to 50, which may contain a heteroatom such as O, N or P and whose melting point ranges from 25 to 120°C;

ii) bis(1,1,1-trimethylolpropane) tetrastearate, sold under the name Hest 2T-4S® by the company Heterene;

iii) dicarboxylic acid diester waxes of general formula R^3-(-OCO-R^4-COO-R^5), in which R^3 and R^5 are identical or different, preferably identical, and represent a C_4-C3o alkyl group (alkyl group comprising from 4 to 30 carbon atoms) and R^4 represents a linear or branched C_4-C3o aliphatic group (alkyl group comprising from 4 to 30 carbon atoms) which may or may not comprise one or more unsaturations and which is preferably linear and unsaturated;

iv) mention may also be made of the waxes obtained by catalytic hydrogenation of animal or vegetable oils having linear or branched C8-C32 fatty chains, for example such as hydrogenated jojoba oil, hydrogenated sunflower oil, hydrogenated castor oil, hydrogenated coconut oil, and also the waxes obtained by hydrogenation of castor oil esterified with cetyl alcohol;

v) beeswax, synthetic beeswax, polyglycerolated beeswax, carnauba wax, candelilla wax, oxypropylenated lanolin wax, rice bran wax, ouricury wax, esparto grass wax, cork fibre wax, sugar cane wax, Japan wax, sumac wax, montan wax, orange wax, laurel wax, hydrogenated jojoba wax, sunflower wax, lemon wax, olive wax or berry wax.

According to another embodiment, the polar wax may be an alcohol wax. According to the invention, the term "*alcohol* wax" means a wax comprising at least one alcohol function, i.e. comprising at least one free hydroxyl (OH) group. Examples of alcohol waxes that may be mentioned include the C30-C50 alcohol wax Performacol® 550 Alcohol sold by the company New Phase Technologies, stearyl alcohol and cetyl alcohol.

It is also possible to use silicone waxes, which may advantageously be substituted polysiloxanes, preferably of low melting point.

The term "*silicone* wax" means an oil comprising at least one silicon atom, and in particular comprising Si-O groups.

Among the commercial silicone waxes of this type, mention may be made in particular of those sold under the names Abilwax 9800®, 9801® or 9810® (Goldschmidt), KF910® and KF7002® (Shin-Etsu), or 176-1118-3® and 176-11481® (General Electric).

The silicone waxes that may be used may also be alkyl or alkoxy dimethicones, and also (C2o-C6o)alkyl dimethicones, in particular (C3o-C_{45})alkyl dimethicones, such as the silicone wax sold under the name SF-1642® by the company GE-Bayer Silicones or C3o-C_{45} alkyl dimethylsilyl polypropylsilsesquioxane under the name SW-8005® C30 Resin Wax® sold by the company Dow Corning.

In the context of the present invention, particularly advantageous waxes that may be mentioned include polyethylene waxes, jojoba wax, candelilla wax and silicone waxes, in particular candelilla wax.

They may be present in the oily phase in a proportion of from 0.5% to 30% by weight relative to the weight of the oily phase, for example from 5% to 20% of the oily phase and more particularly from 2% to 15% by weight relative to the weight of the oily phase.

Modified clays

The composition according to the invention may comprise at least one lipophilic clay.

The clays can be natural or synthetic and they are rendered lipophilic by treatment with an alkylammonium salt, such as a Cio to C_{22} ammonium chloride, for example distearyldimethylammonium chloride.

They can be chosen from bentonites, in particular hectorites and montmorillonites, beidellites, saponites, nontronites, sepiolites, biotites, attapulgites, vermiculites and zeolites.

They are preferably chosen from hectorites.
Hectorites modified with a $C_{1}0$ to C_{22} ammonium chloride, such as hectorite modified with distearyldimethylammonium chloride, for instance the product sold under the name Bentone 38V® by the company Elementis or bentone gel in isododecane sold under the name Bentone Gel ISD V® (87% isododecane/10% disteardimonium hectorite/3% propylene carbonate) by the company Elementis, are preferably used as lipophilic clays.

Lipophilic clay may especially be present in a content ranging from 0.1 % to 15% by weight, in particular from 0.5% to 10% and more particularly from 1% to 10% by weight relative to the total weight of the oily phase.

Silicas

The oily phase of a composition according to the invention may also comprise, as gelling agent, a fumed silica or silica aerogel particles.

a) Fumed silica

Fumed silica which has undergone a hydrophobic surface treatment is most particularly suitable for use in the invention. Specifically, it is possible to chemically modify the surface of silica, by chemical reaction generating a reduced number of silanol groups present at the surface of the silica. It is especially possible to substitute silanol groups with hydrophobic groups: a hydrophobic silica is then obtained.

The hydrophobic groups may be:
- trimethylsiloxyl groups, which are obtained especially by treating fumed silica in the presence of hexamethyldisilazane. Silicas thus treated are known as "Silica silylate" according to the CTFA (8th edition, 2000). They are sold, for example, under the references Aerosil R812® by the company Degussa, and Cab-O-Sil TS-530® by the company Cabot;
- dimethylsilyloxyl or polydimethylsiloxane groups, which are especially obtained by treating fumed silica in the presence of polydimethylsiloxane or dimethyldichlorosilane. Silicas thus treated are known as "silica dimethyl silylate" according to the CTFA (8th Edition, 2000). They are sold, for example, under the references Aerosil R972® and Aerosil R974® by the company Degussa, and Cab-O-Sil TS-610® and Cab-O-Sil TS-720® by the company Cabot.

The fumed silicas may be present in a composition according to the present invention in a content ranging from 0.1 % to 40% by weight, more particularly from 1% to 15% by weight and even more particularly from 2% to 10% by weight relative to the total weight of the oily phase.

b) Hydrophobic silica aerogels

The oily phase of a composition according to the invention may also comprise, as gelling agent, at least silica aerogel particles.

Silica aerogels are porous materials obtained by replacing (by drying) the liquid component of a silica gel with air.

They are generally synthesized via a sol-gel process in a liquid medium and then dried, usually by extraction with a supercritical fluid, the one most commonly used being supercritical CO2. Drying of this type makes it possible to avoid contraction of the pores and of the material. The sol-gel process and the various drying operations are described in detail in Brinker C.J. and Scherer G.W., *Sol-Gel Science,* New York: Academic Press, 1990.

The hydrophobic silica aerogel particles used in the present invention have a specific surface area per unit mass (SM) ranging from 500 to 1500 m^2/g, preferably from 600 to 1200 m^2/g and better still from 600 to 800 m^2/g, and a size expressed as the volume-mean diameter (D[0.5]) ranging from 1 to 1500 μιτι, better still from 1 to 1000 μιτι, preferably from 1 to 100 μιτι, in particular from 1 to 30 μιτι, more preferably from 5 to 25 μιτι, better still from 5 to 20 μιτι and even better still from 5 to 15 μιτι.

According to one embodiment, the hydrophobic silica aerogel particles used in the present invention have a size expressed as the volume mean diameter (D[0.5]) ranging from 1 to 30 μιτι, preferably from 5 to 25 μιτι, better still from 5 to 20 μιτι and even better still from 5 to 15 μιτι.

The specific surface area per unit mass may be determined by the nitrogen absorption method, known as the BET (Brunauer-Emmett-Teller) method, described in *The journal of the American Chemical Society,* vol. 60, page 309, February 1938 and corresponding to international standard ISO 5794/1 (annex D). The BET specific surface area corresponds to the total specific surface area of the particles under consideration.

The sizes of the silica aerogel particles can be measured by static light scattering using a commercial particle size analyser of MasterSizer 2000 type 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, in the case of non-spherical particles, an "effective" particle diameter. This theory is especially described in the publication by Van de Hulst, H.C., *Light Scattering by Small Particles,* Chapters 9 and 10, Wiley, New York, 1957.

According to an advantageous embodiment, the hydrophobic silica aerogel particles used in the present invention have a specific surface area per unit of mass (SM) ranging from 600 to 800 m^2/g.

The silica aerogel particles used in the present invention may advantageously have a tapped density ranging from 0.02 g/cm^3 to 0.10 g/cm^3, preferably from 0.03 g/cm^3 to 0.08 g/cm^3 and in particular ranging from 0.05 g/cm^3 to 0.08 g/cm^3.

In the context of the present invention, this density, known as the tapped density, may be assessed according to the following protocol:

40 g of powder are poured into a measuring cylinder; the measuring cylinder is then placed on a Stav 2003 machine from Stampf Volumeter; the measuring cylinder is then subjected to a series of 2500 tapping actions (this operation is repeated until the difference in volume between two consecutive tests is less than 2%); the final volume Vf of tapped powder is then measured directly on the measuring cylinder. The tapped density is determined by the ratio m/Vf, in this instance 40/Vf (Vf being expressed in cm^3 and m in g).

According to a preferred embodiment, the hydrophobic silica aerogel particles used in the present invention have a specific surface area per unit of volume SV ranging from 5 to 60 m^2/cm^3, preferably from 10 to 50 m^2/cm^3 and better still from 15 to 40 m^2/cm^3.

The specific surface area per unit of volume is given by the relationship:
$Sv = SM \times p$; where p is the tapped density, expressed in g/cm^3, and SM is the specific surface area per unit of mass, expressed in m^2/g, as defined above.

Preferably, the hydrophobic silica aerogel particles according to the invention have an oil-absorbing capacity, measured at the wet point, ranging from 5 to 18 ml/g, preferably from 6 to 15 ml/g and better still from 8 to 12 ml/g.

The absorption capacity, measured at the wet point and denoted Wp, corresponds to the amount of oil which it is necessary to add to 100 g of particles in order to obtain a homogeneous paste.

It is measured according to the "wet point" method or the method for determining the oil uptake of a powder described in standard NF T 30-022. It corresponds to the amount of oil adsorbed onto the available surface of the powder and/or absorbed by the powder by measurement of the wet point, described below:

An amount m = 2 g of powder is placed on a glass plate, and the oil (isononyl isononanoate) is then added dropwise. After addition of 4 to 5 drops of oil to the powder, mixing is carried out using a spatula, and addition of the oil is continued until conglomerates of oil and powder have formed. From this point, the oil is added at the rate of one drop at a time and the mixture is subsequently triturated with the spatula. The addition of oil is stopped when a firm, smooth paste is obtained. This paste must be able to be spread over the glass plate without cracks or the formation of lumps. The volume Vs (expressed in ml) of oil used is then noted.

The oil uptake corresponds to the ratio Vs/m.

The aerogels used according to the present invention are aerogels of hydrophobic silica, preferably of silylated silica (INCI name: silica silylate).

The term *"hydrophobic silica"* means any silica whose surface is treated with silylating agents, for example halogenated silanes such as alkylchlorosilanes, siloxanes, in particular dimethylsiloxanes such as hexamethyldisiloxane, or silazanes, so as to functionalize the OH groups with silyl groups Si-Rn, for example trimethylsilyl groups.

As regards the preparation of hydrophobic silica aerogel particles modified at the surface by silylation, reference may be made to the document US 7 470 725.

Use will preferably be made of hydrophobic silica aerogel particles surface-modified with trimethylsilyl groups, preferably of the INCI name Silica silylate.

As hydrophobic silica aerogels that may be used in the invention, an example that may be mentioned is the aerogel sold under the name VM-2260® or VM-2270® (INCI name: Silica silylate) by the company Dow Corning, the particles of which have a mean size of about 1000 microns and a specific surface area per unit of mass ranging from 600 to 800 m^2/g.

Mention may also be made of the aerogels sold by the company Cabot under the references Aerogel TLD 201®, Aerogel OGD 201® and Aerogel TLD 203®, Enova® Aerogel MT 1100® and Enova Aerogel MT 1200®.

Use will preferably be made of the aerogel sold under the name VM-2270 (INCI name: Silica Silylate) by Dow Corning, the particles of which exhibit a mean size ranging from 5 to 15 microns and a specific surface per unit mass ranging from 600 to 800 m^2/g.

Such an aerogel advantageously makes it possible to promote the resistance of the deposit to sebum and to sweat.

Preferably, the hydrophobic silica aerogel particles are present in the composition according to the invention in a solids content ranging from 0.1 % to 8% by weight, preferably from 0.2% to 5% by weight and preferably from 0.2% to 1.5% by weight relative to the total weight of the oily phase.

II. Organopolysiloxane elastomer

The organopolysiloxane elastomer which can be used as lipophilic gelling agent has the advantage of conferring good application properties on the composition according to the invention. It affords a very soft and mattifying feel after application, which is advantageous in particular for application to the skin. It may also allow efficient filling of the hollows present on keratin materials.

The term *"organopolysiloxane elastomer"* or *"silicone elastomer"* means a supple, deformable organopolysiloxane with viscoelastic properties and especially with the consistency of a sponge or a supple sphere. Its modulus of elasticity is such that this material withstands deformation and has a limited ability to extend and to contract. This material is capable of regaining its original shape after stretching.

It is more particularly a crosslinked organopolysiloxane elastomer.

Thus, the organopolysiloxane elastomer can be obtained by a crosslinking addition reaction of diorganopolysiloxane containing at least one hydrogen bonded to silicon and of diorganopolysiloxane having ethylenically unsaturated groups bonded to silicon, in particular in the presence of a platinum catalyst; or by a dehydrogenation crosslinking condensation reaction between a diorganopolysiloxane comprising hydroxyl end groups and a diorganopolysiloxane containing at least one hydrogen bonded to silicon, in particular in the presence of an organotin compound; or by a crosslinking condensation reaction of a diorganopolysiloxane comprising hydroxyl end groups and of a hydrolysable organopolysilane; or by thermal crosslinking of organopolysiloxane, in particular in the presence of an organic peroxide catalyst; or by crosslinking of organopolysiloxane via high-energy radiation, such as gamma rays, ultraviolet rays or an electron beam.

Preferably, the organopolysiloxane elastomer is obtained by crosslinking addition reaction (A) of diorganopolysiloxane containing at least two hydrogens each bonded to a silicon, and (B) of diorganopolysiloxane containing at least two ethylenically unsaturated groups bonded to silicon, especially in the presence (C) of a platinum catalyst, as described, for instance, in patent application EP-A-295 886.

In particular, the organopolysiloxane elastomer may be obtained by reaction of dimethylpolysiloxane bearing dimethylvinylsiloxy end groups and of methylhydrogenopolysiloxane bearing trimethylsiloxy end groups, in the presence of a platinum catalyst.

Compound (A) is the base reactant for the formation of elastomeric organopolysiloxane, and the crosslinking takes place via an addition reaction of compound (A) with compound (B) in the presence of the catalyst (C).

Compound (A) is in particular an organopolysiloxane containing at least two hydrogen atoms bonded to different silicon atoms in each molecule.

Compound (A) may have any molecular structure, especially a linear-chain or branched-chain structure or a cyclic structure.

Compound (A) may have a viscosity at 25°C ranging from 1 to 50 000 centistokes, especially so as to be readily miscible with compound (B).

The organic groups bonded to the silicon atoms of compound (A) may be alkyl groups such as methyl, ethyl, propyl, butyl, octyl; substituted alkyl groups such as 2-phenylethyl, 2-phenylpropyl or 3,3,3-trifluoropropyl; aryl groups such as phenyl, tolyl, xylyl; substituted aryl groups such as phenylethyl; and substituted monovalent hydrocarbon-based groups such as an epoxy group, a carboxylate ester group or a mercapto group.

Compound (A) may thus be chosen from trimethylsiloxy-terminated methylhydrogenopolysiloxanes, trimethylsiloxy-terminated dimethylsiloxane/methylhydrogenosiloxane copolymers, and dimethylsiloxane/methylhydrogenosiloxane cyclic copolymers.

Compound (B) is advantageously a diorganopolysiloxane containing at least two lower alkenyl groups (for example C_2-C_4); the lower alkenyl group may be chosen from vinyl, allyl and propenyl groups. These lower alkenyl groups may be located in any position on the organopolysiloxane molecule, but are preferably located at the ends of the organopolysiloxane molecule. The organopolysiloxane (B) may have a branched-chain, linear-chain, cyclic or network structure, but the linear-chain structure is preferred. Compound (B) may have a viscosity ranging from the liquid state to the gum state. Preferably, compound (B) has a viscosity of at least 100 centistokes at 25°C.

Besides the abovementioned alkenyl groups, the other organic groups bonded to the silicon atoms in compound (B) may be alkyl groups such as methyl, ethyl, propyl, butyl or octyl; substituted alkyl groups such as 2-phenylethyl, 2-phenylpropyl or 3,3,3-trifluoropropyl; aryl groups such as phenyl, tolyl or xylyl; substituted aryl groups such as phenylethyl; and substituted monovalent hydrocarbon-based groups such as an epoxy group, a carboxylate ester group or a mercapto group.

The organopolysiloxanes (B) can be chosen from methylvinylpolysiloxanes, methylvinylsiloxane-dimethylsiloxane copolymers, dimethylpolysiloxanes comprising dimethylvinylsiloxy end groups, dimethylsiloxane-methylphenylsiloxane copolymers comprising dimethylvinylsiloxy end groups, dimethylsiloxane-diphenylsiloxane-methylvinylsiloxane copolymers comprising dimethylvinylsiloxy end groups, dimethylsiloxane-methylvinylsiloxane copolymers comprising trimethylsiloxy end groups, dimethylsiloxane-methylphenylsiloxane-methylvinylsiloxane copolymers comprising trimethylsiloxy end groups, methyl(3,3,3-trifluoropropyl)polysiloxanes comprising dimethylvinylsiloxy end groups, and dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers comprising dimethylvinylsiloxy end groups.

In particular, the organopolysiloxane elastomer can be obtained by reaction of dimethylpolysiloxane comprising dimethylvinylsiloxy end groups and of methylhydropolysiloxane comprising trimethylsiloxy end groups, in the presence of a platinum catalyst.

Advantageously, the sum of the number of ethylenic groups per molecule in compound (B) and of the number of hydrogen atoms bonded to silicon atoms per molecule in compound (A) is at least 5.

It is advantageous for compound (A) to be added in an amount such that the molecular ratio between the total amount of hydrogen atoms bonded to silicon atoms in compound (A) and the total amount of all the ethylenically unsaturated groups in compound (B) is within the range from 1.5/1 to 20/1.

Compound (C) is the catalyst for the crosslinking reaction, and is especially chloroplatinic acid, chloroplatinic acid-olefin complexes, chloroplatinic acid-alkenylsiloxane complexes, chloroplatinic acid-diketone complexes, platinum black and platinum on a support.

Catalyst (C) is preferably added in an amount of from 0.1 to 1000 parts by weight and better still from 1 to 100 parts by weight, as clean platinum metal, per 1000 parts by weight of the total amount of compounds (A) and (B).

The elastomer is advantageously a non-emulsifying elastomer.

The term *"non-emulsifying"* defines organopolysiloxane elastomers not containing a hydrophilic chain and in particular not containing polyoxyalkylene units (especially polyoxyethylene or polyoxypropylene units) or a polyglyceryl unit. Thus, according to a specific form of the invention, the composition comprises an organopolysiloxane elastomer devoid of polyoxyalkylene units and of polyglyceryl unit.

In particular, the silicone elastomer used in the present invention is chosen from Dimethicone Crosspolymer (INCI name), Vinyl Dimethicone Crosspolymer (INCI name), Dimethicone/Vinyl Dimethicone Crosspolymer (INCI name) or Dimethicone Crosspolymer-3 (INCI name).

The organopolysiloxane elastomer particles may be conveyed in the form of a gel formed from an elastomeric organopolysiloxane included in at least one hydrocarbon-based oil and/or one silicone oil. In these gels, the organopolysiloxane particles are often non-spherical particles.

Non-emulsifying elastomers are especially described in patents EP 242 219, EP 285 886 and EP 765 656 and in patent application JP-A-61-194 009.

The silicone elastomer is generally provided in the form of a gel, a paste or a powder but advantageously in the form of a gel in which the silicone elastomer is dispersed in a linear silicone oil (dimethicone) or cyclic silicone oil (e.g.: cyclopentasiloxane), advantageously in a linear silicone oil.

Non-emulsifying elastomers that may more particularly be used include those sold under the names KSG-6®, KSG-15®, KSG-16®, KSG-18®, KSG-41®, KSG-42®, KSG-43® and KSG-44® by the company Shin-Etsu, DC9040® and DC9041® by Dow Corning and SFE 839® by the company General Electric.

According to a particular mode, use is made of a gel of silicone elastomer dispersed in a silicone oil chosen from a non-exhaustive list comprising cyclopentadimethylsiloxane, dimethicones, dimethylsiloxanes, methyl trimethicone, phenyl methicone, phenyl dimethicone, phenyl trimethicone and cyclomethicone, preferably a linear silicone oil chosen from polydimethylsiloxanes (PDMS) or dimethicones with a viscosity at 25°C ranging from 1 to 500 cSt, optionally modified with optionally fluorinated aliphatic groups, or with functional groups such as hydroxyl, thiol and/or amine groups.

Mention may be made especially of the compounds having the following INCI names:
- dimethicone/vinyl dimethicone crosspolymer, such as USG-105® and USG-107A® from the company Shin-Etsu; DC9506® and DC9701® from the company Dow Corning;
- dimethicone/vinyl dimethicone crosspolymer (and) dimethicone, such as KSG-6® and KSG-16® from the company Shin-Etsu;
- dimethicone/vinyl dimethicone crosspolymer (and) cyclopentasiloxane, such as KSG-15®;
- cyclopentasiloxane (and) dimethicone crosspolymer, such as DC9040®, DC9045® and DC5930® from the company Dow Corning;
- dimethicone (and) dimethicone crosspolymer, such as DC9041® from the company Dow Corning.
- dimethicone (and) dimethicone crosspolymer, such as Dow Corning EL-9240® Silicone Elastomer Blend from the company Dow Corning (mixture of polydimethylsiloxane crosslinked with hexadiene/polydimethylsiloxane (2 cSt));
- C_{4-24} alkyl dimethicone/divinyl dimethicone crosspolymer, such as NuLastic Silk MA® from the company Alzo.

Mention may in particular be made, as examples of silicone elastomers dispersed in a linear silicone oil which can advantageously be used according to the invention, of the following references:
- dimethicone/vinyl dimethicone crosspolymer (and) dimethicone, such as KSG-6® and KSG-1 6® from the company Shin-Etsu;
- dimethicone (and) dimethicone crosspolymer, such as DC9041®, Dow Corning EL-9240® Silicone Elastomer Blend from the company Dow Corning.

The organopolysiloxane elastomer particles may also be used in powder form: mention may be made especially of the powders sold under the names Dow Corning 9505 Powder® and Dow Corning 9506 Powder® by the company Dow Corning, these powders having the INCI name: dimethicone/vinyl dimethicone crosspolymer.

The organopolysiloxane powder may also be coated with silsesquioxane resin, as described, for example, in patent US 5 538 793. Such elastomeric powders are sold under the names KSP-1 00®, KSP-1 01®, KSP-1 02®, KSP-1 03®, KSP-1 04® and KSP-1 05® by the company Shin-Etsu, and have the INCI name: vinyl dimethicone/methicone silsesquioxane crosspolymer.

As examples of organopolysiloxane powders coated with silsesquioxane resin that may advantageously be used according to the invention, mention may be made especially of the reference KSP-1 00® from the company Shin-Etsu.

As preferred lipophilic gelling agent of organopolysiloxane elastomer type, mention may be made especially of crosslinked organopolysiloxane elastomers chosen from Dimethicone Crosspolymer (INCI name), Dimethicone (and) Dimethicone Crosspolymer (INCI name), Vinyl Dimethicone Crosspolymer (INCI name), Dimethicone/Vinyl Dimethicone Crosspolymer (INCI name), Dimethicone Crosspolymer-3 (INCI name), and in particular Dimethicone Crosspolymer (INCI name).

The organopolysiloxane elastomer may be present in a composition of the present invention in a content ranging from 0.1 % to 35% by weight of solids, especially from 1% to 20% and more particularly from 2% to 10% by weight relative to the total weight of the composition.

III. Semi-crystalline polymers

The composition according to the invention may comprise at least one semi-crystalline polymer. Preferably, the semi-crystalline polymer has an organic structure, and a melting point of greater than or equal to 30°C.

For the purposes of the invention, the term *"semi-crystalline polymer"* means polymers comprising a crystallizable portion and an amorphous portion and having a first-order reversible change of phase temperature, in particular of melting point (solid-liquid transition). The crystallizable part is either a side chain (or pendent chain) or a block in the backbone.

When the crystallizable portion of the semi-crystalline polymer is a block of the polymer backbone, this crystallizable block has a chemical nature different than that of the amorphous blocks; in this case, the semi-crystalline polymer is a block copolymer, for example of the diblock, triblock or multiblock type. When the crystallizable part is a chain that is pendent on the backbone, the semi-crystalline polymer may be a homopolymer or a copolymer.

The melting point of the semi-crystalline polymer is preferably less than 150°C.

The melting point of the semi-crystalline polymer is preferably greater than or equal to 30°C and less than 100°C. More preferably, the melting point of the semi-crystalline polymer is greater than or equal to 30°C and less than 70°C.

The semi-crystalline polymer(s) according to the invention are solid at room temperature (25°C) and atmospheric pressure (760 mmHg), with a melting point of greater than or equal to 30°C. The melting point values correspond to the melting point measured using a differential scanning calorimeter (DSC), such as the calorimeter sold under the name DSC 30 by the company Mettler, with a temperature rise of 5 or 10°C per minute (the melting point under consideration is the point corresponding to the temperature of the most endothermic peak in the thermogram).

The semi-crystalline polymer(s) according to the invention preferably have a melting point that is higher than the temperature of the keratinous support intended to receive said composition, in particular the skin, the lips or the eyebrows.

According to the invention, the semi-crystalline polymers are advantageously soluble in the fatty phase, especially to at least 1% by weight, at a temperature that is higher than their melting point. Besides the crystallizable chains or blocks, the blocks of the polymers are amorphous.

For the purposes of the invention, the term *"crystallizable chain or block"* means a chain or block which, if it were alone, would change from the amorphous state to the crystalline state reversibly, depending on whether the temperature is above or below the melting point. For the purposes of the invention, a chain is a group of atoms, which are pendent or lateral relative to the polymer backbone. A "block" is a group of atoms belonging to the backbone, this group constituting one of the repeating units of the polymer.

Preferably, the polymer backbone of the semi-crystalline polymers is soluble in the fatty phase at a temperature above their melting point.

Preferably, the crystallizable blocks or chains of the semi-crystalline polymers represent at least 30% of the total weight of each polymer and better still at least

40%. The semi-crystalline polymers bearing crystallizable side chains are homopolymers or copolymers. The semi-crystalline polymers of the invention bearing crystallizable blocks are block or multiblock copolymers. They may be obtained by polymerizing a monomer bearing reactive (or ethylenic) double bonds or by polycondensation. When the polymers of the invention are polymers bearing crystallizable side chains, these side chains are advantageously in random or statistical form.

Preferably, the semicrystalline polymers of the invention are of synthetic origin.

According to a preferred embodiment, the semi-crystalline polymer is chosen from:
- homopolymers and copolymers comprising units resulting from the polymerization of one or more monomers bearing crystallizable hydrophobic side chain(s),
- polymers bearing in the backbone at least one crystallizable block,
- polycondensates of aliphatic or aromatic or aliphatic/aromatic polyester type,
- copolymers of ethylene and propylene prepared via metallocene catalysis, and
- acrylate/silicone copolymers.

The semi-crystalline polymers that may be used in the invention may be chosen in particular from:
- block copolymers of polyolefins of controlled crystallization, whose monomers are described in EP 0 951 897,
- polycondensates, in particular of aliphatic or aromatic or aliphatic/aromatic polyester type,
- copolymers of ethylene and propylene prepared via metallocene catalysis,
- homopolymers or copolymers bearing at least one crystallizable side chain and homopolymers or copolymers bearing in the backbone at least one crystallizable block, such as those described in document US 5 156 911, such as the $(C_{10}-C_{30})$alkyl polyacrylates corresponding to the Intelimer® products from the company Landec described in the brochure Intelimer® Polymers, Landec IP22® (Rev. 4-97), for example the product Intelimer® IPA 13-1® from the company Landec, which is a polystearyl acrylate with a molecular weight of about 145 000 and a melting point of 49°C,
- homopolymers or copolymers bearing at least one crystallizable side chain, in particular containing fluoro group(s), as described in document WO 01/19333,
- acrylate/silicone copolymers, such as copolymers of acrylic acid and of stearyl acrylate bearing polydimethylsiloxane grafts, copolymers of stearyl methacrylate bearing polydimethylsiloxane grafts, copolymers of acrylic acid and of stearyl methacrylate bearing polydimethylsiloxane grafts, copolymers of methyl methacrylate, butyl methacrylate, 2-ethylhexyl acrylate and stearyl methacrylate bearing polydimethylsiloxane grafts. Mention may be made in particular of the copolymers sold by the company Shin-Etsu under the names KP-561® (CTFA name: acrylates/dimethicone), KP-541® (CTFA name: acrylates/dimethicone and isopropyl alcohol), KP-545® (CTFA name: acrylates/dimethicone and cyclopentasiloxane),
- and mixtures thereof.

Preferably, the amount of semi-crystalline polymer(s), preferably chosen from semi-crystalline polymers bearing crystallizable side chains, represents from 0.1 % to 30% by weight of solids relative to the total weight of the oily phase, for example from 0.5% to 25% by weight, better still from 5% to 20% or even from 5% to 12% by weight, relative to the total weight of the oily phase.

IV. Dextrin esters

The composition according to the invention may comprise as lipophilic gelling agent at least one dextrin ester.

In particular, the composition preferably comprises at least one preferably C_{12} to C_{24} and in particular C_{14} to C_{18} fatty acid ester of dextrin, or mixtures thereof.

Preferably, the dextrin ester is an ester of dextrin and of a C_{12}-C_{18} and in particular C_{14}-C_{18} fatty acid.

Preferably, the dextrin ester is chosen from dextrin myristate and/or dextrin palmitate, and mixtures thereof.

According to a particular embodiment, the dextrin ester is dextrin myristate, especially such as the product sold under the name Rheopearl MKL-2® by the company Chiba Flour Milling.

According to a preferred embodiment, the dextrin ester is dextrin palmitate. This product may be chosen, for example, from those sold under the names Rheopearl TL®, Rheopearl KL® and Rheopearl ® KL2 by the company Chiba Flour Milling.

In a particularly preferred manner, the oily phase of a composition according to the invention may comprise from 0.1 % to 30% by weight, preferably from 2% to 25% and preferably from 7.5% to 17% by weight of dextrin ester(s) relative to the total weight of the oily phase.

In a particularly preferred manner, the composition according to the invention comprises from 0.1 % to 10% by weight and preferably from 0.5% to 5% by weight of dextrin palmitate relative to the total weight of the oily phase. The dextrin palmitate may especially be the product sold under the names Rheopearl TL®, Rheopearl KL® or Rheopearl ® KL2 by the company Chiba Flour Milling.

V. Polymers containing hydrogen bonding

As representatives of polymers containing hydrogen bonding that are suitable for use in the invention, mention may be made most particularly of polyamides and in particular hydrocarbon-based polyamides and silicone polyamides.

Polyamides

The oily phase of a composition according to the invention may comprise at least one polyamide chosen from hydrocarbon-based polyamides and silicone polyamides, and mixtures thereof.

Preferably, the total content of polyamide(s) ranges from 0.1 % to 30% by weight expressed as solids, preferably from 0.1 % to 20% by weight and preferably from 0.5% to 10% by weight relative to the total weight of the oily phase.

For the purposes of the invention, the term *"polyamide"* means a compound containing at least 2 amide repeating units, preferably at least 3 amide repeating units and better still 10 amide repeating units.

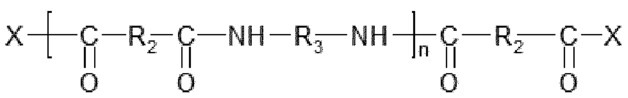
a) Hydrocarbon-based polyamide

The term *"hydrocarbon-based polyamide"* means a polyamide formed essentially of, indeed even consisting of, carbon and hydrogen atoms, and optionally of oxygen or nitrogen atoms, and not comprising any silicon or fluorine atoms. It may contain alcohol, ester, ether, carboxylic acid, amine and/or amide groups.

For the purposes of the invention, the term *"functionalized chain"* means an alkyl chain comprising one or more functional groups or reagents chosen especially from hydroxyl, ether, ester, oxyalkylene and polyoxyalkylene groups.
Advantageously, this polyamide of the composition according to the invention has a weight-average molecular mass of less than 100 000 g/mol (especially ranging from 1000 to 100 000 g/mol), in particular less than 50 000 g/mol (especially ranging from 1000 to 50 000 g/mol) and more particularly ranging from 1000 to 30 000 g/mol, preferably from 2000 to 20 000 g/mol and better still from 2000 to 10 000 g/mol.

This polyamide is insoluble in water, especially at 25°C.

According to a first embodiment of the invention, the polyamide used is a polyamide of formula (I):

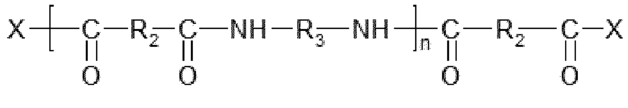


$$X-\left[-\underset{\underset{O}{\|}}{C}-R_2-\underset{\underset{O}{\|}}{C}-NH-R_3-NH-\right]_n\underset{\underset{O}{\|}}{C}-R_2-\underset{\underset{O}{\|}}{C}-X$$

(I)

in which X represents a group -N(Ri)$_2$ or a group -ORi in which R_1 is a linear or branched Cs to C22 alkyl radical which may be identical or different, R_2 is a **C_{28}-C_{42}** diacid dimer residue, **R_3** is an ethylenediamine radical and n is between 2 and 5; and mixtures thereof.

According to a particular mode, the polyamide used is an amide-terminated polyamide of formula (Ia):

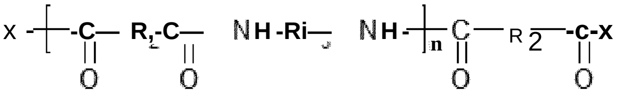


$$X-\left[-\underset{\underset{O}{\|}}{C}-R_2-\underset{\underset{O}{\|}}{C}-NH-R_3-NH-\right]_n\underset{\underset{O}{\|}}{C}-R_2-\underset{\underset{O}{\|}}{C}-X$$

(Ia)

in which X represents a group -N(Ri) $_2$ in which R_1 is a linear or branched Cs to C22 alkyl radical which may be identical or different, R_2 is a C28-C$_4$2 diacid dimer residue, R3 is an ethylenediamine radical and n is between 2 and 5;
and mixtures thereof.

The oily phase of a composition according to the invention may also comprise, additionally in this case, at least one additional polyamide of formula (Ib):



$$X-\left[-\underset{\underset{O}{\|}}{C}-R_2-\underset{\underset{O}{\|}}{C}-NH-R_3-NH-\right]_n-\underset{\underset{O}{\|}}{C}-R_2-\underset{\underset{O}{\|}}{C}-X$$

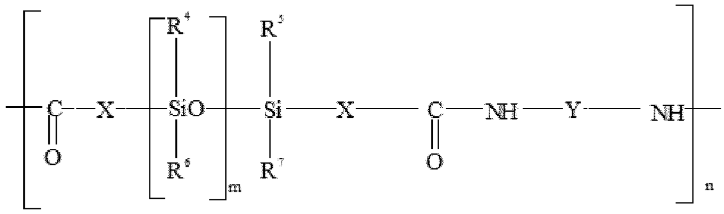
(¾.)

in which X represents a group -OR1 in which R_1 is a linear or branched Cs to C22 and preferably C16 to C22 alkyl radical which may be identical or different, R_2 is a C28-C$_4$2 diacid dimer residue, R3 is an ethylenediamine radical and n is between 2 and 5, such as the commercial products sold by the company Arizona Chemical under the names Unidear 80 and Unidear 100 or Unidear 80 V, Unidear 100 V and Unidear 100 VG, the INCI name of which is Ethylenediamine/stearyl dimer dilinoleate copolymer.

b) Silicone polyamide

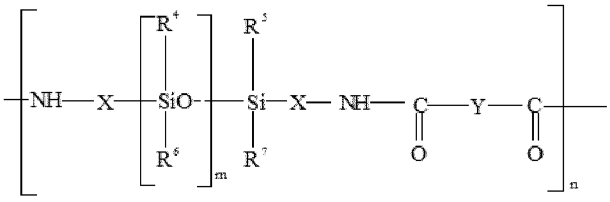
The silicone polyamides are preferably solid at room temperature (25°C) and atmospheric pressure (760 mmHg).

The silicone polyamides may preferentially be polymers comprising at least one unit of formula (III) or (IV):



(III)

or

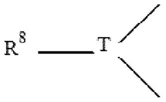


(IV)

in which:
R^4, R^5, R^6 and R^7, which may be identical or different, represent a group chosen from:
- saturated or unsaturated, Ci to C$_4$o linear, branched or cyclic hydrocarbon-based groups, which may contain in their chain one or more oxygen, sulfur and/or

nitrogen atoms, and which may be partially or totally substituted with fluorine atoms,
- C6 to Cio aryl groups, optionally substituted with one or more Ci to C_4 alkyl groups,
- polyorganosiloxane chains possibly containing one or more oxygen, sulfur and/or nitrogen atoms,
- the groups X, which may be identical or different, represent a linear or branched Ci to C30 alkylenediyl group, possibly containing in its chain one or more oxygen and/or nitrogen atoms,
- Y is a saturated or unsaturated Ci to C50 linear or branched alkylene, arylene, cycloalkylene, alkylarylene or arylalkylene divalent group, which may comprise one or more oxygen, sulfur and/or nitrogen atoms, and/or may bear as substituent one of the following atoms or groups of atoms: fluorine, hydroxyl, C3 to Cs cycloalkyl, Ci to C_4o alkyl, C_5 to C10 aryl, phenyl optionally substituted with one to three Ci to C3 alkyl, Ci to C3 hydroxyalkyl and Ci to C6 aminoalkyl groups, or

Y represents a group corresponding to the formula:



in which:
- T represents a linear or branched, saturated or unsaturated, C3 to $C2_4$ trivalent or tetravalent hydrocarbon-based group optionally substituted with a polyorganosiloxane chain, and possibly containing one or more atoms chosen from O, N and S, or T represents a trivalent atom chosen from N, P and Al, and
- R^8 represents a linear or branched C1-C50 alkyl group or a polyorganosiloxane chain, possibly comprising one or more ester, amide, urethane, thiocarbamate, urea, thiourea and/or sulfonamide groups, which may possibly be linked to another chain of the polymer;
- n is an integer ranging from 2 to 500 and preferably from 2 to 200, and m is an integer ranging from 1 to 1000, preferably from 1 to 700 and better still from 6 to 200.

According to a particular mode, the silicone polyamide comprises at least one unit of formula (III) in which m ranges from 50 to 200, in particular from 75 to 150 and is preferably about 100.

More preferably, R^4, R^5, R^6 and R^7 independently represent a linear or branched Ci to C_4o alkyl group, preferably a group CH_3, $C2H_5$, n-CsH_7 or an isopropyl group in formula (III).

As an example of silicone polymers that may be used, mention may be made of one of the silicone polyamides obtained in accordance with Examples 1 to 3 of document
US 5 981 680.

Mention may be made of the compounds sold by the company Dow Corning under the names DC 2-8179 (DP 100) and DC 2-8178 (DP 15), the INCI name of which is Nylon-61 1/dimethicone copolymer, i.e. Nylon-61 1/dimethicone copolymers. The silicone polymers and/or copolymers advantageously have a temperature of transition from the solid state to the liquid state ranging from 45°C to 190°C. Preferably, they have a temperature of transition from the solid state to the liquid state ranging from 70 to 130°C and better still from 80°C to 105°C.

Preferably, the total content of polyamide(s) and/or silicone polyamide(s) ranges from 0.5% to 25% by weight of solids, in particular from 2% to 20% by weight and preferably from 2% to 12% by weight relative to the total weight of the oily phase.

Advantageously, the polymer containing hydrogen bonding is chosen from the ethylenediamine/stearyl dinner dilinoleate copolymer and Nylon-61 1/dimethicone copolymers.

According to an advantageous variant, a composition according to the invention comprises a lipophilic gelling agent chosen from particulate gelling agents, organopolysiloxane elastomers, semi-crystalline polymers, dextrin esters and polymers containing hydrogen bonding, and mixtures thereof, and in particular at least one organopolysiloxane elastomer.

HYDROPHILIC GELLING AGENT/LIPOPHILIC GELLING AGENT SYSTEM

As preferred synthetic polymeric hydrophilic gelling agents, mention may be made more particularly of 2-acrylamido-2-methylpropanesulfonic acid polymers, for instance AMPS®, such as the ammonium 2-acrylamido-2-methylpropanesulfonate polymer sold under the trade name Hostacerin AMPS® by the company Clariant, and 2-acrylamido-2-methyl propanesulfonic acid copolymers and in particular copolymers of AMPS® and of hydroxyethyl acrylate, for instance the AMPS®/hydroxyethyl acrylate copolymer such as that used in the commercial product sold under the name Simulgel NS® by the company SEPPIC (CTFA name: Hydroxyethyl acrylate/sodium acryloyldimethyltaurate copolymer (and) squalane (and) polysorbate 60), or such as the product sold under the name Sodium acrylamido-2-methylpropanesulfonate/hydroxyethyl acrylate copolymer, such as the commercial product Sepinov EMT 10® (INCI name: Hydroxyethyl acrylate/Sodium acryloyldimethyltaurate copolymer).

As preferred lipophilic gelling agents, mention may be made of organopolysiloxane elastomers preferably chosen from Dimethicone Crosspolymer (INCI name), Dimethicone (and) Dimethicone Crosspolymer (INCI name), Vinyl Dimethicone Crosspolymer (INCI name), Dimethicone/Vinyl Dimethicone Crosspolymer (INCI name), Dimethicone Crosspolymer-3 (INCI name), and in particular Dimethicone Crosspolymer (INCI name) and Dimethicone (and) Dimethicone Crosspolymer (INCI name).

According to a preferred mode, as preferred lipophilic gelling agents, mention may be made more particularly of gels of silicone elastomer dispersed in a silicone oil and/or powders of organopolysiloxane elastomer coated with silsesquioxane resin.

Thus, according to a particular mode, use is made of a gel of silicone elastomer dispersed in a silicone oil chosen from a non-exhaustive list comprising cyclopentadimethylsiloxane, dimethicones, dimethylsiloxanes, methyl trimethicone, phenyl methicone, phenyl dimethicone, phenyl trimethicone and cyclomethicone, preferably a linear silicone oil chosen from polydimethylsiloxanes (PDMS) or dimethicones with a viscosity at 25°C ranging from 1 to 500 cSt at 25°C, especially the following references:

- dimethicone/vinyl dimethicone crosspolymer (and) dimethicone, such as KSG-6® and KSG-1 6® from the company Shin-Etsu;
- dimethicone (and) dimethicone crosspolymer, such as DC9041® from the company Dow Corning; and
- dimethicone (and) dimethicone crosspolymer, such as Dow Corning EL-9240® Silicone Elastomer Blend from the company Dow Corning.

As non-limiting illustrations of hydrophilic gelling agent/lipophilic gelling agent systems that are most particularly suitable for use in the invention, mention may be made especially of the polymer or copolymer system of 2-acrylamido-2-methylpropanesulfonic acid/organopolysiloxane elastomer.

Thus, a composition according to the invention may advantageously comprise as hydrophilic gelling agent/lipophilic gelling agent system, a polymer system of 2-acrylamido-2-methylpropanesulfonic acid/organopolysiloxane elastomer(s) or copolymer of 2-acrylamido-2-methylpropanesulfonic acid and of hydroxyethyl acrylate/organopolysiloxane elastomer(s).

Preferably, a composition according to the invention may comprise as hydrophilic gelling agent/lipophilic gelling agent system, a copolymer system of 2-acrylamido-2-methylpropanesulfonic acid and of hydroxyethyl acrylate/organopolysiloxane elastomer powder.

AQUEOUS PHASE

The aqueous phase of a composition according to the invention comprises water and optionally a water-soluble solvent.

In the present invention, the term "water-soluble solvent" denotes a compound that is liquid at room temperature and water-miscible (miscibility with water of greater than 50% by weight at 25°C and atmospheric pressure).

The water-soluble solvents that may be used in the composition of the invention may also be volatile.

Among the water-soluble solvents that may be used in the composition in accordance with the invention, mention may be made especially of lower monoalcohols containing from 1 to 5 carbon atoms such as ethanol and isopropanol, glycols containing from 2 to 8 carbon atoms such as ethylene glycol, propylene glycol, 1,3-butylene glycol and dipropylene glycol, C_3 and C_4 ketones and C_2-C_4 aldehydes.

The aqueous phase (water and optionally the water-miscible solvent) may be present in the composition in a content ranging from 5% to 95%, better still from 30% to 80% by weight and preferably from 40% to 75% by weight relative to the total weight of said composition.

According to another embodiment variant, the aqueous phase of a composition according to the invention may comprise at least one C_2-C_{32} polyol.

For the purposes of the present invention, the term *"polyof* should be understood as meaning any organic molecule comprising at least two free hydroxyl groups.

Preferably, a polyol in accordance with the present invention is present in liquid form at room temperature.

A polyol that is suitable for use in the invention may be a compound of linear, branched or cyclic, saturated or unsaturated alkyl type, bearing on the alkyl chain at least two -OH functions, in particular at least three -OH functions and more particularly at least four -OH functions.

The polyols that are advantageously suitable for formulating a composition according to the present invention are those especially containing from 2 to 32 carbon atoms and preferably 3 to 16 carbon atoms.

Advantageously, the polyol may be chosen, for example, from ethylene glycol, pentaerythritol, trimethylolpropane, propylene glycol, 1,3-propanediol, butylene glycol, isoprene glycol, pentylene glycol, hexylene glycol, glycerol, polyglycerols, such as glycerol oligomers, for instance diglycerol, and polyethylene glycols, and mixtures thereof.

According to a preferred embodiment of the invention, said polyol is chosen from ethylene glycol, pentaerythritol, trimethylolpropane, propylene glycol, glycerol, polyglycerols, polyethylene glycols and mixtures thereof.

According to a particular mode, the composition of the invention may comprise at least propylene glycol.

According to another particular mode, the composition of the invention may comprise at least glycerol.

OILY PHASE

For the purposes of the invention, an oily phase comprises at least one oil.

The term "oil" means any fatty substance that is in liquid form at room temperature (25°C) and atmospheric pressure (760 mmHg).

An oily phase that is suitable for preparing the compositions, especially cosmetic compositions, according to the invention may comprise hydrocarbon-based oils, silicone oils, fluoro oils or non-fluoro oils, or mixtures thereof.

The oils may be volatile or non-volatile.

They may be of animal, plant, mineral or synthetic origin. According to one embodiment variant, oils of silicone origin are preferred.

For the purposes of the present invention, the term "non-volatile oil" means an oil with a vapour pressure of less than 0.13 Pa.

For the purposes of the present invention, the term "silicone oil" means an oil comprising at least one silicon atom, and especially at least one Si-O group.

The term "fluoro oil" means an oil comprising at least one fluorine atom.

The term "hydrocarbon-based oil" means an oil mainly containing hydrogen and carbon atoms.

The oils may optionally comprise oxygen, nitrogen, sulfur and/or phosphorus atoms, for example in the form of hydroxyl or acid radicals.

For the purposes of the invention, the term "volatile oil" means any oil that is capable of evaporating on contact with the skin in less than one hour, at room temperature and atmospheric pressure.

The volatile oil is a volatile cosmetic compound, which is liquid at room temperature, especially having a non-zero vapour pressure, at room temperature and atmospheric pressure, especially having a vapour pressure ranging from 0.13 Pa to 40 000 Pa (10^{-3} to 300 mmHg), in particular ranging from 1.3 Pa to 13 000 Pa (0.01 to 100 mmHg) and more particularly ranging from 1.3 Pa to 1300 Pa (0.01 to 10 mmHg).

Volatile oils

The volatile oils may be hydrocarbon-based oils or silicone oils.

Among the volatile hydrocarbon-based oils containing from 8 to 16 carbon atoms, mention may be made especially of branched C8-C16 alkanes, for instance C8-C16 isoalkanes (also known as isoparaffins), isododecane, isodecane, isohexadecane and, for example, the oils sold under the trade names Isopar or Permethyl, branched C8-C16 esters, for instance isohexyl neopentanoate, and mixtures thereof. Preferably, the volatile hydrocarbon-based oil is chosen from volatile hydrocarbon-based oils containing from 8 to 16 carbon atoms, and mixtures thereof, in particular from isododecane, isodecane and isohexadecane, and is in particular isohexadecane.

Mention may also be made of volatile linear alkanes comprising from 8 to 16 carbon atoms, in particular from 10 to 15 carbon atoms and more particularly from 11 to 13 carbon atoms, for instance n-dodecane (C12) and n-tetradecane (C14) sold by Sasol under the respective references Parafol 12-97® and Parafol 14-97®, and also mixtures thereof, the undecane-tridecane mixture, mixtures of n-undecane (C11) and of n-tridecane (C13) obtained in Examples 1 and 2 of patent application WO 2008/155 059 from the company Cognis, and mixtures thereof.

Volatile silicone oils that may be mentioned include linear volatile silicone oils such as hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, tetradecamethylhexasiloxane, hexadecamethylheptasiloxane and dodecamethylpentasiloxane.
Volatile cyclic silicone oils that may be mentioned include hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane.

Non-volatile oils

The non-volatile oils may, in particular, be selected from non-volatile hydrocarbon-based, fluoro and/or silicone oils.

Non-volatile hydrocarbon-based oils that may especially be mentioned include:
- hydrocarbon-based oils of animal origin,
- hydrocarbon-based oils of plant origin, synthetic ethers containing from 10 to 40 carbon atoms, such as dicaprylyl ether,
- synthetic esters, for instance the oils of formula R1COOR2, in which R1 represents a linear or branched fatty acid residue containing from 1 to 40 carbon atoms and R2 represents a hydrocarbon-based chain, which is especially branched, containing from 1 to 40 carbon atoms, on condition that $R1 + R2 \geq 10$. The esters may be chosen especially from alcohol fatty acid esters, for instance cetostearyl octanoate, isopropyl alcohol esters, such as isopropyl myristate, isopropyl palmitate, ethyl palmitate, 2-ethylhexyl palmitate, isopropyl stearate, octyl stearate, hydroxylated esters, for instance isostearyl lactate, octyl hydroxystearate, alcohol or polyalcohol ricinoleates, hexyl laurate, neopentanoic acid esters, for instance isodecyl neopentanoate, isotridecyl neopentanoate, and isononanoic acid esters, for instance isononyl isononanoate and isotridecyl isononanoate,
- polyol esters and pentaerythritol esters, for instance dipentaerythritol tetrahydroxystearate/tetraisostearate,
- fatty alcohols that are liquid at room temperature, with a branched and/or unsaturated carbon-based chain containing from 12 to 26 carbon atoms, for instance 2-octyldodecanol, isostearyl alcohol and oleyl alcohol,
- C12-C22 higher fatty acids, such as oleic acid, linoleic acid and linolenic acid, and mixtures thereof,
- non-phenyl silicone oils, for instance caprylyl methicone, and

- phenyl silicone oils, for instance phenyl trimethicones, phenyl dimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenyl dimethicones, diphenylmethyldiphenyltrisiloxanes and **2**-phenylethyl trimethylsiloxysilicat.es, dimethicones or phenyl trimethicone with a viscosity of less than or equal to 100 cSt, and trimethyl-pentaphenyl-trisiloxane, and mixtures thereof; and also mixtures of these various oils.

Preferably, a composition according to the invention comprises volatile and/or non-volatile silicone oils. Such silicone oils are particularly appreciated when the lipophilic gelling agent is an organopolysiloxane elastomer.

A composition according to the invention may comprise from 5% to 95% by weight, better still from 5% to 40% by weight and preferably from 7% to 35% by weight of oil(s) relative to the total weight of said composition.

As mentioned above, the gelled oily phase according to the invention may have a threshold stress of greater than 1.5 Pa and preferably greater than 10 Pa. This threshold stress value reflects a gel-type texture of this oily phase.

POLAR OILS

According to a particular form of the invention, when the composition comprises at least one glycol compound of formula **(2),** the gelled oily phase comprises at least one polar oil.

The term "polar oil" means any oil which has solubility parameters in the Hansen solubility space such that $13 < \delta_d < 22$.

The definition of the solubility parameters in the Hansen three-dimensional solubility space are described in the article by CM. Hansen: *The three-dimensional solubility parameters,* J. Paint Technol. 39, 105 (1967).

According to this Hansen space:
- δ_D characterizes the London dispersion forces derived from the formation of dipoles induced during molecular impacts;
- δ_p characterizes the Debye interaction forces between permanent dipoles and also the Keesom interaction forces between induced dipoles and permanent dipoles;
- δ_h characterizes the specific interaction forces (such as hydrogen bonding, acid/base, donor/acceptor, etc.); and
- δ_a is determined by the equation: $\delta_a = (\delta_p^2 + \delta_h^2)^{½}$.

The parameters δ_p, δ_h, δ_D and δ_a are expressed in $(J/cm^3)^{½}$.
The solubility parameters are calculated with the HSPiP v4.1 software.

More preferentially, the polar oil(s) in accordance with the invention will also be characterized by $1 < \delta_a < 10$.

The polar oil(s) in accordance with the invention may be of plant, mineral or synthetic origin.

They may be chosen from hydrocarbon-based oils and silicone oils, and mixtures thereof.

A) Polar hydrocarbon-based oils

Among the hydrocarbon-based polar oils that may be used in the oily phase of the compositions of the invention, mention may be made of:
- phytostearyl esters, such as phytostearyl oleate, phytostearyl isostearate and lauroyl/octyldodecyl/phytostearyl glutamate (Ajinomoto, Eldew PS203®),
- triglycerides constituted of fatty acid esters of glycerol, in particular the fatty acids of which may have chain lengths ranging from C4 to C36, and in particular from C18 to C36, these oils possibly being linear or branched, and saturated or unsaturated; these oils may in particular be heptanoic or octanoic triglycerides, wheatgerm oil, sunflower oil, grapeseed oil, sesame seed oil (820.6 g/mol), corn oil, apricot oil, castor oil, shea oil, avocado oil, olive oil, soybean oil, sweet almond oil, palm oil, rapeseed oil, cottonseed oil, hazelnut oil, macadamia oil, jojoba oil, alfalfa oil, poppy oil, pumpkin oil, marrow oil, blackcurrant oil, evening primrose oil, millet oil, barley oil, quinoa oil, rye oil, safflower oil, candlenut oil, passionflower oil or musk rose oil; shea oil; or alternatively caprylic/capric acid triglycerides, for instance those sold by the company Stearineries Dubois or those sold under the names Miglyol 810®, 812® and 818® by the company Dynamit Nobel;
- synthetic ethers containing from 10 to 40 carbon atoms, such as dicaprylyl ether,
- hydrocarbon-based esters of formula RCOOR' in which RCOO represents a carboxylic acid residue comprising from 2 to 40 carbon atoms, and R' represents a hydrocarbon-based chain containing from 1 to 40 carbon atoms, such as cetostearyl octanoate, isopropyl alcohol esters, such as isopropyl myristate or isopropyl palmitate, ethyl palmitate, 2-ethylhexyl palmitate, isopropyl stearate or isostearate, isostearyl isostearate, octyl stearate, diisopropyl adipate, heptanoates, and in particular isostearyl heptanoate, alcohol or polyalcohol octanoates, decanoates or ricinoleates, for instance propylene glycol dioctanoate, cetyl octanoate, tridecyl octanoate, 2-ethylhexyl 4-diheptanoate and palmitate, alkyl benzoate, polyethylene glycol diheptanoate, propylene glycol 2-diethyl hexanoate, and mixtures thereof, C12 to C15 alcohol benzoates, hexyl laurate, neopentanoic acid esters, for instance isodecyl neopentanoate, isotridecyl neopentanoate, isostearyl neopentanoate and 2-octyldodecyl neopentanoate, isononanoic acid esters, for instance isononyl isononanoate, isotridecyl isononanoate and octyl isononanoate, oleyl erucate, isopropyl lauroyl sarcosinate, diisopropyl sebacate, isocetyl stearate, isodecyl neopentanoate, isostearyl behenate, and myristyl myristate;
- polyesters obtained by condensation of an unsaturated fatty acid dimer and/or trimer and of diol, such as those described in patent application FR 0 853 634, in particular such as dilinoleic acid and 1,4-butanediol. Mention may in particular be made in this respect of the polymer sold by Biosynthis under the name Viscoplast 14436H® (INCI name: Dilinoleic Acid/Butanediol Copolymer), or copolymers of polyols and of diacid dimers, and esters thereof, such as Hailuscent ISDA®,

- polyol esters and pentaerythritol esters, for instance dipentaerythritol tetrahydroxystearate/tetraisostearate,
- fatty alcohols containing from 12 to 26 carbon atoms, for instance octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol and oleyl alcohol,
- dialkyl carbonates, the two alkyl chains possibly being identical or different, such as dicaprylyl carbonate sold under the name Cetiol CC® by Cognis; and
-vinylpyrrolidone copolymers such as the vinylpyrrolidone/1-hexadecene copolymer, Antaron V-216® sold or manufactured by the company ISP,
- linear fatty acid esters with a total carbon number ranging from 35 to 70, such as pentaerythrityl tetrapelargonate,
- hydroxylated esters such as polyglyceryl-2 triisostearate,
- aromatic esters such as tridecyl trimellitate, C12-C15 alcohol benzoate, the 2-phenylethyl ester of benzoic acid, and butyloctyl salicylate,
- C24-C28 esters of branched fatty alcohols or fatty acids such as those described in patent application EP-A-0 955 039, and in particular triisoarachidyl citrate, pentaerythrityl tetraisononanoate, glyceryl triisostearate, glyceryl tris(2-decyl)tetradecanoate, pentaerythrityl tetraisostearate, polyglyceryl-2 tetraisostearate or pentaerythrityl tetrakis(2-decyl)tetradecanoate,
- esters and polyesters of dimer diol and of monocarboxylic or dicarboxylic acid, such as esters of dimer diol and of fatty acid and esters of dimer diol and of dimer dicarboxylic acid, such as Lusplan DD-DA5® and Lusplan DD-DA7® sold by the company Nippon Fine Chemical and described in patent application US 2004-175 338, the content of which is incorporated into the present application by reference,
- and mixtures thereof.

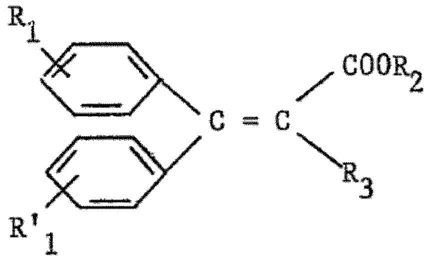
According to one particular mode, the non-volatile hydrocarbon-based oil may be chosen from liquid lipophilic organic UV-screening agents.

The term "liquid lipophilic organic screening agent" means any organic chemical molecule that is capable of absorbing at least UV radiation in the wavelength range between 280 and 400 nm, said molecule being in liquid form at room temperature (20 - 25°C) and at atmospheric pressure (760 mmHg) and capable of being miscible in an oily phase.

The liquid organic UV-screening agents that can be used according to the invention may be chosen from
- liquid lipophilic β,β-diphenylacrylate compounds,
- liquid lipophilic salicylate compounds,
- liquid lipophilic cinnamate compounds,
- and mixtures thereof.

i) β,β-Diphenylacrylate compounds

Among the liquid lipophilic organic UVB-screening agents that can be used according to the invention, mention may be made of the liquid lipophilic alkyl β,β-diphenylacrylate or a-cyano^^-diphenylacrylate compounds of formula (I) below:


(I)

where Ri to R3 can have the following meanings:

- Ri and R'i, which may be identical or different, represent a hydrogen atom, a straight-chain or branched-chain C_1-Cs alkoxy radical or a straight-chain or branched-chain Ci-C_4 alkyl radical;
- R_1 and R'i being in the para meta position;
- R2 represents a straight-chain or branched-chain C 1-C12 alkyl radical;
- R3 represents a hydrogen atom or the CN radical.

Among the straight-chain or branched-chain C_1-Cs alkoxy radicals, mention may for example be made of methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, tert-butoxy, n-amyloxy, isoamyloxy, neopentyloxy, n-hexyloxy, n-heptyloxy, n-octyloxy and 2-ethylhexyloxy radicals.

Among the straight-chain or branched-chain Ci-C_4 alkyl radicals, mention may more particularly be made of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tert-butyl radicals. For the C 1-C12 alkyl radicals, mention may be made, by way of example, in addition to those mentioned above, of n-amyl, isoamyl, neopentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, decyl and lauryl radicals.

Among the compounds of general formula (I), the following compounds are more particularly preferred:

- 2-ethylhexyl a-cyano-p,p-diphenylacrylate or Octocrylene, sold in particular under the trade name UVINUL N539® by BASF;
- ethyl a-cyano-p,p-diphenylacrylate such as Etocrylene, sold in particular under the trade name UVINUL N35® by BASF;
- 2-ethylhexyl β,β-diphenylacrylate;
- ethyl p,p-di(4'-methoxyphenyl)acrylate.

Among the compounds of general formula (I), the compound 2-ethylhexyl 2-cyano-3,3-diphenylacrylate or Octocrylne is even more particularly preferred.

ii) Salicylate compounds

Among the liquid lipophilic salicylate compounds that can be used according to the invention, mention may be made of:

- Homosalate, sold under the name Eusolex HMS® by Rona/EM Industries,

- Ethylhexyl salicylate, sold under the name Neo Heliopan OS® by Symrise.

iii) Cinnamate compounds

Among the liquid lipophilic cinnamate compounds that can be used according to the invention, mention may be made of:
- Ethylhexyl Methoxycinnamate, sold in particular under the trade name Parsol MCX® by DSM Nutritional Products,
- Isopropyl Methoxycinnamate,
- Isoamyl Methoxycinnamate, sold under the trade name Neo Heliopan E 1000 by Symrise.

Among the liquid lipophilic screening agents according to the invention, use will more particularly be made of the compound Ethylhexyl Methoxycinnamate.

Preferentially, the polar hydrocarbon-based oil will be Ethylhexyl Methoxycinnamate.

B) Polar silicone oils

The polar silicone oils that may be used in the oily phase of the compositions of the invention may be chosen from certain non-phenyl silicone oils, phenyl silicone oils, and mixtures thereof.

The term "phenyl silicone" (also referred to as phenyl silicone oil) is understood to mean an organopolysiloxane substituted with at least one phenyl group.

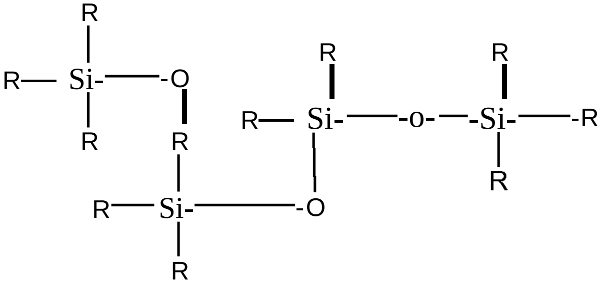
a) Non-phenyl silicone oils

Among the polar non-phenyl silicone oils that may be used in the oily phase of the compositions of the invention, mention may be made of:
- volatile cyclic silicone oils having a viscosity at room temperature of less than 8 cSt and containing in particular from 4 to 7 silicone atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms, such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane (cyclohexasiloxane);
- polydimethylsiloxanes comprising aliphatic groups, in particular alkyl groups, or alkoxy groups, which are pendent and/or at the end of the silicone chain; these groups each comprising from 6 to 24 carbon atoms, for instance caprylyl methicone, such as the commercial product Dow Corning FZ-31 96® from the company Dow Corning.

b) Phenyl silicone oils

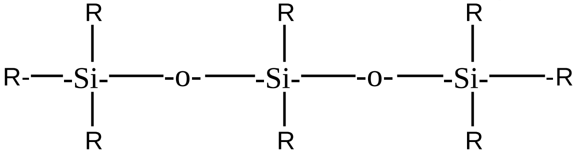
The phenyl silicone oil may be chosen from phenyl trimethicones, phenyl dimethicones, phenyltrimethylsiloxydiphenylsiloxanes, diphenyl dimethicones, diphenylmethyldiphenyltrisiloxanes, trimethylpentaphenyltrisiloxane and 2-phenylethyl trimethylsiloxysilicat.es.

The silicone oil can correspond to the formula:



in which the R groups represent, independently of each other, a methyl or a phenyl. Preferably, in this formula, the silicone oil comprises at least three phenyl groups, for example at least four, at least five or at least six.

According to another embodiment, the silicone oil corresponds to the formula:



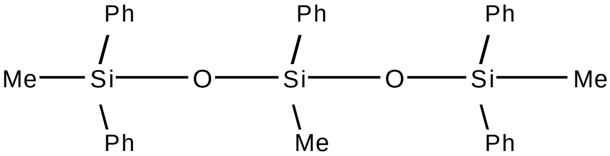
$$R-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-R$$

in which the R groups represent, independently of each other, a methyl or a phenyl. Preferably, in this formula, said organopolysiloxane comprises at least three phenyl groups, for example at least four or at least five.

Mixtures of the phenyl organopolysiloxanes described above can be used.

Mention may be made, for example, of mixtures of triphenylated, tetraphenylated or pentaphenylated organopolysiloxane.

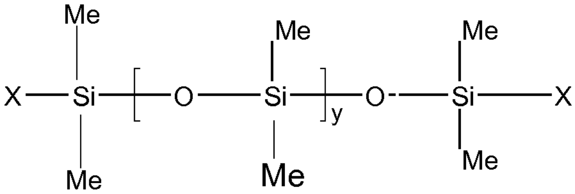
According to another embodiment, the silicone oil corresponds to the formula:



$$Me-\overset{Ph}{\underset{Ph}{Si}}-O-\overset{Ph}{\underset{Me}{Si}}-O-\overset{Ph}{\underset{Ph}{Si}}-Me$$

in which Me represents methyl and Ph represents phenyl. Such a phenyl silicone is especially manufactured by Dow Corning under the reference Dow Corning 555 Cosmetic Fluid® (INCI name: trimethyl pentaphenyl trisiloxane). The reference Dow Corning 554 Cosmetic Fluid® may also be used.

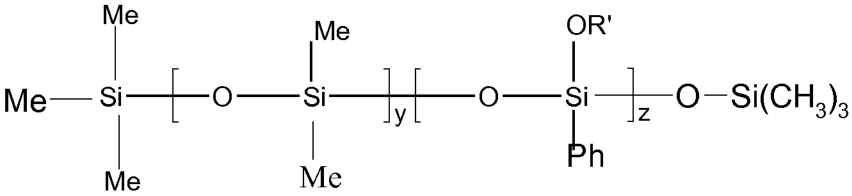
According to another embodiment, the silicone oil corresponds to the formula:



$$X-\overset{Me}{\underset{Me}{Si}}-\left[O-\overset{Me}{\underset{Me}{Si}}\right]_y-O-\overset{Me}{\underset{Me}{Si}}-X$$

in which Me represents methyl, y is between 1 and 1000 and X represents $-CH_2-CH(CH_3)(Ph)$.

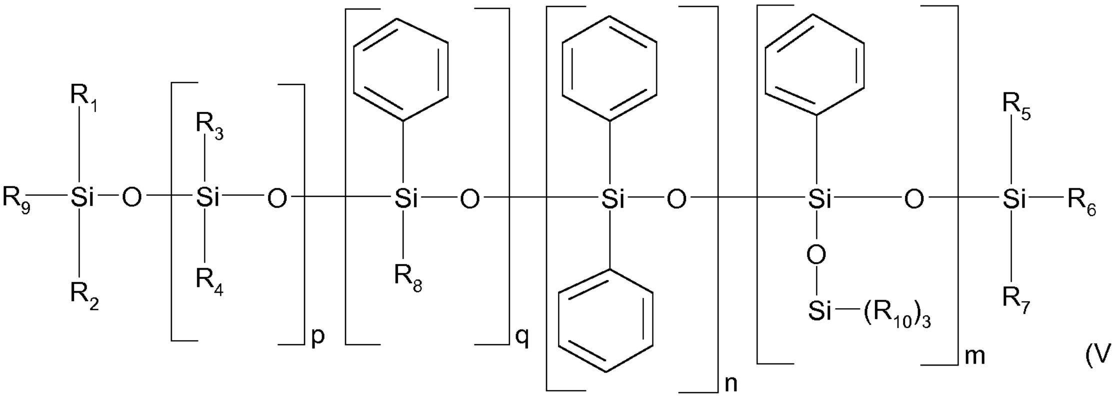
According to another embodiment, the silicone oil corresponds to the formula:



$$Me-\underset{Me}{\overset{Me}{Si}}-\left[O-\underset{Me}{\overset{Me}{Si}}\right]_y-\left[O-\underset{Ph}{\overset{OR'}{Si}}\right]_z-O-Si(CH_3)_3$$

in which -OR' represents -O-SiMe3, y is between 1 and 1000 and z is between 1 and 1000.

The phenyl silicone oil can be chosen from the phenyl silicones of following formula (VI):



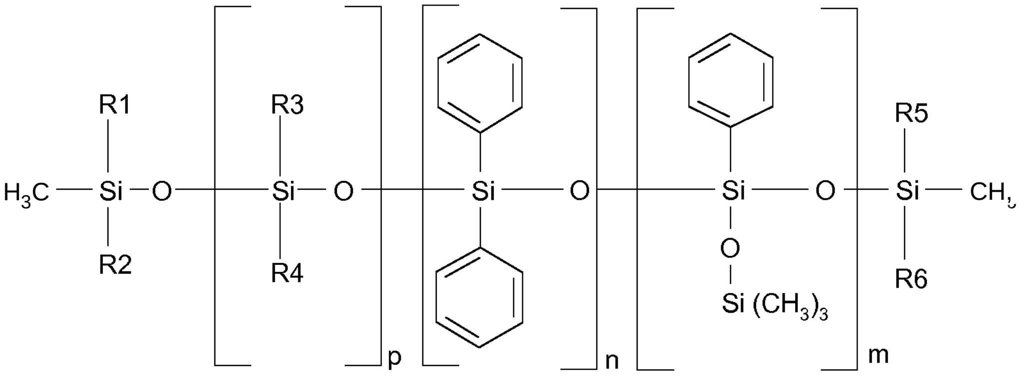
(VI)

in which:

- R_1 to R_{10}, independently of each other, are saturated or unsaturated, linear, cyclic or branched C_1-C_{30} hydrocarbon-based radicals,
- m, n, p and q are, independently of each other, integers between 0 and 900, with the proviso that the sum m+n+q is other than 0.

Preferably, the sum "m+n+p+q" is between 1 and 100. Preferably, the sum "m+n+q" is between 1 and 900 and better still between 1 and 800. Preferably, q is equal to 0.

The phenyl silicone oil can be chosen from the phenyl silicones of following formula (VII):



(VII)

in which:

- Ri to R6, independently of each other, are saturated or unsaturated, linear, cyclic or branched C1-C30 hydrocarbon-based radicals,
- m, n and p are, independently of each other, integers between 0 and 100, with the proviso that the sum n+m is between 1 and 100.

Preferably, Ri to R6, independently of each other, represent a saturated, linear or branched C1-C30 and especially C1-C12 hydrocarbon-based radical and in particular a methyl, ethyl, propyl or butyl radical.

Ri to R6 may especially be identical, and in addition may be a methyl radical.

Preferably, it is possible to have m = 1 or 2 or 3, and/or n = 0 and/or p = 0 or 1, in the formula (VII).

Use may be made of a phenylated silicone oil of formula (VI) having a viscosity at 25°C of between 5 and 1500 mm^2/s (i.e. 5 to 1500 cSt) and preferably having a viscosity of between 5 and 1000 mm^2/s (i.e. 5 to 1000 cSt).

As phenyl silicone oils of formula (VII), it is especially possible to use phenyl trimethicones such as DC556 from Dow Corning (22.5 cSt), the oil Silbione 70663V30 from Rhone-Poulenc (28 cSt) or diphenyl dimethicones such as Belsil oils, especially Belsil PDM1 000® (1000 cSt), Belsil PDM 200® (200 cSt) and Belsil PDM 20 (20 cSt) from Wacker. The values in brackets represent the viscosities at 25°C.

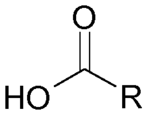
Preferentially, the polar oil will be chosen from ethylhexyl methoxycinnamate, dodecamethylcyclohexasiloxane and caprylyl methicone, and mixtures thereof.

The polar oil(s) are preferably present in the composition in concentrations ranging from 0.5% to 60% and more preferentially from 2% to 30% by weight relative to the total weight of the composition.

The polar oil(s) are preferably present in the composition in concentrations ranging from 2% to 95% and more preferentially from 5% to 80% by weight relative to the total weight of the oily phase.

LIQUID FATTY ACID:

The liquid fatty acids in accordance with the invention correspond to formula (1) below:



(1)

in which R is chosen from:
a) a saturated, branched CM-C22, preferably Cis, alkyl group, or
b) an alkyl group comprising at least one linear or branched C_{14}-C22, preferably c18, double bond.

Among the compounds of formula (1) for which R denotes a saturated branched C_{14}-C22 alkyl, mention may be made in particular of isostearic acid (Cis), such as the products sold under the trade names
- AEC Isostearic Acid® by the company A & E Connock (Perfumery & Cosmetics) Ltd.
- Isostearic Acid EX® by the company Kokyu Alcohol Kogyo Co., Ltd;
- Liponate ISA® by the company Lipo Chemicals, Inc.;
- Prisorine 3505® by the company Croda Europe, Ltd.

Among the compounds of formula (1) for which R represents a linear or branched C_{14}-C22 alkyl group comprising at least one double bond, mention may be made in particular of:
- oleic acid (Cis)
- linoleic acid (Cis)
- linolenic acid (Cis); and
- mixtures thereof.

The liquid fatty acids in accordance with the invention are more particularly chosen from
- isostearic acid (Cis)
- oleic acid (Cis)
- linoleic acid (Cis)
- linolenic acid (Cis); and
- mixtures thereof.

Isostearic acid will be used more particularly.

The liquid fatty acid(s) in accordance with the invention are present in the compositions of the invention preferably in concentrations ranging from 0.1 % to 5% by weight and more preferentially from 0.2% to 3% by weight relative to the total weight of the composition.

GLYCOL COMPOUND

The glycol compound(s) present in the compositions of the invention correspond to formula (2) below:

$$CH_3\text{-}\ [CH_2CH_2]_m\text{-}[COO]n\ \text{-}\ CH_2\text{-}CH(OH)\text{-}CH_2OH$$

(2)

in which:
- m is between 2 and 4
- n is equal to 0 or 1.

Among the preferential compounds of formula (2) that may be mentioned are:
- caprylyl glycol of formula $CH_3(CH_2)_4CH_2CH(OH)CH_2OH$ (m = 2 and n= 0) such as the commercial products sold under the trade names

Botanistat CG® (Botanigenics, Inc.)
Dermosoft Octiol® (Dr. Straetmans)
Hydrolite-8 1091 69® (Symrise)
199602 Hydrolite CG® (Symrise)
Jeecide CAP® (Jeen International Corporation)
Lexgard O® (Inolex Inc.)
OriStar CPG® (Orient Stars LLC)
ParaPure (Paradigm Science, Inc;

- glyceryl caprylate of formula $CH_3(CH_2)_6COOCH_2CH(OH)CH_2OH$ (m = 3, n= 1) such as the commercial products sold under the trade names:

AEC Glyceryl Caprylate (A & E Connock (Perfumery & Cosmetics) Ltd.)
Capmul 708G (Abitec Corporation)
CremerCOOR GC 8 (Cremer Oleo)
Dermosoft GMCY (Dr. Straetmans)
Dub 8G (Stearinerie Dubois Fils)
Imwitor 308 (Cremer Oleo)
Imwitor 988 (Cremer Oleo)
Lexgard GMCY (Inolex Inc.)
OriStar GCC (Orient Stars LLC)
Sunsoft 707 (Taiyo Kagaku Company, Ltd.)
Sunsoft 700 P-2 (Taiyo Kagaku Company, Ltd.)

- glyceryl caprate of formula $CH_3(CH_2)_8COOCH_2CH(OH)CH_2OH$ (m = 4 and n= 1) such as the commercial products sold under the trade names:

AEC Glyceryl Caprate® (A & E Connock (Perfumery & Cosmetics) Ltd.)
Capmul MCM C-1 0® (Abitec Corporation)
Dermosoft GMC® (Dr. Straetmans)
Lexgard GMC® (Inolex Inc.)
Sunsoft 760® (Taiyo Kagaku Company, Ltd.)

- and mixtures thereof.

Mention may also be made of glyceryl caprylate/caprate mixtures such as the commercial products sold under the trade names:
AEC Glyceryl Caprylate/Caprate® (A & E Connock (Perfumery & Cosmetics) Ltd.)
CremerCOOR GC810® (Cremer Oleo)
Dub 810 G® (Stearinerie Dubois Fils)

Use will be made more particularly of caprylyl glycol, glyceryl caprylate, and mixtures thereof.

The compound(s) of formula (2) are present in the compositions of the invention preferably in concentrations ranging from 0.1 % to 5% by weight and more preferentially from 0.2% to 3% by weight relative to the total weight of the composition.

HYDROPHOBIC-COATED PIGMENTS

The term *"pigments"* means white or coloured, mineral or organic particles, which are insoluble in an aqueous medium, and which are intended to colour and/or opacify the resulting composition and/or film. These pigments may be white or coloured, and mineral and/or organic.

The term "hydrophobic-coated pigment" means any pigment coated with at least one lipophilic or hydrophobic compound.

The term "lipophilic compound" means any compound that is soluble or dispersible in an oily phase.

The term "hydrophobic compound" means any compound that is insoluble in water.

According to a particular embodiment, the hydrophobic modified pigments used according to the invention are chosen from mineral pigments.

The term *"mineral pigment'* means any pigment that satisfies the definition in Ullmann's encyclopaedia in the chapter on inorganic pigments. Among the mineral pigments that are useful in the present invention, mention may be made of 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, titanium dioxide, and metal powders, for instance aluminium powder or copper powder. The following mineral pigments may also be used: Ta2O$_5$, Ti$_3$O$_5$, T12O3, TiO, ZrO2 as a mixture with T1O2, ZrO2, Nb2O$_5$, CeO2, ZnS.

The particular size of the coated pigment is strictly greater than 100 nm.

For the purpose of the invention, the "size" of a particle means its D50. The D50, or volume average size, corresponds to the particle size defined such that 50% by volume of the particles have a size greater than D50.

The volume average size may be assessed by light diffraction using a Malvern MasterSizer laser particle size analyser, said particles to be evaluated being dispersed in a liquid medium, for instance octyldodecyl neopentanoate.

According to one embodiment, the size of the pigment particles according to the invention ranges from 100 nm to 25 μιτι, preferably from 200 nm to 10 μιτι.

In the context of the present invention, the hydrophobic modified mineral pigments are more particularly hydrophobic modified pigments of iron oxide and/or titanium dioxide.

They may also be nacres and/or particles with metallic glints.

The term *"nacres"* should be understood as meaning iridescent or non-iridescent coloured particles of any shape, especially produced by certain molluscs in their shell or alternatively synthesized, which have a colour effect via optical interference.

The nacres may be chosen from nacreous pigments such as titanium mica coated with an iron oxide, titanium mica coated with bismuth oxychloride, titanium mica coated with chromium oxide, titanium mica coated with an organic dye and also nacreous pigments based on bismuth oxychloride. They may also be mica particles, at the surface of which are superposed at least two successive layers of metal oxides and/or of organic dyestuffs.

Examples of nacres that may also be mentioned include natural mica covered with titanium oxide, with iron oxide, with natural pigment or with bismuth oxychloride.

The nacres may more particularly have a yellow, pink, red, bronze, orange, brown, gold and/or coppery colour or glint.

Advantageously, the nacres in accordance with the invention are micas covered with titanium dioxide or with iron oxide, and also bismuth oxychloride.

For the purposes of the present invention, the term *"particles with a metallic glint'* means any compound whose nature, size, structure and surface finish allow it to reflect the incident light, especially in a non-iridescent manner.

The particles with a metallic glint that may be used in the invention are in particular chosen from:
- particles of at least one metal and/or of at least one metal derivative;
- particles comprising a monomaterial or multimaterial organic or mineral substrate, at least partially coated with at least one layer with a metallic glint comprising at least one metal and/or at least one metal derivative, and
- mixtures of said particles.

Among the metals that may be present in said particles, mention may be made, for example, of Ag, Au, Cu, Al, Ni, Sn, Mg, Cr, Mo, Ti, Zr, Pt, Va, Rb, W, Zn, Ge, Te and Se, and mixtures or alloys thereof. Ag, Au, Cu, Al, Zn, Ni, Mo and Cr, and mixtures or alloys thereof (for example bronzes and brasses) are preferred metals.

The term *"metal derivatives"* denotes compounds derived from metals, especially oxides, fluorides, chlorides and sulfides.

Coating of the pigment

The composition according to the invention advantageously comprises at least one pigment coated with at least one lipophilic or hydrophobic compound.

The coating may also comprise at least one additional non-lipophilic compound.

For the purposes of the invention, the *"coating"* of a pigment according to the invention generally denotes the total or partial surface treatment of the pigment with a surface agent, absorbed, adsorbed or grafted onto said pigment.

The surface-treated pigments may be prepared according to surface treatment techniques of chemical, electronic, mechanochemical or mechanical nature that are well known to those skilled in the art. Commercial products may also be used.

The surface agent may be absorbed, adsorbed or grafted onto the pigments by evaporation of solvent, chemical reaction and creation of a covalent bond.

According to one variant, the surface treatment is constituted of a coating of the pigments.

The coating may represent from 0.1 % to 20% by weight and in particular from 0.5% to 5% by weight relative to the total weight of the coated pigment.

The coating may be performed, for example, by adsorption of a liquid surface agent onto the surface of the solid particles by simple mixing with stirring of the particles and of said surface agent, optionally with heating, prior to the incorporation of the particles into the other ingredients of the makeup or care composition.

The coating may be performed, for example, by chemical reaction of a surface agent with the surface of the solid pigment particles and creation of a covalent bond between the surface agent and the particles. This method is especially described in patent US 4 578 266.

The chemical surface treatment may consist in diluting the surface agent in a volatile solvent, dispersing the pigments in this mixture and then slowly evaporating off the volatile solvent, so that the surface agent is deposited at the surface of the pigments.

Lipophilic or hydrophobic treatment agent

According to a particular embodiment of the invention, the pigments may be coated according to the invention with at least one compound chosen from silicone surface agents; fluoro surface agents; fluorosilicone surface agents; metal soaps; N-acylamino acids or salts thereof; lecithin and derivatives thereof; isopropyl triisostearyl titanate; isostearyl sebacate; natural plant or animal waxes; polar synthetic waxes; fatty esters; phospholipids; and mixtures thereof.

Silicone surface agent

According to a particular embodiment, the pigments may be totally or partially surface-treated with a compound of silicone nature.
The silicone surface agents may be chosen from organopolysiloxanes, silane derivatives, silicone-acrylate copolymers, silicone resins, and mixtures thereof.

The term *"organopolysiloxane compound"* means a compound having a structure comprising an alternance of silicon atoms and oxygen atoms and comprising organic radicals linked to silicon atoms.

i) Non-elastomeric organopolysiloxane

Non-elastomeric organopolysiloxanes that may in particular be mentioned include polydimethylsiloxanes, polymethylhydrogenosiloxanes and polyalkoxydimethylsiloxanes.

The alkoxy group may be represented by the radical R-O- such that R represents methyl, ethyl, propyl, butyl or octyl, 2-phenylethyl, 2-phenylpropyl or 3,3,3-trifluoropropyl radicals, aryl radicals such as phenyl, tolyl or xylyl, or substituted aryl radicals such as phenylethyl.

One method for surface-treating pigments with a polymethylhydrogenosiloxane consists in dispersing the pigments in an organic solvent and then in adding the silicone compound. On heating the mixture, covalent bonds are created between the silicone compound and the surface of the pigment.
According to a preferred embodiment, the silicone surface agent may be a non-elastomeric organopolysiloxane, especially chosen from polydimethylsiloxanes.
According to one particular form, use may be made of triethoxysilylethyl polydimethylsiloxyethyl dimethicone, such as the commercial product sold under the name KF9908® from Shin-Etsu.

ii) Alkylsilanes and alkoxysilanes

Silanes bearing alkoxy functionality are especially described by Witucki in *"A silane primer, Chemistry and applications of alkoxy silanes, Journal of Coatings Technology, 65, 822, pages 57-60, 1993'.*

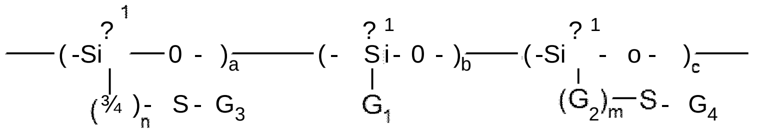
Alkoxysilanes such as the alkyltriethoxysilanes and the alkylthmethoxysilanes sold under the references Silquest A-1 37 (OSI Specialities) and Prosil 9202 (PCR) may be used for coating the pigments.

The use of alkylpolysiloxanes bearing a reactive end group such as alkoxy, hydroxyl, halogen, amino or imino is described in patent application JP H07-196946. They are also suitable for treating the pigments.

Hi) Silicone-acrylate polymers

Grafted silicone-acrylic polymers having a silicone backbone as described in patents US 5 725 882, US 5 209 924, US 4 972 037, US 4 981 903, US 4 981 902 and US 5 468 477 and in patents US 5 219 560 and EP 0 388 582 may be used.

Other silicone-acrylate polymers may be silicone polymers comprising in their structure the unit of formula (I) below:



$$-(-\overset{?^{1}}{\underset{(\text{¾})_n-S-G_3}{Si}}-0-)_a-(-\overset{?^{1}}{\underset{G_1}{Si}}-0-)_b-(-\overset{?^{1}}{\underset{(G_2)_m-S-G_4}{Si}}-o-)_c-$$

(i)

in which the radicals Gi, which may be identical or different, represent hydrogen or a C 1-C10 alkyl radical or alternatively a phenyl radical; the radicals G2, which may be identical or different, represent a C 1-C10 alkylene group; G3 represents a polymeric residue resulting from the (homo)polymerization of at least one ethylenically unsaturated anionic monomer; G_4 represents a polymeric residue resulting from the (homo)polymerization of at least one ethylenically unsaturated hydrophobic monomer; m and n are equal to 0 or 1; a is an integer ranging from 0 to 50; b is an integer that may be between 10 and 350, c is an integer ranging from 0 to 50; with the proviso that one of the parameters a and c is other than 0.

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

- the radicals Gi denote an alkyl radical, preferably a methyl radical;
- n is non-zero, and the radicals G2 represent a divalent C 1-C3 radical, preferably a propylene radical;
- G3 represents a polymeric radical resulting from the (homo)polymerization of at least one monomer of the ethylenically unsaturated carboxylic acid type, preferably acrylic acid and/or methacrylic acid;
- G_4 represents a polymeric radical resulting from the (homo)polymerization of at least one monomer of the (Ci-Cio)alkyl (meth)acrylate type, preferably such as isobutyl or methyl (meth)acrylate.

Examples of silicone polymers corresponding to formula (I) are especially polydimethylsiloxanes (PDMS) onto which are grafted, via a connecting chain unit of thiopropylene type, mixed polymer units of the poly(meth)acrylic acid type and of the polymethyl (meth)acrylate type.

Other examples of silicone polymers corresponding to formula (I) are especially polydimethylsiloxanes (PDMS) onto which are grafted, via a connecting chain unit of thiopropylene type, polymer units of the polyisobutyl (meth)acrylate type.

iv) Silicone resins

The silicone surface agent may be chosen from silicone resins.

The term *"resin"* means a three-dimensional structure.
The silicone resins may be soluble or swellable in silicone oils. These resins are crosslinked polyorganosiloxane polymers.

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

The letter M represents the monofunctional unit of formula $(CH_3)_3SiOi_{/2}$, the silicon atom being connected to only one oxygen atom in the polymer comprising this unit.

The letter D signifies a difunctional unit $(CH_3)_2SiO2_{/}2$ in which the silicon atom is bonded to two oxygen atoms.

The letter T represents a trifunctional unit of formula $(CH_3)SiO3_{/2}$.

In the units M, D and T defined above, at least one of the methyl groups may be substituted with a group R other than a methyl group, such as a hydrocarbon-based radical (especially alkyl) containing from 2 to 10 carbon atoms or a phenyl group, or alternatively a hydroxyl group.

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

Various resins with different properties may be obtained from these different units, the properties of these polymers varying as a function of the type of monomers (or units), of the type and number of substituted radicals, of the length of the polymer chain, of the degree of branching and of the size of the side chains.

Examples of these silicone resins that may be mentioned include:
- siloxysilicates, which may be trimethyl siloxysilicates of formula $[(CH_3)3XSiXO]\ {}_xX(SiO_{4/}2)y$ (MQ units) in which x and y are integers ranging from 50 to 80;
- polysilsesquioxanes of formula $(CH_3SiO3/2)_x$ (T units) in which x is greater than 100 and at least one of the methyl radicals of which may be substituted with a group R as defined above;

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

As examples of commercially available polymethylsilsesquioxane resins, mention may be made of those sold:
- by the company Wacker under the reference Resin MK®, such as Belsil PMS MK®: polymer comprising CH3S1O3/2 repeating units (T units), which may also comprise up to 1% by weight of $(CH_3)_2SiO_{2/2}$ units (D units) and having an average molecular weight of about 10 000;
- by the company Shin-Etsu under the references KR-220L®, which are composed of T units of formula CH3S1O3/2 and contain Si-OH (silanol) end groups, under the reference KR-242A, which comprise 98% of T units and 2% of dimethyl D units and contain Si-OH end groups, or also under the reference KR-251 , comprising 88% of T units and 12% of dimethyl D units and contain Si-OH end groups.

Siloxysilicate resins that may be mentioned include trimethyl siloxysilicate (TMS) resins, optionally in the form of powders. Such resins are sold under the references SR1 000®, E 1 170-002® or SS 4230®, by the company General Electric or under the references TMS 803®, Wacker 803® and 804® by the company Wacker Silicone Corporation.

Mention may also be made of trimethylsiloxysilicate resins sold in a solvent such as cyclomethicone, sold under the name KF-731 2J® by the company Shin-Etsu or DC 749® and DC 593® by the company Dow Corning.

As examples of commercial references of pigments treated with a silicone compound, mention may be made of:
- red iron oxide/dimethicone sold under the reference SA-C 338075-1 0® by the company Miyoshi Kasei; and

Fluoro surface agent

The pigments may be totally or partially surface-treated with a compound of fluoro nature.

The fluoro surface agents may be chosen from perfluoroalkyl phosphates, perfluoropolyethers, polytetrafluoropolyethylenes (PTFE), perfluoroalkanes, perfluoroalkyl silazanes, polyhexafluoropropylene oxides, and polyorganosiloxanes comprising perfluoroalkyl perfluoropolyether groups.

The term *"perfluoroalkyl radicaf* means an alkyl radical in which all of the hydrogen atoms have been replaced with fluorine atoms.

Perfluoropolyethers are in particular described in patent application EP 0 486 135, and sold under the trade name Fomblin® by the company Montefluos.

Perfluoroalkyl phosphates are described in particular in patent application JP H05-86984. The perfluoroalkyl diethanolamine phosphates sold by Asahi Glass under the reference AsahiGuard AG530® may be used.

Among the linear perfluoroalkanes that may be mentioned are perfluorocycloalkanes, perfluoro(alkylcycloalkanes), perfluoropolycycloalkanes, aromatic perfluoro hydrocarbons (perfluoroarenes) and hydrocarbon-based perfluoro organic compounds comprising at least one heteroatom.

Among the perfluoroalkanes, mention may be made of the linear alkane series such as perfluorooctane, perfluorononane or perfluorodecane.

Among the perfluorocycloalkanes and perfluoro(alkylcycloalkanes), mention may be made of perfluorodecalin sold under the name Flutec PP5 GMP® by the company Rhodia, perfluoro(methyldecalin) and perfluoro(C3-C_5 alkylcyclohexanes) such as perfluoro(butylcyclohexane).

Among the perfluoropolycycloalkanes, mention may be made of bicyclo[3.3.1]nonane derivatives such as perfluorotrimethylbicyclo[3.3.1]nonane, adamantane derivatives such as perfluorodimethyladamantane, and hydrogenated perfluorophenanthrene derivatives such as tetracosafluorotetradecahydrophenanthrene.

Among the perfluoroarenes, mention may be made of perfluoronaphthalene derivatives, for instance perfluoronaphthalene and perfluoromethyl-1 -naphthalene.

As examples of commercial references of pigments treated with a fluoro compound, mention may be made of:
- yellow iron oxide/perfluoroalkyl phosphate sold under the reference PF 5 Yellow 601® by the company Daito Kasei;
- red iron oxide/perfluoroalkyl phosphate sold under the reference PF 5 Red R 516L® by the company Daito Kasei;
- black iron oxide/perfluoroalkyl phosphate sold under the reference PF 5 Black BL100® by the company Daito Kasei;
- titanium dioxide/perfluoroalkyl phosphate sold under the reference PF 5 **T1O2** CR 50® by the company Daito Kasei;
- yellow iron oxide/perfluoropolymethyl isopropyl ether sold under the reference Iron oxide yellow BF-25-3® by the company Toshiki;
- DC Red 7/perfluoropolymethyl isopropyl ether sold under the reference D&C Red 7 FHC® by the company Cardre Inc.; and
- DC Red 6/PTFE sold under the reference T 9506® by the company Warner-Jenkinson.

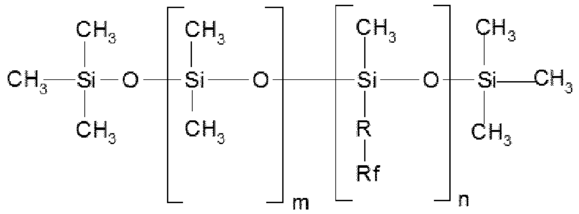
Fluorosilicone surface agent

The pigments may be totally or partially surface-treated with a compound of fluorosilicone nature.

The fluorosilicone compound may be chosen from perfluoroalkyl dimethicones, perfluoroalkyl silanes and perfluoroalkyl trialkoxysilanes.

Perfluoroalkyl silanes that may be mentioned include the products LP-IT® and LP-4T® sold by Shin-Etsu Silicone.

The perfluoroalkyl dimethicones may be represented by the following formula:



in which:
- R represents a linear or branched divalent alkyl group containing from 1 to 6 carbon atoms, preferably a divalent methyl, ethyl, propyl or butyl group;
- Rf represents a perfluoroalkyl radical containing 1 to 9 carbon atoms and preferably 1 to 4 carbon atoms;
- m is chosen between 0 and 150 and preferably from 20 to 100; and
- n is chosen between 1 and 300 and preferably from 1 to 100.

As examples of commercial references of pigments treated with a fluorosilicone compound, mention may be made of titanium dioxide/fluorosilicone sold under the reference Fluorosil Titanium dioxide 100TA® by the company Advanced Dermaceuticals International Inc.

Other lipophilic surface agents

The hydrophobic treatment agent may also be chosen from:
i) metal soaps such as aluminium dimyristate and the aluminium salt of hydrogenated tallow glutamate;

Metal soaps that may especially be mentioned include metal soaps of fatty acids containing from 12 to 22 carbon atoms and in particular those containing from 12 to 18 carbon atoms.

The metal of the metal soap may especially be zinc or magnesium.

Metal soaps that may be used include zinc laurate, magnesium stearate, magnesium myristate and zinc stearate, and mixtures thereof;
ii) fatty acids such as lauric acid, myristic acid, stearic acid and palmitic acid;
iii) N-acylamino acids or salts thereof, which may comprise an acyl group containing from 8 to 22 carbon atoms, for instance a 2-ethylhexanoyl, caproyl, lauroyl, myristoyl, palmitoyl, stearoyl or cocoyl group.

The amino acid may be, for example, lysine, glutamic acid or alanine.

The salts of these compounds may be the aluminium, magnesium, calcium, zirconium, zinc, sodium or potassium salts.

Thus, according to a particularly preferred embodiment, an N-acylamino acid derivative may especially be a glutamic acid derivative and/or a salt thereof, and more particularly a stearoyl glutamate, for instance aluminium stearoyl glutamate. It is, for example, the NAI surface treatment sold by Miyoshi;

iv) lecithin and derivatives thereof, such as hydrogenated lecithin, for instance the HLC surface treatment sold by LCW;

v) isopropyl triisostearyl titanate (INCI name: Isopropyl Titanium Triisostearate).

As examples of isopropyl titanium triisostearate (ITT)-treated pigments, mention may be made of those sold under the commercial references BTD-401® (titanium dioxide CM77891 and isopropyl titanium triisostearate), BBO-12® (iron oxide CI77499 and isopropyl titanium triisostearate), BYO-12® (Iron oxide CI77492 and isopropyl titanium triisostearate) and BRO-12® (Iron oxide CI77491 and isopropyl titanium triisostearate) by the company Kobo;

vi) isostearyl sebacate;
vii) natural plant or animal waxes or polar synthetic waxes;
viii) fatty esters, in particular jojoba esters;
ix) phospholipids; and
x) mixtures thereof.

The waxes mentioned in the compounds mentioned previously may be those generally used in cosmetics, as defined hereinbelow.

They may especially be hydrocarbon, silicone and/or fluoro waxes, optionally comprising ester or hydroxyl functions. They may also be of natural or synthetic origin.

The term *"polar wax"* means a wax containing chemical compounds comprising at least one polar group. Polar groups are well known to those skilled in the art; they may be, for example, alcohol, ester or carboxylic acid groups. Polyethylene waxes, paraffin waxes, microcrystalline waxes, ozokerite and Fischer-Tropsch waxes are not included among polar waxes.

In particular, the polar waxes have a mean Hansen solubility parameter δ_a at 25°C such that $\delta_a > 0$ $(J/cm^3)^{1/2}$ and better still $\delta_a > 1$ $(J/cm^3)^{1/2}$:

$$\delta_a = \sqrt{\delta_p^2 + \delta_h^2}$$

in which δ_p and δ_h are, respectively, the polar contributions and contributions of interaction types specific to the Hansen solubility parameters.

The definition of solvents in the three-dimensional 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):

- δ_h characterizes the specific interaction forces (such as hydrogen bonding, acid/base, donor/acceptor, etc.);
- δ_p characterizes the Debye interaction forces between permanent dipoles and also the Keesom interaction forces between induced dipoles and permanent dipoles.

The solubility parameters are calculated with the HSPiP v4.1 software.

The parameters δ_p and δ_h are expressed in $(J/cm^3)^{1/2}$.

A polar wax is especially formed from molecules comprising, besides carbon and hydrogen atoms in their chemical structure, heteroatoms (such as O, N and P).

Non-limiting illustrations of these polar waxes that may especially be mentioned include natural polar waxes, such as beeswax, lanolin wax, orange wax, lemon wax and Chinese insect waxes, rice bran wax, carnauba wax, candelilla wax, ouricury wax, cork fibre wax, sugarcane wax, Japan wax, sumac wax and montan wax.

According to one particular embodiment, the pigments may be coated with at least one compound chosen from N-acylamino acids or salts thereof, isopropyl triisostearyl titanate; silicone surface agents; natural plant or animal waxes; hydrogenated lecithin, fatty esters; and mixtures thereof.

According to a more particularly preferred embodiment, the pigments may be coated with an N-acylamino acid and/or a salt thereof, in particular with a glutamic acid derivative and/or a salt thereof, especially a stearoyl glutamate, for instance aluminium stearoyl glutamate.

According to one more particularly preferred embodiment, use will be made of hydrophobic coated pigments chosen from titanium dioxides and iron oxides coated with aluminium stearoyl glutamate, sold, for example, under the reference NAI® by Miyoshi Kasei.

According to a more particularly preferred embodiment, use will be made of hydrophobic coated pigments chosen from titanium dioxides and iron dioxides coated with isopropyl titanium triisostearate (ITT); mention may be made of those sold under the commercial references BTD-401® (titanium dioxide CI177891 and isopropyl titanium triisostearate), BBO-I2® (iron oxide CI77499 and isopropyl titanium triisostearate), BYO-I2® (iron oxide CI77492 and isopropyl titanium triisostearate), and BRO-I2® (iron oxide CI77491 and isopropyl titanium triisostearate) by the company Kobo.

The pigments coated with at least one hydrophobic compound are present in a composition of the invention in a proportion preferably of at least 5% by weight, more preferentially ranging from 5% to 25% by weight and even more preferentially ranging from 8% to 15%, relative to the total weight of the composition.

ADDITIONAL DYESTUFFS

A composition according to the invention may also comprise at least one additional dyestuff, preferably in a proportion of at least 0.01 % by weight relative to the total weight of the composition.

For obvious reasons, this amount is liable to vary significantly with regard to the intensity of the desired colour effect and of the colour intensity afforded by the dyestuffs under consideration, and its adjustment clearly falls within the competence of those skilled in the art.

A composition according to the invention may comprise from 0.01 % to 25% by weight, especially from 0.1 % to 25% by weight, in particular from 1% to 20% by weight and preferably from 5% to 15% by weight of dyestuffs relative to the total weight of said composition.

As specified above, the colorants that are suitable for use in the invention may be water-soluble, but may also be liposoluble.

For the purposes of the invention, the term *"water-soluble dyestuff"* means any natural or synthetic, generally organic compound, which is soluble in an aqueous phase or water-miscible solvents and which is capable of imparting colour.

As water-soluble dyes that are suitable for use in the invention, mention may be made in particular of synthetic or natural water-soluble dyes, for instance FDC Red 4, DC Red 6, DC Red 22, DC Red 28, DC Red 30, DC Red 33, DC Orange 4, DC Yellow 5, DC Yellow 6, DC Yellow 8, FDC Green 3, DC Green 5, FDC Blue 1, betanine (beetroot), carmine, copper chlorophylline, methylene blue, anthocyanins (enocianin, black carrot, hibiscus and elder), caramel and riboflavin.

The water-soluble dyes are, for example, beetroot juice and caramel.

For the purposes of the invention, the term *liposoluble dyestuff'* means any natural or synthetic, generally organic compound, which is soluble in an oily phase or in solvents that are miscible with a fatty substance, and which is capable of imparting colour.

As liposoluble dyes that are suitable for use in the invention, mention may be made in particular of synthetic or natural liposoluble dyes, for instance DC Red 17, DC Red 21, DC Red 27, DC Green 6, DC Yellow 11, DC Violet 2, DC Orange 5, Sudan red, carotenes (β-carotene, lycopene), xanthophylls (capsanthin, capsorubin, lutein), palm oil, Sudan brown, quinoline yellow, annatto and curcumin.

They may in particular be non-hydrophobic-coated pigments, non-hydrophobic-coated nacres and/or non-hydrophobic-coated particles with metallic glints.

The term *"non-hydrophobic-coated pigment"* means any pigment which is not coated with at least one lipophilic or hydrophobic compound.

The additional pigments may be white or coloured, and mineral and/or organic.

As non-hydrophobic-coated mineral pigments that may be used in the invention, mention may be made of titanium oxide, titanium dioxide, zirconium oxide, zirconium dioxide, cerium oxide or cerium dioxide and also zinc oxide, iron oxide or chromium oxide, ferric blue, manganese violet, ultramarine blue and chromium hydrate, and mixtures thereof.

They may also be a pigment having a structure that may be, for example, of sericite/brown iron oxide/titanium dioxide/silica type. Such a pigment is sold, for example, under the reference Coverleaf NS® or JS® by the company Chemicals and Catalysts, and has a contrast ratio in the region of 30.

They may also be pigments having a structure that may be, for example, of silica microsphere type containing iron oxide. An example of a pigment having this structure is the product sold by the company Miyoshi under the reference PC Ball PC-LL-1 00 P®, this pigment being constituted of silica microspheres containing yellow iron oxide.

Advantageously, the additional pigments in accordance with the invention are iron oxides and/or titanium dioxides.

The nacres may be chosen from nacreous pigments such as titanium mica coated with an iron oxide, titanium mica coated with bismuth oxychloride, titanium mica coated with chromium oxide, titanium mica coated with an organic dye and also nacreous pigments based on bismuth oxychloride. They may also be mica particles, at the surface of which are superposed at least two successive layers of metal oxides and/or of organic dyestuffs.

Examples of nacres that may also be mentioned include natural mica covered with titanium oxide, with iron oxide, with natural pigment or with bismuth oxychloride.

Among the nacres available on the market, mention may be made of the nacres Timica, Flamenco® and Duochrome® (based on mica) sold by the company Engelhard, the Timiron nacres sold by the company Merck, the Prestige mica-based nacres, sold by the company Eckart, and the Sunshine synthetic mica-based nacres, sold by the company Sun Chemical.

The nacres may more particularly have a yellow, pink, red, bronze, orange, brown, gold and/or coppery colour or glint.

Advantageously, the nacres in accordance with the invention are micas covered with titanium dioxide or with iron oxide, and also bismuth oxychloride.

Illustrations of these additional particles with metallic glints that may be mentioned include aluminium particles, such as those sold under the names Starbrite 1200 EAC® by the company Siberline and Metalure® by the company Eckart and glass particles coated with a metallic layer, in particular those described in documents JP-A-091 88830, JP-A-1 0158450, JP-A-1 0158541 , JP-A-07258460 and JP-A-0501771 0.

FILLERS

Advantageously, a composition according to the invention may also comprise one or more fillers conventionally used in care and/or makeup compositions.

These fillers are colourless or white solid particles of any form, which are in a form that is insoluble and dispersed in the medium of the composition.

These fillers, of mineral or organic, natural or synthetic nature, give the composition containing them softness and give the makeup result a matt effect and uniformity. In addition, these fillers advantageously make it possible to combat various attacking factors such as sebum or sweat.

As illustrations of these fillers, mention may be made of talc, mica, silica, kaolin, poly-β-alanine powder and polyethylene powder, powders of tetrafluoroethylene polymers (Teflon®), lauroyllysine, starch, boron nitride, hollow polymer microspheres such as those of polyvinylidene chloride/acrylonitrile, for instance Expancel® (Nobel Industrie), acrylic acid copolymer microspheres, silicone resin microbeads (for example Tospearls® from Toshiba), polyorganosiloxane elastomer particles, precipitated calcium carbonate, magnesium carbonate, magnesium hydrogen carbonate, hydroxyapatite, barium sulfate, aluminium oxides, polyurethane powders, composite fillers, hollow silica microspheres, and glass or ceramic microcapsules. Use may also be made of particles which are in the form of hollow sphere portions, as described in patent applications JP-2003 128 788 and JP-2000 191 789.

(Meth)acrylic polymer particles

According to a particular form of the invention, the compositions according to the invention may contain (meth)acrylic polymer particles.

The (meth)acrylic polymer particles are especially particles of polymethyl methacrylate, poly(methyl methacrylate/ethylene glycol dimethacrylate), poly(allyl methacrylate/ethylene glycol dimethacrylate), ethylene glycol dimethacrylate/lauryl methacrylate copolymer;

(Meth)acrylic polymer powders that may be mentioned include:

- the polymethyl methacrylate powders sold under the name Covabead LH85® by the company Wackherr;
- the polymethyl methacrylate/ethylene glycol dimethacrylate powders sold under the name Dow Corning 5640 Microsponge Skin Oil Adsorber® by the company Dow Corning and the name Ganzpearl GMP-0820® by the company Ganz Chemical;
- the polyallyl methacrylate/ethylene glycol dimethacrylate powders sold under the names Polypore L200® and Polypore E200® by the company Amcol Health and Beauty Solutions Inc.;
- ethylene glycol dimethacrylate/lauryl methacrylate copolymer powders (INCI name: Lauryl methacrylate/glycol dimethacrylate crosspolymer sold under the name Polytrap 6603 Adsorber® by the company Amcol Health & Beauty Solutions.

Preferably, the (meth)acrylic polymer particles have a number-average size ranging from 50 nm to 350 microns, better still from 100 nm to 100 microns and even more preferentially from 0.5 to 100 microns.

The (meth)acrylic polymer particles are present in the composition according to the invention in a content ranging from 0.01 % to 30% by weight, preferably ranging from 0.05% to 20% by weight and most preferentially ranging from 0.2% to 10% by weight relative to the total weight of the composition.

In particular, such fillers may be present in a composition according to the invention in a content ranging from 0.01 % to 25% by weight, especially from 0.1 % to 20% by weight, in particular from 1% to 10% by weight, relative to the total weight of the composition.

ACTIVE AGENT

A composition according to the invention may comprise at least one moisturizer (also known as a humectant), in particular for a care application.

Preferably, the moisturizer is glycerol.

The moisturizer(s) may be present in the composition in a content ranging from 0.1 % to 15% by weight, especially from 0.5% to 10% by weight or even from 1% to 6% by weight relative to the total weight of said composition.

As other active agents that may be used in the composition of the invention, examples that may be mentioned include vitamins and sunscreens other than liquid lipophilic organic UV-screening agents, and mixtures thereof.

Preferably, a composition according to the invention comprises at least one active agent.

HYDROPHOBIC FILM-FORMING POLYMERS

According to a particularly preferred form of the invention, the compositions according to the invention comprise at least one hydrophobic film-forming polymer.

This type of polymer is particularly advantageous insofar as it makes it possible to significantly increase the persistence of the matt effect over time. As indicated previously, the performance of these polymers is advantageously increased by means of using them in a composition according to the invention.

For the purposes of the invention, the term "polymer" means a compound corresponding to the repetition of one or more units (these units resulting from compounds known as monomers). This or these unit(s) are repeated at least twice and preferably at least three times.

For the purposes of the present invention, the term "hydrophobic film-forming polymer" is intended to denote a film-forming polymer that has no affinity for water and, in this respect, does not lend itself to a formulation in the form of a solute in an aqueous medium. In particular, the term "hydrophobic polymer" means a polymer which has a solubility in water at 25°C of less than 1% by weight.

The term "film-forming polymer" means a polymer that is capable of forming, by itself or in the presence of an auxiliary film-forming agent, a macroscopically continuous film on a support, especially on keratin materials, and preferably a cohesive film, and better still a film whose cohesion and mechanical properties are such that said film may be isolable and manipulable in isolation, for example when said film is prepared by pouring onto a non-stick surface, for instance a Teflon-coated or silicone-coated surface.

In particular, the hydrophobic film-forming polymer is a polymer chosen from the group comprising:

- film-forming polymers that are soluble in an organic solvent medium, in particular liposoluble polymers; this means that the polymer is soluble or miscible in the organic medium and forms a single homogeneous phase when it is incorporated into the medium;
- film-forming polymers that are dispersible in an organic solvent medium, which means that the polymer forms an insoluble phase in the organic medium, the polymer remaining stable and/or compatible once incorporated into this medium. In particular, such polymers may be in the form of non-aqueous dispersions of polymer particles, preferably dispersions in silicone oils or hydrocarbon-based oils; in one embodiment, the non-aqueous polymer dispersions comprise polymer particles stabilized on their surface with at least one stabilizer; these non-aqueous dispersions are often referred to as NADs;

- film-forming polymers in the form of aqueous dispersions of polymer particles, which means that the polymer forms an insoluble phase in water, the polymer remaining stable and/or compatible once incorporated into the water, the polymer particles possibly being stabilized at their surface with at least one stabilizer. These polymer particles are often known as *latices.*

Hydrophobic film-forming polymers that may especially be mentioned include homopolymers and copolymers of a compound bearing an ethylenic unit, acrylic polymers and copolymers, polyurethanes, polyesters, polyureas, cellulose-based polymers such as nitrocellulose, silicone polymers such as silicone resins, silicone polyamides, polymers bearing a non-silicone organic backbone grafted with monomers containing a polysiloxane, polyamide polymers and copolymers, and polyisoprenes.

A composition according to the invention may comprise from 0.1 % to 30% by weight, preferably from 0.2% to 20% by weight and even more preferentially from 0.5% to 15% by weight of hydrophobic film-forming polymer(s) relative to the total weight of the composition.

In particular, said hydrophobic film-forming polymer(s) are present totally or partially, and preferably solely, in the gelled oily phase.

As hydrophobic film-forming polymers that are most particularly suitable for use in the invention, mention may be made especially of block ethylenic polymers, vinyl polymers comprising at least one carbosiloxane dendrimer derivative and silicone resins (T resin, MQ resin).

1. Silicone resins

According to one embodiment variant, a composition according to the invention may comprise, as hydrophobic film-forming polymer, at least one silicone resin.

More generally, the term "resin" is understood to mean a compound, the structure of which is three-dimensional. "Silicone resins" are also referred to as "siloxane resins". Thus, within the meaning of the present invention, a polydimethylsiloxane is not a silicone resin.

The nomenclature of silicone resins (also known as siloxane resins) is known under the name "MDTQ", the resin being described as a function of the various siloxane monomer units it comprises, each of the letters "MDTQ" characterizing a type of unit.

The letter "M" represents the Monofunctional unit of formula R 1R2R3S1O1/2, the silicon atom being connected to only one oxygen atom in the polymer comprising this unit.

The letter "D" signifies a Difunctional unit R 1R2S1O2/2 in which the silicon atom is connected to two oxygen atoms.

The letter "T" represents a Trifunctional unit of formula $R_1SiO_{3/2}$.

Such resins are described, for example, in the *Encyclopedia of Polymer Science and Engineering,* vol. 15, John Wiley and Sons, New York, (1989), pp. 265-270, and US 2 676 182, US 3 627 851 , US 3 772 247, US 5 248 739 or else US 5 082 706, US 5 319 040, US 5 302 685 and US 4 935 484.

In the units M, D and T defined previously, R, namely R_1 and R_2, represents a hydrocarbon-based radical (in particular alkyl) containing from 1 to 10 carbon atoms, a phenyl group, a phenylalkyl group or even a hydroxyl group.

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

Various silicone resins with different properties may be obtained from these different units, the properties of these polymers varying as a function of the type of monomer (or unit), the nature and number of the radical R, the length of the polymer chain, the degree of branching and the size of the pendent chains.
As silicone resins that may be used in the compositions according to the invention, use may be made, for example, of silicone resins of MQ type, of T type or of MQT type.

MQ resins

As examples of silicone resins of MQ type, mention may be made of the alkyl siloxysilicates of formula $[(R_1)_3SiO_{1/2}]_x(SiO_{4/2})_y$ (MQ units) in which x and y are integers ranging from 50 to 80, and such that the group R_1 represents a radical as defined previously, and is preferably an alkyl group containing from 1 to 8 carbon atoms or a hydroxyl group, preferably a methyl group.

As examples of solid silicone resins of MQ type of trimethyl siloxysilicate type, mention may be made of those sold under the reference SR1000® by the company General Electric, under the reference TMS 803® by the company Wacker, or under the name KF-7312J® by the company Shin-Etsu or DC749® or DC593® by the company Dow Corning.

As silicone resins comprising MQ siloxysilicate units, mention may also be made of phenylalkylsiloxysilicate resins, such as phenylpropyldimethylsiloxysilicate (Silshine 151® sold by the company General Electric). The preparation of such resins is described especially in patent US 5 817 302.

T resins

Examples of silicone resins of type T that may be mentioned include the polysilsesquioxanes of formula $(RSiO_{3/2})_x$ (units T) in which x is greater than 100 and such that the group R is an alkyl group containing from 1 to 10 carbon atoms, said polysilsesquioxanes also possibly comprising Si-OH end groups.

Polymethylsilsesquioxane resins that may preferably be used are those in which R represents a methyl group, for instance those sold:

- by the company Wacker under the reference Resin MK®, such as Belsil PMS MK®: polymer comprising **CH3S1O3/2** repeating units (units T), which may also comprise up to 1% by weight of $(CH_3)_2SiO2/2$ units (units D) and having an average molecular weight of about 10 000 g/mol, or
- by the company Shin-Etsu under the reference KR220L®, which are composed of units T of formula **CH3S1O3/2** and have Si-OH (silanol) end groups, under the reference KR242A, which comprise 98% of units T and 2% of dimethyl units D and have Si-OH end groups, or alternatively under the reference KR251® comprising 88% of units T and 12% of dimethyl units D and have Si-OH end groups.

MQT resins

Resins comprising MQT units that are especially known are those mentioned in document US 5 110 890.

A preferred form of resins of MQT type are MQT-propyl (also known as MQTpr) resins. Such resins that may be used in the compositions according to the invention are especially the resins described and prepared in patent application WO 2005/075 542.

The MQ-T-propyl resin preferably comprises the following units:

(i) $(R1_3SiO_{1/2})_a$
(ii) $(R2_2SiO_{2/2})_b$
(iii) $(R3SiO_{3/2})_c$ and
(iv) $(SiO_{4/2})_d$
with:

- Ri, R2 and R3 independently representing a hydrocarbon-based (in particular alkyl) radical containing from 1 to 10 carbon atoms, a phenyl group, a phenylalkyl group or alternatively a hydroxyl group and preferably an alkyl radical containing from 1 to 8 carbon atoms or a phenyl group,
- a being between 0.05 and 0.5,
- b being between 0 and 0.3,
- c being greater than zero,
- d being between 0.05 and 0.6,
- a + b + c + d = 1, and a, b, c and d being mole fractions,

on condition that more than 40 mol% of the groups R3 of the siloxane resin are propyl groups.

Preferably, the siloxane resin comprises the following units:

(i) $(R1_3SiO_{1/2})_a$
(iii) $(R3SiO_{3/2})_c$; and
(iv) $(SiO_{4/2})d$
with:

- R1 and R3 independently representing an alkyl group containing from 1 to 8 carbon atoms, R1 preferably being a methyl group and R3 preferably being a propyl group,
- a being between 0.05 and 0.5 and preferably between 0.15 and 0.4,
- c being greater than zero, preferably between 0.15 and 0.4,
- d being between 0.05 and 0.6, preferably between 0.2 and 0.6 or alternatively between 0.2 and 0.55,
- a + b + c + d = 1, and a, b, c and d being mole fractions,

on condition that more than 40 mol% of the groups R3 of the siloxane resin are propyl groups.

The siloxane resins that may be used according to the invention may be obtained via a process comprising the reaction of:

A) an MQ resin comprising at least 80 mol% of units $(R1_3SiOi_{/2})_a$ and $(SiO_{4/2})_d$; with

- R1 representing an alkyl group containing from 1 to 8 carbon atoms, an aryl group, a carbinol group or an amino group,
- a and d being greater than zero,
- the ratio a/d being between 0.5 and 1.5;

and:

B) a T-propyl resin comprising at least 80 mol% of units $(R3SiO3/2)_c$; with

- R3 representing an alkyl group containing from 1 to 8 carbon atoms, an aryl group, a carbinol group or an amino group,
- c being greater than zero,

on condition that at least 40 mol% of the groups R3 are propyl groups, in which the mass ratio A/B is between 95/5 and 15/85, and preferably mass ratio A/B is 30/70.

Advantageously, the A/B weight ratio is between 95/5 and 15/85. Preferably, the A/B ratio is less than or equal to 70/30. These preferred ratios have proven to allow comfortable deposits due to the absence of percolation of the rigid particles of MQ resin in the deposit.

Thus, preferably, the silicone resin is chosen from the group comprising:

a) a resin of MQ type, chosen especially from (i) alkyl siloxysilicates, which may be trimethyl siloxysilicates, of formula $[Rl_3SiOi_{/2}]_x(SiO_{4/2})_y$, in which x and y are integers ranging from 50 to 80, and such that the group R1 represents a hydrocarbon-based radical containing from 1 to 10 carbon atoms, a phenyl group, a phenylalkyl group or a hydroxyl group, and preferably is an alkyl group containing from 1 to 8 carbon atoms, preferably a methyl group, and (ii) phenylalkyl siloxysilicate resins, such as phenylpropyldimethyl siloxysilicate, and/or

b) a resin of T type, chosen especially from the polysilsesquioxanes of formula $(RSiO3/_2)_x$, in which x is greater than 100 and the group R is an alkyl group containing from 1 to 10 carbon atoms, for example a methyl group, said polysilsesquioxanes also possibly comprising Si-OH end groups, and/or

c) a resin of MQT type, especially of MQT-propyl type, which may comprise units (i) $(R1_3SiOi/_2)_a$, (ii) $(R2_2SiO_{2/2})_b$, (in) $(R3SiO_{3/2})_c$ and (iv) $(SiO_{4/2})_d$,

- with R1, R2 and R3 independently representing a hydrocarbon-based radical, especially alkyl, containing from 1 to 10 carbon atoms, a phenyl group, a

phenylalkyl group or a hydroxyl group and preferably an alkyl radical containing from 1 to 8 carbon atoms or a phenyl group,
- a being between 0.05 and 0.5,
- b being between 0 and 0.3,
- c being greater than zero,
- d being between 0.05 and 0.6,
- a + b + c + d = 1, and a, b, c and d being mole fractions,

on condition that more than 40 mol% of the groups R3 of the siloxane resin are propyl groups.

Advantageously, a composition according to the invention may comprise, as hydrophobic film-forming polymer, at least one trimethyl siloxysilicate resin.

II. Lipodispersible film-forming polymers in the form of non-aqueous dispersions of polymer particles, also known as NADs

According to another embodiment variant, a composition according to the invention may comprise, as hydrophobic film-forming polymer, at least one polymer chosen from lipodispersible film-forming polymers in the form of non-aqueous dispersions of polymer particles, also known as NADs.

Non-aqueous dispersions of hydrophobic film-forming polymer that may be used include dispersions of particles of a grafted ethylenic polymer, preferably an acrylic polymer, in a liquid oily phase:
- either in the form of ethylenic polymer particles dispersed in the absence of additional stabilizer at the surface of the particles, as described especially in document WO 04/055 081,
- or in the form of surface-stabilized particles dispersed in the liquid fatty phase.

The dispersion of surface-stabilized polymer particles may be manufactured as described in document EP-A-749 747. The polymer particles may in particular be surface-stabilized by means of a stabilizer that may be a block polymer, a grafted polymer and/or a random polymer, alone or as a mixture. Dispersions of film-forming polymer in the liquid fatty phase, in the presence of stabilizers, are especially described in documents EP-A-748 746, EP-A-923 928, EP-A-930 060.

Advantageously, dispersions of ethylenic polymer particles dispersed in the absence of additional stabilizer at the surface of said particles are used.
Examples of polymers of NAD type that may be mentioned more particularly include acrylic dispersions in isododecane, for instance Mexomer PAP® (acrylic copolymer as a dispersion in isododecane (25%) with pyrene/isoprene copolymer) sold by the company Chimex.

III. Block ethylenic copolymer

According to a first embodiment of the invention, the hydrophobic film-forming polymer is a block ethylenic copolymer, containing at least one first block with a glass transition temperature (Tg) of greater than or equal to 40°C and being totally or partly derived from one or more first monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature of greater than or equal to 40°C, and at least one second block with a glass transition temperature of less than or equal to 20°C and being derived totally or partly from one or more second monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature of less than or equal to 20°C, said first block and said second block being connected together via a random intermediate segment comprising at least one of said first constituent monomers of the first block and at least one of said second constituent monomers of the second block, and said block copolymer having a polydispersity index I of greater than 2.

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

The term "at least one block" means one or more blocks.

The term "block" polymer means a polymer comprising at least two different blocks and preferably at least three different blocks.

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

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

This means that the block ethylenic polymer used according to the present invention does not contain any multifunctional monomers, which make it possible to break the linearity of a polymer so as to obtain a branched or even crosslinked polymer, as a function of the content of multifunctional monomer. The polymer used according to the invention does not, either, contain any macromonomers (the term "macromonomer" means a monofunctional monomer containing pendent groups of polymeric nature, and preferably having a molecular mass of greater than 500 g/mol, or alternatively a polymer comprising on only one of its ends a polymerizable (or ethylenically unsaturated) end group), which are used in the preparation of a grafted polymer.

It is pointed out that, in the text hereinabove and hereinbelow, the terms "first" and "second" blocks do not in any way condition the order of said blocks in the structure of the polymer.

The first block and the second block of the polymer used in the invention may be advantageously mutually incompatible.

The term "mutually incompatible blocks" means that the mixture formed from a polymer corresponding to the first block and from a polymer corresponding to the second block is not miscible in the polymerization solvent that is in major amount by weight for the block polymer, at room temperature (25°C) and atmospheric pressure (10^5 Pa), for a content of the mixture of said polymers of greater than or equal to 5% by weight, relative to the total weight of the mixture of said polymers and of said polymerization solvent, it being understood that:

i) said polymers are present in the mixture in a content such that the respective weight ratio ranges from 10/90 to 90/10, and that
ii) each of the polymers corresponding to the first and second blocks has an average (weight-average or number-average) molar mass equal to that of the block polymer ± 15%.

In the case of a mixture of polymerization solvents, and in the event that two or more solvents are present in identical mass proportions, said polymer mixture is immiscible in at least one of them.

Needless to say, in the case of a polymerization performed in a single solvent, this solvent is the solvent that is in major amount.

The block polymer according to the invention comprises at least one first block and at least one second block that are connected together via an intermediate segment comprising at least one constituent monomer of the first block and at least one constituent monomer of the second block. The intermediate segment (also known as the intermediate block) has a glass transition temperature Tg that is between the glass transition temperatures of the first and second blocks.

The intermediate segment is a block comprising at least one constituent monomer of the first block and at least one constituent monomer of the second block of the polymer allowing these blocks to be "compatibilized".
Advantageously, the intermediate segment comprising at least one constituent monomer of the first block and at least one constituent monomer of the second block of the polymer is a statistical polymer.

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

The term "essentially" means at least 85%, preferably at least 90%, better still 95% and even better still 100%.

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

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

The term "film-forming polymer" means a polymer that is capable of forming, by itself or in the presence of an auxiliary film-forming agent, a continuous deposit on a support, especially on keratin materials.

Preferentially, the polymer according to the invention does not comprise any silicon atoms in its backbone. The term "backbone" means the main chain of the polymer, as opposed to the pendent side chains.

Preferably, the polymer according to the invention is not water-soluble, i.e. the polymer is not soluble in water or in a mixture of water and linear or branched lower monoalcohols containing from 2 to 5 carbon atoms, for instance ethanol, isopropanol or n-propanol, without modifying the pH, at the solids content of at least 1% by weight, at room temperature (25°C).

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

The term "non-elastomeric polymer" means a polymer which, when it is subjected to a constraint intended to pull it (for example by 30% relative to its initial length), does not return to a length substantially identical to its initial length when the constraint ceases.

More specifically, the term "non-elastomeric polymer" denotes a polymer with an instantaneous recovery Ri < 50% and a delayed recovery R2h < 70% after having been subjected to a 30% elongation. Preferably, Ri is < 30% and R2h < 50%.

More specifically, the non-elastomeric nature of the polymer is determined according to the following protocol:

A polymer film is prepared by pouring a solution of the polymer in a Teflon-coated mould, followed by drying for 7 days in an environment conditioned at 23 ± 5°C and 50 ± 10% relative humidity.

A film about 100 µm thick is thus obtained, from which are cut rectangular test specimens (for example using a punch) 15 mm wide and 80 mm long.

This sample is subjected to a tensile stress using a machine sold under the reference Zwick, under the same temperature and humidity conditions as for the drying.

The specimens are stretched at a speed of 50 mm/min and the distance between the jaws is 50 mm, which corresponds to the initial length (l0) of the specimen.

The instantaneous recovery Ri is determined in the following manner:
- the specimen is stretched by 30% (ε_{max}), i.e. approximately 0.3 times its initial length (l0);
- the stress is released by applying a return speed equal to the pull speed, i.e. 50 mm/min, and the residual elongation of the test specimen is measured as a percentage, after returning to zero stress load (ε_i).

The percentage instantaneous recovery (Ri) is given by the formula below:

$$\mathbf{Ri = ((\varepsilon_{max} - \varepsilon_i)/\varepsilon_{max}) \times 100}$$

To determine the delayed recovery, the percentage residual elongation of the test specimen (ε_{2h}) is measured after 2 hours, 2 hours after returning to zero stress load.

The percentage delayed recovery (R2h) is given by the following formula:

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

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

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

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

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

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

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

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

Preferably, the polydispersity index of the polymer according to the invention is greater than 2, for example ranging from 2 to 9, preferably greater than or equal to 2.5, for example ranging from 2.5 to 8, and better still greater than or equal to 2.8, and in particular ranging from 2.8 to 6.

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

The block with a Tg of greater than or equal to 40°C has, for example, a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C.

The glass transition temperatures indicated for the first and second blocks may be theoretical Tg values determined from the theoretical Tg values of the constituent monomers of each of the blocks, which may be found in a reference manual such as the Polymer Handbook, 3rd Edition, 1989, John Wiley, according to the following relationship, known as Fox's law:

$$1/Tg = \Sigma (\omega_i / Tg_i),\ i$$

ω_i being the mass fraction of the monomer i in the block under consideration and Tgi being the glass transition temperature of the homopolymer of the monomer i. Unless otherwise indicated, the Tg values indicated for the first and second blocks in the present patent application are theoretical Tg values.

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

In the present invention, the expression: "between ... and ..." is intended to denote a range of values for which the limits mentioned are excluded, and "from ... to ..." and "ranging from ... to ..." are intended to denote a range of values for which the limits are included.

The block with a Tg of greater than or equal to 40°C may be a homopolymer or a copolymer.

The block with a Tg of greater than or equal to 40°C may be derived totally or partially from one or more monomers which are such that the homopolymer prepared from these monomers has a glass transition temperature of greater than or equal to 40°C. This block may also be referred to as a "rigid block".

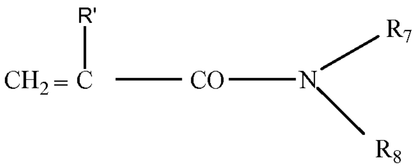
In the case where this block is a homopolymer, it is derived from monomers which are such that the homopolymers prepared from these monomers have glass transition temperatures of greater than or equal to 40°C. This first block may be a homopolymer consisting of only one type of monomer (for which the Tg of the corresponding homopolymer is greater than or equal to 40°C).

In the case where the first block is a copolymer, it may be totally or partially derived from one or more monomers, the nature and concentration of which are chosen such that the Tg of the resulting copolymer is greater than or equal to 40°C.

The copolymer may comprise, for example:
- monomers which are such that the homopolymers prepared from these monomers have Tg values of greater than or equal to 40°C, for example a Tg ranging from 40 to 150°C, preferably greater than or equal to 50°C, for example ranging from 50°C to 120°C and better still greater than or equal to 60°C, for example ranging from 60°C to 120°C, and
- monomers which are such that the homopolymers prepared from these monomers have Tg values of less than 40°C, chosen from monomers with a Tg of between 20°C and 40°C and/or monomers with a Tg of less than or equal to 20°C, for example a Tg ranging from -100°C to 20°C, preferably less than 15°C, especially ranging from -80°C to 15°C and better still less than 10°C, for example ranging from -50°C to 0°C, as described later.

The first monomers whose homopolymers have a glass transition temperature of greater than or equal to 40°C are chosen, preferably, from the following monomers, also known as the main monomers:

- the methacrylates of formula $CH_2 = C(CH_3)$-COORi, in which R_1 represents a linear or branched unsubstituted alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group or R_1 represents a C_4 to C12 cycloalkyi group, preferably a Cs to C12 cycloalkyi, such as isobornyl methacrylate,
- the acrylates of formula $CH_2 = CH-COOR_2$ in which R_2 represents a C_4 to C12 cycloalkyi group such as an isobornyl group or a tert-butyl group,
- the (meth)acrylamides of formula:



$$CH_2=C(R')-CO-N(R_7)(R_8)$$

in which R_7 and Rs, which may be identical or different, each represent a hydrogen atom or a linear or branched C1 to C12 alkyl group such as an n-butyl, t-butyl, isopropyl, isohexyl, isooctyl or isononyl group; or R_7 represents H and Rs represents a 1,1-dimethyl-3-oxobutyl group, and R' denotes H or methyl.

Examples of monomers that may be mentioned include N-butylacrylamide, N-tert-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide, and mixtures thereof.

The first block is advantageously obtained from at least one acrylate monomer of formula CH_2=CH-COOR2 and from at least one methacrylate monomer of formula $CH_2=C(CH_3)$-COOR2 in which R_2 represents a C_4 to Ci_2 cycloalkyi group, preferably a Cs to Ci_2 cycloalkyi, such as isobornyl. The monomers and the proportions thereof are preferably chosen such that the glass transition temperature of the first block is greater than or equal to 40°C.

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

i) at least one acrylate monomer of formula $CH_2=CH-COOR_2$ in which R_2 represents a C_4 to Ci_2 cycloalkyi group, preferably a Cs to Ci_2 cycloalkyi group, such as isobornyl,

ii) and at least one methacrylate monomer of formula $CH_2 = C(CH_3)-COOR'_2$ in which R'_2 represents a C_4 to Ci_2 cycloalkyi group, preferably a Cs to Ci_2 cycloalkyi group, such as isobornyl.

According to one embodiment, the first block is obtained from at least one acrylate monomer of formula $CH_2=CH-COOR_2$ in which R_2 represents a Cs to Ci_2 cycloalkyi group, such as isobornyl, and from at least one methacrylate monomer of formula $CH_2=C(CH_3)-COOR'_2$ in which R'_2 represents a Cs to Ci_2 cycloalkyi group, such as isobornyl.

Preferably, R_2 and R'_2 represent, independently or simultaneously, an isobornyl group.
Preferably, the block copolymer comprises from 50% to 80% by weight of isobornyl methacrylate/acrylate, from 10% to 30% by weight of isobutyl acrylate and from 2% to 10% by weight of acrylic acid.

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

The acrylate monomer and the methacrylate monomer are preferably in mass proportions of between 30/70 and 70/30, preferably between 40/60 and 60/40 and in particular of the order of 50/50.

The proportion of the first block advantageously ranges from 20% to 90%, better still from 30% to 80% and even better still from 60% to 80% by weight of the polymer.

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

Second block with a glass transition temperature of less than 20°C

The second block advantageously has a glass transition temperature Tg of less than or equal to 20°C, for example, a Tg ranging from -100°C to 20°C, preferably less than or equal to 15°C, especially ranging from -80°C to 15°C and better still less than or equal to 10°C, for example ranging from -100°C to 10°C, especially ranging from -30°C to 10°C.

The second block is totally or partially derived from one or more second monomers, which are such that the homopolymer prepared from these monomers has a glass transition temperature of less than or equal to 20°C.
This block may also be referred to as a "flexible block".

The monomer with a Tg of less than or equal to 20°C (known as the second monomer) is preferably chosen from the following monomers:
- the acrylates of formula **CH_2=CHCOOR3, R3** representing a linear or branched Ci to C12 unsubstituted alkyl group, with the exception of the tert-butyl group, in which one or more heteroatoms chosen from O, N and S are optionally intercalated,
- the methacrylates of formula $CH_2=C(CH_3)-COOR_4$, R_4 representing a linear or branched C_6 to C12 unsubstituted alkyl group, in which one or more heteroatoms chosen from O, N and S are optionally intercalated,
- the vinyl esters of formula R_5-CO-O-CH=CH2 in which R_5 represents a linear or branched C_4 to C12 alkyl group,
- ethers of vinyl alcohol and of a C_4 to C12 alcohol,
- N-(C_4 to Ci2)alkyl acrylamides, such as N-octylacrylamide,
- and mixtures thereof.

The preferred monomers with a Tg of less than or equal to 20°C are isobutyl acrylate, 2-ethylhexyl acrylate or mixtures thereof in all proportions.

Each of the first and second blocks may contain in small proportion at least one constituent monomer of the other block.

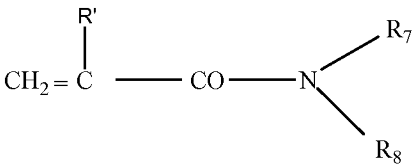
Thus, the first block may contain at least one constituent monomer of the second block, and vice versa.

Each of the first and/or second blocks may comprise, in addition to the monomers indicated above, one or more other monomers known as additional monomers, which are different from the main monomers mentioned above.

The nature and amount of this or these additional monomer(s) are chosen such that the block in which they are present has the desired glass transition temperature.

This additional monomer is chosen, for example, from:
- ethylenically unsaturated monomers comprising at least one tertiary amine function, for instance 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate and dimethylaminopropylmethacrylamide, and salts thereof,
- the methacrylates of formula $CH_2 = C(CH_3)$-COOR6, in which R_6 represents a linear or branched alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group, said alkyl group being substituted with one or more substituents chosen from hydroxyl groups (for instance 2-hydroxypropyl methacrylate and 2-hydroxyethyl methacrylate) and halogen atoms (Cl, Br, I or F), such as trifluoroethyl methacrylate,
- the methacrylates of formula $CH_2=C(CH_3)$-COOR9, Rg representing a linear or branched C6 to C12 alkyl group in which one or more heteroatoms chosen from O, N and S are optionally intercalated, said alkyl group being substituted with one or more substituents chosen from hydroxyl groups and halogen atoms (Cl, Br, I and F),
- the acrylates of formula CH_2=CHCOORio, Rio representing a linear or branched Ci to **Ci2** alkyl group substituted with one or more substituents chosen from hydroxyl groups and halogen atoms (Cl, Br, I or F), such as 2-hydroxypropyl acrylate and 2-hydroxyethyl acrylate, or Rio represents a C1 to C12 alkyl-O-POE (polyoxyethylene) with repetition of the oxyethylene unit 5 to 10 times, for example methoxy-POE, or Rio represents a polyoxyethylenated group comprising from 5 to 10 ethylene oxide units.

In particular, the first block may comprise as additional monomer:
- (meth)acrylic acid, preferably acrylic acid,
- tert-butyl acrylate,
- the methacrylates of formula $CH_2 = C(CH_3)$-COORi, in which R_1 represents a linear or branched unsubstituted alkyl group containing from 1 to 4 carbon atoms, such as a methyl, ethyl, propyl or isobutyl group,
- the (meth)acrylamides of formula:



$$CH_2=C(R')—CO—N(R_7)(R_8)$$

in which R_7 and Rs, which may be identical or different, each represent a hydrogen atom or a linear or branched Ci to c12 alkyl group such as an n-butyl, t-butyl, isopropyl, isohexyl, isooctyl or isononyl group; or R7 represents H and R8 represents a 1,1-dimethyl-3-oxobutyl group, and
R' denotes H or methyl. Examples of monomers that may be mentioned include N-butylacrylamide, N-tert-butylacrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide and N,N-dibutylacrylamide,
- and mixtures thereof.

The additional monomer may represent 0.5% to 30% by weight relative to the weight of the polymer. According to one embodiment, the polymer of the invention does not contain any additional monomer.

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

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

Preferably, the polymer comprises at least isobornyl acrylate and isobornyl methacrylate monomers in equivalent weight proportion in the first block, and isobutyl acrylate and acrylic acid monomers in the second block, the first block representing 70% by weight of the polymer.

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

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

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

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

The constituent monomers of the second block and the proportions thereof are chosen such that the glass transition temperature of the second block is less than or equal to 20°C.

Intermediate segment

The intermediate segment (also known as the intermediate block) connects the first block and the second block of the polymer used according to the present invention. The intermediate segment results from the polymerization:

i) of the first monomer(s), and optionally of the additional monomer(s), which remain available after their polymerization to a maximum degree of conversion of 90% to form the first block,

ii) and of the second monomer(s), and optionally of the additional monomer(s), added to the reaction mixture.

The formation of the second block is initiated when the first monomers no longer react or are no longer incorporated into the polymer chain either because they are all consumed or because their reactivity no longer allows them to be.

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

The intermediate segment of the block polymer is a statistical polymer (which may also be referred to as a statistical block). This means that it comprises a statistical distribution of the first monomer(s) and of the second monomer(s) and also of the additional monomer(s) that may be present.

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

Process for preparing the copolymer

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

The free radical polymerization is performed in the presence of an initiator, the nature of which is adapted, in a known manner, as a function of the desired polymerization temperature and of the polymerization solvent. In particular, the initiator may be chosen from initiators bearing a peroxide function, redox couples or other free radical polymerization initiators known to those skilled in the art.

In particular, examples of initiators bearing a peroxide function that may be mentioned include:
- peroxyesters such as tert-butyl peroxyacetate, tert-butyl perbenzoate, tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S from Akzo Nobel) or 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane (Trigonox 141 from Akzo Nobel);
- peroxydicarbonates such as diisopropyl peroxydicarbonate;
- peroxy ketones such as methyl ethyl ketone peroxide;
- hydroperoxides such as aqueous hydrogen peroxide solution (H2O2) or tert-butyl hydroperoxide;
- diacyl peroxides such as acetyl peroxide or benzoyl peroxide;
- dialkyl peroxides such as di-tert-butyl peroxide;
- mineral peroxides such as potassium peroxodisulfate (K2S2O8).

As initiator in the form of a redox couple, mention may be made of the potassium thiosulfate + potassium peroxodisulfate couple, for example.

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

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

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

The block copolymer may be prepared by free radical polymerization, and in particular by a process that consists in mixing, in the same reactor, a polymerization solvent, an initiator, at least one monomer with a glass transition temperature of greater than or equal to 40°C, and at least one monomer with a glass transition temperature of less than or equal to 20°C, according to the following sequence:
- some of the polymerization solvent and optionally some of the initiator and of the monomers for the first addition are poured into the reactor, and the mixture is heated to a reaction temperature of between 60°C and 120°C,
- said at least one first monomer with a Tg of greater than or equal to 40°C and optionally some of the initiator are then poured in, in a first addition, and the

mixture is left to react for a time T corresponding to a maximum degree of conversion of said monomers of 90%,
- further polymerization initiator and said at least one second monomer with a glass transition temperature of less than or equal to 20°C are then poured into the reactor, in a second addition, and the mixture is left to react for a time T' after which the degree of conversion of said monomers reaches a plateau,
- the reaction mixture is cooled to room temperature.

Preferably, the copolymer may be prepared by free radical polymerization, in particular by a process that consists in mixing, in the same reactor, a polymerization solvent, an initiator, an acrylic acid monomer, at least one monomer with a glass transition temperature of less than or equal to 20°C, at least one acrylate monomer of formula CH2=CH-COOR2 in which R2 represents a C_4 to Ci2 cycloalkyl group and at least one methacrylate monomer of formula $CH_2=C(CH_3)-COOR'2$ in which R'_2 represents a C_4 to C12 cycloalkyl group, according to the following sequence of steps:
- some of the polymerization solvent and optionally some of the initiator and of the monomers for the first addition are poured into the reactor, and the mixture is heated to a reaction temperature of between 60°C and 120°C,
- said at least one acrylate monomer of formula CH_2 = CH-COOR2 and said at least one methacrylate monomer of formula CH_2 = $C(CH_3)$-COOR'2, as monomers with a Tg of greater than or equal to 40°C, and optionally some of the initiator, are then poured in, in a first addition, and the mixture is left to react for a time T corresponding to a maximum degree of conversion of said monomers of 90%,
- further polymerization initiator, the acrylic acid monomer and said at least one monomer with a glass transition temperature of less than or equal to 20°C are then poured into the reactor, in a second addition, and the mixture is left to react for a time T' after which the degree of conversion of said monomers reaches a plateau,
- the reaction mixture is cooled to room temperature.

The term "polymerization solvent" means a solvent or a mixture of solvents.

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

Conventionally, the polymerization solvent is a volatile oil with a flash point of less than 80°C. The flash point is measured in particular according to standard ISO 3679.
The polymerization solvent may be chosen especially from ethyl acetate, butyl acetate, alcohols such as isopropanol or ethanol, and aliphatic alkanes such as isododecane, and mixtures thereof. Preferably, the polymerization solvent is a mixture of butyl acetate and isopropanol or isododecane.

According to another embodiment, the copolymer may be prepared by free radical polymerization according to a preparation process that consists in mixing, in the same reactor, a polymerization solvent, an initiator, at least one monomer with a glass transition temperature of less than or equal to 20°C and at least one monomer with a Tg of greater than or equal to 40°C, according to the following sequence of steps:
- some of the polymerization solvent and optionally some of the initiator and of the monomers for the first addition are poured into the reactor, and the mixture is heated to a reaction temperature of between 60°C and 120°C,
- said at least one monomer with a glass transition temperature of less than or equal to 20°C and optionally some of the initiator are then poured in, in a first addition, and the mixture is left to react for a time T corresponding to a maximum degree of conversion of said monomers of 90%,
- further polymerization initiator and said at least one monomer with a Tg of greater than or equal to 40°C are then poured into the reactor, in a second addition, and the mixture is left to react for a time T' after which the degree of conversion of said monomers reaches a plateau, and the reaction mixture is cooled to room temperature.

According to one preferred embodiment, the copolymer may be prepared by free radical polymerization according to a preparation process that consists in mixing, in the same reactor, a polymerization solvent, an initiator, an acrylic acid monomer, at least one monomer with a glass transition temperature of less than or equal to 20°C, at least one monomer with a Tg of greater than or equal to 40°C, and in particular, as monomers with a Tg of greater than or equal to 40°C, at least one acrylate monomer of formula $CH_2=CH-COOR2$ in which R_2 represents a C_4 to Ci2 cycloalkyl group and at least one methacrylate monomer of formula $CH_2=C(CH_3)-COOR'2$ in which R'_2 represents a C_4 to C12 cycloalkyl group, according to the following sequence of steps:
- some of the polymerization solvent and optionally some of the initiator and of the monomers for the first addition are poured into the reactor, and the mixture is heated to a reaction temperature of between 60°C and 120°C,
- the acrylic acid monomer and said at least one monomer with a glass transition temperature of less than or equal to 20°C and optionally some of the initiator are then poured in, in a first addition, and the mixture is left to react for a time T corresponding to a maximum degree of conversion of said monomers of 90%,
- further polymerization initiator, said at least one acrylate monomer of formula $CH_2=CH-COOR2$ and said at least one methacrylate monomer of formula $CH2=C(CH_3)-COOR'2$, as monomer with a Tg of greater than or equal to 40°C, are

then poured into the reactor, in a second addition, and the mixture is left to react for a time T' after which the degree of conversion of said monomers reaches a plateau,
- the reaction mixture is cooled to room temperature.

The polymerization temperature is preferably about 90°C. The reaction time after the second addition is preferably between 3 and 6 hours.

Preferably, the block ethylenic copolymer is present in the composition in a solids content ranging from 0.1 % to 60%, better still from 0.5% to 50%, better still from 1% to 30% and even better still from 1% to 40% by weight relative to the total weight of the composition.

Distillation of the synthesis solvent

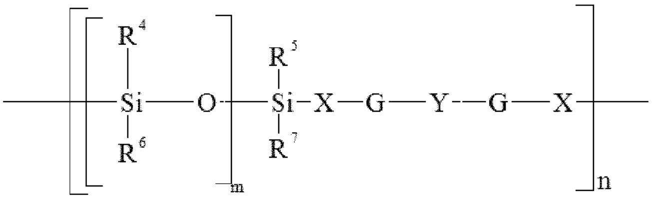
It is possible to perform a step of total or partial removal of said volatile oil or solvent (conventionally isododecane). This is then performed in particular by distillation, optionally under vacuum, and optional addition of non-volatile hydrocarbon-based ester oil comprising at least 16 carbon atoms and having a molar mass of less than 650 g/mol, such as octyldodecyl neopentanoate (especially 2-octyldodecyl neopentanoate).

This step is performed at elevated temperature and optionally under vacuum to distil off a maximum amount of volatile synthesis solvent, and is known to those skilled in the art.

III. Polyamide silicone block polymer

According to another embodiment variant, a composition according to the invention comprises, as hydrophobic film-forming polymer, at least one polyamide silicone block polymer, also known as a silicone polyamide.
The silicone polyamides are preferably solid at room temperature (25°C) and atmospheric pressure (760 mmHg).
For the purposes of the invention, the term "polymer" means a compound containing at least two repeating units, preferably at least three repeating units and better still
ten repeating units.
The silicone polyamides of the composition of the invention may be polymers of the polyorganosiloxane type, for instance those described in documents US-A-5 874 069, US-A-5 919 441 , US-A-6 051 216 and US-A-5 981 680. According to the invention, the silicone polymers may belong to the following two families:
(1) polyorganosiloxanes comprising at least two amide groups, these two groups being located in the polymer chain, and/or
(2) polyorganosiloxanes comprising at least two amide groups, these two groups being located on grafts or branches.
According to a first variant, the silicone polymers are polyorganosiloxanes as defined above in which the units capable of establishing hydrogen interactions are located in the polymer chain.

The silicone polymers may be more particularly polymers comprising at least one unit corresponding to the general formula I:

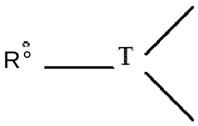


$$-\left[\left[-\underset{R^6}{\overset{R^4}{Si}}-O-\right]_m-\underset{R^7}{\overset{R^5}{Si}}-X-G-Y-G-X-\right]_n-$$

(I)

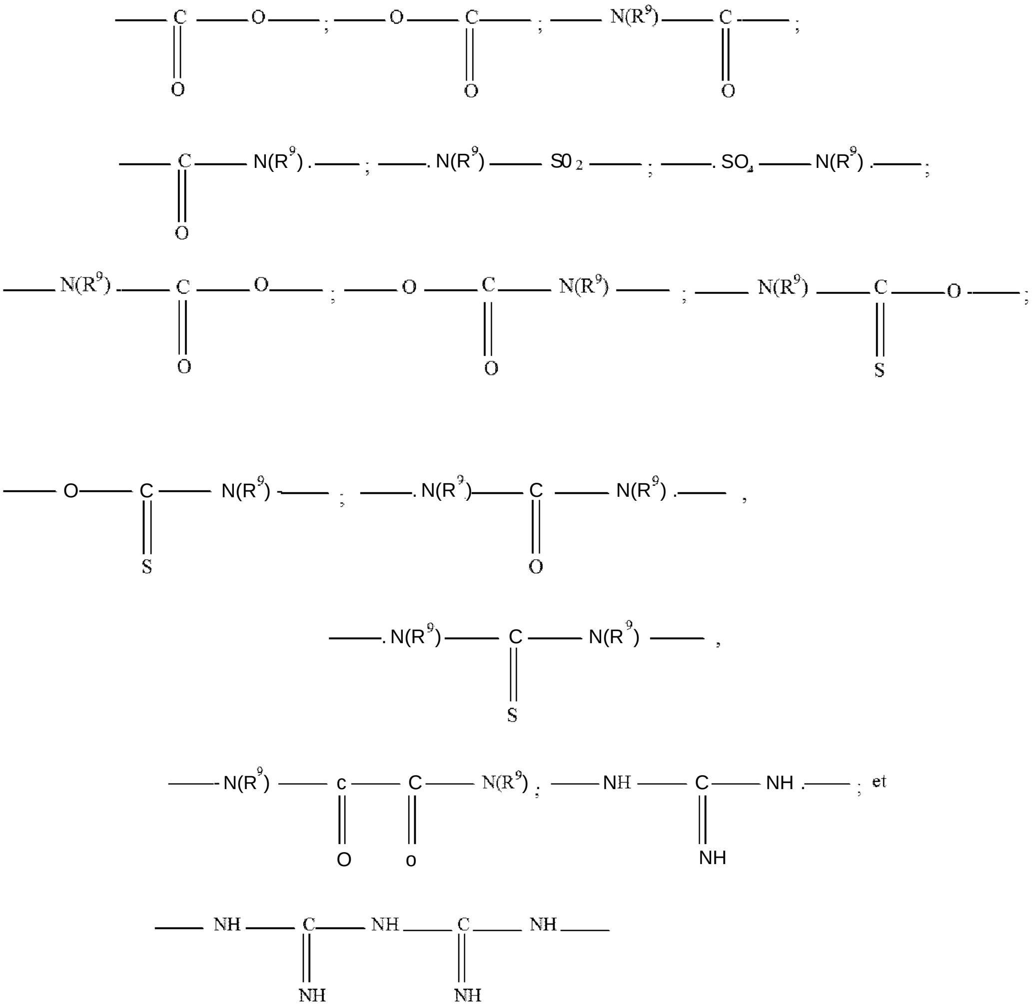
in which:

- R^4, R^5, R^6 and R^7, which may be identical or different, represent a group chosen from:
- saturated or unsaturated, C1 to C40 linear, branched or cyclic hydrocarbon-based groups, which may contain in their chain one or more oxygen, sulfur and/or nitrogen atoms, and which may be partially or totally substituted with fluorine atoms,
- C6 to Cio aryl groups, optionally substituted with one or more Ci to C_4 alkyl groups,
- polyorganosiloxane chains possibly containing one or more oxygen, sulfur and/or nitrogen atoms,
- the groups X, which may be identical or different, represent a linear or branched Ci to C30 alkylenediyl group, which may contain in its chain one or more oxygen and/or nitrogen atoms;
- Y is a saturated or unsaturated C1 to C50 linear or branched alkylene, arylene, cycloalkylene, alkylarylene or arylalkylene divalent group, which may comprise one or more oxygen, sulfur and/or nitrogen atoms, and/or may bear as substituent one of the following atoms or groups of atoms: fluorine, hydroxyl, C3 to Cs cycloalkyl, Ci to C_4o alkyl, C_5 to C10 aryl, phenyl optionally substituted with 1 to 3 Ci to C3 alkyl, Ci to C3 hydroxyalkyl and Ci to C_6 aminoalkyl groups, or
- Y represents a group corresponding to the formula:



in which:

- T represents a linear or branched, saturated or unsaturated, C3 to $C2_4$ trivalent or tetravalent hydrocarbon-based group optionally substituted with a polyorganosiloxane chain, and possibly containing one or more atoms chosen from O, N and S, or T represents a trivalent atom chosen from N, P and Al, and
- R^8 represents a linear or branched C1-C50 alkyl group or a polyorganosiloxane chain, possibly comprising one or more ester, amide, urethane, thiocarbamate, urea, thiourea and/or sulfonamide groups, which may possibly be linked to another chain of the polymer;
- the groups G, which may be identical or different, represent divalent groups chosen from:



$-\underset{\underset{O}{\|}}{C}-O-$; $-O-\underset{\underset{O}{\|}}{C}-$; $-N(R^9)-\underset{\underset{O}{\|}}{C}-$;

$-\underset{\underset{O}{\|}}{C}-N(R^9)-$; $-N(R^9)-SO_2-$; $-SO_2-N(R^9)-$;

$-N(R^9)-\underset{\underset{O}{\|}}{C}-O-$; $-O-\underset{\underset{O}{\|}}{C}-N(R^9)-$; $-N(R^9)-\underset{\underset{S}{\|}}{C}-O-$;

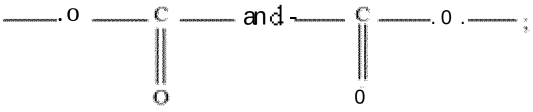
$-O-\underset{\underset{S}{\|}}{C}-N(R^9)-$; $-N(R^9)-\underset{\underset{O}{\|}}{C}-N(R^9)-$,

$-N(R^9)-\underset{\underset{S}{\|}}{C}-N(R^9)-$,

$-N(R^9)-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-N(R^9)$; $-NH-\underset{\underset{NH}{\|}}{C}-NH-$; et

$-NH-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-NH-$

in which R^9 represents a hydrogen atom or a linear or branched C_1 to C_{20} alkyl group, on condition that at least 50% of the groups R^9 of the polymer represent a hydrogen atom and that at least two of the groups G of the polymer are a group other than:



$-O-\underset{\underset{O}{\|}}{C}-$ and $-\underset{\underset{O}{\|}}{C}-O-$;

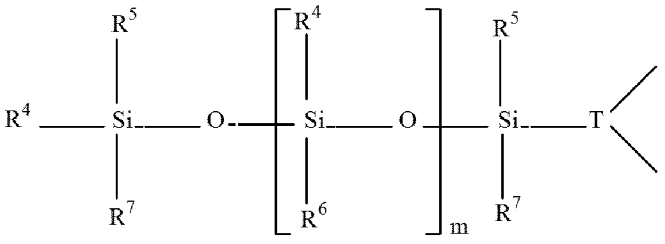
n is an integer ranging from 2 to 500 and preferably from 2 to 200, and m is an integer ranging from 1 to 1000, preferably from 1 to 700 and better still from 6 to 200.

According to the invention, 80% of the groups R^4, R^5, R^6 and R^7 of the polymer are preferably chosen from methyl, ethyl, phenyl and 3,3,3-trifluoropropyl groups.

According to the invention, Y may represent various divalent groups, furthermore optionally comprising one or two free valencies to establish bonds with other units of the polymer or copolymer. Preferably, Y represents a group chosen from:

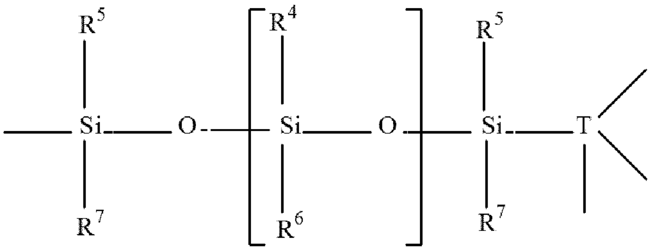
- linear C_1 to C_{20} and preferably C_1 to C_{10} alkylene groups,
- C_{30} to C_{56} branched alkylene groups possibly comprising rings and unconjugated unsaturations,

- C_5-C_6 cycloalkylene groups,
- phenylene groups optionally substituted with one or more C_1 to C_{40} alkyl groups,
- C_1 to C_{20} alkylene groups comprising from 1 to 5 amide groups,
- C_1 to C_{20} alkylene groups comprising one or more substituents chosen from hydroxyl, C_3 to C_s cycloalkane, C_1 to C_3 hydroxyalkyl and C_1 to C_6 alkylamine groups,
- polyorganosiloxane chains of formula:

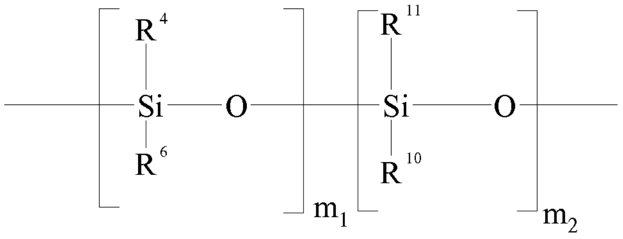


in which R^4, R^5, R^6, R^7, T and m are as defined above, and

- polyorganosiloxane chains of formula:



According to the second variant, the polyorganosiloxanes may be polymers comprising at least one unit corresponding to formula (II):



(II)

in which:

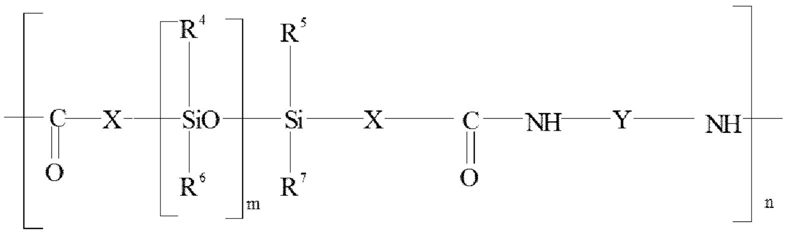
- R^4 and R^6, which may be identical or different, are as defined above for formula (I),
- R^{10} represents a group as defined above for R^4 and R^6, or represents the group of formula -X-G-R^{12} in which X and G are as defined above for formula (I) and R^{12} represents a hydrogen atom or a linear, branched or cyclic, saturated or unsaturated C_1 to C_{50} hydrocarbon-based group optionally comprising in its chain one or more atoms chosen from O, S and N, optionally substituted with one or more fluorine atoms and/or one or more hydroxyl groups, or a phenyl group optionally substituted with one or more C_1 to C_4 alkyl groups,
- R^{11} represents a group of formula -X-G-R^{12} in which X, G and R^{12} are as defined above,
- m_1 is an integer ranging from 1 to 998, and
- m_2 is an integer ranging from 2 to 500.

According to the invention, the silicone polymer used as structuring agent may be a homopolymer, that is to say a polymer comprising several identical units, in particular units of formula (I) or of formula (II).
According to the invention, it is also possible to use a silicone polymer formed from a copolymer comprising several different units of formula (I), that is to say a polymer in which at least one of the groups R4, R5, R6, R7, X, G, Y, m and n is different in one of the units. The copolymer may also be formed from several units of formula (II), in which at least one of the groups R4, R6, R10, R11, m1 and m2 is different in at least one of the units.

It is also possible to use a polymer comprising at least one unit of formula (I) and at least one unit of formula (II), the units of formula (I) and the units of formula (II) possibly being identical to or different than each other.
According to one variant of the invention, it is also possible to use a polymer furthermore comprising at least one hydrocarbon-based unit comprising two groups capable of establishing hydrogen interactions, chosen from ester, amide, sulfonamide, carbamate, thiocarbamate, urea, urethane, thiourea, oxamido, guanidino and biguanidino groups, and combinations thereof.

These copolymers may be block polymers or grafted polymers.

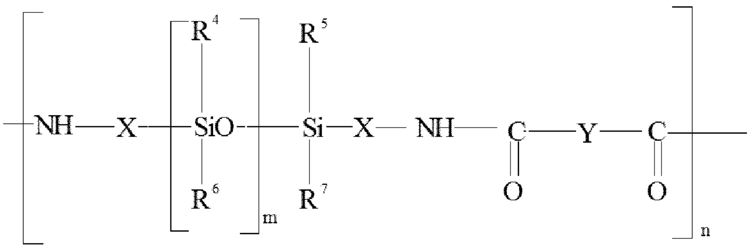
According to a first advantageous embodiment of the invention, the groups capable of establishing hydrogen interactions are amide groups of formulae -C(O)NH- and -HN-C(O)-.
In this case, the structuring agent may be a polymer comprising at least one unit of formula (III) or (IV):



$$\left[-\underset{\substack{\| \\ O}}{C}-X-\left[\underset{R^6}{\overset{R^4}{\mathrm{SiO}}} \right]_m-\underset{R^7}{\overset{R^5}{\mathrm{Si}}}-X-\underset{\substack{\| \\ O}}{C}-NH-Y-NH- \right]_n$$

(HI)

or



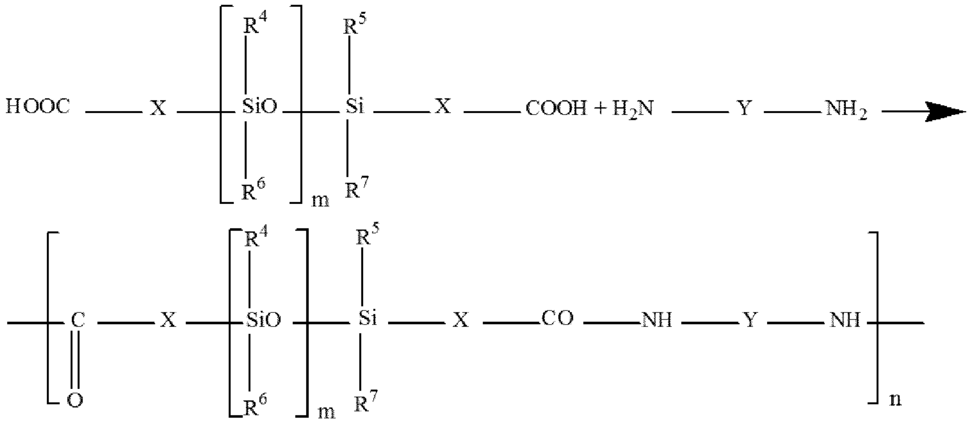
$$\left[-NH-X-\left[\underset{R^6}{\overset{R^4}{\mathrm{SiO}}} \right]_m-\underset{R^7}{\overset{R^5}{\mathrm{Si}}}-X-NH-\underset{\substack{\| \\ O}}{C}-Y-\underset{\substack{\| \\ O}}{C}- \right]_n$$

(IV)

in which R^4, R^5, R^6, R^7, X, Y, m and n are as defined above.

Such a unit may be obtained:

either by a condensation reaction between a silicone containing α,ω-carboxylic acid ends and one or more diamines, according to the following reaction scheme:

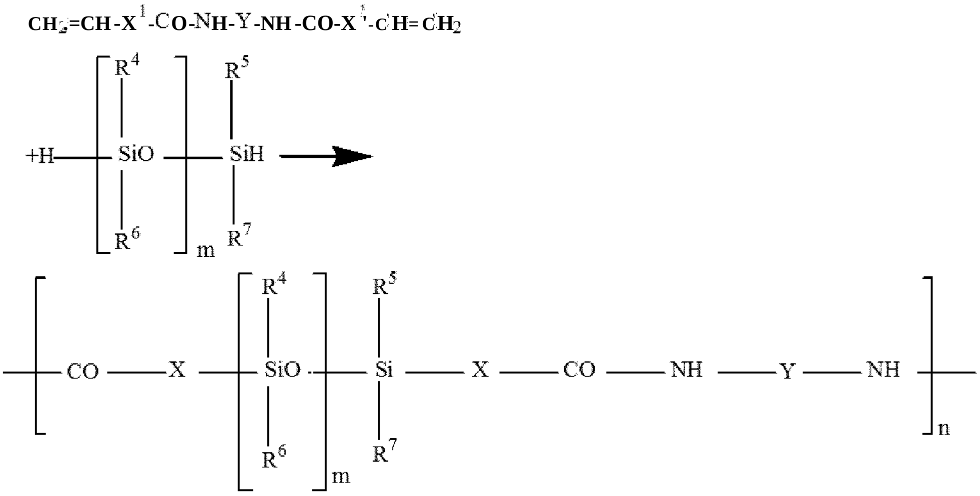


or by reaction of two molecules of a-unsaturated carboxylic acid with a diamine according to the following reaction scheme:

$$CH_2{=}CH\text{-}X^1\text{-}COOH{+}H_2N\text{-}Y\text{-}NH_2 \longrightarrow$$

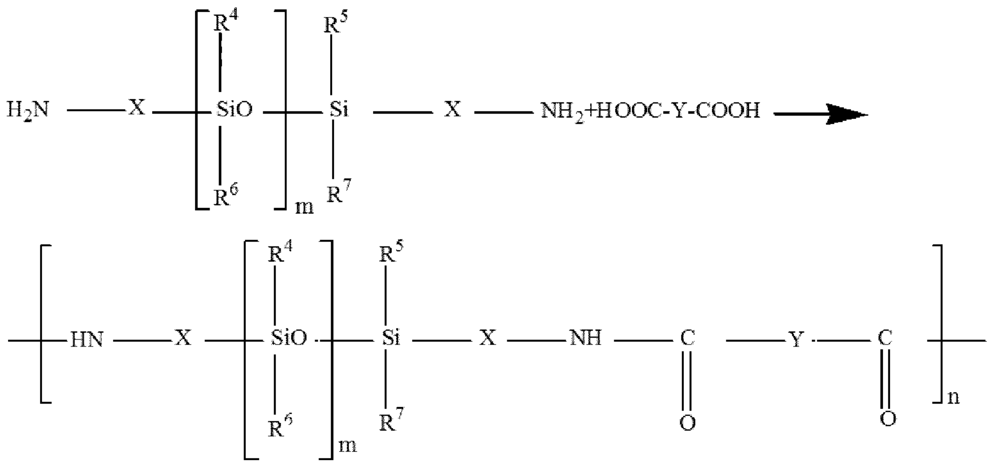
$$CH_2{=}CH\text{-}X^1\text{-}CO\text{-}NH\text{-}Y\text{-}NH\text{-}CO\text{-}X^1\text{-}CH{=}CH_2$$

followed by the addition of a siloxane to the ethylenic unsaturations, according to the following scheme:



in which X^1-$(CH_2)_2$- corresponds to X defined above and Y, R^4, R^5, R^6, R^7 and m are as defined above;

or by reaction of a silicone containing α,ω-NH_2 ends and a diacid of formula HOOC-Y-COOH according to the following reaction scheme:



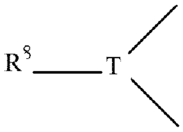
In these polyamides of formula (III) or (IV), m ranges from 1 to 700, in particular from 15 to 500 and especially from 50 to 200, and n ranges in particular from 1 to 500, preferably from 1 to 100 and better still from 4 to 25.

X is preferably a linear or branched alkylene chain containing from 1 to 30 carbon atoms, in particular 1 to 20 carbon atoms, especially from 5 to 15 carbon atoms and more particularly 10 carbon atoms, and Y is preferably an alkylene chain that is linear or branched, or which may comprise rings and/or unsaturations, containing from 1 to 40 carbon atoms, in particular 1 to 20 carbon atoms and better still from 2 to 6 carbon atoms, in particular 6 carbon atoms.

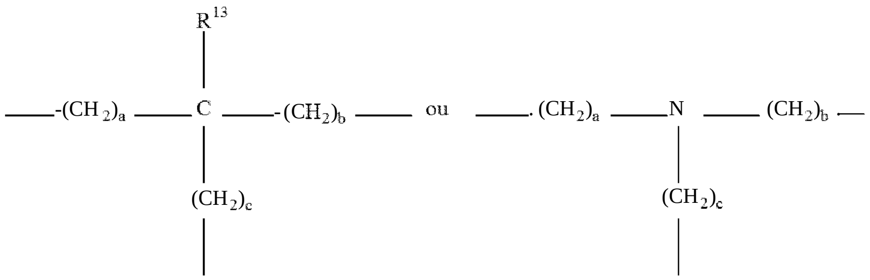
In formulae (III) and (IV), the alkylene group representing X or Y can optionally contain in its alkylene part at least one of the following components:
- one to five amide, urea, urethane or carbamate groups,
- a C_5 or C_6 cycloalkyl group, and
- a phenylene group optionally substituted with 1 to 3 identical or different C_1 to C_3 alkyl groups.

In formulae (III) and (IV), the alkylene groups may also be substituted with at least one component chosen from the group consisting of:
- a hydroxyl group,
- a C_3 to C_8 cycloalkyl group,
- one to three C_1 to C_{40} alkyl groups,
- a phenyl group optionally substituted with one to three C_1 to C_3 alkyl groups,
- a C_1 to C_3 hydroxyalkyl group, and
- a C_1 to C_6 aminoalkyl group.

In these formulae (III) and (IV), Y may also represent:



in which R^8 represents a polyorganosiloxane chain and T represents a group of formula:



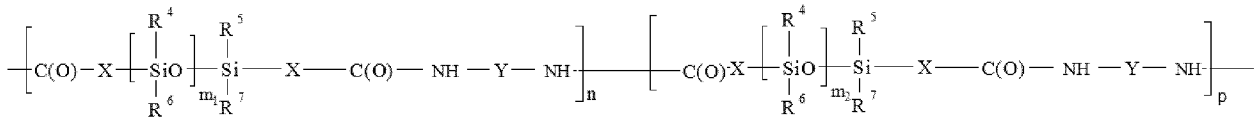
$$-(CH_2)_a-\underset{\underset{|}{(CH_2)_c}}{\overset{\overset{R^{13}}{|}}{C}}-(CH_2)_b- \quad \text{ou} \quad -(CH_2)_a-\underset{\underset{|}{(CH_2)_c}}{N}-(CH_2)_b-$$

in which a, b and c are, independently, integers ranging from 1 to 10, and R^{13} is a hydrogen atom or a group such as those defined for R^4, R^5, R^6 and R^7.

In formulae (III) and (IV), R^4, R^5, R^6 and R^7 preferably represent, independently, a linear or branched Ci to C_4o alkyl group, preferably a CH_3, C2H$_5$, n-CsH$_7$ or isopropyl group, a polyorganosiloxane chain or a phenyl group optionally substituted with one to three methyl or ethyl groups.

As has been seen previously, the polymer may comprise identical or different units of formula (III) or (IV).

Thus, the polymer may be a polyamide containing several units of formula (III) or (IV) of different lengths, i.e. a polyamide corresponding to formula (V):

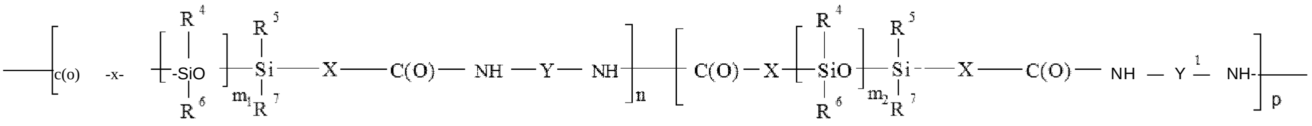


$$\left[C(O)-X-\left[\underset{R^6}{\overset{R^4}{SiO}}\right]_{m_1}-\underset{R^7}{\overset{R^5}{Si}}-X-C(O)-NH-Y-NH\right]_n-\left[C(O)-X-\left[\underset{R^6}{\overset{R^4}{SiO}}\right]_{m_2}-\underset{R^7}{\overset{R^5}{Si}}-X-C(O)-NH-Y-NH\right]_p$$

(V)

in which X, Y, n and R^4 to R^7 have the meanings given above, m_1 and m_2, which are different, are chosen in the range from 1 to 1000, and p is an integer ranging from 2 to 300.

In this formula, the units may be structured to form either a block copolymer, or a random copolymer or an alternating copolymer. In this copolymer, the units may be not only of different lengths, but also of different chemical structures, for example containing different groups Y. In this case, the polymer may correspond to formula VI:



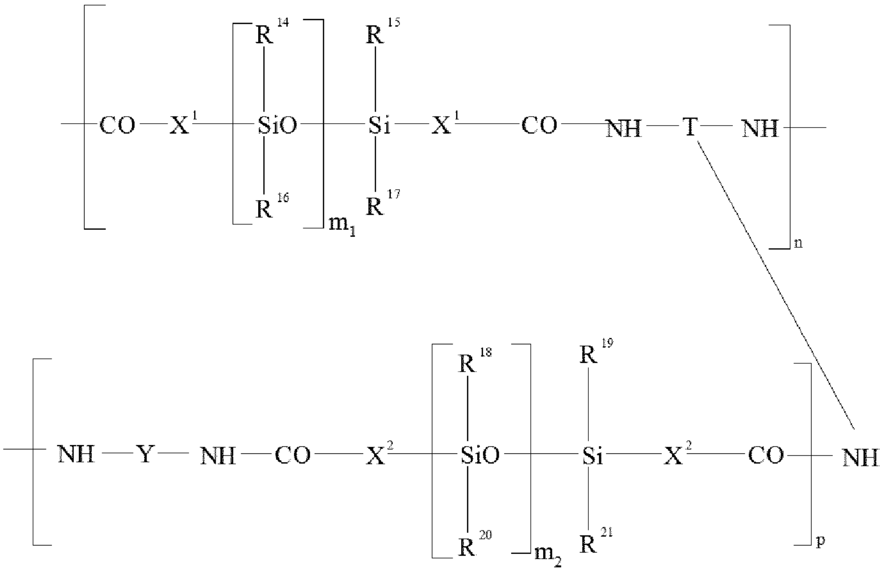
$$\left[c(o)-x-\left[\underset{R^6}{\overset{R^4}{SiO}}\right]_{m_1}-\underset{R^7}{\overset{R^5}{Si}}-X-C(O)-NH-Y-NH\right]_n-\left[C(O)-X-\left[\underset{R^6}{\overset{R^4}{SiO}}\right]_{m_2}-\underset{R^7}{\overset{R^5}{Si}}-X-C(O)-NH-Y^1-NH\right]_p$$

(VI)

in which R^4 to R^7, X, Y, mi, m_2, n and p have the meanings given above and Y1 is different than Y but chosen from the groups defined for Y.

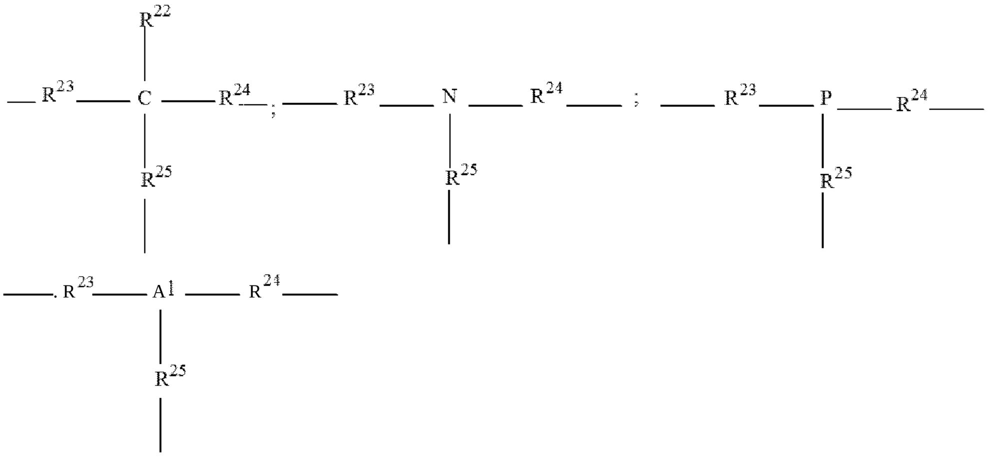
As previously, the various units may be structured to form either a block copolymer, or a random copolymer or an alternating copolymer.
In this first embodiment of the invention, the structuring agent may also consist of a grafted copolymer. Thus, the polyamide containing silicone units may be grafted and optionally crosslinked with silicone chains containing amide groups. Such polymers may be synthesized with trifunctional amines.

In this case, the polymer may comprise at least one unit of formula (VII):



(VII)

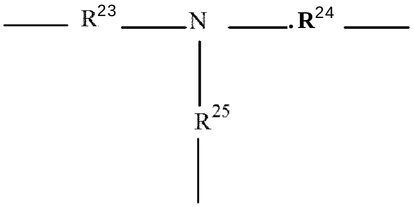
in which X^1 and X^2, which are identical or different, have the meaning given for X in formula (I), n is as defined in formula (I), Y and T are as defined in formula (I), R^{14} to R^{21} are groups chosen from the same group as R^4 to R^7, m_1 and m_2 are numbers in the range from 1 to 1000, and p is an integer ranging from 2 to 500.
In formula (VII), it is preferred that:
- p is in the range from 1 to 25 and better still from 1 to 7,
- R^{14} to R^{21} are methyl groups,
- T corresponds to one of the following formulae:



$$-R^{23}-\underset{\underset{\underset{|}{R^{25}}}{|}}{\overset{\overset{R^{22}}{|}}{C}}-R^{24}- ;\quad -R^{23}-\underset{\underset{\underset{|}{R^{25}}}{|}}{N}-R^{24}- ;\quad -R^{23}-\underset{\underset{\underset{|}{R^{25}}}{|}}{P}-R^{24}-$$

$$-.R^{23}-\underset{\underset{\underset{|}{R^{25}}}{|}}{Al}-R^{24}-$$

in which R^{22} is a hydrogen atom or a group chosen from the groups defined for R^4 to R^7, and R^{23}, R^{24} and R^{25} are, independently, linear or branched alkylene groups, and more preferably correspond to the formula:



$$-R^{23}-\underset{\underset{\underset{|}{R^{25}}}{|}}{N}-.\mathbf{R}^{24}-$$

in particular with R^{23}, R^{24} and R^{25} representing $-CH_2-CH_2-$, m_1 and m_2 are from 15 to 500 and better still from 15 to 45, X^1 and X^2 represent $-(CH_2)io-$, and Y represents $-CH_2-$.

These polyamides containing a grafted silicone unit of formula (VII) may be copolymerized with polyamide-silicones of formula (II) to form block copolymers, alternating copolymers or random copolymers. The weight percentage of grafted silicone units (VII) in the copolymer may range from 0.5% to 30% by weight.

According to the invention, as has been seen previously, the siloxane units may be in the main chain or backbone of the polymer, but they may also be present in grafted or pendent chains. In the main chain, the siloxane units may be in the form of segments as described above. In the pendent or grafted chains, the siloxane units may appear individually or in segments.

According to one embodiment variant of the invention, a copolymer of silicone polyamide and of hydrocarbon-based polyamide, or a copolymer comprising units of formula (III) or (IV) and hydrocarbon-based polyamide units, may be used. In this case, the polyamide-silicone units may be located at the ends of the hydrocarbon-based polyamide.

According to a preferred embodiment, the silicone polyamide comprises units of formula III, preferably in which the groups R^4, R^5, R^6 and R^7 represent methyl groups, one from among X and Y represents an alkylene group of 6 carbon atoms and the other represents an alkylene group of 11 carbon atoms, n representing the degree of polymerization, DP, of the polymer. As examples of such silicone polyamides, mention may be made of the compounds sold by the company Dow Corning under the names DC 2-81 79® (DP 100®) and DC 2-81 78® (DP 15®), the INCI name of which is Nylon-61 1/dimethicone copolymer.

Advantageously, the composition according to the invention comprises at least one polydimethylsiloxane block polymer of general formula (I) with an m value of about 15.

More preferably, the composition according to the invention comprises at least one polymer comprising at least one unit of formula (III) in which m ranges from 5 to 100, in particular from 10 to 75 and even more particularly is about 15; even more preferably, R^4, R^5, R^6 and R^7 independently represent a linear or branched Ci to C_4o alkyl group, preferably a group CH_3, C2H_5, n-CsH_7 or isopropyl in formula (III). According to a preferred mode, use is made of the polyamide silicone polymer sold by the company Dow Corning under the name DC 2-81 79® (DP 100®).

As an example of silicone polymers that may be used, mention may be made of one of the silicone polyamides obtained in accordance with Examples 1 to 3 of document
US-A-5 981 680.

IV. Vinyl polymer comprising at least one carbosiloxane dendrimer-based unit

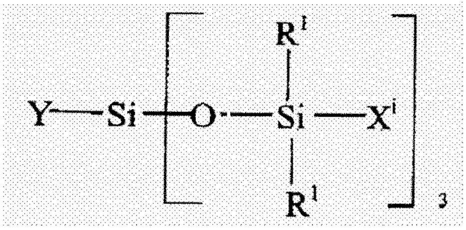
According to one particular embodiment, a composition used according to the invention may comprise, as hydrophobic film-forming polymer, at least one vinyl polymer comprising at least one carbosiloxane dendrimer-based unit.

The vinyl polymer used according to the invention especially has a backbone and at least one side chain, which comprises a carbosiloxane dendrimer-based unit having a carbosiloxane dendrimer structure.

Vinyl polymers comprising at least one carbosiloxane dendrimer unit as described in patent applications WO 03/045 337 and EP 963 751 by the company Dow Corning may be used in particular.

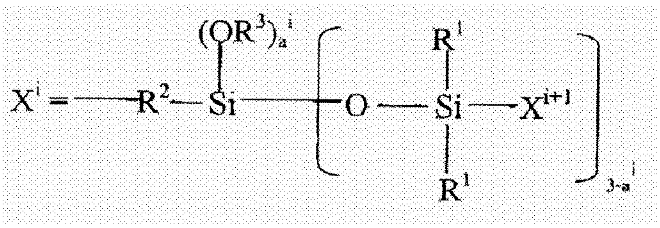
In the context of the present invention, the term "carbosiloxane dendrimer structure" represents a molecular structure containing branched groups of high molecular masses, said structure having high regularity in the radial direction starting from the bond to the backbone. Such carbosiloxane dendrimer structures are described in the form of a highly branched siloxane-silylalkylene copolymer in laid-open Japanese patent application Kokai 9-1 7 1 154.

A vinyl polymer according to the invention may contain carbosiloxane dendrimer-based units that may be represented by the following general formula:



$$Y-Si\left[O-\underset{R^1}{\overset{R^1}{Si}}-X^i\right]_3$$

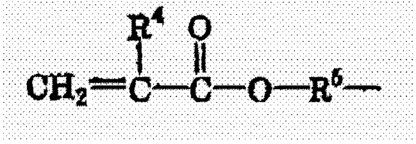
in which R^1 represents an aryl group or an alkyl group containing from 1 to 10 carbon atoms, and X^i represents a silylalkyl group which, when i = 1, is represented by the formula:



$$X^i = -R^2-\overset{(OR^3)_{a^i}}{Si}\left[O-\underset{R^1}{\overset{R^1}{Si}}-X^{i+1}\right]_{3-a^i}$$

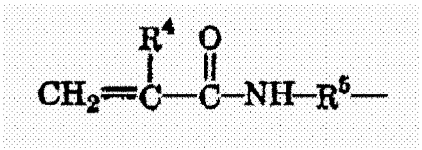
in which R^1 is the same as defined above, R^2 represents an alkylene group containing from 2 to 10 carbon atoms, R^3 represents an alkyl group containing from 1 to 10 carbon atoms, X^{i+1} represents a hydrogen atom, an alkyl group containing from 1 to 10 carbon atoms, an aryl group or the silylalkyl group defined above with i = i + 1; i is an integer from 1 to 10 which represents the generation of said silylalkyl group, and ai is an integer from 0 to 3; Y represents a radical-polymerizable organic group chosen from:

- organic groups containing a methacrylic group or an acrylic group and that are represented by the formulae:



$$CH_2=\overset{R^4}{C}-\overset{O}{\overset{\|}{C}}-O-R^5-$$

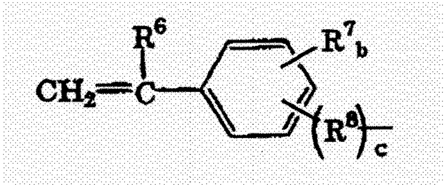
and



$$CH_2=\overset{R^4}{C}-\overset{O}{\overset{\|}{C}}-NH-R^5-$$

in which R^4 represents a hydrogen atom or an alkyl group, R^5 represents an alkylene group containing from 1 to 10 carbon atoms, such as a methylene group, an ethylene group, a propylene group or a butylene group, the methylene group and the propylene group being preferred; and

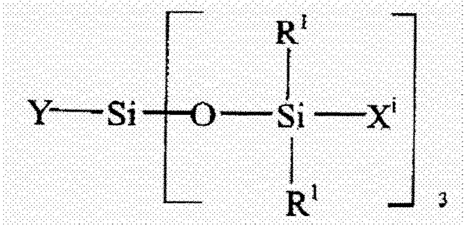
- organic groups containing a styryl group and that are represented by the formula:



in which R^6 represents a hydrogen atom or an alkyl group, R^7 represents an alkyl group containing from 1 to 10 carbon atoms, such as a methyl group, an ethyl group, a propyl group or a butyl group, the methyl group being preferred, R^8 represents an alkylene group containing from 1 to 10 carbon atoms, such as a methylene group, an ethylene group, a propylene group or a butylene group, the ethylene group being preferred, b is an integer from 0 to 4, and c is 0 or 1 such that if c is 0, -(R^8)c- represents a bond.

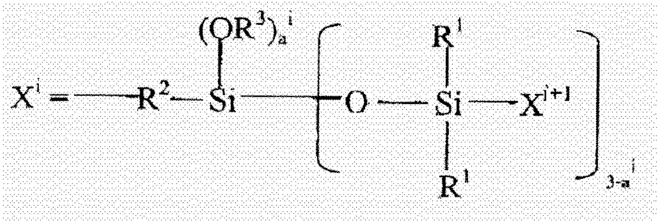
According to one embodiment, R^1 may represent an aryl group or an alkyl group containing from 1 to 10 carbon atoms. The alkyl group may preferably be represented by a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, an isopropyl group, an isobutyl group, a cyclopentyl group or a cyclohexyl group. The aryl group can preferably be represented by a phenyl group and a naphthyl group. The methyl and phenyl groups are more particularly preferred, and the methyl group is most preferred.

A vinyl polymer containing at least one carbosiloxane dendrimer-based unit has a molecular side chain containing a carbosiloxane dendrimer structure, and may be the product of polymerization of:
from 0 to 99.9 parts by weight of a vinyl monomer; and
from 100 to 0.1 part by weight of a carbosiloxane dendrimer containing a radical-polymerizable organic group, represented by the general formula:



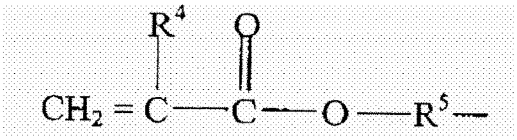
$$Y-Si\left[O-\overset{R^1}{\underset{R^1}{Si}}-X^i\right]_3$$

in which Y represents a radical-polymerizable organic group, R^1 represents an aryl group or an alkyl group containing from 1 to 10 carbon atoms, and X^i represents a silylalkyl group which, when i = 1, is represented by the formula:



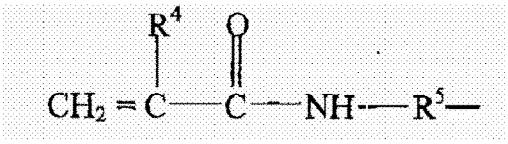
$$X^i = -R^2-\overset{(OR^3)_{a^i}}{Si}\left[O-\overset{R^1}{\underset{R^1}{Si}}-X^{i+1}\right]_{3-a^i}$$

in which R^1 is the same as defined above, R^2 represents an alkylene group containing from 2 to 10 carbon atoms, R^3 represents an alkyl group containing from 1 to 10 carbon atoms, X^{i+1} represents a hydrogen atom, an alkyl group containing from 1 to 10 carbon atoms, an aryl group, or the silylalkyl group defined above with i = i + 1; i is an integer from 1 to 10 that represents the generation of said silylalkyl group, and ai is an integer from 0 to 3;
in which said radical-polymerizable organic group contained in the component (B) is chosen from:
- organic groups containing a methacrylic group or an acrylic group and that are represented by the formulae:



$$CH_2=\overset{R^4}{C}-\overset{O}{\overset{\|}{C}}-O-R^5-$$

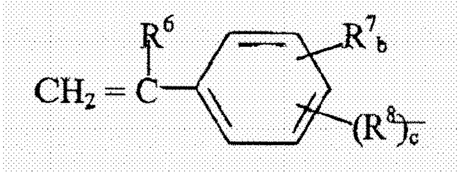
and



$$CH_2=\overset{R^4}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-NH-R^5-$$

in which R4 represents a hydrogen atom or an alkyl group, R5 represents an alkylene group containing from 1 to 10 carbon atoms; and

- organic groups containing a styryl group and that are represented by the formula:



in which R6 represents a hydrogen atom or an alkyl group, R7 represents an alkyl group containing from 1 to 10 carbon atoms, R8 represents an alkylene group containing from 1 to 10 carbon atoms, b is an integer from 0 to 4, and c is 0 or 1, such that if c is 0, -(R8)c- represents a bond.

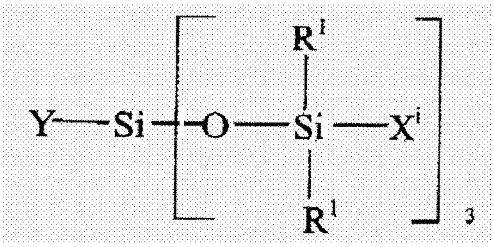
The monomer of vinyl type that is component (A) in the vinyl polymer is a monomer of vinyl type that contains a radical-polymerizable vinyl group.

There is no particular limitation as regards such a monomer.
The following are examples of this monomer of vinyl type: methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate or a methacrylate of an analogous lower alkyl; glycidyl methacrylate; butyl methacrylate, butyl acrylate, n-butyl methacrylate, isobutyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, n-hexyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, octyl methacrylate, lauryl methacrylate, stearyl acrylate, stearyl methacrylate or a higher-analogue methacrylate; vinyl acetate, vinyl propionate or a vinyl ester of an analogous lower fatty acid; vinyl caproate, vinyl 2-ethylhexoate, vinyl laurate, vinyl stearate or an ester of a higher fatty acid analogue; styrene, vinyltoluene, benzyl methacrylate, phenoxyethyl methacrylate, vinylpyrrolidone or similar vinylaromatic monomers; methacrylamide, N-methylolmethacrylamide, N-methoxymethylmethacrylamide, isobutoxymethoxymethacrylamide, N,N-dimethylmethacrylamide or similar monomers of vinyl type containing amide groups; hydroxyethyl methacrylate, hydroxypropyl alcohol methacrylate or similar monomers of vinyl type containing hydroxyl groups; acrylic acid, methacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid or similar monomers of vinyl type containing a carboxylic acid group; tetrahydrofurfuryl methacrylate, butoxyethyl methacrylate, ethoxydiethylene glycol methacrylate, polyethylene glycol methacrylate, polypropylene glycol monomethacrylate, hydroxybutyl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether or a similar monomer of vinyl type with ether bonds; methacryloxypropyltrimethoxysilane, polydimethylsiloxane containing a methacrylic group on one of its molecular ends, polydimethylsiloxane containing a styryl group on one of its molecular ends, or a similar silicone compound containing unsaturated groups; butadiene; vinyl chloride; vinylidene chloride; methacrylonitrile; dibutyl fumarate; anhydrous maleic acid; anhydrous succinic acid; methacryl glycidyl ether; an organic salt of an amine, an ammonium salt, and

an alkali metal salt of methacrylic acid, of itaconic acid, of crotonic acid, of maleic acid or of fumaric acid; a radical-polymerizable unsaturated monomer containing a sulfonic acid group such as a styrenesulfonic acid group; a quaternary ammonium salt derived from methacrylic acid, such as 2-hydroxy-3-methacryloxypropyltrimethylammonium chloride; and a methacrylic acid ester of an alcohol containing a tertiary amine group, such as a methacrylic acid ester of diethylamine.

Multifunctional monomers of vinyl type can also be used.
The following are examples of such compounds: trimethylolpropane trimethacrylate, pentaerythrityl trimethacrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, trimethylolpropane trioxyethylmethacrylate, tris(2-hydroxyethyl)isocyanurate dimethacrylate, tris(2-hydroxyethyl)isocyanurate trimethacrylate, polydimethylsiloxane capped with styryl groups possessing divinylbenzene groups on both ends, or analogous silicone compounds containing unsaturated groups.

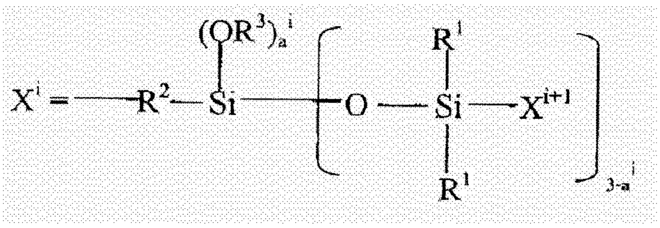
A carbosiloxane dendrimer, which is the component (B), may be represented by the following formula:



$$Y-Si\left[-O-\overset{R^1}{\underset{R^1}{Si}}-X^i\right]_3$$

in which Y represents a radical-polymerizable organic group as defined previously.

The following are preferred examples of radical-polymerizable organic groups Y: an aryloxymethyl group, a 3-acryloxypropyl group, a methacryloxymethyl group, a 3-methacryloxypropyl group, a 4-vinylphenyl group, a 3-vinylphenyl group, a 4-(2-propenyl)phenyl group, a 3-(2-propenyl)phenyl group, a 2-(4-vinylphenyl)ethyl group, a 2-(3-vinylphenyl)ethyl group, a vinyl group, an allyl group, a methallyl group and a 5-hexenyl group.
R' is as defined previously.
X' represents a silylalkyl group that is represented by the following formula, when i is equal to 1:



$$X^i = -R^2-\overset{(OR^3)_{a^i}}{Si}\left[-O-\overset{R^1}{\underset{R^1}{Si}}-X^{i+1}\right]_{3-a^i}$$

in which:
R^1 is as defined above;
R^2 represents an alkylene group containing from 2 to 10 carbon atoms, such as an ethylene group, a propylene group, a butylene group, a hexylene group or a

similar linear alkylene group; a methylmethylene group, a methylethylene group, a 1-methylpentylene group, a 1,4-dimethylbutylene group or a similar branched alkylene group.

The ethylene, methylethylene, hexylene, 1-methylpentylene and 1,4-dimethylbutylene groups are most preferred. R^3 represents an alkyl group containing from 1 to 10 carbon atoms, such as methyl, ethyl, propyl, butyl and isopropyl groups.

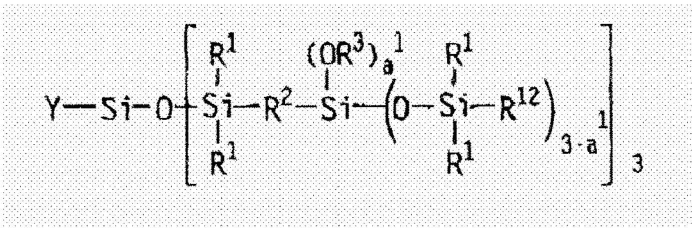
X^{i+1} represents a hydrogen atom, an alkyl group containing from 1 to 10 carbon atoms, an aryl group or the silylalkyl group with i = i + 1.

a' is an integer from 0 to 3, and i is an integer from 1 to 10 that indicates the generation number, which represents the number of repetitions of the silylalkyl group.

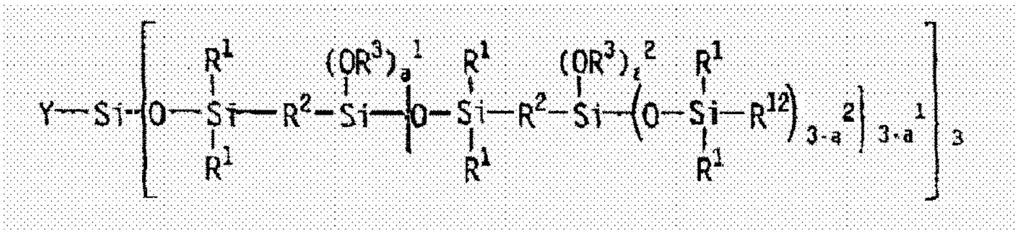
For example, when the generation number is equal to 1, the carbosiloxane dendrimer may be represented by the first general formula shown below, in which Y, R^1, R^2 and R^3 are the same as defined above, R^{12} represents a hydrogen atom or is identical to R^1; a^1 is identical to ai. Preferably, the total average number of OR^3 groups in a molecule is within the range from 0 to 7.

When the generation number is equal to 2, the carbosiloxane dendrimer may be represented by the second general formula shown below, in which Y, R^1, R^2, R^3 and R^{12} are the same as defined above; a1 and a2 represent the ai of the indicated generation. Preferably, the total mean number of groups OR3 in a molecule is within the range from 0 to 25.

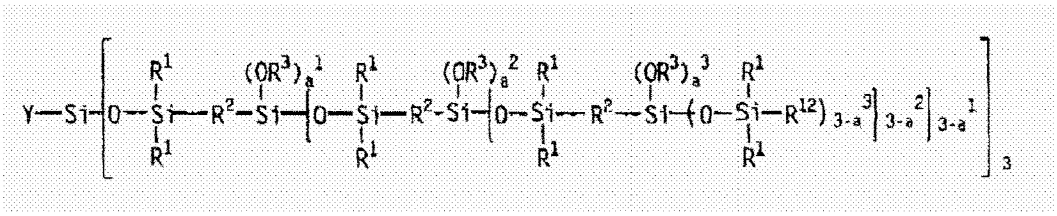
When the generation number is equal to 3, the carbosiloxane dendrimer is represented by the third general formula shown below, in which Y, R^1, R^2, R^3 and $R^{\prime -}$ are the same as defined above; a^1, a^2 and a^3 represent the ai of the indicated generation. Preferably, the total average number of OR^3 groups in a molecule is within the range from 0 to 79.



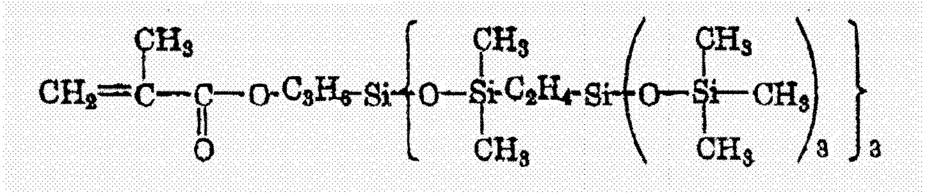
$$Y-Si-O\left[\overset{R^1}{\underset{R^1}{Si}}-R^2-\overset{(OR^3)_a{}^1}{Si}\left(O-\overset{R^1}{\underset{R^1}{Si}}-R^{12}\right)_{3-a}{}^{1}\right]_3$$

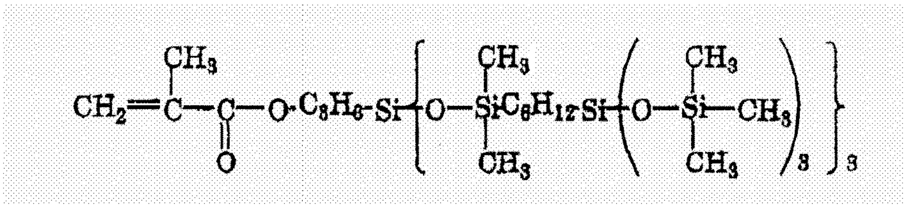


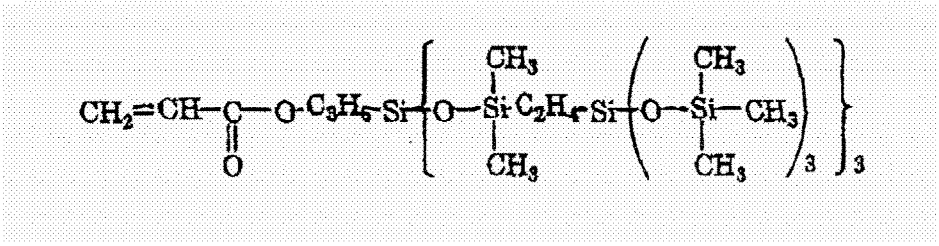
$$Y-Si\left[O-\overset{R^1}{\underset{R^1}{Si}}-R^2-\overset{(OR^3)_a{}^1}{Si}\left\{O-\overset{R^1}{\underset{R^1}{Si}}-R^2-\overset{(OR^3)_a{}^2}{Si}\left(O-\overset{R^1}{\underset{R^1}{Si}}-R^{12}\right)_{3-a}{}^{2}\right\}_{3-a}{}^{1}\right]_3$$

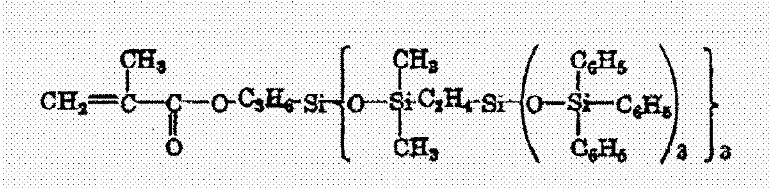

$$Y-Si\left[O-\overset{R^1}{\underset{R^1}{Si}}-R^2-\overset{(OR^3)_a{}^1}{Si}-\left[O-\overset{R^1}{\underset{R^1}{Si}}-R^2-\overset{(OR^3)_a{}^2}{Si}-\left[O-\overset{R^1}{\underset{R^1}{Si}}-R^2-\overset{(OR^3)_a{}^3}{Si}-\left(O-\overset{R^1}{\underset{R^1}{Si}}-R^{12}\right)_{3-a^3}\right]_{3-a^2}\right]_{3-a^1}\right]_3$$

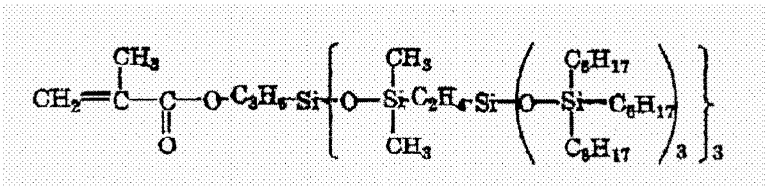
A carbosiloxane dendhmer that contains a radical-polymerizable organic group may be represented by the following mean structural formulae:

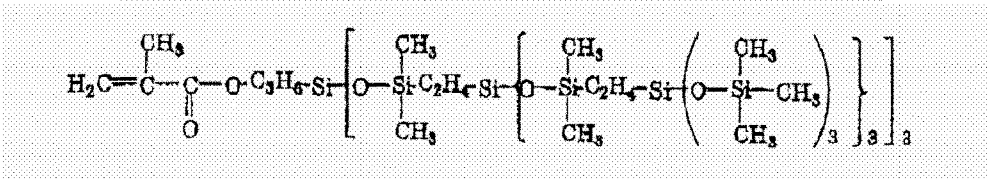

$$CH_2=\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-C_3H_6-Si\left\{O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left(O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3\right)_3\right\}_3$$

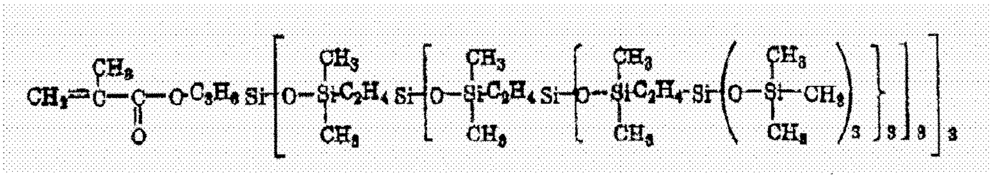

$$CH_2=\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-C_3H_6-Si\left\{O-\overset{CH_3}{\underset{CH_3}{Si}}-C_6H_{12}-Si\left(O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3\right)_3\right\}_3$$

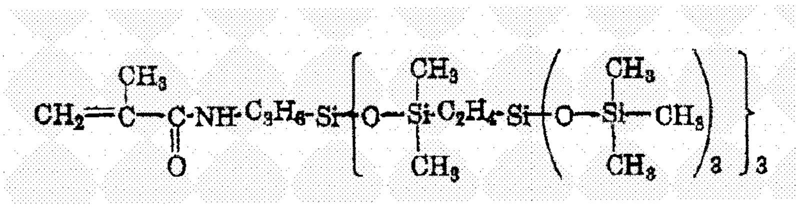

$$CH_2=CH-\underset{\underset{O}{\|}}{C}-O-C_3H_6-Si\left\{O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left(O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3\right)_3\right\}_3$$

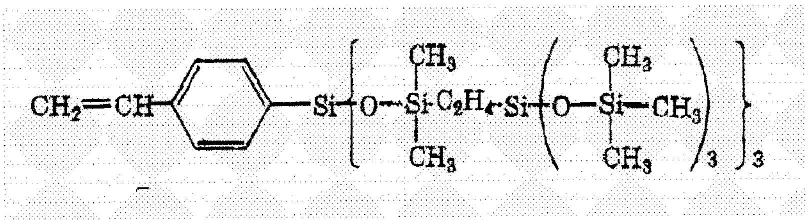

$$CH_2=\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-C_3H_6-Si\left\{O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left(O-\overset{C_6H_5}{\underset{C_6H_5}{Si}}-C_6H_5\right)_3\right\}_3$$

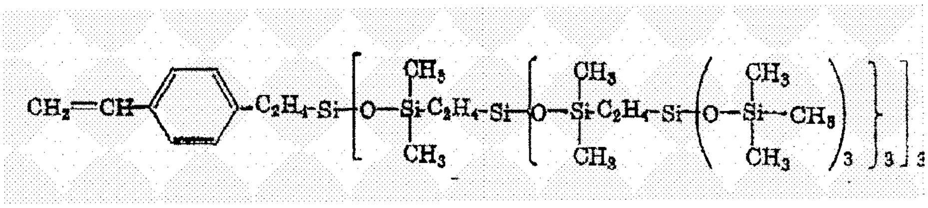

$$CH_2=\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-C_3H_6-Si\left\{O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left(O-\overset{C_8H_{17}}{\underset{C_8H_{17}}{Si}}-C_8H_{17}\right)_3\right\}_3$$

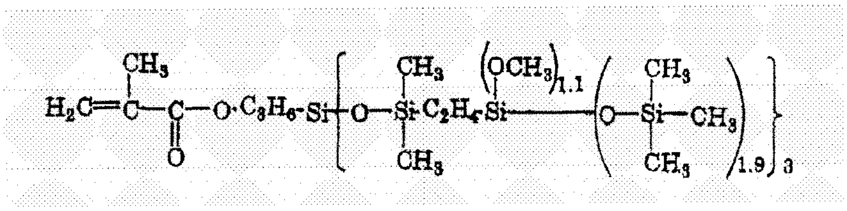

$$H_2C=\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-C_3H_6-Si\left[O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left\{O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left(O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3\right)_3\right\}_3\right]_3$$

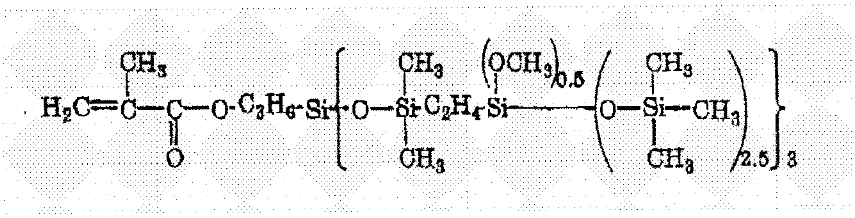

$$CH_2=\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-C_3H_6-Si\left[O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left[O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left\{O-\overset{CH_3}{\underset{CH_3}{Si}}-C_2H_4-Si\left(O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3\right)_3\right\}_3\right]_3\right]_3$$

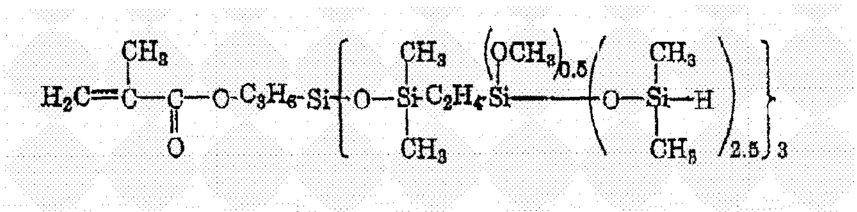


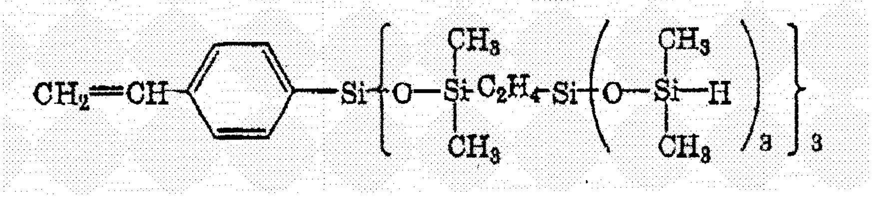






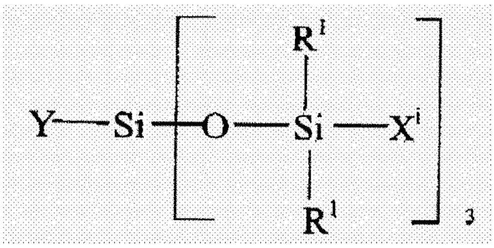






The carbosiloxane dendhmer may be manufactured according to the process for manufacturing a branched silalkylene siloxane described in Japanese patent application Hei 9-1 7 1 154.

For example, it may be produced by subjecting an organosilicon compound containing a hydrogen atom linked to a silicon atom, represented by the following general formula:

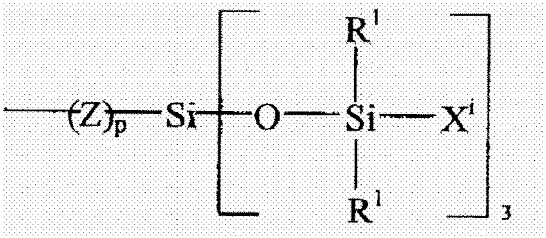


$$Y-Si\left[-O-\underset{R^1}{\overset{R^1}{Si}}-X^i\right]_3$$

and an organosilicon compound containing an alkenyl group, to a hydrosilylation reaction.

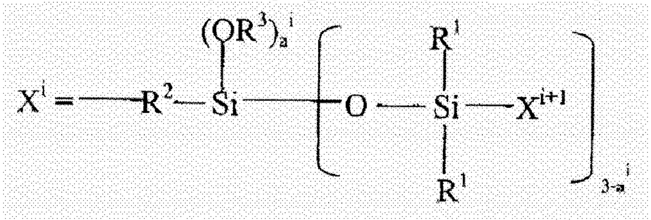
In the above formula, the organosilicon compound may be represented by 3-methacryloxypropyltris(dimethylsiloxy)silane, 3-acryloxypropyltris- may be chosen from the polymers such that the carbosiloxane dendrimer-based unit is (dimethylsiloxy)silane, and 4-vinylphenyltris(dimethylsiloxy)silane. The organosilicon compound that contains an alkenyl group may be represented by vinyltris(trimethylsiloxy)silane, vinyltris(dimethylphenylsiloxy)silane, and 5-hexenyltris(trimethylsiloxy)silane.

The hydrosilylation reaction is performed in the presence of a chloroplatinic acid, a complex of vinylsiloxane and of platinum, or a similar transition metal catalyst.
A vinyl polymer containing at least one carbosiloxane dendrimer-based unit may be chosen from polymers such that the carbosiloxane dendrimer-based unit is a carbosiloxane dendritic structure represented by formula (I):



$$-(Z)_p-Si\left[-O-\underset{R^1}{\overset{R^1}{Si}}-X^i\right]_3$$

in which Z is a divalent organic group, p is 0 or 1, R^1 is an aryl or alkyl group of 1 to 10 carbon atoms and X^i is a silylalkyl group represented by formula (II):



$$X^i=-R^2-\overset{(OR^3)_{a^i}}{Si}\left[-O-\underset{R^1}{\overset{R^1}{Si}}-X^{i+1}\right]_{3-a^i}$$

in which R^1 is as defined above, R^2 is an alkylene group containing from 1 to 10 carbon atoms, R^3 is an alkyl group containing from 1 to 10 carbon atoms and X^{i+1} is a group chosen from the group comprising hydrogen atoms, aryl groups and alkyl groups containing up to 10 carbon atoms, and silylalkyl groups X^i in which the power "i" is an integer from 1 to 10 indicating the generation of the starting silylalkyl group in each carbosiloxane dendritic structure with a value of 1 for the group X^i in formula (I) and the index "a^i" is an integer from 0 to 3.

In a vinyl polymer bearing at least one carbosiloxane dendrimer-based unit, the polymerization ratio between the components (A) and (B), in terms of the weight ratio between (A) and (B), may be within a range from 0/100 to 99.9/0.1, or even from 0.1/99.9 to 99.9/0.1 and preferably within a range from 1/99 to 99/1. A ratio of the component (A) to the component (B) of 0/100 means that the compound becomes a homopolymer of component (B).

A vinyl polymer having at least one unit derived from carbosiloxane dendrimer can be obtained by the copolymerization of the components (A) and (B) or by the polymerization of the component (B) alone.

The polymerization can be a radical polymerization or an ionic polymerization; however, the radical polymerization is preferred.

The polymerization may be performed by bringing about a reaction between the components (A) and (B) in a solution for a period of from 3 to 20 hours in the presence of a radical initiator at a temperature of from 50°C to 150°C.

A suitable solvent for this purpose is hexane, octane, decane, cyclohexane or a similar aliphatic hydrocarbon; benzene, toluene, xylene or a similar aromatic hydrocarbon; diethyl ether, dibutyl ether, tetrahydrofuran, dioxane or similar ethers; acetone, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone or similar ketones; methyl acetate, ethyl acetate, butyl acetate, isobutyl acetate or similar esters; methanol, ethanol, isopropanol, butanol or similar alcohols; octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, hexamethyldisiloxane, octamethyltrisiloxane or a similar organosiloxane oligomer.

A radical initiator can be any compound known in the art for conventional radical polymerization reactions. The specific examples of such radical initiators are 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile) or analogous compounds of azobis type; benzoyl peroxide, lauroyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxy-2-ethylhexanoate or an analogous organic peroxide. These radical initiators can be used alone or in a combination of two or more. The radical initiators can be used in an amount of 0.1 to 5 parts by weight per 100 parts by weight of the components (A) and (B). A chain-transfer agent can be added. The chain-transfer agent can be 2-mercaptoethanol, butyl mercaptan, n-dodecyl mercaptan, (3-mercaptopropyl)trimethoxysilane, a polydimethylsiloxane possessing a mercaptopropyl group or an analogous compound of mercapto type; methylene chloride, chloroform, carbon tetrachloride, butyl bromide, (3-chloropropyl)trimethoxysilane or an analogous halogenated compound.
In the manufacture of the polymer of vinyl type, after the polymerization, the unreacted residual vinyl monomer can be removed under conditions of heating under vacuum.

To facilitate the preparation of starting material mixture for cosmetic products, the number-average molecular weight of the vinyl polymer bearing a carbosiloxane dendrimer may be chosen within the range between 3000 and 2 000 000 and preferably between 5000 and 800 000. It can be a liquid, a gum, a paste, a solid, a powder or any other form. The preferred forms are solutions formed by the dilution of a dispersion or of a powder in solvents.

The vinyl polymer can be a dispersion of a polymer of vinyl type having a carbosiloxane dendrimer structure in its molecular side chain, in a liquid such as a silicone oil, an organic oil, an alcohol or water.

The silicone oil may be a dimethylpolysiloxane with the two molecular ends capped with trimethylsiloxy groups, a copolymer of methylphenylsiloxane and of dimethylsiloxane having the two molecular ends capped with trimethylsiloxy groups, a copolymer of methyl-3,3,3-trifluoropropylsiloxane and of dimethylsiloxane having the two molecular ends capped with trimethylsiloxy groups, or similar unreactive linear silicone oils, and also hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane or a similar cyclic compound. In addition to the unreactive silicone oils, modified polysiloxanes containing functional groups such as silanol groups, amino groups and polyether groups on the ends or within the molecular side chains may be used.

The organic oils can be isododecane, liquid paraffin, isoparaffin, hexyl laurate, isopropyl myristate, myristyl myristate, cetyl myristate, 2-octyldodecyl myristate; isopropyl palmitate, 2-ethylhexyl palmitate, butyl stearate, decyl oleate, 2-octyldodecyl oleate, myristyl lactate, cetyl lactate, lanolin acetate, stearyl alcohol, cetearyl alcohol, oleyl alcohol, avocado oil, almond oil, olive oil, cocoa oil, jojoba oil, gum oil, sunflower oil, soybean oil, camelia oil, squalane, castor oil, cottonseed oil, coconut oil, egg yolk oil, polypropylene glycol monooleate, neopentyl glycol 2-ethylhexanoate or an analogous glycol ester oil; triglyceryl isostearate, the triglyceride of a fatty acid of coconut oil, or an analogous oil of a polyhydric alcohol ester; polyoxyethylene lauryl ether, polyoxypropylene cetyl ether or an analogous polyoxyalkylene ether.
The alcohol may be any type that is suitable for use in combination with a cosmetic product starting material. For example, it can be methanol, ethanol, butanol, isopropanol or analogous lower alcohols.

A solution or a dispersion of the alcohol should have a viscosity within the range from 10 to 10^9 mPa at 25°C. To improve the sensory use properties in a cosmetic product, the viscosity should be within the range from 100 to 5×10^8 mPa.s.

The solutions and dispersions can be easily prepared by mixing a vinyl polymer having at least one unit derived from carbosiloxane dendrimer with a silicone oil, an organic oil, an alcohol or water. The liquids may be present in the step of polymerization of a polymer of vinyl type bearing at least one carbosiloxane dendrimer-based unit. In this case, the unreacted residual vinyl monomer should be completely removed by heat treatment of the solution or dispersion under atmospheric pressure or reduced pressure.

In the case of a dispersion, the dispersity of the polymer of vinyl type can be improved by adding a surfactant.

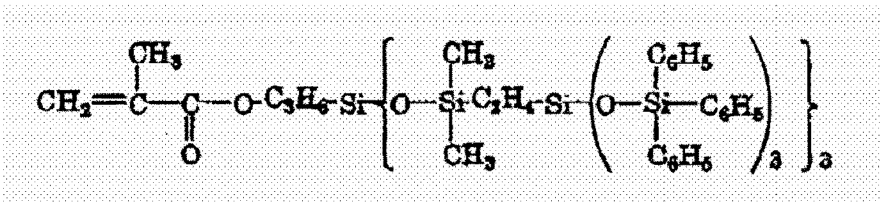
Such an agent may be hexylbenzenesulfonic acid, octylbenzenesulfonic acid, decylbenzenesulfonic acid, dodecylbenzenesulfonic acid, cetylbenzenesulfonic acid, myristylbenzenesulfonic acid or anionic surfactants of the sodium salts of these acids; octyltrimethylammonium hydroxide, dodecyltrimethylammonium hydroxide, hexadecyltrimethylammonium hydroxide, octyldimethylbenzylammonium hydroxide, decyldimethylbenzylammonium hydroxide, dioctadecyldimethylammonium hydroxide, beef tallow-trimethylammonium hydroxide, coconut oil-trimethylammonium hydroxide, or a similar cationic surfactant; a polyoxyalkylene alkyl ether, a polyoxyalkylenealkylphenol, a polyoxyalkylene alkyl ester, the sorbitol ester of polyoxyalkylene, polyethylene glycol, polypropylene glycol, an ethylene oxide additive of diethylene glycol trimethylnonanol, and nonionic surfactants of polyester type, and also mixtures.

In addition, the solvents and dispersions may be combined with iron oxide suitable for use with cosmetic products, or a similar pigment, and also zinc oxide, titanium oxide, silicon oxide, mica, talc or similar mineral oxides in powder form. In the dispersion, a mean particle diameter of the polymer of vinyl type can be within a range of between 0.001 and 100 microns and preferably between 0.01 and 50 microns. The reason for this is that, outside the recommended range, a cosmetic product mixed with the emulsion will not have a nice enough feel on the skin or to the touch, or sufficient spreading properties or a pleasant feel.

A vinyl polymer contained in the dispersion or the solution may have a concentration in the range between 0.1 % and 95% by weight and preferably between 5% and 85% by weight. However, to facilitate the handling and the preparation of the mixture, the range should preferably be between 10% and 75% by weight.

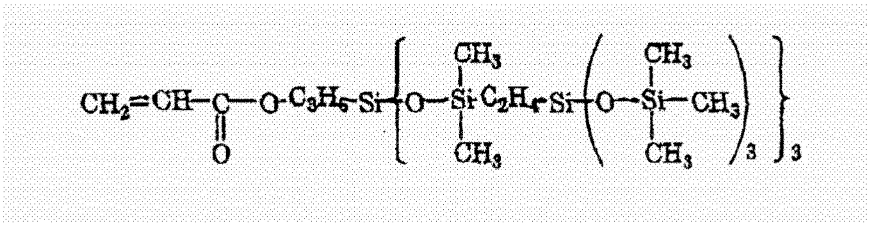
According to a preferred mode, a vinyl polymer that is suitable for use in the invention may be one of the polymers described in the examples of patent application EP 0 963 751 .

According to a preferred embodiment, a vinyl polymer grafted with a carbosiloxane dendrimer may be the product of polymerization of:
of 0.1 to 99 parts by weight of one or more acrylate or methacrylate monomer(s); and
of 100 to 0.1 part by weight of an acrylate or methacrylate monomer of a tris[tri(trimethylsiloxy)silylethyldimethylsiloxy]silylpropyl carbosiloxane dendrimer.
According to one embodiment, a vinyl polymer bearing at least one carbosiloxane dendrimer-based unit may comprise a tris[tri(trimethylsiloxy)silylethyldimethylsiloxy]silylpropyl carbosiloxane dendrimer-based unit corresponding to one of the formulae:



$$CH_2=C(CH_3)-C(=O)-O-C_3H_6-Si\left[O-Si(CH_3)_2-C_2H_4-Si\left(O-Si(C_6H_5)_3\right)_3\right]_3$$

or



$$CH_2=CH-C(=O)-O-C_3H_6-Si\left[O-Si(CH_3)_2-C_2H_4-Si\left(O-Si(CH_3)_3\right)_3\right]_3$$

According to a preferred mode, a vinyl polymer bearing at least one carbosiloxane dendrimer-based unit used in the invention comprises at least one butyl acrylate monomer.

According to one embodiment, a vinyl polymer may also comprise at least one fluoro organic group. A fluorinated vinyl polymer can be one of the polymers described in the examples of application WO 03/045337.

According to a preferred embodiment, a vinyl polymer grafted in the sense of the present invention may be conveyed in an oil or a mixture of oils, which are preferably volatile, chosen in particular from silicone oils and hydrocarbon-based oils, and mixtures thereof.

According to a particular embodiment, a silicone oil that is suitable for use in the invention may be cyclopentasiloxane.

According to another particular embodiment, a hydrocarbon-based oil that is suitable for use in the invention may be isododecane.

Vinyl polymers grafted with at least one carbosiloxane dendrimer-based unit that may be particularly suitable for use in the present invention are the polymers sold under the names TIB 4-1 00®, TIB 4-1 01®, TIB 4-1 20®, TIB 4-1 30®, TIB 4-200®, FA 4002 ID® (TIB 4-202®), TIB 4-220 and FA 4001 CM® (TIB 4-230®) by the company Dow Corning. The polymers sold under the names FA 4002 ID® (TIB 4-202®) and FA 4001 CM® (TIB 4-230®) by the company Dow Corning will preferably be used.

Preferably, the vinyl polymer grafted with at least one carbosiloxane dendrimer-based unit that may be used in a composition of the invention is an acrylate/polytrimethyl siloxymethacrylate copolymer, especially the product sold in isododecane under the name Dow Corning FA 4002 ID® Silicone Acrylate by the company Dow Corning.

V. Silicone acrylate copolymers

According to a particular embodiment, a composition used according to the invention may comprise, as hydrophobic film-forming polymer, at least one copolymer comprising carboxylate groups and polydimethylsiloxane groups.

In the present patent application, the term "copolymer comprising carboxylate groups and polydimethylsiloxane groups" means a copolymer obtained from (a) one or more carboxylic (acid or ester) monomers, and (b) one or more polydimethylsiloxane (PDMS) chains.

In the present patent application, the term "carboxylic monomer" means both carboxylic acid monomers and carboxylic acid ester monomers. Thus, the monomer (a) may be chosen, for example, from acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, esters thereof and mixtures of these monomers. Mention may be made, as esters, of the following monomers: acrylate, methacrylate, maleate, fumarate, itaconate and/or crotonate. According to a preferred embodiment of the invention, the monomers in ester form are more particularly chosen from linear or branched, preferably Ci-$C2_4$ and better still Ci-C22 alkyl acrylates and methacrylates, the alkyl radical preferably being chosen from methyl, ethyl, stearyl, butyl and 2-ethylhexyl radicals, and mixtures thereof.

Thus, according to a particular embodiment of the invention, the copolymer comprises as carboxylate groups at least one group chosen from acrylic acid and methacrylic acid, and methyl, ethyl, stearyl, butyl or 2-ethylhexyl acrylate or methacrylate, and mixtures thereof.

In the present patent application, the term "polydimethylsiloxanes" (also known as organopolysiloxanes and abbreviated as PDMS) is intended to denote, in accordance with what is generally accepted, any organosilicon polymer or oligomer of linear structure, of variable molecular weight, obtained by polymerization and/or polycondensation of suitably functionalized silanes, and formed essentially from a repetition of main units in which the silicon atoms are linked together via oxygen atoms (siloxane bond ≡Si-O-Si≡), comprising trimethyl radicals directly linked via a carbon atom to said silicon atoms. The PDMS chains which can be used to obtain the copolymer used according to the invention comprise at least one radically polymerizable group, preferably located on at least one of the ends of the chain, that is to say that the PDMS can, for example, have a radically polymerizable group on the two ends of the chain or have a radically polymerizable group on one end of the chain and a trimethylsilyl end group on the other end of the chain. The polymerizable radical group may especially be an acrylic or methacrylic group, in particular a group CH_2 = CRi - CO - O - R2, in which R_1 represents a hydrogen or a methyl group and R2 represents $-CH_2-$, $-(CH_2)_n-$ with n = 3, 5, 8 or 10, $-CH_2-CH(CH_3)-CH_2-$, -CH2-CH2-O-CH2-CH2-, -CH2-CH2-O-CH2-CH2-CH(CH3)-CH2-, -CH2-CH2-O-CH2- CH2-O-CH2-CH2-CH2- .

The copolymers used in the composition of the invention are generally obtained according to the usual methods of polymerization and grafting, for example by radical polymerization (A) of a PDMS comprising at least one radically polymerizable group (for example on one of the ends of the chain or on both ends) and (B) of at least one carboxylic monomer, as described, for example, in the documents US-A-5 061 481 and US-A-5 219 560.

The copolymers obtained generally have a molecular weight ranging from about 3000 to 200 000 and preferably from about 5000 to 100 000.

The copolymer used in the composition of the invention can be provided as is or in dispersed form in a solvent, such as lower alcohols comprising from 2 to 8 carbon atoms, for instance isopropyl alcohol, or oils, for instance volatile silicone oils (for example cyclopentasiloxane).

As copolymers that may be used in the composition of the invention, mention may be made, for example, of copolymers of acrylic acid and of stearyl acrylate bearing polydimethylsiloxane grafts, copolymers of stearyl methacrylate bearing polydimethylsiloxane grafts, copolymers of acrylic acid and of stearyl methacrylate bearing polydimethylsiloxane grafts, copolymers of methyl methacrylate, butyl methacrylate, 2-ethylhexyl acrylate and stearyl methacrylate bearing polydimethylsiloxane grafts. As copolymers that may be used in the composition of the invention, mention may be made in particular of the copolymers sold by the company Shin-Etsu under the names KP-561® (CTFA name: acrylates/dimethicone), KP-541® in which the copolymer is dispersed at 60% by weight in isopropyl alcohol (CTFA name: acrylates/dimethicone and isopropyl alcohol), and KP-545® in which the copolymer is dispersed at 30% in cyclopentasiloxane (CTFA name: acrylates/dimethicone and cyclopentasiloxane). According to a preferred embodiment of the invention, KP561® is preferably used; this copolymer is not dispersed in a solvent, but is in waxy form, its melting point being about 30°C.

Mention may also be made of the grafted copolymer of polyacrylic acid and dimethylpolysiloxane dissolved in isododecane, sold by the company Shin-Etsu under the name KP-550®.

Advantageously, a composition according to the invention may comprise, as hydrophobic film-forming polymer, at least one trimethyl siloxysilicate resin.

COSMETIC APPLICATIONS

It is a matter of routine operations for a person skilled in the art to adjust the natures and the amounts of the additives present in the compositions in accordance with the invention so that the cosmetic properties desired for the latter are not affected thereby.

According to one embodiment, a composition of the invention may advantageously be in the form of a composition for caring for the skin and/or keratin fibres, the body or the face, in particular the face.

According to another embodiment, a composition of the invention can advantageously be in the form of a composition for making up keratin materials, in particular the skin of the body or of the face, in particular of the face.

Thus, according to a sub-mode of this embodiment, a composition of the invention may advantageously be in the form of a makeup base composition.

A composition of the invention may advantageously be in the form of a foundation.

According to another sub-mode of this embodiment, a composition of the invention may advantageously be in the form of a composition for making up the skin and in particular the face. It may thus be an eyeshadow or a face powder.

According to yet another sub-mode of this embodiment, a composition of the invention may advantageously be in the form of a product for making up the lips, in particular a lipstick.

According to yet another sub-mode of this embodiment, a composition of the invention may advantageously be in the form of a product for making up and/or caring for the eyebrows.

Such compositions are prepared in particular according to the general knowledge of a person skilled in the art.

Throughout the description, including the claims, the term *"comprising a"* should be understood as being synonymous with *"comprising at least one",* unless otherwise specified.

The terms *"between... and..."* and *"ranging from... to..."* should be understood as being inclusive of the limits, unless otherwise specified.

The invention is illustrated in more detail by the examples and figures presented below. Unless otherwise indicated, the amounts shown are expressed as percentages by weight.

Methodology for the oscillating dynamic rheology measurements

These are harmonic-regime rheology measurements for measuring the elastic modulus.

The measurements are taken using a Haake RS600 rheometer on a product at rest, at 25°C with a plate-plate rotor 0 60 mm and a 2 mm gap.

The harmonic-regime measurements make it possible to characterize the viscoelastic properties of the products. The technique consists in subjecting a material to a stress which varies sinusoidally over time and in measuring the response of the material to this stress. In a range in which the behaviour is linear viscoelastic behaviour (zone in which the strain is proportional to the stress), the stress (τ) and the strain (γ) are two sinusoidal functions of time which are written in the following manner:

$$T(t) = T_o \sin(\omega i)$$
$$Y(t) = Y_o \sin(\omega i + \delta)$$

in which:

T_o represents the maximum amplitude of the stress (Pa);

Y_o represents the maximum amplitude of the strain (-);

$\omega = 2\Pi N$ represents the angular frequency (rad.s^{-1}) with N representing the frequency (Hz); and

δ represents the phase shift of the stress relative to the strain (rad).

Thus, the two functions have the same angular frequency, but they are shifted by an angle δ. Depending on the phase shift δ between $T(t)$ and $\gamma(i)$, the behaviour of the system may be apprehended:

- if $\delta = 0$, the material is purely elastic;
- if $\delta = \Pi/2$, the material is purely viscous (Newtonian fluid); and
- if $0 < \delta < \Pi/2$, the material is viscoelastic.

In general, the stress and the strain are written in complex form:

$$T^*(t) = T_O e^{i\omega t}$$
$$Y^*(t) = {}_Y o\, e^{(iwt + \delta)}$$

A complex stiffness modulus, representing the overall resistance of the material to the strain, whether it is of elastic or viscous origin, is then defined by:

$$G^* = T^*/Y^* = G' + iG''$$

in which:

G' is the storage modulus or elastic modulus, which characterizes the energy stored and totally restituted during a cycle, $G' = (\tau_0/\gamma_o)\cos\delta$; and

G" is the loss modulus or viscous modulus, which characterizes the energy dissipated by internal friction during a cycle, $G'' = (\tau_0/\gamma_o)\sin\delta$.

The parameter retained is the mean stiffness modulus G^* recorded at the plateau measured at a frequency of 1 Hz.

Example 1 of foundation in gel-gel form

Phases	Ingredients	Example 1 (invention)	Example 1A (invention)
A	Trimethyl siloxysilicate	5	5
B	Cyclohexasiloxane	7	7
	Titanium dioxide Isopropyl Titanium Triisostearate (BTD-401® from Kobo)	11.91	11.91
	Iron oxides (and) Isopropyl titanium Triisostearate (BRO-12® from Kobo)	0.43	0.43
	Iron oxides (and) Isopropyl titanium Triisostearate (BYO-12® from Kobo)	1.46	1.46

	Iron oxides (and) Isopropyl Titanium Triisostearate (BBO-12® from Kobo)	0.2	0.2
Bl	Polysilicone-11 (Gransil RPS-D6® from Grant Industries)	11.5	11.5
C	Water	qsp 100	qsp 100
	Butylene glycol	5	5
	Glycerol	5	5
	Isostearic acid (Prisorine 3505-LQ-(GD) ® from Croda)	0.2	0.2
	Phenoxyethanol	0.7	0.7
	Glyceryl caprylate (Dermosoft GMCY®- Dr Straetemans)	0.5	0.5
	Propanediol	3	3
Cl	Hydroxyethyl acrylate/sodium acryloyldimethyltaurate copolymer (Sepinov EMT 10® from SEPPIC)	1.25	1.25
D	Polymethyl methacrylate (Microsphere M-310 from Matsumoto Yushi-Seiyaku)	1.8	1.8
	Lauryl methacrylate/Glycol Dimethacrylate Crosspolymer (Polytrap 6603 Adsorber ® from Amcol Health & Beauty Solutions)	0.5	0.5
	Silica silylate (Dow Corning VM-2270 Aerogel Fine Particles)	0.35	0.35

Procedure:

C was placed in a beaker with moderate stirring using a Rayneri blender. C1 was added, and the gel thickened and became homogeneous after 5 minutes of vigorous stirring with the Rayneri blender. Phase B was ground in 3 treatments (large, medium and then small aperture) using a three-roll mill. The mixture was then placed under slow stirring with the Rayneri blender, followed by addition of B1. When the mixture was homogeneous, A was added very slowly by sprinkling with slow stirring using the Rayneri blender for about 45 minutes until the mixture was homogeneous. Mixture A+B+B1 was added to C+C1 with vigorous stirring using the Rayneri blender for 2 × 2 minutes. The composition then became homogeneous. D was added with vigorous stirring using the Rayneri blender for 2 × 10 minutes until the fillers were fully dispersed in the mixture.

The macroscopic appearance of formulae 1 and 1A was measured with the naked eye after 2 months at room temperature (25°C). There were placed on glass plmates. A smooth and glossy aspect of a formulation corresponds to a homogeneous macroscopic composition.

Contrarily to the formulation 1A without liquid fatty acid of formula (1), formulation 1 comprising a liquid fatty acid compound of formula (1) (ie : isostearic acid) has a smooth, glossy and homogeneous macroscopic appearance after 24 hours.

Exemples 2 to 3

Phase	Ingredients	Exemple 2 (outside the invention)	Exemple 3 (invention)	Exemple 4 (invention)
A	WATER	qsp 100	qsp 100	qsp 100
	GLYCERIN	5,28	5,28	5,28
	PHENOXYETHANOL	0,78	0,78	0,78
B	DIMETHICONE	8	8	8
	DIMETHICONE (and) DIMETHICONE CROSSPOLYMER	14	14	14
	ISOSTEARIC ACID	0	0,2	0
	OLEIC ACID	0	0	0,2
C	HYDROXYETHYL ACRYLATE/SODIUM ACRYLOYLDIMETHYL TAURATE COPOLYMER	2,4	2,4	2,4
D	IRON OXIDES (and) DISODIUM STEAROYL GLUTAMATE (and) ALUMINUM HYDROXIDE (CI 77492)	1,899	1,899	1,899
	IRON OXIDES (and) DISODIUM STEAROYL GLUTAMATE (and) ALUMINUM HYDROXIDE (CI	0,396	0,396	0,396

	77491)			
	IRON OXIDES (and) DISODIUM STEAROYL GLUTAMATE (and) ALUMINUM HYDROXIDE (CI 77499)	0,099	0,099	0,099
	TITANIUM DIOXIDE (and) DISODIUM STEAROYL GLUTAMATE (and) ALUMINUM HYDROXIDE (CI 77891)	15,597	15,597	15,597
	SYNTHETIC FLUORPHLOGOPITE	1,999	1,999	1,999

The ingredients of the aqueous phase A were weighed out and stirred using a Rayneri blender at room temperature. Then, the ingredients of the oily phase B and hydrophilic gelling agent phase C were added to the aqueous phase and mixed under Rayneri stirring. A white and translucid gel gel was formed. When the gel gel was smooth and uniform, the phase D was added under strong stirring until complete homogeneization using a spatula. The walls and base of the beaker were scraped using a spatula and the mixture was left to homogenize with vigorous stirring at room temperature until completely homogeneous.

The macroscopic appearance of formulae 2 to 3 was measured with the naked eye after 24 hours at room temperature (25°C). There were placed on glass plates. A smooth and glossy aspect of a formulation corresponds to a homogeneous macroscopic composition.

Examples	**Macroscopic appearance after 24 hours at 25°C**
Ex. 2 (outside the invention) **Without liquid fatty acid**	Less glossy and less homogeneous
Ex. 3 (invention) **With Isostearic acid**	Smooth and glossy homogeneous texture
Ex. 4 (invention) **With Oleic acid**	Smooth and glossy homogeneous texture

Examples 5 to 12 of foundations in gel-gel form

Phase:	INCI name	Ex. 5*	Ex. 6*	Ex. 7	Ex. 8	Ex. 9	Ex.10	Ex.11	Ex.12
AI	Dimethicone	6.0	6.0						
	Cyclohexasiloxane			6.0	6.0				
	Ethylhexyl methoxycinnamate (Parsol MCX®)					6.0	6.0		
	Caprylyl methicone (Dow Corning FZ-3196®)							6.0	
	Isohexadecane								6.0
A2	Dimethicone crosspolymer (and) dimethicone (Dow Corning EL-9240® Silicone Elastomer Blend)	9.0	9.0				9.0		
	Polysilicone-11 (and) cyclohexasiloxane (Gransil RPS-D6® from Grant Industries)			9.0	9.0	9.0		9.0	
	Vinyl dimethicone/lauryl dimethicone crosspolymer (and) isododecane (KSG-42® from Shin-Etsu)								9.0
B	Water	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100	qs 100
	Glycerol	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	Phenoxyethanol	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
	Caprylyl glycol	0.5		0.5		0.5	0.5	0.5	0.5
	Glyceryl caprylate (Dermosoft GMCY® from Dr Straetmans)		0.5		0.5				
	Hydroxyethyl acrylate/sodium acryloyldimethyltaurate copolymer (Sepinov EMT 10® from SEPPIC)	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
C	Titanium dioxide (and) disodium stearoyl glutamate (and) aluminium hydroxide (NAI-TAO-77891 ® from Myoshi Kasei)	9.9	9.9	9.9	9.9	9.9	9.9	9.9	9.9
	Iron oxides (and) disodium stearoyl glutamate (and) aluminium hydroxide (NAI-C33-8001-10 ® from Myoshi Kasei)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
	Iron oxides (and) disodium stearoyl glutamate (and) aluminium hydroxide (NAI-C33-7001-10 from Myoshi	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

	Kasei)								
	Iron oxides (and) disodium stearoyl glutamate (and) aluminium hydroxide (NAI-C33-9001-10® from Myoshi Kasei)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
D	Fragrance	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

(*) outside the invention

The foundation formulations 5 to 12 were prepared as described below.

The components of phases A1 and A2 were weighed out and stirred using a Rayneri blender at room temperature. The components of phase B were weighed out and stirred using a Rayneri blender at room temperature. The components of phase B, C and D were added to phase A and stirred vigorously with a Rayneri blender at room temperature. The walls and base of the beaker were scraped using a spatula and the mixture was left to homogenize with vigorous stirring at room temperature until completely homogeneous. A gel-gel composition was formed.

The macroscopic appearance of formulae 2 to 8 was measured with the naked eye after 2 months at room temperature (25°C). The results are given in the table below.

Examples	**Macroscopic appearance after 2 months at 25°C**
Ex. 5 (outside the invention)	Granular texture, which changes
Ex. 6 (outside the invention)	Granular texture, which changes
Ex. 7 (invention)	Smooth, homogeneous texture
Ex. 8 (invention)	Smooth, homogeneous texture
Ex. 9 (invention)	Smooth, homogeneous texture
Ex. 10 (invention)	Smooth, homogeneous texture
Ex. 11 (invention)	Smooth, homogeneous texture
Ex. 12 (invention)	Smooth, homogeneous texture

The results showed that formulations 2 and 3 (outside the invention) comprising a glycol compound of formula (1) (caprylyl glycol or glycol caprylate) and an oily phase comprising at least one apolar silicone oil of the linear polydimethylsiloxane type (dimethicone) had a heterogeneous macroscopic appearance after 2 months of storage at 25°C, in contrast with formulations 4 to 9 comprising a glycol compound of formula (1) (caprylyl glycol or glycol caprylate) and an oily phase comprising at least one polar oil (cyclohexasiloxane, caprylyl methicone, ethylhexyl methoxycinnamate).

Comparative Tests showing the influence of the glycol of formula (1)

The fornnulation of exemple 8 as above defined was compared to a counter-type example 8A which was identical but without glyceryl caprylate. The exemple 8A was prepared according to the same conditions as the exemple 8.

The macroscopic appearance of formulae 8 and 8A was measured with the naked eye after 24 hours at room temperature (25°C). The results are given in the table below :

Examples	Macroscopic appearance after 24 hours at 25°C
Ex. 8 (invention) with glyceryl caprylate	Smooth, homogeneous texture No separation of the two phases
Ex. 8A (outside the invention) without glyceryl caprylate	Heterogenous texture, Separation of the two phases

Tests comparing the nature of the hydrophilic gelling agent.

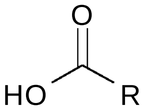
The formulation of exemple 8 as above defined was compared to a counter-type example 8B which was identical but containing as hydrophilic gelling agent : SODIUM CARBOXYMETHYL STARCH (GLYCOLIS® from the company Roquette) instead of the synthetic polymeric hydrophilic agent : Hydroxyethyl acrylate/Sodium Acryloyldimethyltaurate Copolymer (Sepinov EMT 10® from the company SEPPIC) at the same amount 2.4% by weight relative to the total composition. The exemple 8B was prepared according to the same conditions as the exemple 8.

The macroscopic appearance of formulae 4 and 4 was measured with the naked eye after 24 hours at room temperature (25°C). The results are given in the table below :

Examples	Macroscopic appearance after 24 hours at 25°C
Ex. 8 (invention) with Hydroxyethyl acrylate/Sodium Acryloyldimethyltaurate Copolymer	Smooth, homogeneous texture No separation of the two phases
Ex. 8B (outside the invention) with SODIUM CARBOXYMETHYL STARCH	Heterogenous texture, Separation of the two phases

CLAIMS

1. Composition, especially comprising a physiologically acceptable medium, especially for coating keratin materials, more particularly for making up and/or caring for keratin materials, containing:
- at least one aqueous phase gelled with at least one hydrophilic gelling agent selected from synthetic polymeric gelling agents, mixed silicates, fumed silicas, and mixtures thereof ; and
- at least one oily phase gelled with at least one lipophilic gelling agent; said phases forming therein a macroscopically homogeneous mixture and said composition also comprising:
- at least one hydrophobic-coated pigment; and
- at least one liquid fatty acid of formula (1) below:



in which R is chosen from:
a) a saturated, branched CM-C22, preferably C18, alkyl group, or
b) an alkyl group comprising at least one linear or branched CM-C22, preferably C18, double bond; and/or
- at least one glycol compound of formula (2) below:

$$CH_3\text{--}[CH_2CH_2]_m\text{-}[COO]n - CH_2\text{-}CH(OH)\text{-}CH_2OH$$

(2)

in which:
- m is between 2 and 4
- n is equal to 0 or 1; said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2) ; said gelled aqueous phase comprising at least one synthetic polymeric gelling agent and said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2).

2. Composition according to Claim 1, comprising, as hydrophilic gelling agent, at least one synthetic polymeric gelling agent.

3. Composition according to Claim 2, in which the synthetic polymeric hydrophilic gelling agent is chosen from 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers, and in particular is a copolymer of 2-acrylamido-2-methylpropanesulfonic acid and of hydroxyethyl acrylate.

4. Composition according to any one of the preceding claims, in which said lipophilic gelling agent is chosen from particulate gelling agents, organopolysiloxane elastomers, semi-crystalline polymers, dextrin esters and polymers containing hydrogen bonding, and mixtures thereof.

5. Composition according to any one of the preceding claims, comprising as lipophilic gelling agent at least one organopolysiloxane elastomer preferably chosen from Dimethicone Crosspolymer, Dimethicone (and) Dimethicone Crosspolymer, Vinyl Dimethicone Crosspolymer, DimethiconeA/inyl Dimethicone Crosspolymer, Dimethicone Crosspolymer-3, and in particular Dimethicone Crosspolymer and Dimethicone (and) Dimethicone Crosspolymer.

6. Composition according to any one of the preceding claims, containing, as hydrophilic gelling agent/lipophilic gelling agent system, a 2-acrylamido-2-methylpropanesulfonic acid polymer or copolymer/organopolysiloxane elastomer system.

7. Composition according to any one of the preceding claims, containing the aqueous and oily phases in an aqueous phase/oily phase weight ratio of from 95/5 to 5/95 and preferably from 30/70 to 80/20.

8. Composition according to any one of the preceding claims, in which the hydrophobic coated pigments are hydrophobic coated pigments of iron oxide and/or of titanium dioxide.

9. Composition according to any one of the preceding claims, in which the hydrophobic-coated pigments are coated with at least one compound chosen from N-acylamino acids or salts thereof, isopropyl titanium triisostearate; silicone surface agents; natural plant or animal waxes; hydrogenated lecithin, fatty esters; and mixtures thereof.

10. Composition according to any one of the preceding claims, in which the hydrophobic-coated pigments are titanium dioxides and/or iron oxides coated:
- with an N-acylamino acid and/or a salt thereof, more particularly with a glutamic acid derivative and/or a salt thereof, in particular aluminium stearoyl glutamate; or
- with isopropyl titanium triisostearate.

11. Composition according to any one of the preceding claims, in which the liquid fatty acid of formula (1) is chosen from:
- isostearic acid
- oleic acid
- linoleic acid
- linolenic acid; and
- mixtures thereof, and more particularly is isostearic acid.

12. Composition according to any one of the preceding claims, in which the compound of formula (2) is chosen from caprylyl glycol, glyceryl caprylate, glyceryl caprylate/caprate mixtures, and mixtures thereof, and more particularly is chosen from caprylyl glycol, glyceryl caprylate, and mixtures thereof.

13. Composition according to any one of the preceding claims, in which the polar oil is chosen from liquid lipophilic organic UV-screening agents, preferably chosen from:
- liquid lipophilic β,β-diphenylacrylate compounds
- liquid lipophilic salicylate compounds

- liquid lipophilic cinnamate compounds
- mixtures thereof, and more particularly is ethylhexyl methoxycinnamate.

14. Composition according to any one of the preceding claims, in which the polar oil is chosen from:
- volatile cyclic silicone oils having a viscosity at room temperature of less than 8 cSt and containing in particular from 4 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms, such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane (cyclohexasiloxane);
- polydimethylsiloxanes comprising aliphatic groups, in particular alkyl or alkoxy groups, which are pendent and/or at the end of the silicone chain, in particular caprylyl methicone.

15. Composition according to any one of the preceding claims, in which the polar oil is chosen from phenyl silicone oils.

16. Composition according to any one of the preceding claims, in which the polar oil is chosen from ethylhexyl methoxycinnamate, dodecamethylcyclohexasiloxane, caprylyl methicone, and mixtures thereof.

17. Process for preparing a composition as defined in any one of the preceding claims, comprising at least one step of mixing:
- aqueous phase gelled with at least one hydrophilic gelling agent; and
- oily phase gelled with at least one lipophilic gelling agent under conditions suitable for obtaining a macroscopically homogeneous mixture; said composition also comprising at least one hydrophobic-coated pigment and at least one compound of formula (1).

18. Process according to Claim 17, comprising a step of mixing at least three or even more gelled phases.

19. Process according to either of Claims 17 and 18, in which the mixing is performed at room temperature.

20. Cosmetic process for making up and/or caring for a keratin material, in particular the skin and/or the lips and/or the eyebrows, and keratin fibres, especially the eyebrows, comprising at least one step which consists in applying to said keratin material a composition as defined according to any one of Claims 1 to 16.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/079451

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/29 A61K8/36 A61Q1/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61K A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/112072 Al (WANG JAMES J [US] ET AL) 26 May 2005 (2005-05-26) claim 1; examples 5-6 -----	1-20
X	US 2001/044475 Al (MATSUZAKI FUMIAKI [JP] ET AL) 22 November 2001 (2001-11-22) claim 1; examples 23,25-26 -----	1-20
X	US 2013/156831 Al (MATSU0 AYAN0 [JP] ET AL) 20 June 2013 (2013-06-20) claim 1; example 8 -----	1-20
X	W0 2014/167543 Al (0REAL [FR]) 16 October 2014 (2014-10-16) page 71, line 4; claim 1 page 7, lines 30-32 ----- -/-	1-20

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 7 April 2017	Date of mailing of the international search report 20/04/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Vayssié, Stephane

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C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/071453 Al (SOJKA MILAN F [US] ET AL) 21 March 2013 (2013-03-21) examples IX.1-IX.7	1-20
X	W0 2014/161722 Al (0REAL [FR]) 9 October 2014 (2014-10-09) claim 1; examples 1-7	1-20
X	US 2014/356402 Al (LEMOINE CYRIL [CN] ET AL) 4 December 2014 (2014-12-04) paragraphs [0331] - [0335], [0337]; examples 11.2, 11.7	1-20
X,P	W0 2016/030839 Al (0REAL [FR]) 3 March 2016 (2016-03-03) claim 1; example Bl	1-20

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2016/079451

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos. :

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos. :

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: l-20(partially)

Composition, especially comprising a physiologically acceptable medium, especially for coating keratin materials, more particularly for making up and/or caring for keratin materials, containing:
- at least one aqueous phase gelled with at least one hydrophilic gelling agent selected from synthetic polymeric gelling agents, mixed silicates, fumed silicas, and mixtures thereof; and
- at least one oily phase gelled with at least one lipophilic gelling agent; said phases forming therein a macroscopically homogeneous mixture and said composition also comprising:
- at least one hydrophobic-coated pigment; and
- at least one liquid fatty acid of formula (1) in which R is chosen from:
a) a saturated, branched C14-C22, preferably Cis, alkyl group, or
b) an alkyl group comprising at least one linear or branched C14-C22, preferably Cis, double bond.

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2. claims: l-20(partially)

Composition, especially comprising a physiologically acceptable medium, especially for coating keratin materials, more particularly for making up and/or caring for keratin materials, containing:
- at least one aqueous phase gelled with at least one hydrophilic gelling agent selected from synthetic polymeric gelling agents, mixed silicates, fumed silicas, and mixtures thereof; and
- at least one oily phase gelled with at least one lipophilic gelling agent; said phases forming therein a macroscopically homogeneous mixture and said composition also comprising:
- at least one hydrophobic-coated pigment; and
- at least one glycol compound of formula (2) in which:
- m is between 2 and 4
- n is equal to 0 or 1;
said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2); said gelled aqueous phase comprising at least one synthetic polymeric gelling agent and said gelled oily phase comprising at least one polar oil when the composition comprises at least one glycol compound of formula (2).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/079451

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005112072 Al	26-05-2005	NONE	
US 2001044475 Al	22-11-2001	NONE	
US 2013156831 Al	20-06-2013	BR 112012027445 A2	19-07-2016
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		TW 201206491 A	16-02-2012
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		W0 2013107350 Al	25-07-2013
W0 2016030839 Al	03-03-2016	NONE	