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(54) Title: COSMETIC USE OF A FLOCCULANT POLYMER AS ANTIPERSPIRANT

(57) Abstract: The present invention relates to the cosmetic use of a flocculant polymer chosen from: (i) flocculant polymers comprising as side chain non-quaternized pyridine groups directly or indirectly linked to the main chain; (ii) flocculant polymers comprising as side chain non-quaternary amine groups borne by a side substituent directly linked to the main chain; the said polymer comprising at least one non-quaternary cationic monomer and at least one hydrophobic nonionic monomer; (iii) cationic polyurethane flocculant polymers; as antiperspirant active agent, especially in a composition comprising a cosmetically acceptable medium and more particularly not containing any antiperspirant aluminium and/or zirconium salts. A subject of the present invention is also a cosmetic process for treating perspiration, which consists in applying to the surface of the skin a composition comprising, in a cosmetically acceptable medium, at least one flocculant polymer as defined previously, not containing any antiperspirant aluminium and/or zirconium salts.



COSMETIC USE OF A FLOCCULANT POLYMER AS ANTIPERSPIRANT

The present invention relates to the cosmetic use of a flocculant polymer chosen from:

- 5 (i) flocculant polymers comprising as side chain non-quaternized pyridine groups directly linked or indirectly to the main chain, as antiperspirant active agent, particularly in a composition not containing any antiperspirant aluminium and/or zirconium salts;
- 10 (ii) flocculant polymers comprising as side chain non-quaternary amine groups borne by a side substituent directly linked to the main chain; the said polymer comprising at least one non-quaternary cationic monomer and at least one hydrophobic nonionic monomer;
- 15 (iii) cationic polyurethane flocculant polymers;
as antiperspirant active agent, especially in a composition comprising a cosmetically acceptable medium and more particularly not containing any antiperspirant aluminium and/or zirconium salts.

- 20 A subject of the present invention is also a cosmetic process for treating perspiration, which consists in applying to the surface of the skin a composition comprising, in a cosmetically acceptable medium, at least one flocculant polymer as defined previously, not containing any antiperspirant aluminium and/or zirconium salts.

25 In the cosmetic field, it is well known to use, in topical application, antiperspirant products containing substances that have the effect of limiting or even preventing the flow of sweat. These products are generally available in the form of roll-ons, sticks, aerosols or sprays.

- 30 Antiperspirant substances generally consist of aluminium salts or aluminium/zirconium salts. Their antiperspirant efficacy is limited when they are used alone. The use of these active agents at high concentrations in order to obtain good efficacy leads to formulation difficulties. Furthermore, these
35 substances have a skin irritant potential.

There is thus a need to find novel antiperspirant active agents that can replace aluminium salts and aluminium/zirconium salts, and that are efficient and easy to formulate.

- 40 Patent application WO 95/24105 proposes as antiperspirant active agents water-insoluble polymers that form an occlusive film on the skin. The use of standard aluminium salts is unnecessary. The occlusive polymers proposed are of the octylacrylamide/acrylate copolymer or vinyl acetate/butyl maleate/isobornyl
45 acrylate type, alone or in combination with a PVP/linear α -olefin polymer such as PVP/eicosene.

- Antiperspirant active agents also proposed in patent application WO 95/27473 are
50 water-insoluble film-forming polymers whose main chain is hydrocarbon-based and which comprise pendent hydrophobic quaternary ammonium groups.

Patent application WO 01/54658 discloses anhydrous compositions containing a cyanoacrylate monomer that reacts with sweat to form *in situ* by polymerization a film on the skin that blocks the sweat ducts.

5

However, these occlusive film-forming polymers do not make it possible to obtain entirely satisfactory antiperspirant efficacy, and still give rise to formulation problems.

10 Moisture-absorbing polymers have been proposed as substitutes for standard astringent salts in antiperspirant compositions in patent US 4 743 440. These moisture-absorbing polymers may especially be water-soluble and chosen especially from natural gums (xanthan, agar, carrageenans, guar, gelatin),
celluloses (hydroxypropylmethylcellulose, carboxymethylcellulose),
15 polyoxyethylenes, polyvinylpyrrolidones, carboxyvinyl polymers or vinyl ether/maleic anhydride copolymers. In patent application WO 03/030 853, the recommended moisture-absorbing polymers are chosen from grafted starch homopolymers and 2-propenamide-co-propenoic acid sodium salt copolymers.

20 However, these moisture-absorbing polymers do not make it possible to obtain entirely satisfactory antiperspirant efficacy, and still give rise to formulation problems.

Water-soluble quaternary polymers have been proposed in antiperspirant
25 compositions in the presence of standard aluminium salts in order to improve their efficacy. This is the case for dimethyldiallylammonium chloride in patent application EP 222 580, which acts as an agent for retaining the antiperspirant salt. This is the case for the water-soluble polymers comprising a Brønsted acid in patent application WO 02/49590, in particular those derived from maleic acid
30 and/or maleic anhydride, which act as co-gelling agent with the antiperspirant salts. This is the case for polyethyleneimines (PEI) in the article Cosmetics & Toiletries Vol. 108, August 1993, pp. 73-77, which act as agents for complexing the aluminium salts.

35 Dimethyldiallylammonium chloride/acrylic acid copolymers were proposed in patent application EP 478 327 as thickeners in aqueous liquid antiperspirant products containing aluminium salts.

40 In patent US 4 690 817, film-forming polymers of vinyl alcohols containing quaternary amine side groups were proposed in antiperspirant compositions in the presence of standard astringent salts, as skin-conditioning agents that form a moisturizing barrier thereon.

45 In patent application WO 82/01993, polyethyleneimines were used as odour absorbers, in particular for fatty acids, aldehydes or ketones, and more particularly in alcohol-based deodorant products in spray or roll-on form.

The Applicant has discovered, surprisingly, that particular flocculant polymers constitute by themselves excellent antiperspirant agents and can be readily
50 formulated in numerous products intended for treating perspiration and the body

odour associated with perspiration, without it being necessary to use standard astringent salts.

5 The present invention relates to the cosmetic use of a flocculant polymer chosen from:

(i) flocculant polymers comprising as side chain non-quaternized pyridine groups directly linked or indirectly to the main chain, as antiperspirant active agent, particularly in a composition not containing any antiperspirant aluminium and/or zirconium salts;

(ii) flocculant polymers comprising as side chain non-quaternary amine groups borne by a side substituent directly linked to the main chain; the said polymer comprising at least one non-quaternary cationic monomer and at least one hydrophobic nonionic monomer;

(iii) cationic polyurethane flocculant polymers; as antiperspirant active agent, especially in a composition comprising a cosmetically acceptable medium and more particularly not containing any antiperspirant aluminium and/or zirconium salts.

A subject of the present invention is also a cosmetic process for treating perspiration, which consists in applying to the surface of the skin a composition comprising, in a cosmetically acceptable medium, at least one flocculant polymer as defined previously, not containing any antiperspirant aluminium and/or zirconium salts.

The term "antiperspirant agent" means any substance which, by itself, has the effect of reducing or limiting the flow of sweat without it being necessary to use an aluminium and/or zirconium antiperspirant salt.

The term "effective amount of polymer" means an amount of polymer that is sufficient to be able to observe after application to the surface of the skin an antiperspirant effect as defined above.

The term "cosmetically acceptable medium" means a medium that is compatible with the skin and/or its integuments or mucous membranes, having a pleasant colour, odour and feel and not causing any unacceptable discomfort (stinging, tautness or redness) liable to discourage the consumer from using this composition.

The term "flocculant polymer" means any polymer that is capable of destabilizing a colloidal suspension indiscriminantly via a flocculation or coagulation mechanism. The term "destabilizing colloids" means the formation of aggregates that make the suspension unstable. As the terms "flocculation" and "coagulation" are generally interchangeable and equivalent, we will speak in the invention of "flocculation" for one or other of the mechanisms. The definitions of these mechanisms are given in volume 10 of Kirk-Othmer's *Encyclopaedia of Chemical Technology*, 3rd edition.

The term "composition not containing any antiperspirant aluminium and/or zirconium salts" means any composition containing not more than 1% by weight of antiperspirant aluminium and/or zirconium salts.

5 **A/ Flocculant polymers comprising as side chain non-quaternized pyridine groups directly or indirectly linked to the main chain**

The flocculant polymers of the invention may be in the form of homopolymer or copolymer containing at least one monomer of non-quaternized pyridine type.

10

The flocculant polymers of the invention are preferably water-dispersible or water-soluble.

15 The term "water-dispersible polymer" means any polymer which, when introduced into an aqueous phase (into water or into a mixture of water and linear or branched C₂-C₅ monoalcohols, for instance ethanol, isopropanol or n-propanol) at room temperature (25°C and 1 atmosphere), without pH modification, at a solids content allows the production of a dispersion whose mean particle size is between 5 nm and 5 µm.

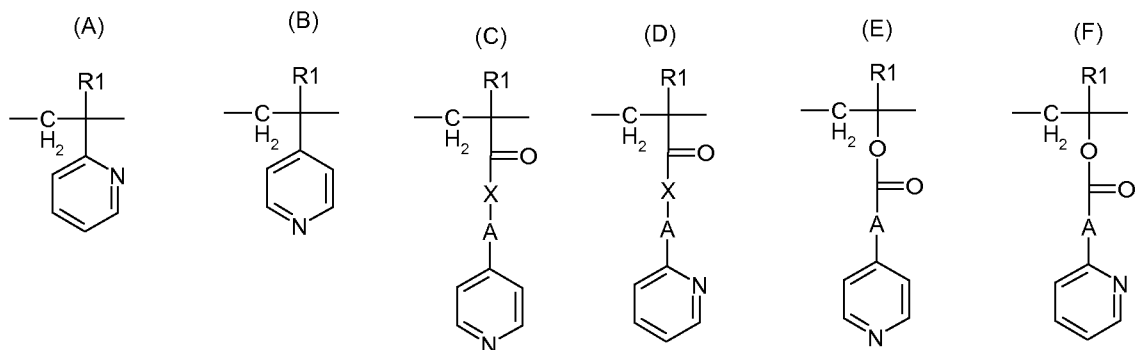
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25 The term "water-soluble polymer" means any polymer which, when introduced into water or into a mixture of water and linear or branched C₂-C₅ monoalcohols, for instance ethanol, isopropanol or n-propanol, without pH modification at 25°C, to a mass concentration equal to 1%, allows the production of a macroscopically homogeneous and transparent solution, i.e. a solution with a minimum light transmission value, at a wavelength equal to 500 nm, through a sample 1 cm thick, of at least 80% and preferably at least 90%.

30 The molar masses of these polymers generally range from 1000 to 20 000 000 g/mol and preferably between 5000 and 1 000 000 g/mol.

The polymers may be crosslinked or non-crosslinked.

35 Among the flocculant polymers comprising non-quaternized pyridine groups that are pendent relative to the main chain, which may be used in the compositions of the invention, mention may be made of homopolymers or copolymers comprising at least one monomer (A) to (F) defined below:



40 where:
X = O, or NH

R1 represents a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, preferably methyl;

A is a linear or branched C₁-C₆ and preferably C₂-C₃ alkyl group; a C₁-C₄ hydroxyalkyl group, preferably monohydroxyalkyl;

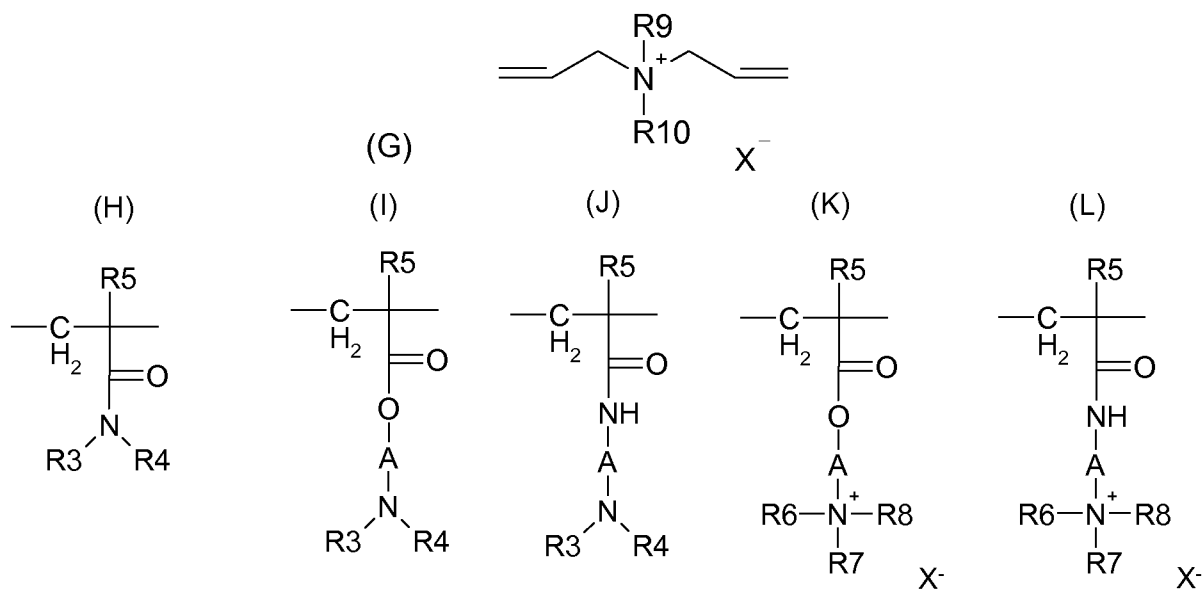
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The monomers corresponding to the preferred units among (A)-(F) are:

2-vinylpyridine; 4-vinylpyridine; N-(4-pyridyl)propylmethacrylamide, N-4(pyridyl)ethyl methacrylate.

10 According to one particular form of the invention, the flocculant polymer also comprises units consisting of at least one cationic monomer other than a pyridine unit, which may be chosen from quaternary ammonium monomers and (meth)acrylamide monomers, or mixtures thereof.

15 Among these additional cationic monomers, mention may be made of those having the following formulae:



20 in which:

R₉ and R₁₀ independently represent a linear or branched C₁-C₈ alkyl group, a benzyl group, a C₁-C₅ hydroxyalkyl group or a linear or branched amido(C₁-C₄)alkyl group;

25 R₃ and R₄ independently represent a hydrogen atom or a linear or branched alkyl group having from 1 to 6 carbon atoms, and preferably methyl or ethyl;

R₃ and R₄ may form with the nitrogen atom a 5- to 8-membered non-aromatic nitrogenous heterocycle, for instance pyrrolidine, piperazine or piperidine;

R₅ represents a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, preferably methyl;

30 A is a linear or branched C₁-C₆ and preferably C₂-C₃ alkyl group; a C₁-C₄ hydroxyalkyl group, preferably monohydroxyalkyl;

R₆, R₇ and R₈, which may be identical or different, represent a hydrogen atom or a linear or branched C₁-C₆ alkyl group or a benzyl radical;

35 X denotes a mineral anion such as a halide (chloride, bromide or iodide) or an organic anion such as a (C₁-C₄) alkyl sulfate (methyl sulfate or ethyl sulfate).

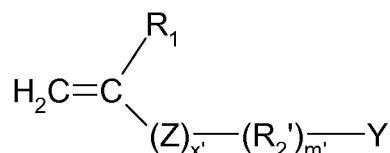
The preferred units of formula (G) are diallyldimethylammonium chloride (DADMAC) and diallyldiethylammonium chloride (DADEAC).

5 The preferred units of formula (H) are methacrylamide or acrylamide and more particularly acrylamide.

The units (I), (J), (K) or (L) may be chosen from methylaminoethyl methacrylate, benzyl dimethylaminoethylacrylate chloride (DMAEA-BCQ), acryloyloxyethyltrimethylammonium chloride (AETAC);
 10 methacryloyloxyethyltrimethylammonium chloride (METAC); methylacrylamidopropyltrimethylammonium chloride (MAPTAC); acrylamidopropyltrimethylammonium chloride (APTAC); acryloyloxyethyltrimethylammonium methosulfate (AETAMS);
 15 methacryloyloxyethyltrimethylammonium methosulfate (METAMS); acryloyloxyethyldiethylmethylammonium chloride; methacryloyloxyethyldiethylmethylammonium chloride or the equivalents thereof neutralized with a methyl sulfate, vinylimidazole, piperidine ethylmethacrylate or piperazine ethylmethacrylate.

20 The most preferential are benzyl dimethylaminoethylacrylate chloride (DMAEA-BCQ), acryloyloxyethyltrimethylammonium chloride (AETAC), methacryloyloxyethyltrimethylammonium methosulfate (METAMS) and methylaminoethyl methacrylate.

25 According to one particular form of the invention, the flocculant polymer also comprises units consisting of at least one anionic monomer preferably chosen from those having the following formula:



30 with

Y is a group chosen from -COOH, -SO₃H, -OSO₃H, -PO₃H₂ and -OPO₃H₂. It is understood that, according to the prior art, the groups SO₄H₂ and PO₄H₂ are linked to R'₂ via the oxygen atom, whereas the groups SO₃H and PO₃H are linked to R'₂, respectively, via the atoms S and P.

35 - R₁ is as defined previously,

- Z is a divalent group chosen from -COO-, -CONH-, -CONCH₃-, -OCO- or -O-, -SO₂-, -CO-O-CO- or -CO-CH₂-CO-, preferably Z is chosen from COO and CONH,

- x' = 0 or 1, preferably 1,

40 - R'₂ is a saturated or unsaturated, optionally aromatic, linear, branched or cyclic carbon-based divalent radical of 1 to 30 carbon atoms, which may comprise 1 to 18 heteroatoms chosen from O, N, S, F, Si and P; the heteroatom(s) may be intercalated in the chain of the said radical R'₂ or alternatively the said radical R'₂ may be substituted with one or more groups comprising them such as hydroxyl or amino.

45

Among the preferred anionic monomers M when they are present, mention may be made of maleic anhydride, acrylic acid, methacrylic acid, crotonic acid, itaconic

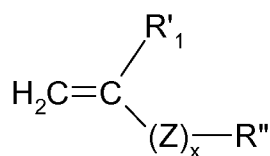
acid, fumaric acid, maleic acid, 2-carboxyethyl acrylate ($\text{CH}_2=\text{CH}-\text{C}(\text{O})-\text{O}-(\text{CH}_2)_2-\text{COOH}$); styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylbenzoic acid, vinylphosphoric acid and sulfopropyl (meth)acrylate, and salts thereof.

5

According to one particular form of the invention, the flocculant polymer also comprises units consisting of at least one nonionic monomer.

10

The additional nonionic monomers may be chosen especially from those having the following formula, alone or as a mixture:



in which:

15

- R'_1 is hydrogen or $-\text{CH}_3$;

- Z is a divalent group chosen from $-\text{COO}-$, $-\text{CONH}-$, $-\text{CONCH}_3-$, $-\text{OCO}-$, $-\text{SO}_2$, $-\text{CO}-\text{O}-\text{CO}-$, $-\text{CO}-\text{CH}_2-\text{CO}-$ and $-\text{O}-$; preferably COO or CONH ;

- x is 0 or 1;

20

- R'' is a saturated or unsaturated, optionally aromatic, linear, branched or cyclic carbon-based radical of 1 to 30 carbon atoms, which may comprise 1 to 18 heteroatoms chosen from O, N, S, F, Si and P; the heteroatom(s) may be intercalated in the chain of the said radical or alternatively the said radical R'' may be substituted with one or more groups comprising them such as hydroxyl, ester, amide, urethane or urea.

25

In particular, R'' may be a methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, phenyl or benzyl radical or a radical of formula $-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$, $-\text{CH}_2-\text{CH}_2-\text{OH}$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$ or furfuryl.

30

The additional nonionic monomers may be chosen especially from the monomers below: methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, tetrahydrofurfuryl methacrylates, butyl methacrylate, 2-ethylhexyl acrylate, stearyl methacrylate, acrolein, tetrahydrofurfuryl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, ethoxyethyl methacrylate, ethoxyethyl acrylate, N-isopropylacrylamide, N-isopropylmethacrylamide, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, vinylpyrrolidone, vinylcaprolactam, N-vinylacetamide, hydroxypropyl acrylate, N-vinylactam, acrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-methyl-N-vinylacetamide, N-vinylformamide, N-methyl-N-vinylformamide, vinyl alcohol (copolymerized in the form of vinyl acetate and then hydrolysed).

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The polymers containing a non-quaternized pyridine unit may advantageously be totally or partially neutralized relative to the pyridine unit with an organic acid or an inorganic acid:

Neutralization of the amine units, belonging to the functionalized pyridine polymer, may be performed with a mineral acid, such as sulfuric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid or boric acid; or alternatively with an organic acid, which may comprise one or more carboxylic, sulfonic or phosphonic acid groups. They may be linear, branched or cyclic aliphatic acids, or alternatively unsaturated or aromatic acids. These acids may also include one or more heteroatoms chosen from O, N, Si, F and P, for example in the form of hydroxyl groups. The neutralizers of organic acid type may be chosen from linear, branched or cyclic aliphatic acids and/or unsaturated or aromatic acids, and may especially comprise 1 to 1000 carbon atoms and especially 2 to 500 carbon atoms. They contain at least one Brønsted acid function, and especially one or more carboxylic, sulfonic and/or phosphonic acid groups. They may also include one or more heteroatoms chosen from O, N, Si, F and P, for example in the form of hydroxyl groups.

Linear, branched or cyclic, saturated or unsaturated, optionally aromatic fatty acids containing 6 to 32 carbon atoms, especially 8 to 28, and comprising at least one COOH or sulfonic acid ($-\text{SO}_3\text{H}$) function, may be used in particular as neutralizer. Linear, branched or cyclic, saturated or unsaturated, optionally aromatic hydroxy acids and especially α -hydroxy acids containing 2 to 32 and especially 6 to 28 carbon atoms, and comprising at least one COOH or sulfonic acid ($-\text{SO}_3\text{H}$) function, may also be used.

Alkylbenzenesulfonic acids in which the alkyl group may comprise from 4 to 30 and especially 6 to 24 carbon atoms may also be used.

Amphoteric neutralizers may also be used, especially of the alkylbetaine or alkylamidopropylbetaine type, in which the alkyl group may comprise 1 to 30, especially 4 to 24 or even 6 to 22 carbon atoms; mention may be made in particular of cocamidopropylbetaine.

Mention may be made especially of α -hydroxyethanoic (or glycolic) acid, α -hydroxyoctanoic acid, α -hydroxycaprylic acid, ascorbic acid, acetic acid, benzoic acid, behenic acid, capric acid, citric acid, caproic acid, caprylic acid, dodecylbenzenesulfonic acid, 2-ethylcaproic acid, folic acid, fumaric acid, galactaric acid, gluconic acid, 2-hexadecyleicosanoic acid, hydroxycaproic acid, 12-hydroxystearic acid, isolauric (or 2-butyloctanoic) acid, isomyristic (or 2-hexyloctanoic) acid, isoarachidic (or 2-octyldodecanoic) acid, isolignoceric (or 2-decyltetradecanoic) acid, lactic acid, lauric acid, malic acid, myristic acid, oleic acid, palmitic acid, propionic acid, sebacic acid, stearic acid, tartaric acid, terephthalic acid, trimesic acid, undecylenic acid, propylbetaine, cocamidopropylbetaine and betaine hydrochloride of formula $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CO}_2\text{H}.\text{Cl}^-]$, and also mixtures thereof.

Preferably, caproic acid, 2-ethylcaproic acid, oleic acid, behenic acid, stearic acid, acetic acid, citric acid, tartaric acid, betaine hydrochloride and/or gluconic acid, and preferentially betaine hydrochloride and/or behenic acid, may be used as neutralizer.

Among the polymers of the invention that are particularly preferred, mention may be made of:

- poly(4-vinylpyridine) homopolymers, such as the products sold under the trade names Reilline 410; Reilline 420; Reilline 4200 sold by Reilly Industries, Inc. or PM 60 K and 160 K sold by Aldrich;
- poly(2-vinylpyridine) homopolymers, such as the products sold under the trade names Raluplate LEV 170; Reilline 2200 by Reilly Industries, Inc.; and Poly(2-vinylpyridine-co-styrene) 130 K (Aldrich);
- poly(4- or 2-vinylpyridine)-co-styrene copolymers such as those sold by Aldrich;
- poly(4- or 2-vinylpyridine)-co-butyl methacrylate copolymers such as those sold by Aldrich;
- poly(4- or 2-vinylpyridine) crosslinked with divinylbenzene, for instance Poly(4-vinylpyridine), 2% crosslinked with divinylbenzene, sold by Aldrich, and Poly(4-vinylpyridine) ReillexTM 402 crosslinked with divinylbenzene, sold by Reilly Industries, Inc.;
- block copolymers comprising at least one block comprising a pyridine monomer, for instance diblock polymers comprising a polyethylene glycol (PEG) or polyisobutylene block and a poly(4- or 2-vinylpyridine) block;
- neutralized polymers, such as Poly(4-vinylpyridinium p-toluenesulfonate) and Poly(4-vinylpyridine hydrochloride) 2% crosslinked with divinylbenzene, sold by Aldrich.

The polymers according to the invention may preferably be conveyed in aqueous medium, i.e. they are preferably water-soluble or water-dispersible. The dissolution or dispersion in water may be performed by direct dissolution of the polymer if it is soluble, or by neutralization of the amine units so as to make the polymer soluble or dispersible in water. The aqueous dissolution or dispersion may also be performed via an intermediate dissolution step in an organic solvent followed by addition of water before evaporation of the organic solvent.

B/ Water-dispersible flocculant polymers comprising as side chain non-quaternary amine groups borne by a side substituent directly linked to the main chain; the said polymer comprising at least one non-quaternary cationic monomer and at least one hydrophobic nonionic monomer;

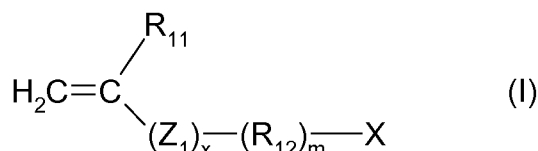
The term "hydrophobic nonionic monomer" means any monomer not comprising any ionic groups (anionic, cationic or amphoteric) and not being soluble in water or in a mixture of water and of linear or branched C₂-C₅ monoalcohols, such as ethanol, isopropanol or n-propanol, without pH modification, at a solids content of 1% by weight, at room temperature (25°C, 1 atm.).

These flocculant polymers of the invention may be in the form of homopolymer or copolymer containing at least one monomer of tertiary, secondary or primary amine type. They may be linear, branched or hyperbranched polymers. These polymers may be in random, block or alternating form. It may be a case of a polymer blend composition.

The molar masses of these polymers generally range from 1000 to 20 000 000 g/mol and preferably between 5000 and 1 000 000 g/mol.

The polymer necessarily comprises at least one non-quaternary cationic monomer and at least one hydrophobic nonionic monomer. It may optionally comprise an anionic monomer. It may also optionally comprise a small amount of difunctional monomer thus allowing the production of crosslinked polymers.

The cationic monomer, or a salt thereof, is preferably chosen from monomers of formula (I):



in which:

R_{11} is a hydrogen atom or a linear or branched hydrocarbon-based radical, of the type $\text{C}_p\text{H}_{2p+1}$, with p being an integer between 1 and 12 inclusive (in particular, R_{11} may represent a methyl, ethyl, propyl or butyl radical (preferably, R_{11} represents hydrogen or a methyl radical));

- Z is a divalent group chosen from $-\text{COO}-$, $-\text{CONH}-$, $-\text{CONCH}_3-$, $-\text{OCO}-$ or $-\text{O}-$, $-\text{SO}_2-$, $-\text{CO-O-CO}-$ or $-\text{CO-CH}_2\text{-CO}-$, (preferably Z is chosen from COO and CONH);

- $x = 0$ or 1 , preferably 1 ;

R_{12} is a saturated or unsaturated, optionally aromatic, linear, branched or cyclic carbon-based divalent radical of 1 to 30 carbon atoms, which may comprise 1 to 18 heteroatoms chosen from O, N, S, F, Si and P; the heteroatom(s) may be intercalated in the chain of the said radical R_2 .

the said radical R_{12} may be substituted with one or more groups comprising them such as hydroxyl or a group NH_2 , NHR' or $\text{NR}'\text{R}''$ with R' and R'' , which may be identical or different, representing a linear or branched $\text{C}_1\text{-C}_{22}$ alkyl, especially methyl or ethyl;

R_{12} may also be an alkylene radical such as methylene, ethylene, propylene, n-butylene, isobutylene, tert-butylene, n-hexylene, n-octylene, n-dodecylene, n-octadecylene, n-tetradecylene or n-docosanylene); a phenylene radical $-\text{C}_6\text{H}_4-$ (ortho, meta or para), optionally substituted with a $\text{C}_1\text{-C}_{12}$ alkyl radical optionally comprising 1 to 25 heteroatoms chosen from N, O, S, F, Si and/or P; or alternatively a benzylene radical $-\text{C}_6\text{H}_4\text{-CH}_2-$, optionally substituted with a $\text{C}_1\text{-C}_{12}$ alkyl radical optionally comprising 1 to 25 heteroatoms chosen from O, N, S, F, Si and P;

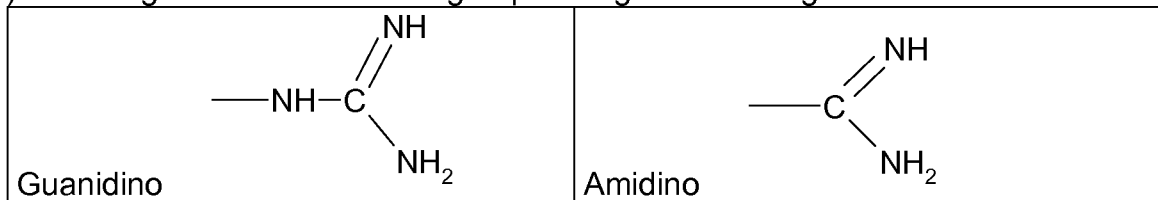
R_{12} may also be a radical of formula $-\text{CH}_2\text{-O-CO-O-}$, $\text{CH}_2\text{-CH}_2\text{-O-CO-O-}$, $-\text{CH}_2\text{-CO-O-}$, $-\text{CH}_2\text{-CH}_2\text{-CO-O-}$, $-\text{[(CH}_2)_5\text{-CO-O]}_n-$, $-\text{CH}_2\text{-CH(CH}_3\text{)-O-}$, $-(\text{CH}_2)_2\text{-O-}$, $-\text{CH}_2\text{-O-CO-NH-}$, $-\text{CH}_2\text{-CH}_2\text{-O-CO-NH-}$; $-\text{CH}_2\text{-NH-CO-NH-}$ or $-\text{CH}_2\text{-CH}_2\text{-NH-CO-NH-}$, $-\text{CH}_2\text{-CHOH-}$, $-\text{CH}_2\text{-CH}_2\text{-CHOH-}$, $-\text{CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-}$, $-\text{CH}_2\text{-CH(NH}_2\text{)-}$, $-\text{CH}_2\text{-CH}_2\text{-CH(NHR')}-$, $-\text{CH}_2\text{-CH(NHR'')-}$, $-\text{CH}_2\text{-CH}_2\text{-CH(NR'''R''')-}$, $-\text{CH}_2\text{-CH(NR'''R''')-}$, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-NR'''-}$, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$; $-\text{CH}_2\text{-CH}_2\text{-CHR'-O-}$ with R''' and R'''' representing a linear or branched $\text{C}_1\text{-C}_{22}$ alkyl optionally comprising 1 to 12 heteroatoms chosen from O, N, S, F, Si and P;

R_{12} may be a mixture of these radicals;

m is 0 or 1;

X is

a) either a guanidino or amidino group having the following formulae:



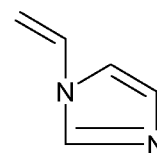
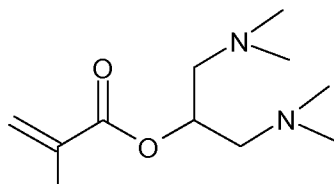
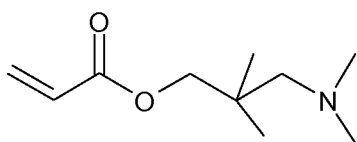
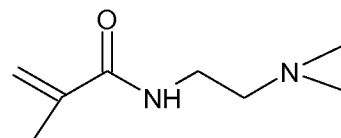
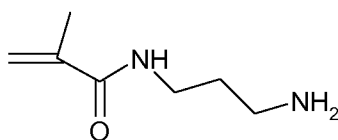
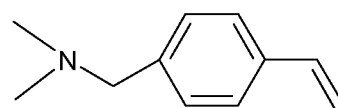
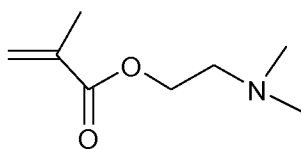
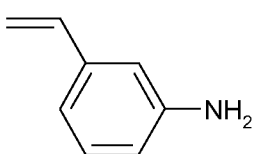
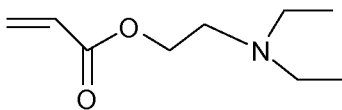
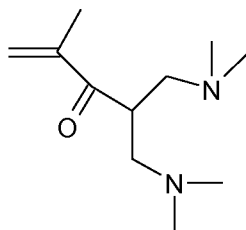
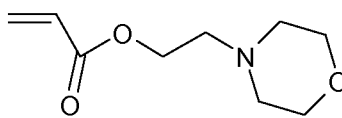
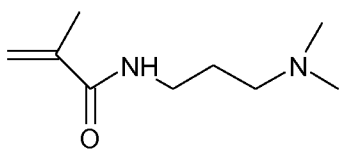
- b) or a group of formula $-N(R_{13})(R_{14})$ or $-P(R_{13})(R_{14})$ with R_{13} and R_{14} representing, independently of each other:
- (i) a hydrogen atom;
 - (ii) a linear, branched or cyclic, saturated or unsaturated, optionally aromatic alkyl group, comprising from 1 to 18 carbon atoms, which may comprise 1 to 10 heteroatoms chosen from O, N, S, F, Si and P;
 - (iii) R_{13} and R_{14} may form, with the nitrogen or phosphorus atom, a first saturated or unsaturated, optionally aromatic ring comprising in total 5, 6, 7 or 8 atoms, and especially 4, 5 or 6 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N; the said first ring possibly being fused with one or more other saturated or unsaturated, optionally aromatic rings, each comprising 5, 6 or 7 atoms, and especially 4, 5, 6 or 7 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N;

For example, R_{13} and R_{14} may be chosen from hydrogen or a methyl, ethyl, propyl, isopropyl, n-butyl, t-butyl, isobutyl, octyl, lauryl or stearyl group. Preferably, R_6 and R_7 are chosen, independently of each other, from H, CH_3 and C_2H_5 .

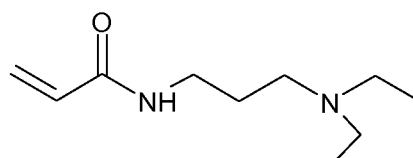
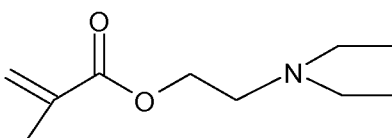
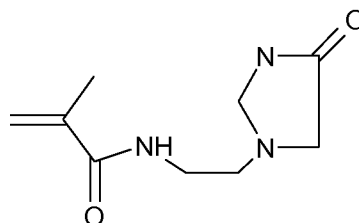
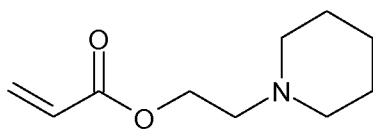
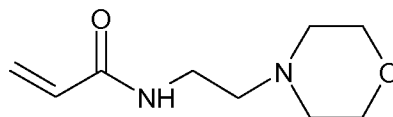
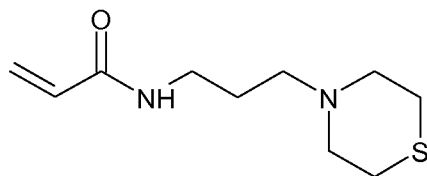
- c) a group $R'_3.N.R'_4$ in which R'_3 and R'_4 form, with the nitrogen atom, a saturated ring comprising in total 5, 6, 7 or 8 atoms, and especially 4, 5 or 6 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N; the said ring possibly being fused with one or more other saturated rings, each comprising 5, 6 or 7 atoms, and especially 4, 5, 6, 7 or 8 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N.

The cationic units (amines) of the monomer of formula (I) may optionally be neutralized at this stage, in the manner described later.

Among the non-quaternary amine cationic monomers of formula (I) that are preferred, mention may be made of:



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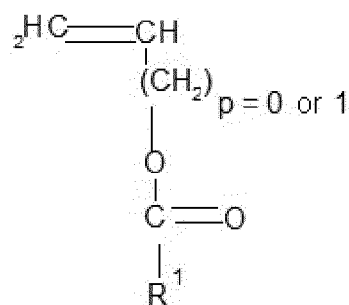


Among the monomers of formula (I) that are particularly preferred, mention may be made of dimethylaminopropyl(meth)acrylamide, dimethylaminoethyl(meth)acrylamide, diethylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, vinylimidazole and morpholinoethyl (meth)acrylate, and mixtures thereof.

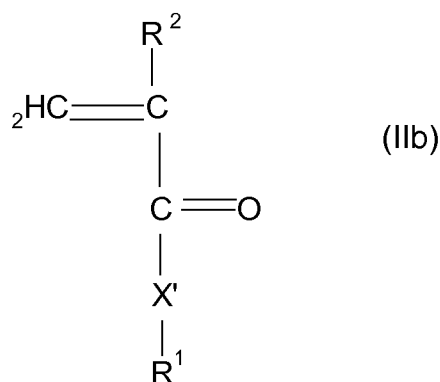
The copolymer may, of course, comprise a mixture of different cationic monomers of formula (I).

The cationic monomers of formula (I) are preferably present in a proportion of from 5% to 80% by weight relative to the weight of the final polymer, especially from 7% to 30% by weight and preferably from 10% to 20% by weight.

The flocculant polymer of the invention also comprises units consisting of at least one hydrophobic nonionic monomer preferably chosen from those of formula (IIa) or (IIb) below:



(IIa)



in which:

X' represents an oxygen atom or a group NH, and
 R¹ represents a linear, branched, cycloaliphatic or aromatic C₂-C₆₀ hydrocarbon-based group, which may contain one or more atoms chosen from O, S and P; the said group may further contain at least a polyoxyalkylenated chain (a polyoxyethylenated and/or polyoxypropylated chain);
 R² represents a hydrogen atom or a methyl group.

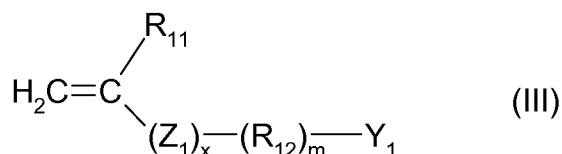
Among these nonionic comonomers, the ones that are preferred in particular are ethyl, isobornyl, n-butyl, n-hexyl, 2-ethylhexyl, n-nonyl, lauryl, n-octadecyl, isooctyl, isodecyl, hydroxyethyl or hydroxypropyl acrylate, methyl, butyl, n-hexyl, 2-ethylhexyl, ethoxyethyl, isodecyl, methoxyethyl methacrylate, C1-30-PEG alkoxy methacrylate (with 5 to 30 ethylene oxide units), vinyl propionate, and vinyl neoalkanoates such as vinyl neononanoate and vinyl neododecanoate, or mixtures thereof.

Particularly preferred comonomers of this group are n-butyl acrylate and 2-ethylhexyl acrylate.

The flocculant polymers of the present invention may also contain a highly hydrophobic nonionic monomer chosen from vinyl monomers bearing a silicone side chain, chlorotrifluoroethylene, tetrafluoroethylene, and vinyl, allylic or (meth)acrylic monomers bearing a perhalogenated, in particular perfluoro, hydrocarbon-based side chain, such as perfluorohexyl (meth)acrylate or perfluorooctyl (meth)acrylate. These monomers will preferably be present in small amounts relative to the weight of the final polymer.

The nonionic monomers of formula (IIa) or (IIb) are preferably present in a proportion of from 10% to 95% by weight relative to the weight of the final polymer, especially from 20% to 90% by weight and preferably from 30% to 85% by weight.

The flocculant polymer of the invention may also comprise units consisting of at least one additional ionic monomer, chosen from the anionic monomers of formula (III)



in which:

- R_{11} , Z_1 , x , R_{12} and m have the same meanings as those given above for formula (I);
- Y_1 is a group chosen from $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{OSO}_3\text{H}$, $-\text{PO}_3\text{H}_2$ and $-\text{OPO}_3\text{H}_2$; it is understood that, according to the prior art, the groups SO_4H_2 and PO_4H_2 are linked to R_{12} via the oxygen atom, whereas the groups SO_3H and PO_3H are linked to R_{12} , respectively, via the S and P atoms.

Among the preferred anionic monomers, mention may be made of maleic anhydride, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, maleic acid, 2-carboxyethyl acrylate ($\text{CH}_2=\text{CH}-\text{C}(\text{O})-\text{O}-(\text{CH}_2)_2-\text{COOH}$); styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylbenzoic acid, vinylphosphoric acid and sulfopropyl (meth)acrylate, and salts thereof.

The introduction of these anionic comonomers makes it possible to adjust the equilibrium of the charges, to modify the hydrophilic nature and thus the solubility of the polymers obtained, or alternatively to modify the compatibility of the polymers with certain other ingredients of the formulation.

It is generally desirable for the overall charge of the polymers of the invention to be positive, i.e. for the total number of positive charges borne by the polymers to be greater than the number of negative charges.

- 5 The anionic monomers of formula (III) are preferably present in a proportion of from 10% to 40% by weight relative to the weight of the final polymer, especially from 15% to 30% by weight and preferably from 20% to 25% by weight.

10 Among the cationic or amphoteric radical copolymers described above, the Applicant has obtained particularly advantageous results with the following polymers:

- copolymers of butyl acrylate and of dimethylaminoethyl methacrylate,
- copolymers of butyl acrylate and of dimethylaminopropylmethacrylamide, and
- copolymers of 2-ethylhexyl acrylate and of dimethylaminopropylmethacrylamide.

15 The cationic flocculant polymers of the present invention may be prepared by statistical radical solution, bulk, dispersion or emulsion polymerization, which are familiar to those skilled in the art, in the presence of a radical initiator. Preferably, the polymers are obtained by solution polymerization.

20 The positive charges of the polymers may be introduced by copolymerization of monomers bearing a protonated tertiary amine function, but the protonation of the amine function may also take place after polymerization. Preferably, the protonation of the amine functions takes place after polymerization.

25 Although, the molecular mass of the cationic polymers of the present invention is not a determining factor for the present invention, polymers with a number-average molar mass of between 1000 and 20 000 000, better still between 5000 and 5 000 000 and preferably between 5000 and 1 000 000 g/mol are preferably used.

30 The cationic flocculant polymers of the present invention that are dispersible in water are in latex form, i.e. in the form of dispersions of fine particles, with a mean size of between 5 nm and 5 μ m, preferably between 5 nm and 600 nm and better still between 5 nm and 400 nm, in an aqueous phase. This water-dispersed form of the polymers of the present invention offers the advantage of having low viscosities and are easier to manipulate and to incorporate into cosmetic compositions than solutions.

40 The protonating agents for the amine functions of the polymers of the present invention are chosen from cosmetically acceptable organic or mineral acids. Among the cosmetically acceptable mineral acids, an example that may be mentioned is hydrochloric acid.

45 The organic acids used as protonating agents may comprise one or more carboxylic, sulfonic or phosphonic acid groups. They may be linear, branched or cyclic aliphatic acids, or alternatively unsaturated or aromatic acids. These acids may also include one or more heteroatoms chosen from O, N, Si, F and P, for example in the form of hydroxyl groups. The neutralizers of organic acid type
50 may be chosen from linear, branched or cyclic aliphatic acids and/or unsaturated

or aromatic acids, and may especially comprise 1 to 1000 carbon atoms and especially 2 to 500 carbon atoms. They contain at least one Brønsted acid function, and especially one or more carboxylic, sulfonic and/or phosphonic acid groups. They may also include one or more heteroatoms chosen from O, N, Si, F and P, for example in the form of hydroxyl groups.

Linear, branched or cyclic, saturated or unsaturated, optionally aromatic fatty acids containing 6 to 32 carbon atoms, especially 8 to 28, and comprising at least one COOH or sulfonic acid ($-\text{SO}_3\text{H}$) function, may be used in particular as neutralizer. Linear, branched or cyclic, saturated or unsaturated, optionally aromatic hydroxy acids and especially α -hydroxy acids containing 2 to 32 and especially 6 to 28 carbon atoms, and comprising at least one COOH or sulfonic acid ($-\text{SO}_3\text{H}$) function, may also be used.

Alkylbenzenesulfonic acids in which the alkyl group may comprise from 4 to 30 and especially 6 to 24 carbon atoms may also be used.

Amphoteric neutralizers may also be used, especially of the alkylbetaine or alkylamidopropylbetaine type, in which the alkyl group may comprise 1 to 30, especially 4 to 24 or even 6 to 22 carbon atoms; mention may be made in particular of cocamidopropylbetaine.

Among the cosmetically acceptable organic acids that may especially be mentioned are α -hydroxyethanoic (or glycolic) acid, α -hydroxyoctanoic acid, α -hydroxycaprylic acid, ascorbic acid, acetic acid, benzoic acid, behenic acid, capric acid, citric acid, caproic acid, caprylic acid, dodecylbenzenesulfonic acid, 2-ethylcaproic acid, folic acid, fumaric acid, galactaric acid, gluconic acid, 2-hexadecyleicosanoic acid, hydroxycaproic acid, 12-hydroxystearic acid, isolauric (or 2-butyloctanoic) acid, isomyristic (or 2-hexyloctanoic) acid, isoarachidic (or 2-octyldodecanoic) acid, isolignoceric (or 2-decyltetradecanoic) acid, lactic acid, lauric acid, malic acid, myristic acid, oleic acid, palmitic acid, propionic acid, sebacic acid, stearic acid, tartaric acid, terephthalic acid, trimesic acid, undecylenic acid, propylbetaine, cocamidopropylbetaine and betaine hydrochloride of formula $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CO}_2\text{H}\cdot\text{Cl}^-]$, and also mixtures thereof.

Preferably, caproic acid, 2-ethylcaproic acid, oleic acid, behenic acid, stearic acid, acetic acid, citric acid, tartaric acid, betaine hydrochloride and/or gluconic acid, and preferentially betaine hydrochloride and/or behenic acid, may be used as neutralizer.

C/ Flocculant cationic polyurethane polymers

The flocculant cationic polyurethane polymers of the invention are preferably water-dispersible or water-soluble.

The molar masses of these polymers generally range from 1000 to 20 000 000 g/mol, preferably between 2000 and 1 000 000 g/mol and even more preferentially between 3000 and 50 000 g/mol.

The polymers may be crosslinked or non-crosslinked.

Among the flocculant cationic polyurethane polymers comprising one or more quaternary cationic or tertiary amine functions that are pendent relative to the main

chain or as an end function, which may be used in the compositions of the invention, mention may be made of the polymers of types (I) and (II) defined below:

- 5 Two types of polyurethane in accordance with the invention may be distinguished:
- polyurethanes of type (1) comprising a tertiary or quaternary amine function as pendent functions on the main chain, and
 - polyurethanes of type (2) necessarily comprising a tertiary or quaternary amine function at the end of the main chain and optionally tertiary or quaternary amine
- 10 functions as pendent functions on the main chain.

The cationic polyurethanes of type (1) according to the invention comprise at least:

15 (a1) cationic units derived from at least one tertiary or quaternary amine bearing at least two reactive functions containing labile hydrogen, and

(a2) nonionic units derived from oligomers or from nonionic polymers bearing at their ends reactive functions containing labile hydrogen, and

(a3) nonionic units derived from nonionic monomer compounds containing at least two functions containing labile hydrogen, and

20 (b) units derived from at least one diisocyanate.

The cationic polyurethanes of type (2) according to the invention comprise at least:

(a2) nonionic units derived from oligomers or from nonionic polymers bearing at their ends reactive functions containing labile hydrogen, and

(a3) nonionic units derived from nonionic monomer compounds containing at least

25 two functions containing labile hydrogen, and

(a4) units consisting of at least one tertiary amine and containing only one function containing labile hydrogen, the tertiary amine function possibly being quaternized, and

(b) units derived from at least one diisocyanate, and

30 (a1) optionally cationic units derived from at least one tertiary or quaternary amine bearing at least two reactive functions containing labile hydrogen.

The term "reactive functions containing labile hydrogen" means functions that are capable, after loss of a hydrogen atom, of forming covalent bonds with the

35 isocyanate functions of the compounds forming the units (b). Examples of such functions that may be mentioned include hydroxyl, primary amine (-NH₂) or secondary amine (-NHR) groups, or alternatively thiol groups (-SH). The polycondensation of compounds bearing these reactive functions containing labile hydrogen with diisocyanates makes it possible, depending on the nature of the

40 reactive functions bearing the labile hydrogen (-OH, -NH₂, -NHR or -SH), to obtain, respectively, polyurethanes, polyureas or polythio-urethanes. For the sake of simplicity, all these polymers are grouped in the present patent application under the term "polyurethanes".

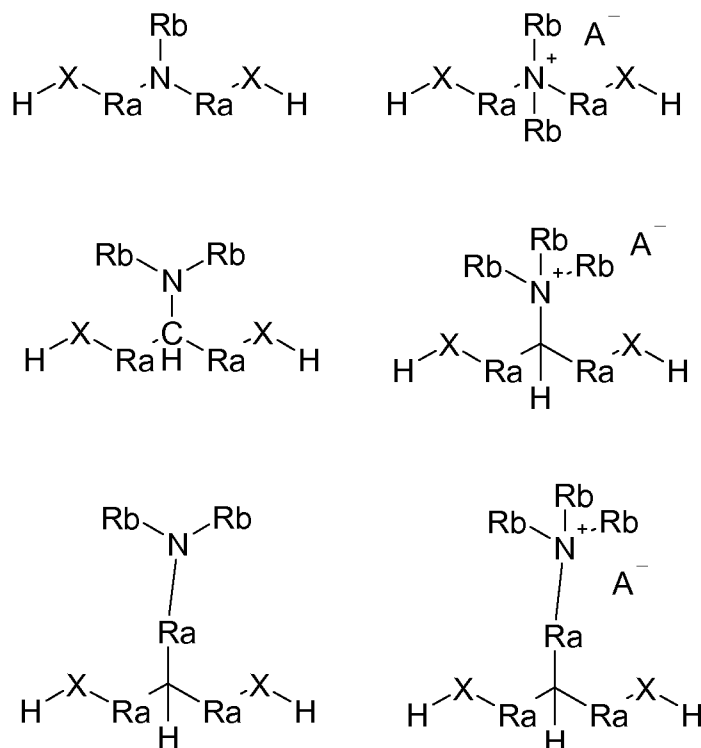
45 When the tertiary or quaternary amines forming the units (a1) bear more than two functions containing labile hydrogen, the polyurethanes obtained have a branched structure.

In one preferred embodiment of the polyurethanes of the present invention, the

50 tertiary or quaternary amines forming the cationic units (a1) bear only two reactive

functions containing labile hydrogen and the polyurethanes obtained by polycondensation consequently have an essentially linear structure. It is also obviously possible to use a mixture of difunctional amines containing a small proportion of amines bearing more than two reactive functions containing labile hydrogen.

The tertiary or quaternary amines forming the cationic units (a1) are preferably chosen from compounds corresponding to one of the following formulae:



10

in which each Ra independently represents a linear or branched C₁-C₆ alkylene, C₃-C₆ cycloalkylene or arylene group (preferably phenylene or benzylene), all possibly being substituted with one or more halogen atoms and comprising one or more heteroatoms chosen from O, N, P and S, each Rb independently represents a C₁-C₆ alkyl, C₃-C₆ cycloalkyl or aryl group (preferably phenyl or benzyl), all possibly being substituted with one or more halogen atoms and comprising one or more heteroatoms chosen from O, N, P and S, each X independently represents an oxygen or sulfur atom or a group NH or NRc, in which Rc represents a C₁-C₆ alkyl group, and A⁻ represents a physiologically acceptable counterion.

As tertiary amines that are particularly preferred for obtaining the cationic polyurethanes of elastic nature of the present invention, mention may be made of N-methyldiethanolamine and N-tert-butyldiethanolamine.

25

The tertiary and quaternary amines forming the cationic units (a1) of the polyurethanes of the present invention may also be polymers containing tertiary and/or quaternary amine functions, bearing at their ends reactive functions containing labile hydrogen. The weight-average molar mass of these polymers

bearing tertiary and/or quaternary amine functions is preferably between 400 and 10 000.

5 Examples of such suitable polymers bearing amine functions that may be mentioned include polyesters derived from the polycondensation of N-methyldiethanolamine and of adipic acid. When the amines forming the cationic units (a1) are compounds bearing tertiary amine function(s), some or all of these amine functions must be neutralized with a suitable neutralizer chosen from physiologically acceptable organic or mineral acids. Examples of preferred acids
10 that may be mentioned include hydrochloric acid and acetic acid.

The term "unit (a2)" means a water-soluble or water-insoluble oligomeric or polymeric group terminated at each of its ends with a group containing labile hydrogens. Examples of hydrophilic polymers that may be mentioned include
15 polyethers, sulfonated polyesters and sulfonated polyamides, or a mixture of these polymers. The hydrophilic compound is preferably a polyether and especially a poly(ethylene oxide) or poly(propylene oxide). Examples of hydrophobic polymers that may be mentioned include polyethylenes and polyisobutylenes, and copolymers thereof.

20 The term "unit (a3)" included in the preparation of the polyurethanes of formulae (I) and (II) means a compound of formula: $HX-R_2-XH$ in which each X independently represents an oxygen or sulfur atom or a group NH or NRc, in which Rc represents a C_1-C_6 alkyl group and more particularly each X is an oxygen atom; R_2
25 represents a linear or branched alkylene radical containing from 1 to 20 carbon atoms, optionally comprising a saturated or unsaturated ring, an arylene radical, one or more of the carbon atoms possibly being replaced with a heteroatom chosen from N, S, O and P. When they are not polymers, examples that may be mentioned include ethylene glycol, diethylene glycol and propylene glycol.

30 Monomers (a4) that may be mentioned include compounds comprising on the same molecule a tertiary amine unit and a primary or secondary amine unit. Examples that may be mentioned include the following diamines: N,N-dimethyl-1,4-butanediamine, N,N-dimethyl-1,3-propanediamine, N,N-diethyl-1,3-propanediamine,
35 N,N-dibutyl-1,3-propanediamine, N,N-dimethyl-1,2-propanediamine, N,N-dimethyl-1,2-ethanediamine, N,N-diethyl-1,2-ethanediamine.

Compound (b) included in the preparation of the polyurethanes of types (1) and (2) is a diisocyanate corresponding to the formula: $O=C=N-R_1-N=C=O$ in which R_1
40 represents a linear or branched alkylene radical containing from 1 to 20 carbon atoms, optionally comprising a saturated or unsaturated ring, an arylene radical, one or more of the carbon atoms possibly being replaced with a heteroatom chosen from N, S, O and P. Examples that may be mentioned include methylenediphenyl diisocyanate, methylenecyclohexane diisocyanate, isophorone
45 diisocyanate, toluene diisocyanate, naphthalene diisocyanate, butane diisocyanate and hexane diisocyanate.

The synthesis of the polyurethanes of type I is described in patent FR 0 116 598.

The polyurethanes of the invention containing tertiary amine cationic units may advantageously be totally or partially neutralized relative to the tertiary amine units with an organic acid or an inorganic acid.

- 5 Neutralization of the amine units, belonging to the polyurethane polymer, may thus be performed with a mineral acid, such as sulfuric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid or boric acid; or alternatively with an organic acid, which may comprise one or more carboxylic, sulfonic or phosphonic acid groups. They may be linear, branched or cyclic aliphatic acids, or
10 alternatively unsaturated or aromatic acids. These acids may also include one or more heteroatoms chosen from O, N, Si, F and P, for example in the form of hydroxyl groups. The neutralizers of organic acid type may be chosen from linear, branched or cyclic aliphatic acids and/or unsaturated or aromatic acids, and may especially comprise 1 to 1000 carbon atoms and especially 2 to 500 carbon
15 atoms. They contain at least one Brønsted acid function, and especially one or more carboxylic, sulfonic and/or phosphonic acid groups. They may also include one or more heteroatoms chosen from O, N, Si, F and P, for example in the form of hydroxyl groups.
- 20 Linear, branched or cyclic, saturated or unsaturated, optionally aromatic fatty acids containing 6 to 32 carbon atoms, especially 8 to 28, and comprising at least one COOH or sulfonic acid ($-\text{SO}_3\text{H}$) function, may be used in particular as neutralizer. Linear, branched or cyclic, saturated or unsaturated, optionally aromatic hydroxy
25 acids and especially α -hydroxy acids containing 2 to 32 and especially 6 to 28 carbon atoms, and comprising at least one COOH or sulfonic acid ($-\text{SO}_3\text{H}$) function, may also be used.

Alkylbenzenesulfonic acids in which the alkyl group may comprise from 4 to 30 and especially 6 to 24 carbon atoms may also be used.

- 30 Amphoteric neutralizers may also be used, especially of the alkylbetaine or alkylamidopropylbetaine type, in which the alkyl group may comprise 1 to 30, especially 4 to 24 or even 6 to 22 carbon atoms; mention may be made in particular of cocamidopropylbetaine.

- 35 Mention may be made especially of α -hydroxyethanoic (or glycolic) acid, α -hydroxyoctanoic acid, α -hydroxycaprylic acid, ascorbic acid, acetic acid, benzoic acid, behenic acid, capric acid, citric acid, caproic acid, caprylic acid, dodecylbenzenesulfonic acid, 2-ethylcaproic acid, folic acid, fumaric acid,
40 galactaric acid, gluconic acid, glycolic acid, 2-hexadecyleicosanoic acid, hydroxycaproic acid, 12-hydroxystearic acid, isolauric (or 2-butyloctanoic) acid, isomyristic (or 2-hexyloctanoic) acid, isoarachidic (or 2-octyldodecanoic) acid, isolignoceric (or 2-decyltetradecanoic) acid, lactic acid, lauric acid, malic acid, myristic acid, oleic acid, palmitic acid, propionic acid, sebacic acid, stearic acid,
45 tartaric acid, terephthalic acid, trimesic acid, undecylenic acid, propylbetaine, cocamidopropylbetaine and betaine hydrochloride of formula $[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CO}_2\text{H}\cdot\text{Cl}^-]$, and also mixtures thereof.

- Preferably, caproic acid, 2-ethylcaproic acid, oleic acid, behenic acid, stearic acid,
50 acetic acid, citric acid, tartaric acid, betaine hydrochloride and/or gluconic acid,

and preferentially betaine hydrochloride and/or behenic acid, may be used as neutralizer.

The polyurethanes of the invention containing tertiary amine cationic units may advantageously be quaternized. Preferably, the quaternizing agent, when it exists, is a hydrophobic group. Thus, the hydrophobic group is introduced via the quaternizing agent. This quaternizing agent is a compound of the type RQ or R'Q, in which R and R' are such that:

Q denotes a leaving group such as a halide, a sulfate, etc.

R and R' both independently represent a hydrophobic group.

The term "hydrophobic group" means a radical or polymer containing a saturated or unsaturated, linear or branched hydrocarbon-based chain, which may contain one or more heteroatoms such as P, O, N or S, or a radical containing a perfluoro or silicone chain. When the hydrophobic group denotes a hydrocarbon-based radical, it comprises at least 1 carbon atom, preferably from 4 to 25 carbon atoms and in particular from 6 to 21 carbon atoms. Preferentially, the hydrocarbon-based group is derived from a monofunctional compound.

The second types of units forming the polyurethanes of the present invention are macromolecular units, known as units (a2), derived from nonionic polymers bearing at their ends reactive functions containing labile hydrogen and preferably having a glass transition temperature (Tg), measured by differential enthalpy analysis, of less than 10°C. These polymers preferably have a weight-average molar mass of between 400 and 30 000 and more particularly between 1000 and 10 000 g/mol. The nonionic polymers capable of forming the nonionic units (a2) are chosen, for example, from polyethers, polyesters, polysiloxanes, copolymers of ethylene and of butylene, polycarbonates and fluoro polymers. Polyethers are most particularly preferred, and, among these, poly(tetramethylene oxide) and hydrogenated or non-hydrogenated polymers of ethylene and butylene.

The diisocyanates forming the units (b) are preferably chosen from aliphatic, alicyclic and aromatic diisocyanates. Diisocyanates that are more preferred are chosen from methylenediphenyl diisocyanates, methylenecyclohexane diisocyanate, isophorone diisocyanate, toluene diisocyanate, naphthalene 10-diisocyanate, butane diisocyanate and hexyl diisocyanate. Needless to say, these diisocyanates may be used alone or in the form of a mixture of two or more diisocyanates.

As indicated above, the cationic polyurethanes of the present invention may contain, in addition to the units (a1), (a2) and (b), preferably present in the polyurethanes of the present invention, a certain fraction of units (a3) derived from nonionic monomer compounds containing at least two functions containing labile hydrogen. These units (a3) are derived, for example, from neopentyl glycol, hexaethylene glycol or aminoethanol.

The units (a1) must be present in a sufficient amount to give the polymers their positive charge responsible for their flocculation property.

In general, the units (a1) represent from 1% to 90% and preferably from 5% to 60% by weight, the units (a2) from 10% to 80% and preferably from 40% to 70% by weight, the units (a3) from 0 to 50% by weight and preferably from 0 to 30% by weight, and the units (a4) from 0 to 10% and preferably from 0 to 5% by weight of the total polymer.

The units (b) are present in an essentially stoichiometric amount relative to the sum of the units (a1), (a2), (a3) and optionally (a4). Specifically, the production of polyurethanes with high molar masses assumes a number of isocyanate functions that is virtually identical to the number of functions containing a labile hydrogen. A person skilled in the art will select an optional molar excess of one or other type of function to adjust the molar mass to the desired value.

The polyurethanes in accordance with the invention may be prepared according to the standard polyaddition techniques used for the manufacture of polyurethanes.

The polymers according to the invention are preferably conveyed in aqueous medium, i.e. they are water-soluble or water-dispersible. Preferably, the polymers are water-dispersible. The dissolution or dispersion in water may be performed by direct dissolution of the polymer if it is soluble, or by neutralization of the amine units so as to make the polymer soluble or dispersible in water. The aqueous dissolution or dispersion may also be performed via an intermediate dissolution step in an organic solvent followed by addition of water before evaporation of the organic solvent.

The flocculant polymers used as antiperspirant active agents are preferably present in the compositions according to the invention in amounts ranging from 0.1% to 50% by weight and more preferentially from 1% to 20% by weight relative to the total weight of the composition.

GALENICAL FORMS

The composition according to the invention may be in any galenical form conventionally used for topical application and especially in the form of aqueous gels, or aqueous or aqueous-alcoholic solutions. By adding a fatty or oily phase, it may also be in the form of dispersions of lotion type, emulsions of liquid or semi-liquid consistency of milk type, obtained by dispersing a fatty phase in an aqueous phase (O/W) or conversely (W/O), or suspensions or emulsions of soft, semi-solid or solid consistency of the cream or gel type, or alternatively multiple emulsions (W/O/W or O/W/O), microemulsions, vesicular dispersions of ionic and/or nonionic type, or wax/aqueous phase dispersions. These compositions are prepared according to the usual methods.

The compositions may especially be conditioned in pressurized form in an aerosol device or in a pump-action bottle; conditioned in a device equipped with a perforated wall, especially a grille; conditioned in a device equipped with a ball applicator ("roll-on"); conditioned in the form of wands (sticks) or in the form of

loose or compacted powder. In this regard, they contain the ingredients generally used in products of this type, which are well known to those skilled in the art.

5 According to one particular form of the invention, the compositions according to the invention may be anhydrous.

The term "anhydrous composition" means a composition containing less than 2% by weight of water, or even less than 0.5% water, and especially free of water, the water not being added during the preparation of the composition but
10 corresponding to the residual water provided by the mixed ingredients.

According to another particular form of the invention, the compositions according to the invention may be solid, in particular in wand or stick form.

15 The term "solid composition" means that the maximum force measured by texturometry during the penetration of a probe into the sample of formula must be at least equal to 0.25 newtons, in particular at least equal to 0.30 newtons and especially at least equal to 0.35 newtons, assessed under precise measuring conditions as follows.

20 The formulae are poured hot into jars 4 cm in diameter and 3 cm deep. Cooling is performed at room temperature. The hardness of the formulae is measured after an interval of 24 hours. The jars containing the samples are characterized in texturometry using a texturometer such as the machine sold by the company Rheo
25 TA-XT2, according to the following protocol: a stainless-steel ball probe 5 mm in diameter is brought into contact with the sample at a speed of 1 mm/s. The measuring system detects the interface with the sample, with a detection threshold equal to 0.005 newtons. The probe penetrates 0.3 mm into the sample, at a speed of 0.1 mm/s. The measuring machine records the change in force measured in
30 compression over time, during the penetration phase. The hardness of the sample corresponds to the average of the maximum force values detected during penetration, over at least three measurements.

AQUEOUS PHASE

35 The compositions according to the invention intended for cosmetic use may comprise at least one aqueous phase. They are especially formulated as aqueous lotions or as water-in-oil or oil-in-water emulsions or as multiple emulsions (oil-in-water-in-oil or water-in-oil-in-water triple emulsion (such emulsions are known and
40 described, for example, by C. Fox in "Cosmetics and Toiletries" - November 1986 - Vol. 101 - pages 101-112)).

The aqueous phase of the said compositions contains water and generally other water-soluble or water-miscible solvents. The water-soluble or water-miscible
45 solvents comprise monoalcohols with a short chain, for example of C₁-C₄, such as ethanol or isopropanol; diols or polyols, for instance ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, 2-ethoxyethanol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether and sorbitol. Propylene glycol and glycerol, propane-1,3-diol,
50 will be used more particularly.

EMULSIFIERSa) Oil-in-water emulsifiers

5

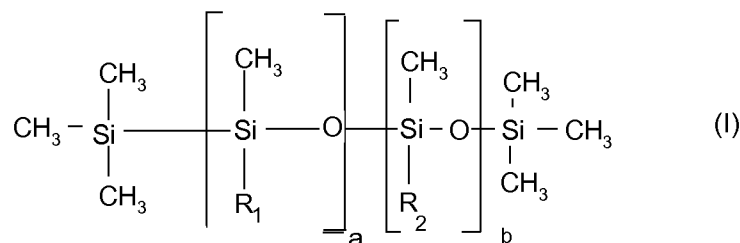
As emulsifiers that may be used in the oil-in-water emulsions or oil-in-water-in-oil triple emulsions, examples that may be mentioned include nonionic emulsifiers such as oxyalkylenated (more particularly polyoxyethylenated) fatty acid esters of glycerol; oxyalkylenated fatty acid esters of sorbitan; oxyalkylenated (oxyethylenated and/or oxypropylenated) fatty acid esters; oxyalkylenated (oxyethylenated and/or oxypropylenated) fatty alcohol ethers; sugar esters such as sucrose stearate; and mixtures thereof, such as the mixture of glyceryl stearate and PEG-40 stearate.

15 Mention may also be made of fatty alcohol/alkylpolyglycoside emulsifying mixtures as described in patent applications WO 92/06778, WO 95/13863 and WO 98/47610, for instance the commercial products sold by the company SEPPIC under the name Montanov®.

20 b) Water-in-oil emulsifiers

Among the emulsifiers that may be used in the water-in-oil emulsions or water-in-oil-in-water-in-oil triple emulsions, examples that may be mentioned include alkyl dimethicone copolyols corresponding to formula (I) below

25



in which:

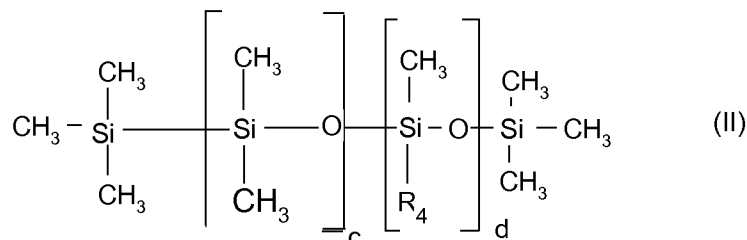
- 30 R_1 denotes a linear or branched C_{12} - C_{20} and preferably C_{12} - C_{18} alkyl group;
 R_2 denotes the group: $-\text{C}_n\text{H}_{2n}-(-\text{OC}_2\text{H}_4-)_x-(-\text{OC}_3\text{H}_6-)_y-\text{O}-\text{R}_3$,
 R_3 denotes a hydrogen atom or a linear or branched alkyl radical comprising from 1 to 12 carbon atoms;
 a is an integer ranging from 1 to 500;
 b is an integer ranging from 1 to 500;
35 n is an integer ranging from 2 to 12 and preferably from 2 to 5;
 x is an integer ranging from 1 to about 50 and preferably from 1 to 30;
 y is an integer ranging from 0 to about 49 and preferably from 0 to 29, with the proviso that when y is other than zero, the ratio x/y is greater than 1 and preferably ranges from 2 to 11.

40

Among the alkyl dimethicone copolyol emulsifiers of formula (I) that are preferred, mention will be made more particularly of Cetyl PEG/PPG-10/1 Dimethicone and more particularly the mixture Cetyl PEG/PPG-10/1 Dimethicone and Dimethicone (INCI name), for instance the product sold under the trade name Abil EM90 by the

company Goldschmidt, or alternatively the mixture (Polyglyceryl-4 Stearate and Cetyl PEG/PPG-10 (and) Dimethicone (and) Hexyl Laurate), for instance the product sold under the trade name Abil WE09 by the same company.

- 5 Among the water-in-oil emulsifiers, mention may also be made of the dimethicone copolyols corresponding to formula (II) below



- 10 in which:

R_4 denotes the group: $--\text{C}_m\text{H}_{2m}--(-\text{OC}_2\text{H}_4-)_s--(-\text{OC}_3\text{H}_6-)_t--\text{O}--\text{R}_5$,

R_5 denotes a hydrogen atom or a linear or branched alkyl radical comprising from 1 to 12 carbon atoms,

c is an integer ranging from 1 to about 500;

- 15 d is an integer ranging from 1 to about 500;

m is an integer ranging from 2 to 12 and preferably from 2 to 5;

s is an integer ranging from 1 to about 50 and preferably from 1 to 30;

t is an integer ranging from 0 to about 50 and preferably from 0 to 30; with the proviso that the sum $s+t$ is greater than or equal to 1.

- 20

Among these preferential dimethicone copolyol emulsifiers of formula (II), use will particularly be made of PEG-18/PPG-18 Dimethicone and more particularly the mixture Cyclopentasiloxane (and) PEG-18/PPG-18 Dimethicone (INCI name), such as the product sold by the company Dow Corning under the trade name
25 Silicone DC5225 C or KF-6040 from the company Shin-Etsu.

According to one particularly preferred form, use will be made of a mixture of at least one emulsifier of formula (I) and of at least one emulsifier of formula (II).

- 30 Use will be made more particularly of a mixture of PEG-18/PPG-18 Dimethicone and Cetyl PEG/PPG-10/1 Dimethicone and even more particularly a mixture of (Cyclopentasiloxane (and) PEG-18/PPG-18 Dimethicone) and of Cetyl PEG/PPG-10/1 Dimethicone and Dimethicone or of (Polyglyceryl-4-stearate and Cetyl PEG/PPG-10 (and) Dimethicone (and) Hexyl Laurate).

- 35

Among the water-in-oil emulsifiers, mention may also be made of nonionic emulsifiers derived from fatty acids and polyol, alkylpolyglycosides (APG) and sugar esters, and mixtures thereof.

- 40 As nonionic emulsifiers derived from fatty acids and polyol, use may be made especially of fatty acid esters of polyol, the fatty acid especially containing a C8-C24 alkyl chain, and the polyols being, for example, glycerol and sorbitan.

Fatty acid esters of polyol that may especially be mentioned include isostearic acid esters of polyols, stearic acid esters of polyols, and mixtures thereof, in particular isostearic acid esters of glycerol and/or sorbitan.

- 5 Stearic acid esters of polyols that may especially be mentioned include the polyethylene glycol esters, for instance PEG-30 Dipolyhydroxystearate, such as the product sold under the name Arlacel P135 by the company ICI.

- 10 Glycerol and/or sorbitan esters that may be mentioned, for example, include polyglyceryl isostearate, such as the product sold under the name Isolan GI 34 by the company Goldschmidt; sorbitan isostearate, such as the product sold under the name Arlacel 987 by the company ICI; sorbitan glyceryl isostearate, such as the product sold under the name Arlacel 986 by the company ICI, the mixture of sorbitan isostearate and polyglyceryl isostearate (3 mmol) sold under the name
15 Arlacel 1690 by the company Uniqema, and mixtures thereof.

The emulsifier may also be chosen from alkylpolyglycosides with an HLB of less than 7, for example those represented by the general formula (1) below:



- in which R represents a branched and/or unsaturated alkyl radical comprising from 14 to 24 carbon atoms, G represents a reduced sugar comprising 5 or 6 carbon atoms, and x is a value ranging from 1 to 10 and preferably from 1 to 4, and G
25 especially denotes glucose, fructose or galactose.

The unsaturated alkyl radical may comprise one or more ethylenic unsaturations, and in particular one or two ethylenic unsaturations.

- 30 As alkylpolyglycosides of this type, mention may be made of alkylpolyglucosides (G = glucose in formula (I)), and especially the compounds of formula (I) in which R more particularly represents an oleyl radical (unsaturated C₁₈ radical) or isostearyl (saturated C₁₈ radical), G denotes glucose, x is a value ranging from 1 to 2, especially isostearyl glucoside or oleyl glucoside, and mixtures thereof. This
35 alkylpolyglucoside may be used as a mixture with a coemulsifier, more especially with a fatty alcohol and especially a fatty alcohol containing the same fatty chain as that of the alkylpolyglucoside, i.e. comprising from 14 to 24 carbon atoms and containing a branched and/or unsaturated chain, for example isostearyl alcohol when the alkylpolyglucoside is isostearyl glucoside, and oleyl alcohol when the
40 alkylpolyglucoside is oleyl glucoside, optionally in the form of a self-emulsifying composition, as described, for example, in document WO-A-92/06778. Use may be made, for example, of the mixture of isostearyl glucoside and isostearyl alcohol, sold under the name Montanov WO 18 by the company SEPPIC, and also the mixture octyldodecanol and octyldodecyl xyloside sold under the name Fludanov
45 20X by the company SEPPIC.

Mention may also be made of succinic-terminated polyolefins, for instance esterified succinic-terminated polyisobutylenes and salts thereof, especially the diethanolamine salts, such as the commercial products sold under the names

Lubrizol 2724, Lubrizol 2722 and Lubrizol 5603 by the company Lubrizol or the commercial product Chemcinnate 2000.

5 The total amount of emulsifiers in the composition will preferably be, in the composition according to the invention, in active material contents ranging from 1% to 8% by weight and more particularly from 2% to 6% by weight relative to the total weight of the composition.

FATTY PHASE

10

The compositions according to the invention may contain at least one water-immiscible organic liquid phase, known as a fatty phase. This phase generally comprises one or more hydrophobic compounds that make the said phase water-immiscible. The said phase is liquid (in the absence of structuring agent) at room temperature (20-25°C). Preferentially, the water-immiscible organic-liquid organic phase in accordance with the invention generally comprises at least one volatile oil and/or non-volatile oil and optionally at least one structuring agent.

20 The term "oil" means a fatty substance that is liquid at room temperature (25°C) and atmospheric pressure (760 mmHg, i.e. 105 Pa). The oil may be volatile or non-volatile.

25 For the purposes of the invention, the term "volatile oil" means an oil that is capable of evaporating on contact with the skin or the keratin fibre in less than one hour, at room temperature and atmospheric pressure. The volatile oils of the invention are volatile cosmetic oils, which are liquid at room temperature, having a non-zero vapour pressure, at room temperature and atmospheric pressure, ranging in particular 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).

35 The term "non-volatile oil" means an oil that remains on the skin or the keratin fibre at room temperature and atmospheric pressure for at least several hours, and that especially has a vapour pressure of less than 10^{-3} mmHg (0.13 Pa).

The oil may be chosen from any physiologically acceptable oil and in particular cosmetically acceptable oil, especially mineral, animal, plant or synthetic oils; in particular volatile or nonvolatile hydrocarbon-based oils and/or silicone oils and/or fluoro oils, and mixtures thereof.

40

More precisely, the term "hydrocarbon-based oil" means an oil mainly comprising carbon and hydrogen atoms and optionally one or more functions chosen from hydroxyl, ester, ether and carboxylic functions. Generally, the oil has a viscosity of from 0.5 to 100 000 mPa.s, preferably from 50 to 50 000 mPa.s and more preferably from 100 to 300 000 mPa.s.

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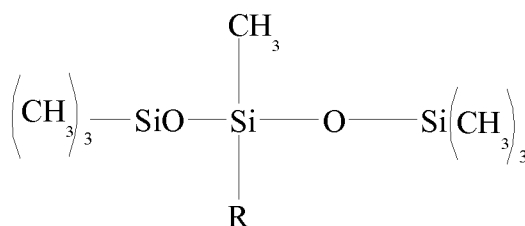
As examples of volatile oils that may be used in the invention, mention may be made of:

50 - volatile hydrocarbon-based oils chosen from hydrocarbon-based oils containing from 8 to 16 carbon atoms, and especially C_8 - C_{16} isoalkanes of petroleum origin

(also known as isoparaffins), for instance isododecane (also known as 2,2,4,4,6-pentamethylheptane), isodecane and isohexadecane, for example the oils sold under the trade names Isopar or Permethyl, branched C₈-C₁₆ esters and isohexyl neopentanoate, and mixtures thereof. Other volatile hydrocarbon-based oils, for instance petroleum distillates, especially those sold under the name Shell Solt by the company Shell, may also be used; volatile linear alkanes, such as those described in patent application DE10 2008 012 457 from the company Cognis.

- volatile silicones, for instance volatile linear or cyclic silicone oils, especially those with a viscosity ≤ 8 centistokes (8×10^{-6} m²/s) and especially containing from 2 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms. As volatile silicone oils that may be used in the invention, mention may be made especially of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane and dodecamethylpentasiloxane; - and mixtures thereof.

Mention may also be made of linear volatile alkyltrisiloxane oils of general formula (I):



in which R represents an alkyl group containing from 2 to 4 carbon atoms, of which one or more hydrogen atoms may be substituted with a fluorine or chlorine atom.

Among the oils of general formula (I) that may be mentioned are:

3-butyl-1,1,1,3,5,5,5-heptamethyltrisiloxane,
3-propyl-1,1,1,3,5,5,5-heptamethyltrisiloxane, and
3-ethyl-1,1,1,3,5,5,5-heptamethyltrisiloxane,
corresponding to the oils of formula (I) for which R is, respectively, a butyl group, a propyl group or an ethyl group.

As examples of nonvolatile oils that may be used in the invention, mention may be made of:

- hydrocarbon-based oils of animal origin, such as perhydrosqualene;
- hydrocarbon-based plant oils such as liquid triglycerides of fatty acids of 4 to 24 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or wheatgerm oil, olive oil, sweet almond oil, palm oil, rapeseed oil, cottonseed 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, passion flower oil, musk rose oil, sunflower oil, corn oil, soybean oil, grapeseed oil, sesame seed oil, hazelnut oil, apricot oil, macadamia oil, castor oil, avocado oil, caprylic/capric acid triglycerides, for instance those sold by the company Stéarineries Dubois or those sold under the names Miglyol 810, 812 and 818 by the company Sasol, jojoba oil and shea butter oil,

- linear or branched hydrocarbons, of mineral or synthetic origin, such as liquid paraffins and derivatives thereof, petroleum jelly, polydecenes, polybutenes, hydrogenated polyisobutene such as Parleam, and squalane,
- synthetic ethers containing from 10 to 40 carbon atoms;
- 5 - synthetic esters, especially of fatty acids, for instance the oils of formula R_1COOR_2 in which R_1 represents a linear or branched higher fatty acid residue containing from 1 to 40 carbon atoms and R_2 represents a hydrocarbon-based chain, which is especially branched, containing from 1 to 40 carbon atoms, with $R_1 + R_2 \geq 10$, for instance purcellin oil (cetostearyl octanoate), isononyl isononanoate,
- 10 isopropyl myristate, isopropyl palmitate, C_{12} - C_{15} alkyl benzoates, hexyl laurate, diisopropyl adipate, isononyl isononanoate, 2-ethylhexyl palmitate, 2-octyldodecyl stearate, 2-octyldodecyl erucate, isostearyl isostearate or tridecyl trimellitate; alcohol or polyalcohol octanoates, decanoates or ricinoleates, for instance propylene glycol dioctanoate; hydroxylated esters, for instance isostearyl lactate,
- 15 octyl hydroxystearate, octyldodecyl hydroxystearate, diisostearyl malate, triisocetyl citrate, and fatty alcohol heptanoates, octanoates or decanoates; polyol esters, for instance propylene glycol dioctanoate, neopentyl glycol diheptanoate or diethylene glycol diisononanoate; and pentaerythritol esters, for instance pentaerythrityl tetraistearate,
- 20 - fatty alcohols that are liquid at room temperature, containing a branched and/or unsaturated carbon-based chain containing from 12 to 26 carbon atoms, for instance octyldodecanol, isostearyl alcohol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol or oleyl alcohol,
- higher fatty acids such as oleic acid, linoleic acid or linolenic acid;
- 25 - carbonates;
- acetates;
- citrates;
- fluoro oils that are optionally partially hydrocarbon-based and/or silicone-based, for instance fluorosilicone oils, fluoro polyethers and fluorosilicones as described in
- 30 document EP-A-847 752;
- silicone oils, for instance linear or cyclic non-volatile polydimethylsiloxanes (PDMS); polydimethylsiloxanes comprising alkyl, alkoxy or phenyl groups, which are pendant or at the end of a silicone chain, these groups containing from 2 to 24 carbon atoms; phenyl silicones, for instance phenyl trimethicones, phenyl
- 35 dimethicones, phenyl trimethylsiloxy diphenyl siloxanes, diphenyl dimethicones, diphenyl methyldiphenyl trisiloxanes and 2-phenylethyl trimethylsiloxy silicates, and
- mixtures thereof.

40 **STRUCTURING AGENT**

The compositions according to the invention comprising a fatty phase may also contain at least one agent for structuring the said fatty phase, which may preferably be chosen from waxes, pasty compounds, and mineral or organic

45 lipophilic gelling agents, and mixtures thereof.

It is understood that the amount of these compounds may be adjusted by a person skilled in the art so as not to harm the desired effect in the context of the present invention.

Wax(es)

The wax is in general 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.

In particular, the waxes that are suitable for the invention may have a melting point of greater than or equal to 45°C and in particular greater than or equal to 55°C.

For the purposes of the invention, the melting point corresponds to the temperature of the most endothermic peak observed on thermal analysis (DSC) as described in 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 increase ranging from -20°C to 100°C at a heating rate of 5°C/minute. During the second temperature increase, the variation of 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.

As illustrations of waxes that are suitable for the invention, mention may be made especially of hydrocarbon-based waxes, for instance beeswax, lanolin wax, Chinese insect waxes, rice bran wax, carnauba wax, candelilla wax, ouricury wax, esparto grass wax, berry wax, shellac wax, Japan wax and sumach wax; montan wax, orange wax and lemon wax, refined sunflower wax sold under the name Sunflower Wax by Koster Keunen, microcrystalline waxes, paraffins and ozokerite; polyethylene waxes, the waxes obtained by Fischer-Tropsch synthesis and waxy copolymers, and also esters thereof.

Mention may also be made of waxes obtained by catalytic hydrogenation of animal or plant oils containing linear or branched C₈-C₃₂ fatty chains. Among these waxes that may especially be mentioned are isomerized jojoba oil such as the trans-isomerized partially hydrogenated jojoba oil manufactured or sold by the company Desert Whale under the commercial reference Iso-Jojoba-50®, hydrogenated sunflower oil, hydrogenated castor oil, hydrogenated coconut oil, hydrogenated lanolin oil and bis(1,1,1-trimethylolpropane) tetrastearate sold under the name Hest 2T-4S® by the company Heterene.

Mention may also be made of silicone waxes (C₃₀₋₄₅ alkyl dimethicone) and fluoro waxes.

5 The waxes obtained by hydrogenation of castor oil esterified with cetyl alcohol, sold under the names Phytowax ricin 16L64® and 22L73® by the company Sophim, may also be used. Such waxes are described in patent application FR-A-2 792 190.

10 A wax that may be used is a C₂₀-C₄₀ alkyl (hydroxystearoxy)stearate (the alkyl group containing from 20 to 40 carbon atoms), alone or as a mixture.

Such a wax is especially sold under the names Kester Wax K 82 P®, Hydroxypolyester K 82 P® and Kester Wax K 80 P® by the company Koster
15 Keunen.

As microwaxes that may be used in the compositions according to the invention, mention may be made especially of carnauba microwaxes, such as the product sold under the name MicroCare 350® by the company Micro Powders, synthetic
20 microwaxes, such as the product sold under the name MicroEase 114S® by the company Micro Powders, microwaxes consisting of a mixture of carnauba wax and polyethylene wax, such as the products sold under the names Micro Care 300® and 310® by the company Micro Powders, microwaxes consisting of a mixture of carnauba wax and of synthetic wax, such as the product sold under the name
25 Micro Care 325® by the company Micro Powders, polyethylene microwaxes, such as the products sold under the names Micropoly 200®, 220®, 220L® and 250S® by the company Micro Powders, the commercial products Performalene 400, Polyethylene and Performalene 500-L Polyethylene from New Phase Technologies, Performalene 655, Polyethylene or paraffin waxes, for instance the
30 wax having the INCI name Microcrystalline Wax and Synthetic Wax and sold under the trade name Microlease by the company Sochibo; polytetrafluoroethylene microwaxes such as those sold under the names Microslip 519® and 519 L® by the company Micro Powders.

35 The composition according to the invention may preferably comprise a content of wax(es) ranging from 3% to 20% by weight relative to the total weight of the composition, in particular from 5% to 15% and more particularly from 6% to 15% thereof.

40 According to one particular form of the invention, in the context of anhydrous solid compositions in stick form, use will be made of polyethylene microwaxes in the form of crystallites with an aspect ratio at least equal to 2, and with a melting point ranging from 70 to 110°C and preferably from 70 to 100°C, so as to reduce or even eliminate the presence of strata in the solid composition.

45 These crystallites in needle form and especially the dimensions thereof may be characterized visually according to the following method.

The wax is deposited on a microscope slide, which is placed on a hotplate. The
50 slide and the wax are heated to a temperature generally at least 5°C higher than

the melting point of the wax or of the mixture of waxes under consideration. At the end of melting, the liquid thus obtained and the microscope slide are allowed to cool to solidify. Observation of the crystallites is performed using a Leica DMLB100 optical microscope, with an objective lens selected as a function of the size of the objects to be viewed, and under polarized light. The dimensions of the crystallites are measured using image analysis software such as that sold by the company Microvision.

The crystallite polyethylene waxes in accordance with the invention preferably have an average length ranging from 5 to 10 μm . The term "average length" denotes the dimension given by statistical granulometric distribution of half the population, which is written as D50.

Use will be made more particularly of a mixture of the waxes Performalene 400 Polyethylene and Performalene 500-L Polyethylene from New Phase Technologies.

Pasty compounds

For the purposes of the present invention, the term "pasty compound" is intended to denote a lipophilic fatty compound that undergoes a reversible solid/liquid change of state, which has in solid form an anisotropic crystal organization, and that comprises, at a temperature of 23°C, a liquid fraction and a solid fraction.

The pasty compound is preferably chosen from synthetic compounds and compounds of plant origin. A pasty compound may be obtained by the synthesis from starting materials of plant origin.

The pasty compound may be advantageously chosen from:

- lanolin and derivatives thereof,
- polymeric or non-polymeric silicone compounds,
- polymeric or non-polymeric fluoro compounds,
- vinyl polymers, especially:
 - olefin homopolymers,
 - olefin copolymers,
 - hydrogenated diene homopolymers and copolymers,
 - linear or branched oligomers, homopolymers or copolymers of alkyl (meth)acrylates preferably containing a C₈-C₃₀ alkyl group,
 - oligomers, homopolymers and copolymers of vinyl esters containing C₈-C₃₀ alkyl groups,
 - oligomers, homopolymers and copolymers of vinyl ethers containing C₈-C₃₀ alkyl groups,
 - liposoluble polyethers resulting from the polyetherification between one or more C₂-C₁₀₀ and preferably C₂-C₅₀ diols,
- esters,
- mixtures thereof.

Among the esters, the following are especially preferred:

- esters of a glycerol oligomer, especially diglycerol esters, in particular condensates of adipic acid and of glycerol, for which some of the hydroxyl groups

- of the glycerols have reacted with a mixture of fatty acids such as stearic acid, capric acid, stearic acid and isostearic acid, and 12-hydroxystearic acid, especially such as those sold under the brand name Softisan 649 by the company Sasol,
- the arachidyl propionate sold under the brand name Waxenol 801 by Alzo,
 - 5 - phytosterol esters,
 - fatty acid triglycerides and derivatives thereof,
 - pentaerythritol esters,
 - non-crosslinked polyesters resulting from polycondensation between a linear or branched C₄-C₅₀ dicarboxylic acid or polycarboxylic acid and a C₂-C₅₀ diol or
 - 10 polyol,
 - aliphatic esters of an ester, resulting from the esterification of an aliphatic hydroxycarboxylic acid ester with an aliphatic carboxylic acid,
 - polyesters resulting from the esterification, with a polycarboxylic acid, of an aliphatic hydroxycarboxylic acid ester, the said ester comprising at least two
 - 15 hydroxyl groups, such as the products Risocast DA-H® and Risocast DA-L®,
 - esters of a diol dimer and of a diacid dimer, where appropriate esterified on their free alcohol or acid function(s) with acid or alcohol radicals, such as Plandool-G,
 - mixtures thereof.
- 20 Among the pasty compounds of plant origin that will preferably be chosen is a mixture of oxyethylenated (5 OE) oxypropylenated (5 OP) soybean sterols and pentaerythritol, sold under the reference Lanolide by the company Vevy.

Lipophilic gelling agents

25

Mineral gelling agents

Mineral lipophilic gelling agents that may be mentioned include optionally modified clays, for instance hectorites modified with a C₁₀-C₂₂ ammonium chloride, for

30 instance hectorite modified with distearyldimethylammonium chloride, for instance the product sold under the name Bentone 38V® by the company Elementis.

Mention may also be made of fumed silica optionally subjected to a hydrophobic surface treatment, the particle size of which is less than 1 µm. Specifically, it is

35 possible to chemically modify the surface of the 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 trimethylsiloxy groups, which are obtained especially by treating fumed silica in

40 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, Cab-O-Sil TS-530® by the company Cabot, dimethylsiloxy or polydimethylsiloxane groups, which are obtained especially by treating fumed silica in the presence of

45 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.

50

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

Organic gelling agents

5

The polymeric organic lipophilic gelling agents are, for example, partially or totally crosslinked elastomeric organopolysiloxanes of three-dimensional structure, for instance those sold under the names KSG6®, KSG16® and KSG18® from Shin-Etsu, Trefil E-505C® or Trefil E-506C® from Dow Corning, Gransil SR-CYC®, SR DMF10®, SR-DC556®, SR 5CYC gel®, SR DMF 10 gel® and SR DC 556 gel® from Grant Industries and SF 1204® and JK 113® from General Electric; ethylcellulose, for instance the product sold under the name Ethocel® by Dow Chemical; galactomannans comprising from one to six and in particular from two to four hydroxyl groups per saccharide, substituted with a saturated or unsaturated alkyl chain, for instance guar gum alkylated with C1 to C6, and in particular C1 to C3, alkyl chains, and mixtures thereof. Block copolymers of "diblock", "triblock" or "radial" type, of the polystyrene/polyisoprene or polystyrene/polybutadiene type, such as the products sold under the name Luvitol HSB® by the company BASF, of the polystyrene/copoly(ethylene-propylene) type, such as the products sold under the name Kraton® by the company Shell Chemical Co., or of the polystyrene/copoly(ethylene-butylene) type, and mixtures of triblock and radial (star) copolymers in isododecane, such as those sold by the company Penreco under the name Versagel®, for instance the mixture of butylene/ethylene/styrene triblock copolymer and of ethylene/propylene/styrene star copolymer in isododecane (Versagel M 5960).

Lipophilic gelling agents that may also be mentioned include polymers with a weight-average molecular mass of less than 100 000, comprising a) a polymer backbone with hydrocarbon-based repeating units containing at least one heteroatom, and optionally b) at least one optionally functionalized pendent fatty chain and/or terminal fatty chain, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, as described in patent applications WO-A-02/056 847 and WO-A-02/47619, in particular polyamide resins (especially comprising alkyl groups containing from 12 to 22 carbon atoms) such as those described in US-A-5 783 657.

Among the lipophilic gelling agents that may be used in the compositions according to the invention, mention may also be made of fatty acid esters of dextrin, such as dextrin palmitates, especially the products sold under the name Rheopearl TL® or Rheopearl KL® by the company Chiba Flour.

Silicone polyamides of the polyorganosiloxane type may also be used, such as those described in documents US-A-5 874 069, US-A-5 919 441, US-A-6 051 216 and US-A-5 981 680.

45

These silicone polymers may belong to the following two families:

- polyorganosiloxanes comprising at least two groups capable of establishing hydrogen interactions, these two groups being in the chain of the polymer, and/or
- polyorganosiloxanes comprising at least two groups capable of establishing hydrogen interactions, these two groups being located on grafts or branches.

50

MOISTURE ABSORBERS

5 It is also possible to add moisture absorbers, for instance perlites and preferably expanded perlites.

The perlites that may be used according to the invention are generally aluminosilicates of volcanic origin and have as the composition:

- 70.0-75.0% by weight of silica SiO_2
- 12.0-15.0% by weight of oxide of aluminium oxide Al_2O_3
- 10 3.0-5.0% of sodium oxide Na_2O
- 3.0-5.0% of potassium oxide K_2O
- 0.5-2% of iron oxide $\text{Fe}_2\text{O}_3 \rightarrow$
- 0.2-0.7% of magnesium oxide MgO
- 0.5-1.5% of calcium oxide CaO
- 15 0.05-0.15% of titanium oxide TiO_2

The perlite is ground, dried and then calibrated in a first step. The product obtained, known as perlite ore, is grey-coloured and has a size of about 100 μm .

- 20 The perlite ore is then expanded (1000°C/2 seconds) to give more or less white particles. When the temperature reaches 850-900°C, the water trapped in the structure of the material evaporates and brings about the expansion of the material relative to its original volume. The expanded perlite particles in accordance with the invention may be obtained via the expansion process described in patent US 5
- 25 002 698.

Preferably, the perlite particles used are ground: in this case, they are known as Expanded Milled Perlite (EMP). They preferably have a particle size defined by a median diameter D_{50} ranging from 0.5 to 50 μm and preferably from 0.5 to 40 μm .

30 Preferably, the perlite particles used have an untamped apparent density at 25°C ranging from 10 to 400 kg/m^3 (standard DIN 53468) and preferably from 10 to 300 kg/m^3 .

35 Preferably, the expanded perlite particles according to the invention have a water-absorbing capacity, measured at the wet point, ranging from 200% to 1500% and preferably from 250% to 800%.

40 The wet point corresponds to the amount of water that needs to be added to 1 g of particle in order to obtain a homogeneous paste. This method is derived directly from that of the oil uptake applied to solvents. The measurements are taken in the same manner by means of the wet point and the flow point, which have, respectively, the following definition:

45 wet point: mass expressed in grams per 100 g of product corresponding to the production of a homogeneous paste during the addition of a solvent to a powder;

flow point: mass expressed in grams per 100 g of product at and above which the amount of solvent is greater than the capacity of the powder to retain it. This is

reflected by the production of a more or less homogeneous mixture that flows on a glass plate.

The wet point and the flow point are measured according to the following protocol:

5

Protocol for measuring the water absorption

1) Materials used

Glass plate (25 x 25 mm)

10

Spatula (wooden and partly metallic handle, 15 x 2.7 mm)

Silk-bristled brush

Balance

2) Procedure

15

The glass plate is placed on the balance and 1 g of perlite particles is weighed out. The beaker containing the solvent and the sampling pipette is placed on the balance. The solvent is gradually added to the powder, the whole being regularly blended (every 3 to 4 drops) with the spatula.

20

The mass of solvent needed to obtain the wet point is noted. Further solvent is added and the mass required to reach the flow point is noted. The average of three tests is determined.

25

The expanded perlite particles sold under the trade names Optimat 1430 OR or Optimat 2550 by the company World Minerals will be used in particular.

DEODORANTS

30

The deodorant active agents may be bacteriostatic agents or bactericides that act on underarm odour microorganisms, such as 2,4,4'-trichloro-2'-hydroxydiphenyl ether (®Triclosan), 2,4-dichloro-2'-hydroxydiphenyl ether, 3',4',5'-trichlorosalicylanilide, 1-(3',4'-dichlorophenyl)-3-(4'-chlorophenyl)urea (®Triclocarban) or 3,7,11-trimethyldodeca-2,5,10-trienol (®Farnesol); quaternary ammonium salts such as cetyltrimethylammonium salts, cetylpyridinium salts, DPTA (1,3-diaminopropanetetraacetic acid), 1,2-decanediol (Symclariol from the company Symrise), glycerol derivatives, for instance caprylic/capric glycerides (Capmul MCM from Abitec), glyceryl caprylate or caprate (Dermosoft GMCY and Dermosoft GMC, respectively from Straetmans), Polyglyceryl-2 caprate (Dermosoft DGMC from Straetmans), and biguanide derivatives, for instance polyhexamethylene biguanide salts, - chlorhexidine and salts thereof; 4-phenyl-4,4-dimethyl-2-butanol (Symdeo MPP from Symrise).

35

Among the deodorant active agents in accordance with the invention, mention may also be made of - zinc salts, for instance zinc salicylate, zinc gluconate, zinc pidolate; zinc sulfate, zinc chloride, zinc lactate, zinc phenolsulfonate; salicylic acid and derivatives thereof such as 5-n-octanoylsalicylic acid.

45

The deodorant active agents may be odour absorbers such as zinc ricinoleate, sodium bicarbonate; metallic or non-metallic zeolites, cyclodextrins or alum.

It may also be a chelating agent such as Dissolvine GL-47-S from Akzo Nobel, EDTA; DPTA.

It may also be a polyol such as glycerol or propane-1,3-diol (Zemea Propane diol sold by Dupont Tate and Lyle Bioproducts).

Alternatively, it may be an enzyme inhibitor such as triethyl citrate.

In the event of incompatibility or to stabilize them, some of the agents mentioned above may be incorporated into spherules, especially ionic or nonionic vesicles and/or nanoparticles (capsules and/or spheres).

The deodorant agents may preferably be present in the compositions according to the invention in weight concentrations ranging from 0.01% to 15% by weight relative to the total weight of the composition.

ORGANIC POWDER

According to one particular form of the invention, the compositions according to the invention will also contain an organic powder.

In the present patent application, the term "organic powder" means any solid that is insoluble in the medium at room temperature (25°C).

As organic powders that may be used in the composition of the invention, examples that may be mentioned include polyamide particles and especially those sold under the name Orgasol by the company Atochem; nylon-6,6 fibres, especially the polyamide fibres sold by Etablissements P Bonte under the name Polyamide 0.9 Dtex 0.3 mm (INCI name: Nylon-6,6 or Polyamide 6,6) with a mean diameter of 6 µm, a weight of about 0.9 dtex and a length ranging from 0.3 mm to 1.5 mm; polyethylene powders; microspheres based on acrylic copolymers, such as those made of ethylene glycol dimethacrylate/lauryl methacrylate copolymer, sold by the company Dow Corning under the name Polytrap; polymethyl methacrylate microspheres, sold under the name Microsphere M-100 by the Company Matsumoto or under the name Covabead LH85 by the Company Wackher; hollow polymethyl methacrylate microspheres (particle size: 6.5-10.5 µm) sold under the name Ganzpearl GMP 0800 by Ganz Chemical; methyl methacrylate/ethylene glycol dimethacrylate copolymer microbeads (size: 6.5-10.5 µm) sold under the name Ganzpearl GMP 0820 by Ganz Chemical or Microsponge 5640 by the company Amcol Health & Beauty Solutions; ethylene-acrylate copolymer powders, such as those sold under the name Flobeads by the company Sumitomo Seika Chemicals; expanded powders such as hollow microspheres and especially microspheres formed from a terpolymer of vinylidene chloride, acrylonitrile and methacrylate and sold under the name Expancel by the company Kemanord Plast under the references 551 DE 12 (particle size of about 12 µm and mass per unit volume of 40 kg/m³), 551 DE 20 (particle size of about 30 µm and mass per unit volume of 65 kg/m³), 551 DE 50 (particle size of about 40 µm), or the microspheres sold under the name Micropearl F 80 ED by the company Matsumoto; powders of natural organic materials such as starch powders, especially of crosslinked or non-crosslinked corn, wheat or rice starch, such as the powders of starch crosslinked with octenylsuccinic anhydride, sold

under the name Dry-Flo by the company National Starch; silicone resin microbeads such as those sold under the name Tospearl by the company Toshiba Silicone, especially Tospearl 240; amino acid powders such as the lauroyllysine powder sold under the name Amihope LL-11 by the company Ajinomoto; particles
5 of wax microdispersion, which preferably have mean sizes of less than 1 μm and especially ranging from 0.02 μm to 1 μm , and which are formed essentially from a wax or a mixture of waxes, such as the products sold under the name Aquacer by the company Byk Cera, and especially: Aquacer 520 (mixture of synthetic and natural waxes), Aquacer 514 or 513 (polyethylene wax), Aquacer 511 (polymeric
10 wax), or such as the products sold under the name Jonwax 120 by the company Johnson Polymer (mixture of polyethylene wax and paraffin wax) and under the name Ceraflour 961 by the company Byk Cera (micronized modified polyethylene wax); and mixtures thereof.

15 **ADDITIVES**

The cosmetic compositions according to the invention may also comprise cosmetic adjuvants chosen from softeners, antioxidants, opacifiers, stabilizers, moisturizers, vitamins, bactericides, preserving agents, polymers, fragrances, thickeners or
20 suspension agents, propellants or any other ingredient usually used in cosmetics for this type of application.

Needless to say, a person skilled in the art will take care to select this or these optional additional compounds such that the advantageous properties intrinsically
25 associated with the cosmetic composition in accordance with the invention are not, or are not substantially, adversely affected by the envisaged addition(s).

THICKENERS AND SUSPENSION AGENTS

The thickeners may be chosen from carboxyvinyl polymers, such as Carbopols (Carbomers) and the Pemulens (acrylate/ $\text{C}_{10}\text{-C}_{30}$ alkyl acrylate copolymer); polyacrylamides, for instance the crosslinked copolymers sold under the names Sepigel 305 (CTFA name: polyacrylamide/ $\text{C}_{13\text{-}14}$ isoparaffin/Laureth 7) or Simulgel 600 (CTFA name: acrylamide/sodium acryloyldimethyltaurate
35 copolymer/isohexadecane/polysorbate 80) by the company SEPPIC; 2-acrylamido-2-methylpropanesulfonic acid polymers and copolymers, optionally crosslinked and/or neutralized, for instance poly(2-acrylamido-2-methylpropanesulfonic acid) sold by the company Hoechst under the trade name Hostacerin AMPS (CTFA name: ammonium polyacryloyldimethyl taurate or
40 Simulgel 800 sold by the company SEPPIC (CTFA name: sodium polyacryloyldimethyltaurate/polysorbate 80/sorbitan oleate); copolymers of 2-acrylamido-2-methylpropanesulfonic acid and of hydroxyethyl acrylate, for instance Simulgel NS and Sepinov EMT 10 sold by the company SEPPIC; cellulose derivatives such as hydroxyethylcellulose or cetylhydroxyethylcellulose;
45 polysaccharides and especially gums such as xanthan gum and hydroxypropyl guar gums; silicas, for instance Bentone Gel MIO sold by the company NL Industries or Veegum Ultra sold by the company Polyplastic.

The thickeners may also be cationic, for instance Polyquaternium-37 sold under
50 the name Salcare SC95 (Polyquaternium-37 (and) Mineral Oil (and) PPG-1

Trideceth-6) or Salcare SC96 (Polyquaternium-37 (and) Propylene Glycol Dicaprylate/Dicaprate (and) PPG-1 Trideceth-6) or other crosslinked cationic polymers, for instance those of the CTFA name Ethyl Acrylate/Dimethylaminoethyl Methacrylate Cationic Copolymer In Emulsion.

5

SUSPENSION AGENTS

In order to improve the homogeneity of the product, it is also possible to use one or more suspension agents preferably chosen from hydrophobic modified montmorillonite clays such as hydrophobic modified bentonites or hectorites. Examples that may be mentioned include the product Stearalkonium Bentonite (CTFA name) (product of reaction of bentonite and the quaternary ammonium stearalkonium chloride) such as the commercial product sold under the name Tixogel MP 250 by the company Sud Chemie Rheologicals, United Catalysts Inc. or the product Distearldimonium Hectorite (CTFA name) (product of reaction of hectorite and distearyldimonium chloride) sold under the name Bentone 38 or Bentone Gel by the company Elementis Specialities.

Other suspension agents may be used, in the present case in hydrophilic media (aqueous and/or ethanolic). They may be cellulose, xanthan, guar, starch, locust bean or agar derivatives.

The suspension agents are preferably present in amounts ranging from 0.1% to 5% by weight and more preferentially from 0.2% to 2% by weight relative to the total weight of the composition.

The amounts of these various constituents that may be present in the cosmetic composition according to the invention are those conventionally used in compositions for treating perspiration.

30

AEROSOLS

The compositions according to the invention may also be pressurized and may be conditioned in an aerosol device formed by:

- (A) a container comprising an antiperspirant composition as defined previously,
(B) at least one propellant and a means for dispensing the said aerosol composition.

The propellants generally used in products of this type and that are well known to those skilled in the art are, for instance, dimethyl ether (DME); volatile hydrocarbons such as n-butane, propane, isobutane and mixtures thereof, optionally with at least one chlorohydrocarbon and/or fluorohydrocarbon; among these derivatives, mention may be made of the compounds sold by the company DuPont de Nemours under the names Freon® and Dymel®, and in particular monofluorotrichloromethane, difluorodichloromethane, tetrafluorodichloroethane and 1,1-difluoroethane sold especially under the trade name Dymel 152 A by the company DuPont. Carbon dioxide, nitrous oxide, nitrogen or compressed air may also be used as propellant.

The compositions containing perlite particles as defined previously and the propellant(s) may be in the same compartment or in different compartments in the aerosol container. According to the invention, the concentration of propellant generally ranges from 5% to 95% by weight of pressurized composition, and more preferentially from 50% to 85% by weight relative to the total weight of the pressurized composition.

The dispensing means, which forms a part of the aerosol device, is generally formed by a dispensing valve controlled by a dispensing head, which itself comprises a nozzle via which the aerosol composition is vaporized. The container containing the pressurized composition may be opaque or transparent. It may be made of glass, a polymer or a metal, optionally coated with a protective varnish coat.

15 **Example 1: Antiperspirant stick**

Ingredients	Amounts in weight %
Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	33
PPG-14 butyl ether (Ucon Fluid AP - Amerchol)	10
Hydrogenated castor oil (Cutina HR Pulver - Cognis)	4
Talc	2
Poly(4-vinylpyridine) PM 60K (Aldrich)	20
Stearyl alcohol	14
PEG-8 distearate (Stéarineries Dubois)	2
C12-15 alkyl benzoate (Finsolv TN - Witco)	15

Procedure:

20 The cyclopentasiloxane is heated to 65°C. The other ingredients are added one by one, while keeping the temperature at 65-70°C. The whole is homogenized (transparent solution) for 15 minutes. The product is cooled to about 55°C (a few degrees Celsius above the thickening point of the mixture) and is poured into sticks. The sticks are placed at 4°C for 30 minutes.

25

Example 2: Antiperspirant emulsion (roll-on)

Phase	Ingredients	Amounts in weight %

A	Crosslinked poly(4-vinylpyridine) (Reillex 402)	8
	Zinc gluconate (Givobio G Zn - SEPPIC)	2
B	Steareth-21 (Brij 721 - ICI)	2
	Steareth-2 (Brij 72 - ICI)	2
	Steareth-5 Stearate (Arlatone 985 - ICI)	1
	PPG-15 stearyl ether (Arlamol E - ICI)	1.5
	Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	3.5
C	Water	68

Procedure:

- 5 Phases (B) and (C) are separately heated to 70°C. (B) and (C) are mixed together by Turrax blending for 5 minutes, and the mixture is then cooled to 55°C with continued stirring. Phase A is then added slowly with stirring. The mixture is homogenized for 1 to 3 minutes. It is cooled to 35°C with stirring.

10

Example 3: Antiperspirant vaporizer (PIT emulsion)

Ingredients	Amounts in weight %
Poly(2-vinylpyridine) Aldrich PM 159 K neutralized 50% HCl	10
Cetearyl isononanoate (and) Cetearyl alcohol (and) Ceteareth-20 (and) Glycerin (and) Glyceryl stearate (and) Ceteareth-12 (and) Cetyl palmitate (Emulgade CM - Cognis)	15
Water	65

Procedure:

- 15 Poly(vinylpyridine) from Aldrich is dissolved in water, and Emulgade CM is added to the mixture with moderate stirring.

Example 4: Antiperspirant aerosol

20

Ingredients	Amounts in weight %
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Stearalkonium Bentonite (Tixogel MP 250 - Süd Chemie)	0.5
Poly(4-vinylpyridine-co-styrene 10%) Aldrich neutralized 100% HCl	5
C12-15 alkyl benzoate (Finsolv TN - Witco)	3
Triethyl citrate (Citroflex 2; Morflex)	1
Isopropyl palmitate	1
Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	9.5
Isobutane (propellant)	80

Examples of synthesis of flocculant polymers comprising as side chain non-quaternary amine groups and at least one hydrophobic nonionic monomer

5 Polymer 1: copolymer (NMDEA -PEG 200-IPDI) (weight%: 20/20.22/59.78) neutralized HCl

The monomers and solvents below are introduced into a thermostatically controlled reactor equipped with a mechanical stirring system and a condenser:

10 - 1 mol of a mixture of monomers of diol type, i.e. a mixture of N-methyldiethanolamine (0.62 mol) and of PEG-200 (0.38 mol),
and

- an amount of methyl ethyl ketone such that the concentration of monomers of diol type is equal to 75% by weight.

15 The mixture is heated with stirring to a temperature of 70°C, followed by dropwise addition with stirring, over a period of about 2 hours, of a small molar excess, i.e. 1.03 mol, of isophorone diisocyanate. During this addition, an increase in temperature up to the reflux point of the solvent is observed. Samples are withdrawn at regular intervals and the IR absorption spectrum is plotted to monitor
20 the disappearance of the band corresponding to the isocyanate functions (2260 cm⁻¹). When the absorption band of the -NCO functions no longer decreases, which is generally the case after about 5 hours, the reaction mixture is allowed to cool to room temperature and is then diluted with acetone to a polymer concentration of about 40% by weight. 20 cm³ of ethanol are then added to the
25 mixture obtained in order to destroy the residual -NCO functions, and stirring is continued at room temperature until all these -NCO functions have disappeared, i.e. until the disappearance of the IR absorption band at 2260 cm⁻¹. 2M hydrochloric acid solution is then added in an amount such that the amine groups are neutralized to the desired proportion. The various organic solvents (methyl
30 ethyl ketone, acetone and ethanol) are then removed by distillation under vacuum at a temperature of 40°C. After removal of the organic phase, an amount of water sufficient to obtain a final polymer concentration in the water of about 25% by weight is added to the aqueous polymer solution.

35 Polymers 2 to 5 are synthesized according to a similar procedure, replacing the methyl ethyl ketone with THF for the polymers based on Krasol LBH P 2000.

40 Polymer 2: copolymer (NMDEA -PEG 100 000 g/mol - IPDI) (weight%: 20/37.4/42.6) neutralized HCl

Polymer 3: copolymer (NMDEA -Krasol LBH P 2000 - IPDI) (weight%: 19.1/40.7/40.2) neutralized HCl

45 Polymer 4: copolymer (NMDEA -Krasol LBH P 2000 - IPDI) (weight%: 11.6/60/28.4) neutralized HCl

Polymer 5: copolymer (NMDEA -Krasol LBH P 2000 - IPDI) (weight%: 15.5/50/34.5) neutralized HCl

Polymer 6: copolymer (PEG 10 000 g/mol - Desmodur W - 2-dimethylaminoethanol quaternized with dodecyl(2-hydroxyethyl)dimethylammonium) bromide (weight% 95.5/2/0.5/2)

- 5 A 500 ml reactor equipped with a central mechanical stirrer, a thermometer, a condenser and a nitrogen inlet is charged with 0.01 mol of PEG 10 000 g/mol + 0.0006 mol of tin 2-ethylhexanoate + 100 cm³ of tetrahydrofuran (THF). The mixture is stirred at room temperature to obtain a homogeneous solution, followed by dropwise addition of 0.02 mol of methylenedicyclohexyl 4,4'-diisocyanate (Desmodur W 2) while remaining at room temperature. The mixture is then heated to the reflux temperature of the solvent (66°C) over about 30 minutes, and is left at this temperature for about 5 hours. 0.02 mol of N-methyldiethanolamine is then introduced and the mixture is left to react for 2 hours at 66°C (the disappearance of the NCO band of the isocyanate is monitored by IR), followed by addition of 15 0.02 mol of methylenedicyclohexyl 4,4'-diisocyanate, which is left to react for 3 hours (the disappearance of the NCO band of the isocyanate is also monitored by IR) and finally 0.02 mol of dodecanol. The mixture is left for a further 3 hours at reflux temperature of the solvent.
- 20 The polymer is then quaternized by addition of 0.022 mol of dimethyl sulfate. The reaction medium becomes opaque, and heating is maintained at 66°C for 48 hours. The mixture is then allowed to cool to room temperature. The polyurethane is purified by precipitation from petroleum ether, filtered off and dried under vacuum at 55°C to a constant weight.

25

Example 5: Antiperspirant stick

Ingredients	Amounts in weight %
Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	33
PPG-14 butyl ether (Ucon Fluid AP - Amerchol)	10
Hydrogenated castor oil (Cutina HR Pulver - Cognis)	4
Talc	2
Polymer 1	20
Stearyl alcohol	14
PEG-8 distearate (Stéarineries Dubois)	2
C12-15 alkyl benzoate (Finsolv TN - Witco)	15

Procedure:

30

The cyclopentasiloxane is heated to 65°C. The other ingredients are added one by one, while keeping the temperature at 65-70°C. The whole is homogenized for 15 minutes. The product is cooled to about 55°C (a few degrees Celsius above the

thickening point of the mixture) and is poured into sticks. The sticks are placed at 4°C for 30 minutes.

Example 6: Antiperspirant emulsion (roll-on)

5

Phase	Ingredients	Amounts in weight %
A	Polymer 2	20
	Zinc gluconate (Givobio G Zn - SEPPIC)	2
B	Steareth-21 (Brij 721 - ICI)	2
	Steareth-2 (Brij 72 - ICI)	2
	Steareth-5 Stearate (Arlatone 985 - ICI)	1
	PPG-15 stearyl ether (Arlamol E - ICI)	1.5
	Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	3.5
C	Water	68

Procedure:

10

Phases (B) and (C) are separately heated to 70°C. (B) and (C) are mixed together by Turrax blending for 5 minutes, and the mixture is then cooled to 55°C with paddle stirring. Phase A is then added slowly with stirring. The mixture is homogenized for 1 to 3 minutes. The mixture is cooled to 35°C with stirring.

Example 7: Antiperspirant vaporizer (Phase-Inversion Technique Emulsion)

Ingredients	Amounts in weight %
Polymer 2 (20%)	20
Cetearyl isononanoate (and) Cetearyl alcohol (and) Ceteareth-20 (and) Glycerin (and) Glyceryl stearate (and) Ceteareth-12 (and) Cetyl palmitate (Emulgade CM - Cognis)	15
Water	65

Procedure:

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Polymer 2 is dissolved in water, and Emulgade CM is added to the mixture with moderate stirring.

Examples of synthesis of polyurethane flocculant polymers

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Polymer 1': copolymer (NMDEA -PEG 200-IPDI) (weight%: 20/20.22/59.78) neutralized HCl

The monomers and solvents below are introduced into a thermostatically controlled reactor equipped with a mechanical stirring system and a condenser:

15 - 1 mol of a mixture of monomers of diol type, i.e. a mixture of N-methyldiethanolamine (0.62 mol) and of PEG-200 (0.38 mol),
and

20 - an amount of methyl ethyl ketone such that the concentration of monomers of diol type is equal to 75% by weight.

The mixture is heated with stirring to a temperature of 70°C, followed by dropwise addition with stirring, over a period of about 2 hours, of a small molar excess, i.e. 1.03 mol, of isophorone diisocyanate. During this addition, an increase in
25 temperature up to the reflux point of the solvent is observed. Samples are withdrawn at regular intervals and the IR absorption spectrum is plotted to monitor the disappearance of the band corresponding to the isocyanate functions (2260 cm⁻¹). When the absorption band of the -NCO functions no longer decreases, which is generally the case after about 5 hours, the reaction mixture is allowed to
30 cool to room temperature and is then diluted with acetone to a polymer concentration of about 40% by weight. 20 cm³ of ethanol are then added to the mixture obtained in order to destroy the residual -NCO functions, and stirring is continued at room temperature until all these -NCO functions have disappeared, i.e. until the disappearance of the IR absorption band at 2260 cm⁻¹. 2M
35 hydrochloric acid solution is then added in an amount such that the amine groups are neutralized to the desired proportion. The various organic solvents (methyl ethyl ketone, acetone and ethanol) are then removed by distillation under vacuum at a temperature of 40°C. After removal of the organic phase, an amount of water

sufficient to obtain a final polymer concentration in the water of about 25% by weight is added to the aqueous polymer solution.

Polymers 2 to 5 are synthesized according to a similar procedure, replacing the methyl ethyl ketone with THF for the polymers based on Krasol LBH P 2000.

5

Polymer 2': copolymer (NMDEA -PEG 100 000 g/mol - IPDI) (weight%: 20/37.4/42.6) neutralized HCl

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Polymer 3': copolymer (NMDEA -Krasol LBH P 2000 - IPDI) (weight%: 19.1/40.7/40.2) neutralized HCl

Polymer 4': copolymer (NMDEA -Krasol LBH P 2000 - IPDI) (weight%: 11.6/60/28.4) neutralized HCl

15

Polymer 5': copolymer (NMDEA -Krasol LBH P 2000 - IPDI) (weight%: 15.5/50/34.5) neutralized HCl

20

Polymer 6': copolymer (PEG 10 000 g/mol - Desmodur W - 2-dimethylaminoethanol quaternized with dodecyl(2-hydroxyethyl)dimethylammonium) bromide (weight% 95.5/2/0.5/2)

25

A 500 ml reactor equipped with a central mechanical stirrer, a thermometer, a condenser and a nitrogen inlet is charged with 0.01 mol of PEG 10 000 g/mol + 0.0006 mol of tin 2-ethylhexanoate + 100 cm³ of tetrahydrofuran (THF). The mixture is stirred at room temperature to obtain a homogeneous solution, followed by dropwise addition of 0.02 mol of methylenedicyclohexyl 4,4'-diisocyanate (Desmodur W 2) while remaining at room temperature. The mixture is then heated to the reflux temperature of the solvent (66°C) over about 30 minutes, and is left at this temperature for about 5 hours. 0.02 mol of N-methyldiethanolamine is then introduced and the mixture is left to react for 2 hours at 66°C (the disappearance of the NCO band of the isocyanate is monitored by IR), followed by addition of 0.02 mol of methylenedicyclohexyl 4,4'-diisocyanate, which is left to react for 3 hours (the disappearance of the NCO band of the isocyanate is also monitored by IR) and finally 0.02 mol of dodecanol. The mixture is left for a further 3 hours at reflux temperature of the solvent.

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The polymer is then quaternized by addition of 0.022 mol of dimethyl sulfate. The reaction medium becomes opaque, and heating is maintained at 66°C for 48 hours. The mixture is then allowed to cool to room temperature. The polyurethane is purified by precipitation from petroleum ether, filtered off and dried under vacuum at 55°C to a constant weight.

45

Example 8: Antiperspirant stick

Ingredients	Amounts in weight %
Cyclopentasiloxane	33

(DC 245 Fluid from Dow Corning)	
PPG-14 butyl ether (Ucon Fluid AP - Amerchol)	10
Hydrogenated castor oil (Cutina HR Pulver - Cognis)	4
Talc	2
Polymer 6'	20
Stearyl alcohol	14
PEG-8 distearate (Stéarineries Dubois)	2
C12-15 alkyl benzoate (Finsolv TN - Witco)	15

Procedure:

The cyclopentasiloxane is heated to 65°C. The other ingredients are added one by one, while keeping the temperature at 65-70°C. The whole is homogenized (transparent solution) for 15 minutes. The product is cooled to about 55°C (a few degrees Celsius above the thickening point of the mixture) and is poured into sticks. The sticks are placed at 4°C for 30 minutes.

Example 9: Antiperspirant stick

Ingredients	Amounts in weight %
Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	33
PPG-14 butyl ether (Ucon Fluid AP - Amerchol)	10
Hydrogenated castor oil (Cutina HR Pulver - Cognis)	4
Talc	2
Polymer 3'	20
Stearyl alcohol	14
PEG-8 distearate (Stéarineries Dubois)	2
C12-15 alkyl benzoate (Finsolv TN - Witco)	15

Procedure:

The cyclopentasiloxane is heated to 65°C. The other ingredients are added one by one, while keeping the temperature at 65-70°C. The whole is homogenized (transparent solution) for 15 minutes. The product is cooled to about 55°C (a few degrees Celsius above the thickening point of the mixture) and is poured into sticks. The sticks are placed at 4°C for 30 minutes.

Example 10: Antiperspirant emulsion (roll-on)

Phase	Ingredients	Amounts in weight %
A	Polymer 4'	8
	Zinc gluconate (Givobio G Zn - SEPPIC)	2
B	Steareth-21 (Brij 721 - ICI)	2
	Steareth-2 (Brij 72 - ICI)	2
	Steareth-5 Stearate (Arlatone 985 - ICI)	1
	PPG-15 stearyl ether (Arlamol E - ICI)	1.5
	Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	3.5
C	Water	68

5 **Procedure:**

Phases (B) and (C) are separately heated to 70°C. (B) and (C) are mixed together by Turrax blending for 5 minutes, and the mixture is then cooled to 55°C with paddle stirring. Phase A is then added slowly with stirring. The mixture is
 10 homogenized for 1 to 3 minutes. The mixture is cooled to 35°C with stirring.

Example 11: Antiperspirant emulsion (roll-on)

Phase	Ingredients	Amounts in weight %
A	Polymer 1'	8
	Zinc gluconate (Givobio G Zn - SEPPIC)	2
B	Steareth-21 (Brij 721 - ICI)	2
	Steareth-2 (Brij 72 - ICI)	2
	Steareth-5 Stearate (Arlatone 985 - ICI)	1
	PPG-15 stearyl ether (Arlamol E - ICI)	1.5
	Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	3.5
C	Water	68

Procedure:

Phases (B) and (C) are separately heated to 70°C. (B) and (C) are mixed together by Turrax blending for 5 minutes, and the mixture is then cooled to 55°C with paddle stirring. Phase A is then added slowly with stirring. The mixture is homogenized for 1 to 3 minutes. The mixture is cooled to 35°C with stirring.

Example 12: Antiperspirant vaporizer (Emulsion obtained by phase inversion)

Ingredients	Amounts in weight %
Polymer 5'	10
Cetearyl isononanoate (and) Cetearyl alcohol (and) Ceteareth-20 (and) Glycerin (and) Glyceryl stearate (and) Ceteareth-12 (and) Cetyl palmitate (Emulgade CM - Cognis)	15
Water	65

Procedure:

Polymer 5 is dissolved in water, and Emulgade CM is added to the mixture with moderate stirring.

Example 12: Antiperspirant aerosol

Ingredients	Amounts in weight %
Stearalkonium Bentonite (Tixogel MP 250 - Süd Chemie)	0.5
Polymer 2'	5
C12-15 alkyl benzoate (Finsolv TN - Witco)	3
Triethyl citrate (Citroflex 2; Morflex)	1
Isopropyl palmitate	1
Cyclopentasiloxane (DC 245 Fluid from Dow Corning)	9.5
Isobutane (propellant)	80

CLAIMS

5 1. Cosmetic use of a flocculant polymer chosen from:

(i) flocculant polymers comprising as side chain non-quaternized pyridine groups directly or indirectly linked to the main chain;

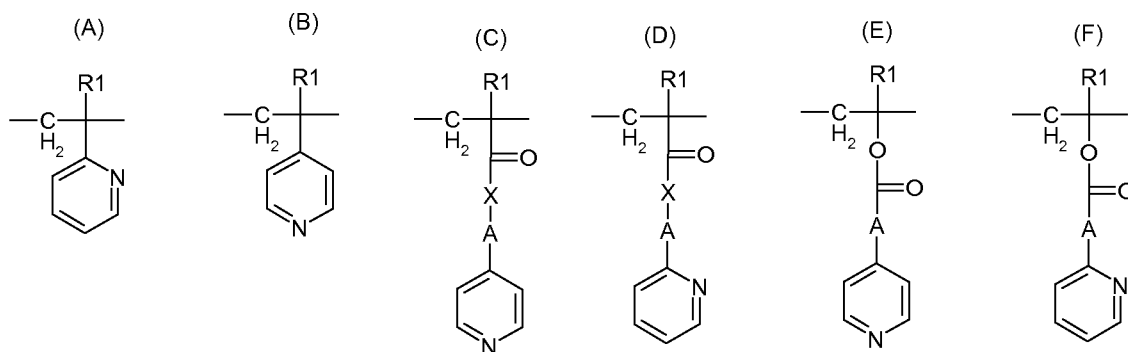
10 (ii) flocculant polymers comprising as side chain non-quaternary amine groups borne by a side substituent directly linked to the main chain; the said polymer comprising at least one non-quaternary cationic monomer and at least one hydrophobic nonionic monomer;

15 (iii) cationic polyurethane flocculant polymers; as antiperspirant active agent.

2. Use according to Claim 1, in which the flocculant polymer is contained in a composition comprising a cosmetically acceptable medium, in particular not containing any antiperspirant aluminium and/or zirconium salts.

20

3. Use according to Claim 1 or 2, in which the flocculant polymer of paragraph i) is chosen from homopolymers or copolymers comprising at least one monomer (A) to (F) defined below:



25

where:

X = O, or NH

R₁ represents a hydrogen atom or an alkyl group containing from 1 to 3 carbon atoms, preferably methyl;

30 A is a linear or branched C₁-C₆ and preferably C₂-C₃ alkyl group; a C₁-C₄ hydroxyalkyl group, preferably monohydroxyalkyl;

4. Use according to Claim 3, in which the pyridine monomers (A) to (F) are chosen from 2-vinylpyridine; 4-vinylpyridine; N-(4-pyridyl)propylmethacrylamide and N-4-(pyridyl)ethyl methacrylate.

35

5. Use according to Claim 3 or 4, in which the flocculant polymer may also comprise:

40 - units consisting of at least one additional cationic monomer preferably chosen from benzyl dimethylaminoethylacrylate chloride (DMAEA-BCQ), acryloyloxyethyltrimethylammonium chloride (AETAC),

methacryloyloxyethyltrimethylammonium methosulfate (METAMS) and methylaminoethyl methacrylate;

- units consisting of at least one anionic monomer preferably chosen from maleic anhydride, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, maleic acid, 2-carboxyethyl acrylate ($\text{CH}_2=\text{CH}-\text{C}(\text{O})-\text{O}-(\text{CH}_2)_2-\text{COOH}$);
- styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylbenzoic acid, vinylphosphoric acid and sulfopropyl (meth)acrylate, and salts thereof;
- units consisting of at least one nonionic monomer preferably chosen from methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, tetrahydrofurfuryl methacrylates, butyl methacrylate, 2-ethylhexyl acrylate, stearyl methacrylate, acrolein, tetrahydrofurfuryl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, ethoxyethyl methacrylate, ethoxyethyl acrylate, N-isopropylacrylamide, N-isopropylmethacrylamide, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, vinyl acetate, methyl vinyl ether, ethyl vinyl ether, vinylpyrrolidone, vinylcaprolactam, N-vinylacetamide, hydroxypropyl acrylate, N-vinylactam, acrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-methyl-N-vinylacetamide, N-vinylformamide, N-methyl-N-vinylformamide, vinyl alcohol (copolymerized in the form of vinyl acetate and then hydrolysed).

20

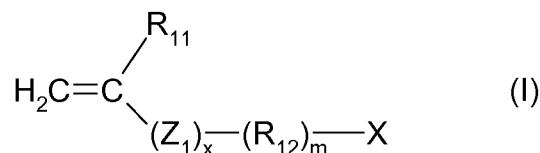
6. Use according to any one of Claims 3 to 5, in which the flocculant polymer of paragraph i) is chosen from:

- poly(2-vinylpyridine) homopolymers;
- poly(4- or 2-vinylpyridine)-co-styrene copolymers;
- poly(4- or 2-vinylpyridine)-co-butyl methacrylate copolymers;
- poly(4- or 2-vinylpyridine) crosslinked with divinylbenzene;
- diblock polymers comprising a polyethylene glycol (PEG) or polyisobutylene block and a poly(4- or 2-vinylpyridine) block;
- poly(4-vinylpyridinium) p-toluenesulfonate;
- poly(4-vinylpyridine hydrochloride) 2% crosslinked with divinylbenzene.

30

7. Use according to Claim 1 or 2, in which, in the flocculant polymer of paragraph ii), the non-quaternary cationic monomer is chosen from those of formula (I) below, or a salt thereof:

35



in which:

- R_{11} is a hydrogen atom or a linear or branched hydrocarbon-based radical, of the type $\text{C}_p\text{H}_{2p+1}$, with p being an integer between 1 and 12 inclusive (in particular, R_{11} may represent a methyl, ethyl, propyl or butyl radical (preferably, R_{11} represents hydrogen or a methyl radical));

40

- Z_1 is a divalent group chosen from $-\text{COO}-$, $-\text{CONH}-$, $-\text{CONCH}_3-$, $-\text{OCO}-$ or $-\text{O}-$, $-\text{SO}_2-$, $-\text{CO}-\text{O}-\text{CO}-$ or $-\text{CO}-\text{CH}_2-\text{CO}-$, (preferably Z is chosen from COO and CONH);

45

- $x = 0$ or 1 , preferably 1 ;

R_{12} is a saturated or unsaturated, optionally aromatic, linear, branched or cyclic carbon-based divalent radical of 1 to 30 carbon atoms, which may comprise 1 to 18 heteroatoms chosen from O, N, S, F, Si and P; the heteroatom(s) may be intercalated in the chain of the said radical R_2 .

5 the said radical R_{12} may be substituted with one or more groups comprising them such as hydroxyl or a group NH_2 , NHR' or $NR'R''$ with R' and R'' , which may be identical or different, representing a linear or branched C_1 - C_{22} alkyl, especially methyl or ethyl;

10 R_{12} may also be an alkylene radical such as methylene, ethylene, propylene, n-butylene, isobutylene, tert-butylene, n-hexylene, n-octylene, n-dodecylene, n-octadecylene, n-tetradecylene or n-docosanylene); a phenylene radical $-C_6H_4-$ (ortho, meta or para), optionally substituted with a C_1 - C_{12} alkyl radical optionally comprising 1 to 25 heteroatoms chosen from N, O, S, F, Si and/or P; or alternatively a benzylene radical $-C_6H_4-CH_2-$, optionally substituted with a C_1 - C_{12} alkyl radical optionally comprising 1 to 25 heteroatoms chosen from O, N, S, F, Si and P;

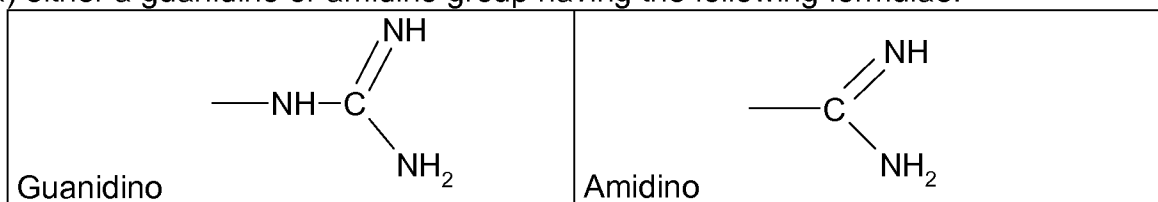
15 R_{12} may also be a radical of formula $-CH_2-O-CO-O-$, $CH_2-CH_2-O-CO-O-$, $-CH_2-CO-O-$, $-CH_2-CH_2-CO-O-$, $-[(CH_2)_5-CO-O]_n-$, $-CH_2-CH(CH_3)-O-$, $-(CH_2)_2-O-$, $-CH_2-O-CO-NH-$, $-CH_2-CH_2-O-CO-NH-$, $-CH_2-NH-CO-NH-$ or $-CH_2-CH_2-NH-CO-NH-$, $-CH_2-CHOH-$, $-CH_2-CH_2-CHOH-$, $-CH_2-CH_2-CH(NH_2)-$, $-CH_2-CH(NH_2)-$, $-CH_2-CH_2-CH(NHR')-$, $-CH_2-CH(NHR'')$, $-CH_2-CH_2-CH(NR'''R''')$, $-CH_2-CH(NR'''R''')$, $-CH_2-CH_2-CH_2-NR'''-$, $-CH_2-CH_2-CH_2-O-$, $-CH_2-CH_2-CH_2-R'$ with R''' and R'''' representing a linear or branched C_1 - C_{22} alkyl optionally comprising 1 to 12 heteroatoms chosen from O, N, S, F, Si and P;

25 R_{12} may be a mixture of these radicals;

m is 0 or 1;

X is

a) either a guanidino or amidino group having the following formulae:



30

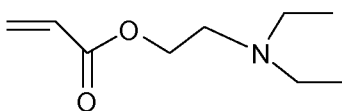
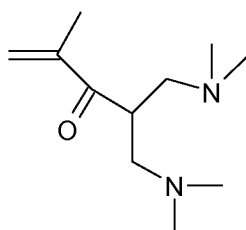
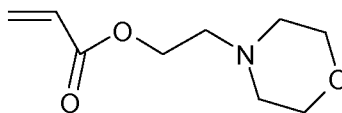
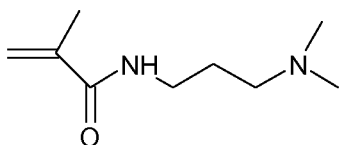
b) or a group of formula $-N(R_{13})(R_{14})$ or $-P(R_{13})(R_{14})$ with R_{13} and R_{14} representing, independently of each other:

- 35 (i) a hydrogen atom;
- (ii) a linear, branched or cyclic, saturated or unsaturated, optionally aromatic alkyl group, comprising from 1 to 18 carbon atoms, which may comprise 1 to 10 heteroatoms chosen from O, N, S, F, Si and P;
- 40 (iii) R_{13} and R_{14} may form, with the nitrogen or phosphorus atom, a first saturated or unsaturated, optionally aromatic ring comprising in total 5, 6, 7 or 8 atoms, and especially 4, 5 or 6 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N; the said first ring possibly being fused with one or more other saturated or unsaturated, optionally aromatic rings, each comprising 5, 6 or 7 atoms, and especially 4, 5, 6 or 7 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N;

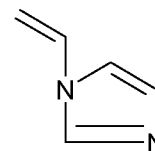
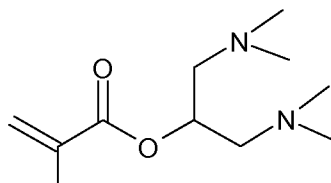
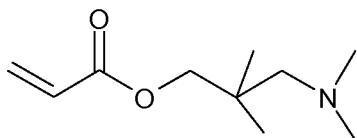
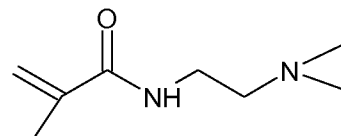
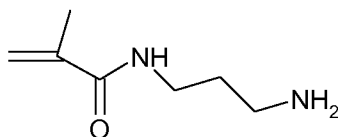
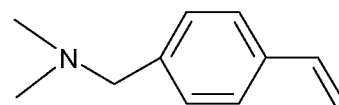
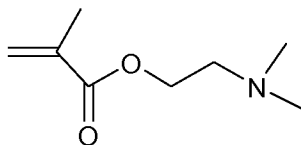
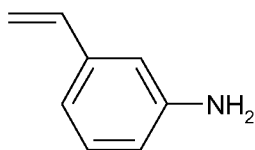
45 c) a group $R'_3-N-R'_4$ in which R'_3 and R'_4 form, with the nitrogen atom, a saturated

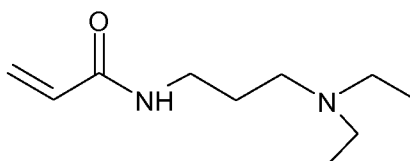
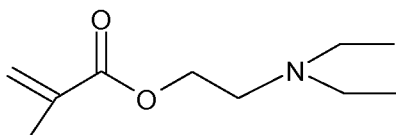
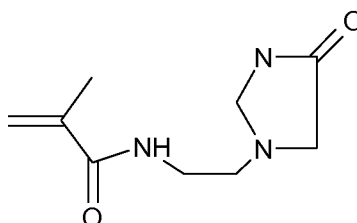
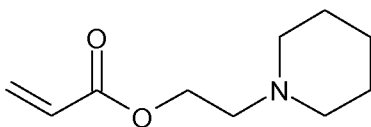
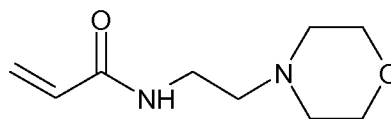
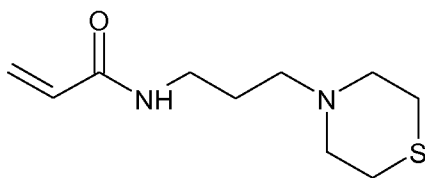
ring comprising in total 5, 6, 7 or 8 atoms, and especially 4, 5 or 6 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N; the said ring possibly being fused with one or more other saturated rings, each comprising 5, 6 or 7 atoms, and especially 4, 5, 6, 7 or 8 carbon atoms and/or 2 to 4 heteroatoms chosen from O, S and N.

8. Use according to Claim 7, in which the non-quaternary amine cationic monomers of formula (I) are chosen from the following monomers:



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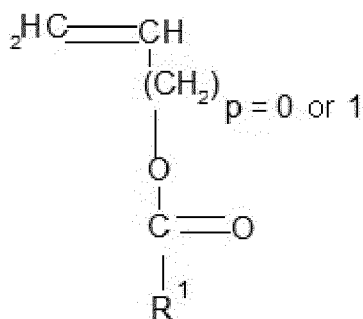




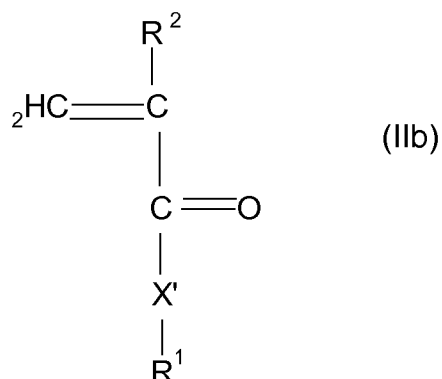
and preferably chosen from dimethylaminopropyl(meth)acrylamide, dimethylaminoethyl(meth)acrylamide, diethylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, vinylimidazole and morpholinoethyl (meth)acrylate, and mixtures thereof.

9. Use according to Claim 7 or 8, in which the non-quaternary amine cationic monomers of formula (I) are present in a proportion of from 5% to 80% by weight relative to the weight of the final polymer, especially from 7% to 30% by weight and preferably from 10% to 20% by weight.

10. Use according to any one of Claims 7 to 9, in which the flocculant polymer of paragraph ii) comprises units consisting of at least one hydrophobic nonionic monomer preferably chosen from those of formula (IIa) or (IIb) below:



(IIa)



in which:

X' represents an oxygen atom or a group NH, and

- 5 R¹ represents a linear, branched, cycloaliphatic or aromatic C₂-C₆₀ hydrocarbon-based group, which may contain one or more atoms chosen from O, S and P; ; the said group may further contain at least a polyoxyalkylenated chain ;
 R² represents a hydrogen atom or a methyl group.

- 10 **11.** Use according to Claim 10, in which the nonionic monomers of formula (IIa) or (IIb) are present in a proportion of from 10% to 95% by weight relative to the weight of the final polymer, especially from 20% to 90% by weight and preferably from 30% to 85% by weight.

- 15 **12.** Use according to any one of Claims 7 to 11, in which the flocculant polymer of paragraph ii) may also comprise:

- units consisting of at least one hydrophobic nonionic monomer preferably chosen from vinyl monomers bearing a silicone side chain, chlorotrifluoroethylene, tetrafluoroethylene, and vinyl, allylic or (meth)acrylic monomers bearing a
 20 perhalogenated, in particular perfluoro, hydrocarbon-based side chain, such as perfluorohexyl (meth)acrylate or perfluorooctyl (meth)acrylate. These monomers will preferably be present in small amounts relative to the weight of the final polymer;
 - units consisting of at least one anionic monomer preferably chosen from maleic
 25 anhydride, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, maleic acid, 2-carboxyethyl acrylate (CH₂=CH-C(O)-O-(CH₂)₂-COOH); styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylbenzoic acid, vinylphosphoric acid and sulfopropyl (meth)acrylate, and salts thereof.

- 30 **13.** Use according to any one of Claims 7 to 11, in which the flocculant polymer of paragraph ii) is chosen from the following polymers:

- copolymers of butyl acrylate and of dimethylaminoethyl methacrylate,
- copolymers of butyl acrylate and of dimethylaminopropylmethacrylamide, and
- copolymers of 2-ethylhexyl acrylate and of dimethylaminopropylmethacrylamide.

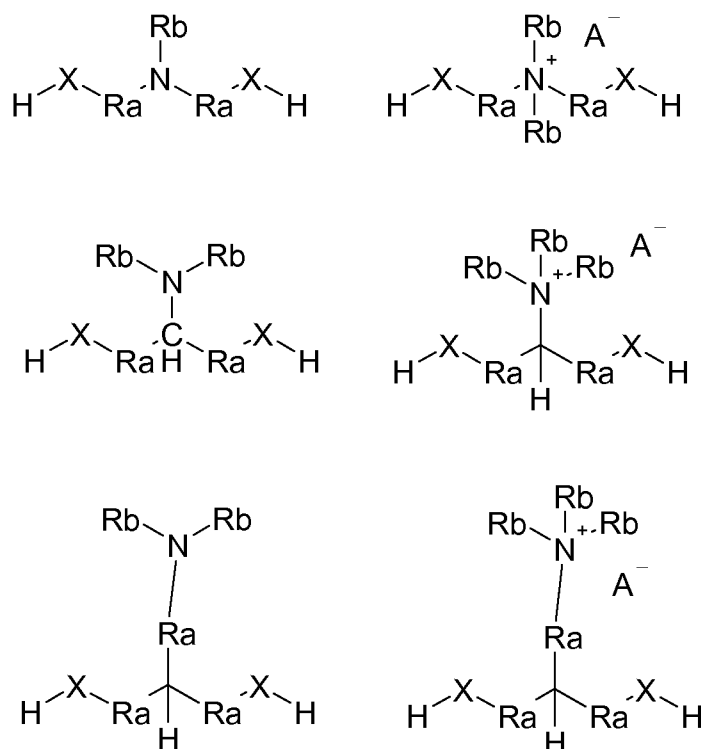
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- 14.** Use according to any one of Claims 1 to 3, in which the flocculant cationic polyurethane polymer is chosen from:

- polyurethanes of type (1) comprising a tertiary or quaternary amine function as pendent functions on the main chain, and

- polyurethanes of type (2) necessarily comprising a tertiary or quaternary amine function at the end of the main chain and optionally tertiary or quaternary amine functions as pendent functions on the main chain.

- 5 **15.** Use according to Claim 14, in which the cationic polyurethanes of type (1) comprise at least:
- (a1) cationic units derived from at least one tertiary or quaternary amine bearing at least two reactive functions containing labile hydrogen, and
- 10 (a2) nonionic units derived from oligomers or from nonionic polymers bearing at their ends reactive functions containing labile hydrogen, and
- (a3) nonionic units derived from nonionic monomer compounds containing at least two functions containing labile hydrogen, and
- (b) units derived from at least one diisocyanate.
- 15 **16.** Use according to Claim 14, in which the cationic polyurethanes of type (2) comprise at least:
- (a2) nonionic units derived from oligomers or from nonionic polymers bearing at their ends reactive functions containing labile hydrogen, and
- (a3) nonionic units derived from nonionic monomer compounds containing at least
- 20 two functions containing labile hydrogen, and
- (a4) units consisting of at least one tertiary amine and containing only one function containing labile hydrogen; the tertiary amine function possibly being quaternized, and
- (b) units derived from at least one diisocyanate, and
- 25 (a1) optionally cationic units derived from at least one tertiary or quaternary amine bearing at least two reactive functions containing labile hydrogen.
- 17.** Use according to Claim 15 or 16, in which the tertiary or quaternary amines forming the cationic units (a1) are chosen from:
- 30 (i) compounds corresponding to one of the following formulae:



in which each Ra independently represents a linear or branched C₁-C₆ alkylene, C₃-C₆ cycloalkylene or arylene group, all possibly being substituted with one or more halogen atoms and comprising one or more heteroatoms chosen from O, N, P and S, each Rb independently represents a C₁-C₆ alkyl, C₃-C₆ cycloalkyl or aryl group, all possibly being substituted with one or more halogen atoms and comprising one or more heteroatoms chosen from O, N, P and S, each X independently represents an oxygen or sulfur atom or a group NH or NRc, in which Rc represents a C₁-C₆ alkyl group, and A⁻ represents a physiologically acceptable counterion.

(ii) polymers containing tertiary and/or quaternary amine functions, bearing at their ends reactive functions containing labile hydrogen and more preferentially chosen from N-methyldiethanolamine and N-tert-butyldiethanolamine, and polyesters derived from the polycondensation of N-methyldiethanolamine and of adipic acid.

18. Use according to any one of Claims 15 to 17, in which the units (a2) are derived from nonionic polymers bearing at their ends reactive functions containing labile hydrogen and preferably having a glass transition temperature (T_g) of less than 10°C; the said units preferably being chosen from polyethers, polyesters, polysiloxanes, copolymers of ethylene and butylene, polycarbonates and fluoro polymers, and more particularly polyethers and even more particularly poly(tetramethylene oxide) and hydrogenated or non-hydrogenated polymers of ethylene and butylene.

19. Use according to any one of Claims 15 to 18, in which the units (a3) are compounds of formula: HX-R₂-XH in which each X independently represents an oxygen or sulfur atom or a group NH or NRc, in which Rc represents a C₁-C₆ alkyl group and more particularly each X is an oxygen atom, and are preferably neopentyl glycol, hexaethylene glycol or aminoethanol derivatives.

5 **20.** Use according to any one of Claims 15 to 19, in which the units (a4) are chosen from diamines comprising on the same molecule a tertiary amine unit and a primary or secondary amine unit, chosen in particular from N,N-dimethyl-1,4-butanediamine, N,N-dimethyl-1,3-propanediamine, N,N-diethyl-1,3-propanediamine, N,N-dibutyl-1,3-propanediamine, N,N-dimethyl-1,2-propanediamine, N,N-dimethyl-1,2-ethanediamine, N,N-diethyl-1,2-ethanediamine.

10 **21.** Use according to any one of Claims 15 to 20, in which the diisocyanates forming the units (b) include aliphatic, alicyclic or aromatic diisocyanates and are preferably chosen from methylenediphenyl diisocyanate, methylenecyclohexane diisocyanate, isophorone diisocyanate, toluene diisocyanate, naphthalene 10-diisocyanate, butane diisocyanate and hexyl diisocyanate.

15 **22.** Use according to any one of Claims 15 to 21, in which the units (a1) represent from 1% to 90% and preferably from 5% to 60% by weight, the units (a2) from 10% to 80% and preferably from 40% to 70% by weight, the units (a3) from 0 to 50% by weight and preferably from 0 to 30% by weight, and the units (a4) from 0 to 10% and preferably from 0 to 5% by weight of the total polymer.

20 **23.** Cosmetic process for treating perspiration, which consists in applying to the surface of the skin a composition comprising, in a cosmetically acceptable medium, at least one flocculant polymer as defined in any one of Claims 1 to 22, not containing any antiperspirant aluminium and/or zirconium salts.

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