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(54) Title: COMPOSITION COMPRISING A POLYURETHANE, A CATIONIC POLYMER, AN ORGANOSILANE AND A POLYSACCHARIDE

(57) Abstract: The present invention relates to a composition, notably a cosmetic hair composition, comprising one or more polyurethanes, one or more cationic polymers other than polyurethanes, one or more organosilanes and one or more polysaccharides. The invention also relates to the use of the composition according to the invention for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair, and notably for defining the hair curls.



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COMPOSITION COMPRISING A POLYURETHANE, A CATIONIC POLYMER, AN ORGANOSILANE AND A POLYSACCHARIDE

The present invention relates to a composition, notably a cosmetic composition,
5 notably a hair composition, comprising one or more polyurethanes, one or more cationic polymers, one or more organosilanes and one or more polysaccharides.

The invention also relates to a process for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres the composition according to the invention.

10 The invention lastly relates to the use of the composition according to the invention for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair, and notably for defining the hair curls.

Many people are unsatisfied with the appearance of their hair: in particular people who have curly hair may wish to maintain the curls but to obtain better curl definition and
15 better regularity, better movement and less volume and frizziness. Furthermore, certain people find it difficult to control, define and/or style their curly hair.

The conventional processes for modifying curly hair comprise straightening or relaxing the hair.

The processes for straightening or relaxing the hair generally involve reducing
20 agents based on thiol or strong alkaline agents.

These two techniques are based on cleavage of the disulfide covalent bonds present in keratin.

The first technique consists, in a first stage, in opening the disulfide bonds using a composition comprising a reducing agent, and then, in a second stage, after having
25 generally rinsed the hair, in reconstituting said disulfide bonds by applying to the hair, which has been placed beforehand under tension, for example by means of rollers, an oxidizing composition also known as a "fixer" (fixing step), so as to give the head of hair the desired shape.

The second technique consists in performing a lanthionization operation, using a
30 composition containing a base belonging to the hydroxide family. Contrary to the first one, this second technique does not require a fixing step, since the formation of the lanthionine bonds is irreversible. Thus, this technique makes it possible, without preference, to perform waving, relaxing, uncurling or straightening of the hair. In particular, it is mainly used for relaxing naturally curly hair.

35 However, these two techniques have many drawbacks. In particular, they lead to unpleasant odours during their use, a certain level of discomfort of the scalp and substantial degradation of the keratin fibres.

More recently, another technique has been developed, which consists in combining a heat treatment step and a step of applying a composition comprising formaldehyde. This technique is particularly effective for imparting a better appearance to damaged hair and/or for treating long hair and curly hair.

5 Formaldehyde, subjected to a temperature that may be up to 200°C or more, for example by means of an iron, crosslinks the proteins of the keratin fibres by reaction on their nucleophilic sites.

However, it is sought to avoid the use of substances such as formaldehyde, which may prove to be irritant or even highly toxic.

10 In addition, all these techniques are used to straighten and/or relax the hair for the purpose of removing the curls from the hair.

There is a need to provide compositions that can simplify the styling routine in the case of people with curly hair.

15 In particular, there is a need to provide compositions which can maintain hair curls while at the same time giving them good definition and regularity, and which make it possible to obtain good control of the frizziness and volume of the hair, while at the same time providing haircare, which may be persistent on shampooing several times.

20 Now, the applicant has just discovered, surprisingly, that a composition comprising a combination of one or more polyurethanes with one or more cationic polymers, one or more organosilanes and one or more polysaccharides makes it possible to solve the abovementioned problems.

One subject of the present invention is thus a composition comprising:

- one or more polyurethanes,
- one or more cationic polymers other than polyurethanes,
- 25 - one or more organosilanes, and
- one or more polysaccharides other than cationic polymers,

the organosilane(s) being chosen from the compounds of formula (X), oligomers thereof, hydrolysis products thereof and/or mixtures thereof:

30
$$R_1Si(OR_2)_z(R_3)_x(OH)_y \quad (X)$$

in which

- R₁ is a cyclic or acyclic, linear or branched, saturated or unsaturated C₁ to C₂₂, notably C₂ to C₂₀, hydrocarbon-based chain, which may be substituted with one or more groups chosen from amine groups NH₂ or NHR (R being a linear or branched C₁ to C₂₀, notably C₁ to C₆, alkyl, or a C₃ to C₄₀ cycloalkyl or a C₆ to C₃₀ aromatic radical); a hydroxyl group (OH); a thiol group; an aryl group (more particularly benzyl) which is
- 35 unsubstituted or substituted with an NH₂ or NHR group; it being possible for R₁ to be

interrupted with one or more oxygen, sulfur and/or nitrogen heteroatoms and/or with one or more carbonyl groups (CO);

- R2 and R3, which may be identical or different, represent a linear or branched alkyl group comprising from 1 to 6 carbon atoms,

- 5 - y denotes an integer ranging from 0 to 3,
 - z denotes an integer ranging from 0 to 3, and
 - x denotes an integer ranging from 0 to 2,
 - with $z + x + y = 3$.

10 The Applicant has notably observed that the composition according to the invention makes it possible to obtain well-defined curls, good control of the frizziness and volume of the hair, and to give the hair good manageability, these effects also persisting throughout the day, or even for several days.

15 In addition, the composition according to the invention affords a hair conditioning effect and makes it possible in particular to give a pleasant cosmetic feel, notably a smooth feel, to facilitate the disentangling of the hair and to provide sheen.

20 Moreover, the use of the composition according to the invention makes it possible to improve the persistence of the shaping of keratin fibres and of the conditioning properties; the shaping, manageability, frizz-control and conditioning properties can in particular be persistent with respect to at least one shampoo wash, in particular to at least two shampoo washes, better still to at least three shampoo washes, or even to at least four shampoo washes.

Furthermore, the composition according to the invention is easy to use, notably being applied to wet hair after shampooing, to obtain a styling effect.

25 A subject of the invention is also a process for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres the composition according to the invention.

Other subjects, characteristics, aspects and advantages of the invention will emerge even more clearly on reading the description and the example that follows.

30 In the present description, the expression "at least one" is equivalent to the expression "one or more" and can be substituted for said expression; the expression "between" is equivalent to the expression "ranging from" and can be substituted for said expression, and implies that the limits are included.

35 The composition according to the invention comprises a **polyurethane**.

The polyurethane may be associative or non-associative.

For the purposes of the present invention, the term "non-associative polyurethanes" refers to polycondensates comprising at least one polyurethane block and not comprising in their structure a terminal or pendent alkyl or alkenyl chain, including more than 10 carbon atoms. They are described in particular in the patents EP 0 751 162, EP 0 637 600, EP 0 648 485 and FR 2 743 297, of which the applicant is the proprietor, and also in the patents EP 0 656 021 and WO 94/03510 from the company BASF and EP 0 619 111 from the company National Starch.

The non-associative polyurethanes used in accordance with the invention may be soluble in the cosmetically acceptable aqueous medium, notably after neutralization with an organic or mineral base, or else may form a dispersion in this medium. The dispersion may then comprise at least 0.05% of surfactant allowing the setting in dispersion and the maintenance in dispersion of the non-associative polyurethane.

According to the invention, any type of surfactant may be used in said dispersion, but preferably a nonionic surfactant. The mean size of the non-associative polyurethane particles in the dispersion is preferably between 0.1 and 1 micrometre.

By way of example, the non-associative polyurethane may be formed by an arrangement of blocks, this arrangement being obtained notably from:

- (1) at least one compound which contains two or more than two active hydrogen atoms per molecule;
- (2) at least one diol or a mixture of diols containing acid functions or salts thereof; and
- (3) at least one diisocyanate or polyisocyanate.

Advantageously, the compounds (1) are chosen from the group comprising diols, diamines, polyesterols and polyetherols, or mixtures thereof.

The compounds (1) that are preferred are linear polyethylene glycols and polypropylene glycols, in particular those that are obtained by reaction of ethylene oxide or propylene oxide with water or diethylene or dipropylene glycol in the presence of sodium hydroxide as catalyst. These polyalkylene glycols generally have a molecular mass of between about 600 and 20 000.

Other preferred organic compounds are those which contain mercapto, amino, carboxyl or hydroxyl groups. Among these, mention is made more particularly of polyhydroxylated compounds such as polyether-diols, polyester-diols, polyacetal-diols, polyamide-diols, polyester-polyamide-diols, poly(alkylene ether)-diols, polythioether-diols and polycarbonate-diols.

The preferred polyether-diols are, for example, the products of condensation of ethylene oxide, of propylene oxide or of tetrahydrofuran, the grafted or block copolymerization or condensation products thereof, such as mixtures of condensates of

ethylene oxide and of propylene oxide, and products of polymerization of olefins, under high pressure, with alkylene oxide condensates. Suitable polyether-diols are prepared, for example, by condensation of alkylene oxides and of polyhydric alcohols, such as ethylene glycol, 1,2-propylene glycol and 1,4-butanediol.

5 The polyester-diols, polyester-amides and polyamide-diols are preferably saturated and are obtained, for example, from the reaction of saturated or unsaturated polycarboxylic acids with polyhydric alcohols, diamines or polyamines. To prepare these compounds, use may be made, for example, of adipic acid, succinic acid, phthalic acid, terephthalic acid and maleic acid. Suitable polyhydric alcohols for preparing the
10 polyesters include, for example, ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, neopentyl glycol and hexanediol. Use may also be made of amino alcohols, for instance ethanolamine. Suitable diamines for preparing the amide-polyesters are ethylenediamine and hexamethylenediamine.

 Suitable polyacetals may be prepared, for example, from 1,4-butanediol or
15 hexanediol and from formaldehyde. Suitable polythioethers may be prepared, for example, by condensation reaction between thioglycols alone or in combination with other glycols such as ethylene glycol, 1,2-propylene glycol or with other polyhydroxylated compounds. Polyhydroxylated compounds already containing urethane groups, natural polyols, which may be further modified, for example castor oil and carbohydrates, may
20 also be used.

 More preferentially, the compound of group (1) is a polyesterol, notably a polyester-diol formed by reaction of at least one (di)-polyol (1_a) and of at least one acid (1_b). The (di)-polyol (1_a) is chosen in particular from the group comprising neopentyl glycol, 1,4-butanediol, hexanediol, ethylene glycol, diethylene glycol, propylene glycol, butylene
25 glycol, neopentyl glycol and (di)-polyethylene glycol. The acid (1_b) is chosen in particular from the group comprising phthalic acid, isophthalic acid, adipic acid and (poly)lactic acid.

 As compound (2), use may be made notably of a hydroxycarboxylic acid such as dimethylolpropanoic acid (DMPA) or a 2,2-hydroxymethylcarboxylic acid. In general,
30 compound (2) is useful as a coupling block. The compounds that are preferred as compounds (2) are those comprising at least one poly(α,α -dihydroxylated carboxylic acid).

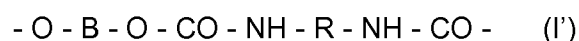
 The compounds (2) that are particularly preferred in accordance with the invention are those chosen from the group comprising 2,2-bis(hydroxymethyl)acetic acid, 2,2-dihydroxymethylpropionic acid, 2,2-dihydroxymethylbutyric acid and 2,2-dihydroxymethylpentanoic acid.
35

The diisocyanate or polyisocyanate (3) may be chosen in particular from the group comprising hexamethylene diisocyanate, isophorone diisocyanate (IPDI), tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate (DPMD) and 4,4'-dicyclohexylmethane diisocyanate (DCMD), methylenedi-p-phenyl diisocyanate, methylenebis(4-cyclohexyl isocyanate), toluene diisocyanates, 1,5-naphthalene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,2'-dimethyl-4,4'-diphenylmethane diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, mixtures of 2,4- and 2,6-toluene diisocyanates, 2,2'-dichloro-4,4'-diisocyanatodiphenylmethane, 2,4-dibromo-1,5-diisocyanatonaphthalene, 1,4-butane diisocyanate, 1,6-hexane diisocyanate and 1,4-cyclohexane diisocyanate.

The non-associative polyurethane may be formed using an additional compound (4) generally serving to extend its chain. These compounds (4) may be chosen from the group notably comprising saturated or unsaturated glycols such as ethylene glycol, diethylene glycol, neopentyl glycol, triethylene glycol; amino alcohols such as ethanolamine, propanolamine, butanolamine; heterocyclic, aromatic, cycloaliphatic and aliphatic primary amines; diamines; carboxylic acids such as aliphatic, aromatic and heterocyclic carboxylic acids, for instance oxalic acid, succinic acid, glutaric acid, adipic acid, sebacic acid and terephthalic acid; and aminocarboxylic acids. The preferred compounds (4) are aliphatic diols.

The non-associative polyurethanes used according to the invention may also be formed from additional compounds (5) bearing a silicone backbone, such as polysiloxanes, polyalkylsiloxanes or polyarylsiloxanes, notably polyethylsiloxanes, polymethylsiloxanes and polyphenylsiloxanes, optionally including hydrocarbon-based chains grafted onto the silicon atoms.

The non-associative polyurethanes advantageously used comprise a base repeating unit corresponding to the general formula (I'):



in which:

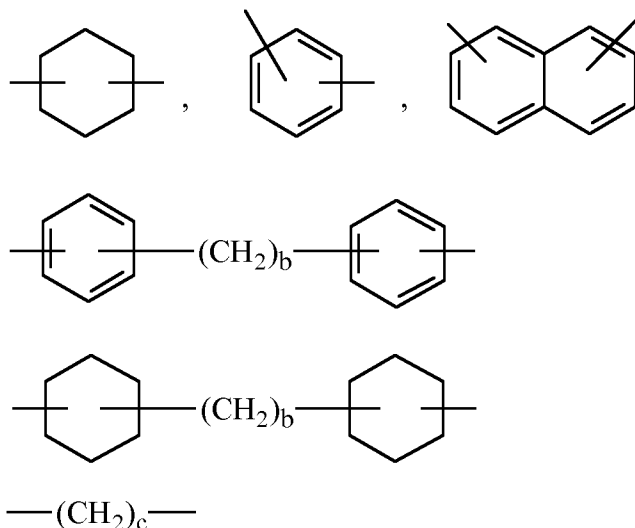
- B is a C₁ to C₃₀ divalent hydrocarbon-based group, this group being optionally substituted with a group including one or more carboxylic acid functions and/or one or more sulfonic acid functions, said carboxylic acid and/or sulfonic acid functions being in free form or else partially or totally neutralized with a mineral or organic base, and

- R is a divalent group chosen from C₁ to C₂₀ aliphatic, C₃ to C₂₀ cycloaliphatic and C₆ to C₂₀ aromatic hydrocarbon-based groups, for instance C₁ to C₂₀ alkylene, C₆ to C₂₀

arylene, C₃ to C₂₀ cycloalkylene groups, or combinations thereof, these groups being optionally substituted.

The group R is advantageously chosen from the groups corresponding to the following formulae:

5



10

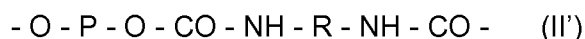
in which b is an integer between 0 and 3 and c is an integer between 1 and 20 and preferably between 2 and 12.

In particular, the group R is chosen from hexamethylene, 4,4'-biphenylenemethane, 2,4- and/or 2,6-tolylene, 1,5-naphthylene, p-phenylene and methylene-4,4-bis(cyclohexyl) groups and the divalent group derived from isophorone.

15

The non-associative polyurethane used in the present invention may also advantageously comprise at least one polysiloxane block, the base repeating unit of which corresponds, for example, to the general formula (II'):

20



in which:

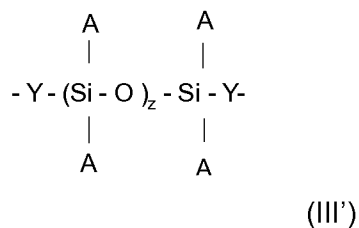
- P is a polysiloxane segment, and

- R is a divalent group chosen from C₁ to C₂₀ aliphatic, C₃ to C₂₀ cycloaliphatic and

25

C₆ to C₂₀ aromatic hydrocarbon-based groups, for instance C₁ to C₂₀ alkylene, C₆ to C₂₀ arylene, C₃ to C₂₀ cycloalkylene groups, or combinations thereof, these groups being optionally substituted.

Advantageously, the polysiloxane segment P corresponds to the general formula (III') below:



in which:

- the groups A, which may be identical or different, are chosen firstly from C₁-C₂₀ monovalent hydrocarbon-based groups that are free or substantially free of ethylenic unsaturation and, secondly, from aromatic groups,

- Y represents a divalent hydrocarbon-based group, and

- z represents an integer chosen such that the weight-average molecular mass of the polysiloxane segment is between 300 and 10 000.

Preferably, the divalent group Y is chosen from the alkylene groups of formula - (CH₂)_a-, in which a represents an integer that may be between 1 and 10.

The groups A may be chosen from C₁₋₈ alkyl groups, in particular methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl and octyl groups; C₃₋₈ cycloalkyl groups, in particular the cyclohexyl group; C₆₋₁₀ aryl groups, notably phenyl; C₇₋₁₀ arylalkyl groups, notably benzyl and phenylethyl, and also tolyl and xylyl groups.

Examples of non-associative polyurethanes that may notably be mentioned include the dimethylolpropionic acid/isophorone diisocyanate/neopentyl glycol/polyesterdiols copolymer (also known under the name polyurethane-1, INCI name) sold under the brand name Luviset® PUR by the company BASF, and the dimethylolpropionic acid/isophorone diisocyanate/neopentyl glycol/polyesterdiols/silicone diamine copolymer (also known under the name polyurethane-6, INCI name) sold under the brand name Luviset® Si PUR A by the company BASF.

The term "associative polyurethane" refers to a polyurethane bearing at least one terminal or pendent alkyl chain including at least 10 carbon atoms. This type of polymer is capable of interacting with itself or with particular compounds such as surfactants to lead to thickening of the medium.

The associative polyurethanes used in the invention may be cationic, anionic or nonionic. They are preferably anionic or nonionic.

An example of an anionic associative polyurethane that may notably be mentioned is an alkali-soluble or alkali-swellaable acrylic terpolymer. It is characterized in that it comprises:

a) about 20% to 70% by weight, preferably 25% to 55% by weight, of an α,β-monoethylenically unsaturated carboxylic acid;

b) about 20% à 80% by weight, preferably 30% to 65% by weight, of a non-surfactant monoethylenically unsaturated monomer other than a) and

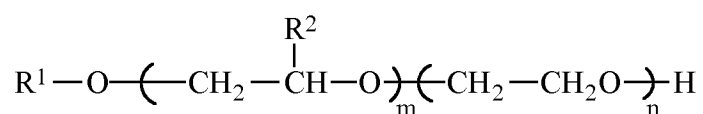
c) about 0.5% to 60% by weight, preferably 10% to 50% by weight, of a nonionic urethane monomer which is the reaction product of a monohydric nonionic surfactant
5 with a monoethylenically unsaturated monoisocyanate.

The α,β -monoethylenically unsaturated carboxylic acid a) may be chosen from numerous acids and in particular acrylic acid, methacrylic acid, itaconic acid and maleic acid. Methacrylic acid is preferred. A large proportion of acid is essential to give a polymer structure which dissolves and gives thickening by reaction with an alkaline
10 compound such as sodium hydroxide, alkanolamines, aminomethylpropanol or aminomethylpropanediol.

The terpolymer must also contain a large proportion indicated above of a monoethylenically unsaturated monomer b) which has no surfactant properties. The preferred monomers are those which give water-insoluble polymers when they are
15 homopolymerized and are illustrated by C₁-C₄ alkyl acrylates and methacrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, or the corresponding methacrylates. The monomers that are more particularly preferred are methyl and ethyl (meth)acrylates. Other monomers that may be used are styrene, vinyltoluene, vinyl acetate, acrylonitrile and vinylidene chloride. Unreactive monomers are preferred, these monomers being
20 those in which the single ethylenic group is the only group that is reactive under the polymerization conditions. However, monomers which contain groups that are reactive under the action of heat may be used in certain situations, such as hydroxyethyl acrylate.

The monohydric nonionic surfactants used to obtain the nonionic urethane monomer c) are well known and are generally alkoxyated hydrophobic compounds
25 containing an alkylene oxide forming the hydrophilic part of the molecule. The hydrophobic compounds generally consist of an aliphatic alcohol or an alkylphenol in which a carbon-based chain containing at least six carbon atoms constitutes the hydrophobic part of the surfactant.

The preferred monohydric nonionic surfactants have the formula:
30



in which R¹ is a C₆-C₃₀ alkyl or C₈-C₃₀ aralkyl group, R² is a C₁-C₄ alkyl group, n is an average number ranging from about 5 to 150 and m is an average number ranging
35 from about 0 to 50, on condition that n is at least as big as m and that n + m = 5-150.

As preferred C₆-C₃₀ alkyl groups, mention may be made of dodecyl and C₁₈-C₂₆ alkyl radicals. As aralkyl groups, mention may be made more particularly of (C₈-C₁₃)alkylphenyl groups. The preferred group R² is the methyl group.

5 The monoethylenically unsaturated monoisocyanate used to form the nonionic urethane monomer c) may be chosen from very varied compounds. Use may be made of a compound containing any copolymerizable unsaturation such as acrylic or methacrylic unsaturation. Use may also be made of allylic unsaturation imparted by allyl alcohol. The preferred monoethylenic monoisocyanates are α,α -dimethyl-m-isopropenylbenzyl isocyanate and methylstyreneisopropyl isocyanate.

10 The acrylic terpolymer defined above is obtained by aqueous emulsion copolymerization of the components a), b) and c) which is common and described in patent application EP-A-0 173 109.

As examples of anionic associative polyurethanes that may be used according to the present invention, mention may be made notably of methacrylic or acrylic acid
15 copolymers comprising at least one C₁₋₃₀ alkyl (meth)acrylate unit and a urethane unit substituted with a fatty chain. Mention may be made in particular of the methacrylic acid/methyl methacrylate/methylstyreneisopropyl isocyanate/polyethoxylated behenyl alcohol (including 40 ethoxy units) copolymer sold under the brand name Viscophobe[®] DB 1000 sold by the company Union Carbide.

20 The nonionic associative polyurethanes may notably be polyurethane polyethers including in their chain both hydrophilic blocks most usually of polyoxyethylenated nature and hydrophobic blocks which may be aliphatic sequences alone and/or cycloaliphatic and/or aromatic sequences.

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

30 The polyurethane polyethers may be multiblock, in particular in triblock form. The hydrophobic blocks may be at each end of the chain (for example: triblock copolymer bearing a hydrophilic central block) or distributed both at the ends and in the chain (for example, multiblock copolymer). These same polymers may also be graft polymers or starburst polymers.

35 The nonionic fatty-chain polyurethane polyethers may be triblock copolymers, the hydrophilic block of which is a polyoxyethylene chain including from 50 to 1000 ethoxyl

groups. The nonionic polyurethane polyethers include a urethane bond between the hydrophilic blocks, whence arises the name.

By extension, also included among the nonionic fatty-chain polyurethane polyethers are those in which the hydrophilic blocks are linked to the lipophilic blocks via
5 other chemical bonds.

As examples of nonionic fatty-chain polyurethane polyethers that may be used in the invention, mention may also be made of Rheolate 205 bearing a urea function, sold by the company Rheox, or Rheolate 208, 204 or 212, and also Acrysol® RM 184.

Mention may also be made of the product Elfacos T210 containing a C₁₂₋₁₄ alkyl
10 chain, and the product Elfacos® T212 containing a C¹⁸ alkyl chain, from Akzo.

The product DW 1206B from Röhm & Haas bearing a C₂₀ alkyl chain and a urethane bond, sold at a solids content of 20% in water, may also be used.

Use may also be made of solutions or dispersions of these polymers, notably in water or in aqueous-alcoholic medium. Examples of such polymers that may be
15 mentioned include Rheolate® 255, Rheolate® 278 and Rheolate® 244 sold by the company Rheox. Use may also be made of the products DW 1206F and DW 1206J sold by the company Röhm & Haas.

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

As preferred examples of nonionic associative polyurethanes, mention may be made of polyurethane polyethers that may be obtained by polycondensation of at least three compounds comprising (i) at least one polyethylene glycol comprising from 150 to 180 mol of ethylene oxide, (ii) stearyl alcohol or decyl alcohol, and (iii) at least one
25 diisocyanate.

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

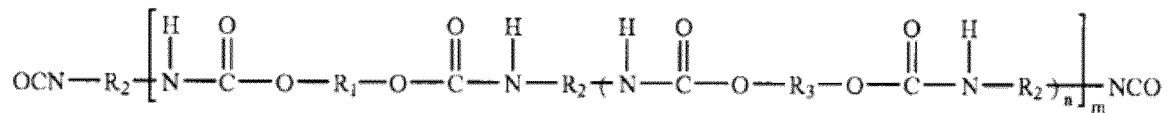
35 Preferably, the polyurethane is non-associative.

Preferably, the polyurethane is in the form of an aqueous dispersion of polyurethane particles.

The dispersion(s) may be simple dispersions in the aqueous medium of the composition. As a particular case of dispersions, mention may be made of latexes.

More particularly, the polyurethane(s) present in the aqueous dispersions used in the present invention result from the reaction of:

- 5 - a prepolymer of formula (A) below:



(A)

in which:

- 10- R_1 represents a divalent radical of a dihydroxylated compound,
 - R_2 represents a radical of an aliphatic or cycloaliphatic polyisocyanate,
 - R_3 represents a radical of a low molecular weight diol, optionally substituted with one or more ionic groups,
 - n represents an integer ranging from 1 to 5, and
 15- m is greater than 1;

- at least one chain extender according to the formula $\text{H}_2\text{N}-\text{R}_4-\text{NH}_2$ (B), in which R_4 represents an alkylene or alkylene oxide radical which is not substituted with one or more ionic or potentially ionic groups; and

- at least one chain extender according to the formula $\text{H}_2\text{N}-\text{R}_5-\text{NH}_2$ (C), in which R_5
 20 represents an alkylene radical substituted with one or more ionic or potentially ionic groups.

- Among the dihydroxylated compounds that may be used according to the present invention, mention may be made notably of the compounds containing two hydroxyl groups and having a number-average molecular weight from about 700 to about 16 000,
 25 and preferably from about 750 to about 5000. By way of example of dihydroxylated compounds having a high molecular weight, mention may be made of polyol polyesters, polyol polyethers, polyhydroxylated polycarbonates, polyhydroxylated polyacetates, polyhydroxylated polyacrylates, polyhydroxylated amide polyesters, polyhydroxylated polyalkadienes, polyhydroxylated polythioethers, and mixtures thereof. Preferably, the
 30 hydroxylated compounds are chosen from polyol polyesters, polyol polyethers, polyhydroxylated polycarbonates, and mixtures thereof.

The polyisocyanates that may be used according to the present invention are notably chosen from organic diisocyanates with a molecular weight of about 112 to 1000, and preferably about 140 to 400.

Preferably, the polyisocyanates are chosen from diisocyanates and more particularly from those represented by the general formula $R_2(NCO)_2$, in which R_2 represents a divalent aliphatic hydrocarbon-based group containing from 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon-based group containing from 5 to 15 carbon atoms, a divalent araliphatic hydrocarbon-based group containing from 7 to 15 carbon atoms or a divalent aromatic hydrocarbon-based group containing from 6 to 15 carbon atoms.

Preferably, R_2 represents an organic diisocyanate. By way of example of organic diisocyanates, the following may notably be chosen: tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,5,5-trimethylcyclohexane isocyanate (isophorone diisocyanate or IPDI), bis(4-isocyanatocyclohexyl)methane, 1,3-bis(isocyanatomethyl)cyclohexane, 1,4-bis(isocyanatomethyl)cyclohexane, bis(4-isocyanato-3-methyl-cyclohexyl)methane, isomers of toluene diisocyanate (TDI) such as toluene 2,4-diisocyanate, toluene 2,6-diisocyanate and mixtures thereof, hydrogenated toluene diisocyanate, diphenylmethane 4,4'-diisocyanate and mixtures with its diphenylmethane 2,4-diisocyanate isomers and optionally diphenylmethane 2,2'-diisocyanate, naphthalene 1,5-diisocyanate isomers, and mixtures thereof.

Preferably, the diisocyanates are aliphatic and cycloaliphatic diisocyanates, and are more preferentially chosen from 1,6-hexamethylene diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexane isocyanate, and mixtures thereof.

According to the present invention, the term "low molecular weight diol" refers to a diol with a molecular weight from about 62 to 700, and preferably from 62 to 200. These diols may comprise aliphatic, alicyclic or aromatic groups. Preferably, they comprise only aliphatic groups.

Preferably, R_3 represents a low molecular weight diol containing more than 20 carbon atoms, more preferentially chosen from ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,3-butylene glycol, neopentyl glycol, butylethylpropanediol, cyclohexanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, bisphenol A (2,2-bis(4-hydroxyphenyl)propane), hydrogenated bisphenol A (2,2-bis(4-hydroxycyclohexyl)propane), and mixtures thereof.

The low molecular weight diols may optionally comprise ionic or potentially ionic groups. Examples of low molecular weight diols containing ionic or potentially ionic groups are notably described in patent US 3 412 054. Such compounds are preferably chosen from dimethylolbutanoic acid, dimethylolpropionic acid, polycaprolactone diols containing a carboxyl group, and mixtures thereof.

If low molecular weight diols containing ionic or potentially ionic groups are used, they are preferably used in an amount such that less than 0.30 meq of COOH per gram of polyurethane is present in the polyurethane dispersion.

The prepolymer is extended by means of two chain extender families. The first
5 chain extender family corresponds to the compounds of general formula $H_2N-R_4-NH_2$ (B), in which R_4 represents an alkylene or alkylene oxide radical which is not substituted with one or more ionic or potentially ionic groups.

The chain extenders of formula (B) are preferably chosen from alkylenediamines, such as hydrazine, ethylenediamine, propylenediamine, 1,4-butylenediamine,
10 piperazine; alkylene oxide diamines, such as 3-{2-[2-(3-aminopropoxy)ethoxy]ethoxy}propylamine (also known as dipropylamine diethylene glycol or DPA-DEG available from Tomah Products, Milton, Wis.), 2-methyl-1,5-pentanediamine (Dytec A from DuPont), hexanediamine, isophorone diamine, 4,4-methylenedi(cyclohexylamine), ether-amines of the DPA series, available from Tomah
15 Products, Milton, Wis., such as dipropylamine propylene glycol, dipropylamine dipropylene glycol, dipropylamine tripropylene glycol, dipropylamine poly(propylene glycol), dipropylamine ethylene glycol, dipropylamine poly(ethylene glycol), dipropylamine 1,3-propanediol, dipropylamine 2-methyl-1,3-propanediol, dipropylamine 1,4-butanediol, dipropylamine 1,3-butanediol, dipropylamine 1,6-hexanediol and
20 dipropylamine cyclohexane-1,4-dimethanol; and mixtures thereof.

The second chain extender family corresponds to the compounds of general formula $H_2N-R_5-NH_2$ (C), in which R_5 represents an alkylene radical substituted with one or more ionic or potentially ionic groups. Such compounds preferably have an ionic or potentially ionic group and two groups that can react with isocyanate groups. Such
25 compounds can optionally comprise two groups that react with isocyanate groups and one group which is ionic or capable of forming an ionic group.

The ionic or potentially ionic group may preferably be chosen from ternary or quaternary ammonium groups or groups that can be converted into such groups, a carboxyl group, a carboxylate group, a sulfonic acid group and a sulfonate group. The at
30 least partial conversion of groups that can be converted into a ternary or quaternary ammonium group salt may be performed before or during the mixing with water.

The chain extenders of formula (C) are preferably chosen from diaminosulfonates, for instance the sodium salt of N-(2-aminoethyl)-2-aminoethanesulfonic acid (ASA), the sodium salt of N-(2-aminoethyl)-2-aminopropionic acid, and mixtures thereof.

35 The polyurethane that may be used according to the present invention may optionally also comprise compounds which are located, respectively, at the chain ends

and terminate said chains (chain terminators). Such compounds are notably described in patents US 7 445 7 452 770 and/or US 7 452 770.

Preferably, the aqueous dispersion of polyurethane particles has a viscosity of less than 2000 mPa.s at 23°C, more preferentially less than 1500, and even better still less than 1000. Even more preferably, the aqueous polyurethane dispersion has a glass transition temperature of less than 0°C.

Preferably also, the aqueous polyurethane dispersion has a solids (or active material, or dry matter) content, on the basis of the weight of the dispersion, of from 20% to 60% by weight, more preferentially from 25% to 55% by weight and even better still from 30% to 50% by weight. This is intended to mean that the polyurethane content (dry matter) of the aqueous dispersion is preferably from 20% to 60% by weight, more preferentially from 25% to 55% by weight and even better still from 30% to 50% by weight, relative to the total weight of the dispersion.

Preferably also, the aqueous dispersion of polyurethane particles has a glass transition temperature (T_g) of less than or equal to -25°C, preferably less than -35°C and more preferentially less than -40°C.

The polyurethane particles may have an average diameter ranging up to about 1000 nm, for example from about 50 nm to about 800 nm, better still from about 100 nm to about 500 nm. These particle sizes may be measured with a laser particle sizer (for example Brookhaven BI90).

As non-limiting examples of aqueous polyurethane dispersions, mention may be made of those sold under the name Baycusan® by Bayer, for instance Baycusan® C1000 (INCI name: polyurethane-34), Baycusan® C1001 (INCI name: polyurethane-34), Baycusan® C1003 (INCI name: polyurethane-32), Baycusan® C1004 (INCI name: polyurethane-35) and Baycusan® C1008 (INCI name: polyurethane-48).

Mention may also be made of the aqueous polyurethane dispersions of isophthalic acid/adipic acid copolymer/hexylene glycol/neopentyl glycol/dimethylol acid/isophorone diisocyanate (INCI name: polyurethane-1, such as Luviset® Pur, BASF), the polyurethane of polycarbonate, polyurethane and aliphatic polyurethane of aliphatic polyester (such as the Neorez® series, DSM, such as Neorez® R989, Neorez® and R-2202).

According to a preferred embodiment, the aqueous dispersion of polyurethane particles may be chosen from aqueous dispersions of adipic acid copolymer/hexylene glycol/neopentyl glycol/hexamethylene diisocyanate/sodium N-(2-aminoethyl)-2-aminoethanesulfonate/ethylenediamine.

According to a particularly preferred embodiment, the polyurethane is the compound having the INCI name polyurethane-34, preferably in the form of an aqueous particle dispersion.

- 5 The composition according to the invention may comprise a total amount of one or more polyurethanes ranging from 0.01% to 20% by weight, preferably from 0.1% to 10% by weight, more preferentially from 0.2% to 5% by weight and better still from 0.3% to 2% by weight, relative to the total weight of the composition.
- 10 The composition according to the present invention also comprises one or more **cationic polymers** other than polyurethanes, preferably having a cationic charge density greater than or equal to 4 milliequivalents/gram (meq/g), better still greater than or equal to 5 meq/g, or even ranging from 5 to 20 meq/g.

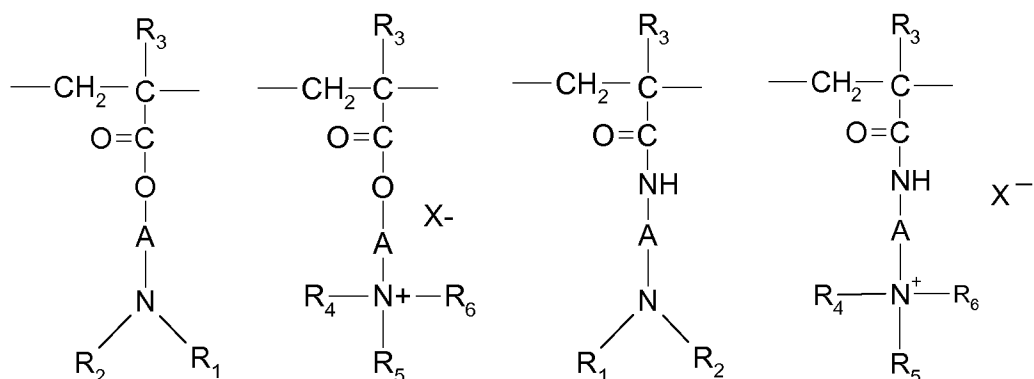
The cationic charge density of a polymer corresponds to the number of moles of cationic charges per unit mass of polymer under conditions in which it is totally ionized. It may be determined by calculation if the structure of the polymer is known, i.e. the structure of the monomers constituting the polymer and their molar proportion or weight proportion. It may also be determined experimentally by the Kjeldahl method.

For the purposes of the present invention, the expression "cationic polymer" denotes any non-silicone (not comprising any silicon atoms) polymer containing cationic groups and/or groups that can be ionized into cationic groups and not containing any anionic groups and/or groups that can be ionized into anionic groups.

The cationic polymers preferably have a weight-average molar mass (Mw) of between 500 and 5×10^6 approximately and preferably between 10^3 and 3×10^6 approximately.

Among the cationic polymers, mention may be made more particularly of:

(1) homopolymers or copolymers derived from acrylic or methacrylic esters or amides and including at least one of the units of formula (I), (II), (III) or (IV) below:



(I)

(II)

(III)

(IV)

in which:

- R3, which may be identical or different, denote a hydrogen atom or a CH3 radical;
- A, which may be identical or different, represent a linear or branched divalent alkyl group of 1 to 6 carbon atoms, preferably 2 or 3 carbon atoms, or a hydroxyalkyl group of 1 to 4 carbon atoms;
- R4, R5 and R6, which may be identical or different, represent an alkyl group containing from 1 to 18 carbon atoms or a benzyl radical, preferably an alkyl group containing from 1 to 6 carbon atoms;
- R1 and R2, which may be identical or different, represent a hydrogen atom or an alkyl group containing from 1 to 6 carbon atoms, preferably methyl or ethyl;
- X- denotes an anion derived from a mineral or organic acid, such as a methosulfate anion or a halide such as chloride or bromide.

The copolymers of family (1) may also contain one or more units derived from comonomers that may be chosen from the family of acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides substituted on the nitrogen with lower (C1-C4) alkyls, acrylic or methacrylic acid esters, vinyl lactams such as vinylpyrrolidone or vinylcaprolactam, and vinyl esters.

Among these copolymers of family (1), mention may be made of:

- copolymers of acrylamide and of dimethylaminoethyl methacrylate quaternized with dimethyl sulfate or with a dimethyl halide, such as that sold under the name Hercofloc by the company Hercules,
- copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium chloride, such as those sold under the name Bina Quat P 100 by the company Ciba Geigy,
- the copolymer of acrylamide and of methacryloyloxyethyltrimethylammonium methosulfate, such as that sold under the name Reten by the company Hercules,
- vinylpyrrolidone/methacrylamidopropyldimethylamine copolymers, such as those sold under the name Styleze CC 10 by ISP;
- preferably crosslinked polymers of methacryloyloxy(C1-C4)alkyltri(C1-C4)alkylammonium salts, such as the polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride, or by copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized with methyl chloride, the homopolymerization or copolymerization being followed by crosslinking with an olefinically unsaturated compound, in particular methylenebisacrylamide. Use may be made more particularly of a crosslinked acrylamide/methacryloyloxyethyltrimethylammonium chloride copolymer (20/80 by

weight) in the form of a dispersion comprising 50% by weight of said copolymer in mineral oil. This dispersion is sold under the name Salcare® SC 92 by the company Ciba. Use may also be made of a crosslinked methacryloyloxyethyltrimethylammonium chloride homopolymer comprising approximately 50% by weight of the homopolymer in mineral oil or in a liquid ester. These dispersions are sold under the names Salcare® SC 95 and Salcare® SC 96 by the company Ciba.

More preferentially, the cationic polymers of family (1) are chosen from quaternized or non-quaternized vinylpyrrolidone/dialkylaminoalkyl (meth)acrylate copolymers; crosslinked polymers of methacryloyloxy(C1-C4)alkyl tri(C1-C4)alkylammonium salts, such as the polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride, or by copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized with methyl chloride, the homo- or copolymerization being followed by crosslinking with an olefinically unsaturated compound, in particular methylenebisacrylamide; and mixtures thereof.

(2) cationic polysaccharides, in particular cationic galactomannan gums and celluloses. Among the cationic polysaccharides, mention may be made more particularly of cellulose ether derivatives including quaternary ammonium groups, cationic cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer and cationic galactomannan gums.

The cellulose ether derivatives including quaternary ammonium groups are notably described in FR 1 492 597, and mention may be made of the polymers sold under the name Ucare Polymer JR (JR 400 LT, JR 125 and JR 30M) or LR (LR 400 and LR 30M) by the company Amerchol. These polymers are also defined in the CTFA dictionary as quaternary ammoniums of hydroxyethylcellulose that have reacted with an epoxide substituted with a trimethylammonium group.

Cationic cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer are described notably in patent US 4 131 576, and mention may be made of hydroxyalkyl celluloses, for instance hydroxymethyl, hydroxyethyl or hydroxypropyl celluloses notably grafted with a methacryloylethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt. The commercial products corresponding to this definition are more particularly the products sold under the names Celquat L 200 and Celquat H 100 by the company National Starch.

The cationic galactomannan gums are described more particularly in patents US 3 589 578 and US 4 031 307, and mention may be made of guar gums comprising cationic trialkylammonium groups. Use is made, for example, of guar gums modified with

a 2,3-epoxypropyltrimethylammonium salt (for example, a chloride). Such products are in particular sold under the names Jaguar C13 S, Jaguar C 15, Jaguar C 17 and Jaguar C162 by the company Rhodia.

5 (3) polymers constituted of piperaziny units and of divalent alkylene or hydroxyalkylene radicals bearing linear or branched chains, optionally interrupted with oxygen, sulfur or nitrogen atoms or with aromatic or heterocyclic rings, and also the oxidation and/or quaternization products of these polymers.

10 (4) water-soluble polyaminoamides prepared in particular by polycondensation of an acidic compound with a polyamine; these polyaminoamides can be crosslinked with an epihalohydrin, a diepoxide, a dianhydride, an unsaturated dianhydride, a bis-unsaturated derivative, a bis-halohydrin, a bis-azetidinium, a bis-haloacyldiamine, a bis-alkyl halide or alternatively with an oligomer resulting from the reaction of a difunctional
15 compound which is reactive with a bis-halohydrin, a bis-azetidinium, a bis-haloacyldiamine, a bis-alkyl halide, an epihalohydrin, a diepoxide or a bis-unsaturated derivative; the crosslinking agent being used in proportions ranging from 0.025 to 0.35 mol per amine group of the polyaminoamide; these polyaminoamides can be alkylated or, if they include one or more tertiary amine functions, they can be quaternized.

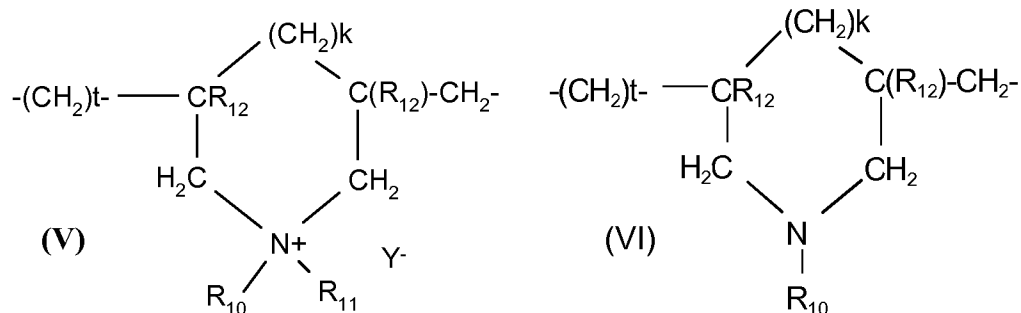
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(5) polyaminoamide derivatives resulting from the condensation of polyalkylene polyamines with polycarboxylic acids followed by alkylation with difunctional agents. Mention may be made, for example, of adipic acid/dialkylaminohydroxyalkyldialkylenetriamine polymers in which the alkyl radical
25 includes from 1 to 4 carbon atoms and preferably denotes methyl, ethyl or propyl. Among these derivatives, mention may be made more particularly of the adipic acid/dimethylaminohydroxypropyl/diethylenetriamine polymers sold under the name Cartaretine F, F4 or F8 by the company Sandoz.

30 (6) polymers obtained by reacting a polyalkylene polyamine including two primary amine groups and at least one secondary amine group with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids containing from 3 to 8 carbon atoms; the mole ratio between the polyalkylene polyamine and the dicarboxylic acid preferably being between 0.8:1 and 1.4:1; the resulting polyaminoamide being
35 reacted with epichlorohydrin in a mole ratio of epichlorohydrin relative to the secondary amine group of the polyaminoamide preferably of between 0.5:1 and 1.8:1. Polymers of this type are sold in particular under the name Hercosett 57 by the company Hercules

Inc. or else under the name PD 170 or Delsette 101 by the company Hercules in the case of the adipic acid/epoxypropyl/diethylenetriamine copolymer.

(7) cyclopolymers of alkyldiallylamine or of dialkyldiallylammonium, such as the
5 homopolymers or copolymers including, as main constituent of the chain, units
corresponding to formula (V) or (VI):

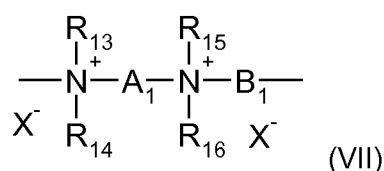


in which

- 10 - k and t are equal to 0 or 1, the sum $k + t$ being equal to 1;
 - R12 denotes a hydrogen atom or a methyl radical;
 - R10 and R11, independently of each other, denote a C1-C6 alkyl group, a C1-C5 hydroxyalkyl group, a C1-C4 amidoalkyl group; or alternatively R10 and R11 may denote, together with the nitrogen atom to which they are attached, a heterocyclic group such as
 15 piperidyl or morpholinyll; R10 and R11, independently of each other, preferably denote a C1-C4 alkyl group;
 - Y- is an anion such as bromide, chloride, acetate, borate, citrate, tartrate, bisulfate, bisulfite, sulfate or phosphate.

20 Mention may be made more particularly of the homopolymer of dimethyldiallylammonium salts (for example chloride) for example sold under the name Merquat 100 by the company Nalco and the copolymers of diallyldimethylammonium salts (for example chloride) and of acrylamide, sold in particular under the name Merquat 550 or Merquat 7SPR.

25 (8) quaternary diammonium polymers comprising repeating units of formula (VII)
below:



in which:

- R13, R14, R15 and R16, which may be identical or different, represent aliphatic, alicyclic or arylaliphatic radicals comprising from 1 to 20 carbon atoms or C1-C12 hydroxyalkyl aliphatic radicals;

5 or else R13, R14, R15 and R16, together or separately, form, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second non-nitrogen heteroatom;

or else R13, R14, R15 and R16 represent a linear or branched C1-C6 alkyl radical substituted with a nitrile, ester, acyl, amide or -CO-O-R17-D or -CO-NH-R17-D group, where R17 is an alkylene and D is a quaternary ammonium group;

10 - A1 and B1 represent linear or branched, saturated or unsaturated, divalent polymethylene groups comprising from 2 to 20 carbon atoms, which may contain, linked to or intercalated in the main chain, one or more aromatic rings or one or more oxygen or sulfur atoms or sulfoxide, sulfone, disulfide, amino, alkylamino, hydroxyl, quaternary ammonium, ureido, amide or ester groups, and

15 - X- denotes an anion derived from a mineral or organic acid;

it being understood that A1, R13 and R15 can form, with the two nitrogen atoms to which they are attached, a piperazine ring;

in addition, if A1 denotes a linear or branched, saturated or unsaturated alkylene or hydroxyalkylene radical, B1 may also denote a group $(CH_2)_n-CO-D-OC-(CH_2)_p-$ with
20 n and p, which may be identical or different, being integers ranging from 2 to 20, and D denoting:

a) a glycol residue of formula $-O-Z-O-$, in which Z denotes a linear or branched hydrocarbon-based radical or a group corresponding to one of the following formulae: $-(CH_2CH_2O)_x-CH_2CH_2-$ and $-[CH_2CH(CH_3)O]_y-CH_2CH(CH_3)-$, in which x and y denote
25 an integer from 1 to 4, representing a defined and unique degree of polymerization or any number from 1 to 4 representing an average degree of polymerization;

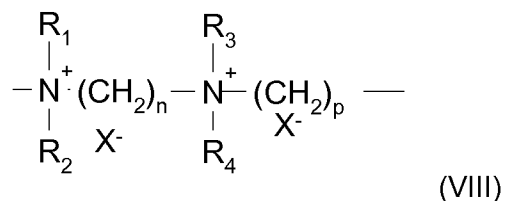
b) a bis-secondary diamine residue, such as a piperazine derivative;

c) a bis-primary diamine residue of formula $-NH-Y-NH-$, in which Y denotes a linear or branched hydrocarbon-based radical, or else the divalent radical $-CH_2-CH_2-S-S-CH_2-$
30 CH_2- ;

d) an ureylene group of formula $-NH-CO-NH-$.

Preferably, X- is an anion such as chloride or bromide. These polymers have a number-average molar mass (M_n) generally of between 1000 and 100 000.

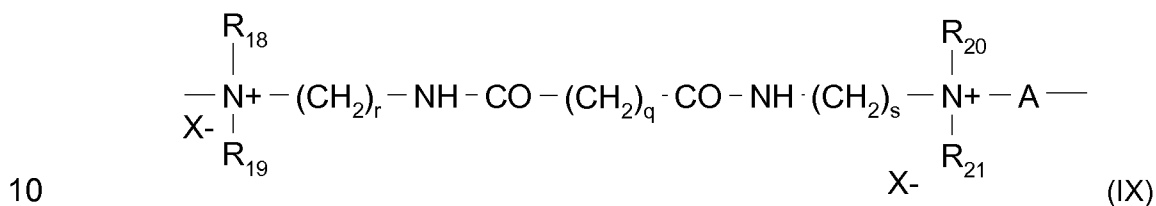
35 Mention may be made more particularly of polymers that are composed of repeating units corresponding to the formula (VIII):



in which R1, R2, R3 and R4, which may be identical or different, denote an alkyl or hydroxyalkyl radical containing from 1 to 4 carbon atoms, n and p are integers ranging from 2 to 20, and X⁻ is an anion derived from a mineral or organic acid.

- 5 A particularly preferred compound of formula (X) is the one for which R1, R2, R3 and R4 represent a methyl radical and n = 3, p = 6 and X = Cl, known as hexadimethrine chloride according to the INCI (CTFA) nomenclature.

(9) polyquaternary ammonium polymers comprising units of formula (IX):



in which:

- R18, R19, R20 and R21, which may be identical or different, represent a hydrogen atom or a methyl, ethyl, propyl, β-hydroxyethyl, β-hydroxypropyl or -CH₂CH₂(OCH₂CH₂)_pOH radical, in which p is equal to 0 or to an integer between 1 and 6, with the proviso that R18, R19, R20 and R21 do not simultaneously represent a hydrogen atom,
- r and s, which may be identical or different, are integers between 1 and 6,
- q is equal to 0 or to an integer between 1 and 34,
- X⁻ denotes an anion such as a halide,
- A denotes a divalent dihalide radical or preferably represents -CH₂CH₂OCH₂CH₂-.

Examples that may be mentioned include the products Mirapol® A 15, Mirapol® AD1, Mirapol® AZ1 and Mirapol® 175 sold by the company Miranol.

- 25 (10) Polyamines such as Polyquart® H sold by Cognis, referred to under the name Polyethylene glycol (15) tallow polyamine in the CTFA dictionary; and

(11) Mixtures of the above polymers.

Other cationic polymers that may be used in the context of the invention are cationic proteins or cationic protein hydrolysates, polyalkyleneimines, in particular polyethyleneimines, polymers comprising vinylpyridine or vinylpyridinium units, condensates of polyamines and of epichlorohydrin, quaternary polyureylenes and chitin
5 derivatives.

Preferably, the cationic polymers are chosen from those of families (1), (7) and (8) mentioned above, and mixtures thereof.

10 Among the cationic polymers mentioned above, use may preferably be made of cationic cyclopolymers, in particular homopolymers or copolymers of dimethyldiallylammonium salts (for example chloride), sold under the names Merquat 100, Merquat 550 and Merquat S by the company Nalco, optionally crosslinked homopolymers or copolymers of methacryloyloxy(C1-C4)alkyltri(C1-C4)alkylammonium
15 salts, and mixtures thereof.

According to a preferred embodiment of the invention, the cationic polymer(s) are chosen from:

alkyldiallylamine or dialkyldiallylammonium cyclopolymers,
20 homopolymers or copolymers derived from acrylic or methacrylic esters or amides and including units as defined in family (1),
and mixtures thereof.

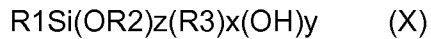
More preferentially, according to this embodiment of the invention, the cationic polymer(s) are chosen from 2-methacryloyloxyethyltrimethylammonium chloride
25 homopolymers or copolymers, dimethyldiallylammonium chloride homopolymers, and mixtures thereof.

Preferably, the composition comprises at least two cationic polymers other than polyurethanes.

According to the invention, the total content of the cationic polymer(s) other than
30 polyurethanes present in the composition is preferably between 0.01% and 15% by weight, preferably between 0.05% and 10% by weight, even more preferentially between 0.1% and 5% by weight and better still between 1% and 3% by weight, relative to the total weight of the composition.

35 The composition according to the present invention comprises one or more **organosilanes**.

The organosilane(s) that may be used according to the invention are preferably chosen from the compounds of formula (X), oligomers thereof, hydrolysis products thereof and/or mixtures thereof:



5 in which

- R1 is a cyclic or acyclic, linear or branched, saturated or unsaturated C1 to C22, notably C2 to C20, hydrocarbon-based chain, which may be substituted with one or more groups chosen from amine groups NH₂ or NHR (R being a linear or branched C1 to C20, notably C1 to C6, alkyl, or a C3 to C40 cycloalkyl or a C6 to C30 aromatic radical); a
10 hydroxyl group (OH); a thiol group; an aryl group (more particularly benzyl) which is unsubstituted or substituted with one or more NH₂ or NHR groups; it being possible for R1 to be interrupted with one or more oxygen, sulfur and/or nitrogen heteroatoms and/or with one or more carbonyl groups (CO);

- R2 and R3, which may be identical or different, represent a linear or branched
15 alkyl group comprising from 1 to 6 carbon atoms,

- y denotes an integer ranging from 0 to 3,

- z denotes an integer ranging from 0 to 3, and

- x denotes an integer ranging from 0 to 2,

- with $z + x + y = 3$.

20 For the purposes of the present invention, the term "oligomer" refers to the polymerization products of the compounds of formula (X) including from 2 to 10 silicon atoms.

Preferably, R1 is a linear or branched, more preferentially linear, saturated C1 to C22 and notably C2 to C12 hydrocarbon-based chain, which may be substituted with an
25 amine group NH₂ or NHR, R being a C1 to C20, and notably C1 to C6, alkyl.

Preferably, R2 represents an alkyl group comprising from 1 to 4 carbon atoms, more preferentially a linear alkyl group comprising from 1 to 4 carbon atoms, and in particular the ethyl group.

Preferably, z ranges from 1 to 3.

30 Preferably, y is equal to 0.

Preferentially, z is equal to 3.

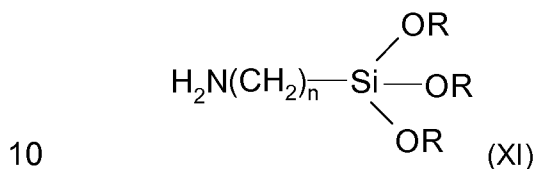
Even more preferentially, x and y are equal to 0 and z is equal to 3.

In one embodiment of the invention, the organosilane(s) are chosen from the
35 compounds of formula (X) in which R1 represents a linear alkyl group including from 1 to 18 carbon atoms and more particularly from 1 to 12 carbon atoms, or a C1 to C6 and preferably C2 to C4 aminoalkyl group.

Particularly preferably, in this embodiment, R1 represents a methyl or octyl group.

In another embodiment of the invention, the organosilane(s) are chosen from the compounds of formula (X) in which R1 is a linear or branched, saturated or unsaturated C1 to C22 hydrocarbon-based chain, substituted with one or more amine groups NH₂ or
 5 NHR, R being a linear or branched C1 to C20, preferably C1 to C6, alkyl, or a C3 to C40 cycloalkyl or a C6 to C30 aromatic.

Particularly preferably, in this other embodiment, the organosilane(s) are chosen from the compounds of formula (XI), oligomers thereof, hydrolysis products thereof and/or mixtures thereof:



in which

the radicals R, which may be identical or different, are chosen from linear or branched C1 to C6, more preferentially C2 to C4, alkyl radicals; and

n is an integer ranging from 1 to 6, more preferentially from 2 to 4.

15

Preferably, the organosilane(s) that may be used according to the invention are chosen from methyltriethoxysilane, octyltriethoxysilane (OTES), dodecyltriethoxysilane, octadecyltriethoxysilane, hexadecyltriethoxysilane, 3-aminopropyltriethoxysilane (APTES), 2-aminoethyltriethoxysilane (AETES), 3-aminopropylmethyldiethoxysilane, N-
 20 (2-aminoethyl)-3-aminopropyltriethoxysilane, 3-(m-aminophenoxy)propyltrimethoxysilane, p-aminophenyltrimethoxysilane, N-(2-aminoethylaminomethyl)phenethyltrimethoxysilane, oligomers thereof, hydrolysis products thereof, and mixtures thereof; and preferably the organosilane(s) are chosen from methyltriethoxysilane, octyltriethoxysilane (OTES) and 3-
 25 aminopropyltriethoxysilane (APTES), oligomers thereof, hydrolysis products thereof, and mixtures thereof; and even more preferentially from 3-aminopropyltriethoxysilane (APTES), oligomers thereof, hydrolysis products thereof, and mixtures thereof.

The organosilanes used in the composition of the invention, notably those including a basic function, may be partially or totally neutralized in order to improve the water
 30 solubility thereof. In particular, the neutralizer may be chosen from organic or mineral acids, such as citric acid, tartaric acid, lactic acid and hydrochloric acid.

Preferably, the optionally neutralized organosilane(s) that may be used according to the invention are water-soluble and notably soluble at a concentration of 2% by weight, better still at a concentration of 5% by weight and even better still at a concentration of

10% by weight in water at a temperature of 25°C and at atmospheric pressure (1 atm). The term "soluble" implies the formation of a single macroscopic phase.

According to the invention, the total content of the organosilane(s) present in the composition is between 0.1% and 15% by weight, preferably between 1% and 10% by weight, and more preferentially between 2% and 8% by weight, relative to the total weight of the composition.

As indicated previously, the composition according to the invention comprises one or more **polysaccharides** other than the cationic polymers described previously.

10 Preferably, the polysaccharide(s) according to the invention are chosen from nonionic, anionic and amphoteric polysaccharides.

For the purposes of the present invention, the term "polysaccharides" refers to a polymer constituted of sugar units.

15 For the purposes of the present invention, the term "sugar unit" refers to an oxygen-bearing hydrocarbon-based compound containing several alcohol functions, with or without aldehyde or ketone functions, and which includes at least 4 carbon atoms.

The sugar units may be optionally modified by substitution, and/or by oxidation and/or by dehydration.

20 The sugar units that may be included in the composition of the polysaccharides of the invention are preferably derived from the following sugars: glucose, galactose, arabinose, rhamnose, mannose, xylose, fucose, anhydrogalactose, galacturonic acid, glucuronic acid, mannuronic acid, galactose sulfate, anhydrogalactose sulfate and fructose.

Polysaccharides that may notably be mentioned include native gums such as:

25 a) tree or shrub exudates, including:

- gum arabic (branched polymer of galactose, arabinose, rhamnose and glucuronic acid);

- ghatti gum (polymer derived from arabinose, galactose, mannose, xylose and glucuronic acid);

30 - karaya gum (polymer derived from galacturonic acid, galactose, rhamnose and glucuronic acid);

- gum tragacanth (polymer of galacturonic acid, galactose, fucose, xylose and arabinose);

b) gums derived from algae, including:

35 - agar (polymer derived from galactose and anhydrogalactose);

- alginates (polymers of mannuronic acid and of glucuronic acid);

- carrageenans and furcellerans (polymers of galactose sulfate and of anhydrogalactose sulfate);

c) gums derived from seeds or tubers, including:

- guar gum (polymer of mannose and galactose);
- 5 - locust bean gum (polymer of mannose and galactose);
- fenugreek gum (polymer of mannose and galactose);
- tamarind gum (polymer of galactose, xylose and glucose);
- konjac gum (polymer of glucose and mannose);

d) microbial gums, including:

- 10 - xanthan gum (polymer of glucose, mannose acetate, mannose/pyruvic acid and glucuronic acid);

- gellan gum (polymer of partially acylated glucose, rhamnose and glucuronic acid);

- scleroglucan gum (glucose polymer);

e) polymers extracted from plants, including:

- 15 - celluloses (glucose polymers);
- starches (glucose polymers) and
- inulin.

The polysaccharide(s) of the composition according to the invention may also be chosen from mixtures of the polysaccharides above.

- 20 These polymers may be physically or chemically modified. As physical treatment, mention may notably be made of a heat treatment.

Chemical treatments that may be mentioned include esterification, etherification, amidation and oxidation reactions. These treatments make it possible to produce polymers that may notably be nonionic, anionic or amphoteric.

- 25 Preferably, these chemical or physical treatments are applied to guar gums, locust bean gums, starches and celluloses.

The nonionic guar gums that may be used according to the invention may be modified with C1-C6 (poly)hydroxyalkyl groups.

- 30 Among the C1-C6 (poly)hydroxyalkyl groups, examples that may be mentioned include hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl groups.

These guar gums are well known from the prior art and may be prepared, for example, by reacting corresponding alkene oxides, for instance propylene oxides, with the guar gum so as to obtain a guar gum modified with hydroxypropyl groups.

- 35 The degree of hydroxyalkylation preferably ranges from 0.4 to 1.2 and corresponds to the number of alkylene oxide molecules consumed by the number of free hydroxyl functions present on the guar gum.

Such nonionic guar gums optionally modified with hydroxyalkyl groups are sold, for example, under the trade names Jaguar HP8, Jaguar HP60 and Jaguar HP120, Jaguar DC 293 and Jaguar HP 105 by the company Rhodia Chimie or under the name Galactasol 4H4FD2 by the company Aqualon.

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

10 Distarch phosphates or compounds rich in distarch phosphate will preferentially be used, for instance the product sold under the references Prejel VA-70-T AGGL (gelatinized hydroxypropyl cassava distarch phosphate), Prejel TK1 (gelatinized cassava distarch phosphate) or Prejel 200 (gelatinized acetyl cassava distarch phosphate) by the company Avebe, or Structure Zea from National Starch (gelatinized corn distarch phosphate).

15 According to the invention, amphoteric starches may also be used, these amphoteric starches comprising one or more anionic groups and one or more cationic groups. The anionic and cationic groups may be bonded to the same reactive site of the starch molecule or to different reactive sites; they are preferably bonded to the same reactive site. The anionic groups may be of carboxylic, phosphate or sulfate type, preferably carboxylic. The cationic groups may be of primary, secondary, tertiary or
20 quaternary amine type.

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

 The polysaccharides that may be used according to the invention may be cellulose-based polymers.

 According to the invention, the term "cellulose-based polymer" refers to any polysaccharide compound bearing in its structure sequences of glucose residues linked
30 together via β -1,4 bonds; in addition to unsubstituted celluloses, the cellulose derivatives may be anionic, cationic, amphoteric or nonionic.

 Thus, the cellulose-based polymers that may be used according to the invention may be chosen from unsubstituted celluloses, including those in a microcrystalline form, and cellulose ethers.

35 Among these cellulose-based polymers, cellulose ethers, cellulose esters and cellulose ester ethers are distinguished.

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

Among the nonionic cellulose ethers, mention may be made of (C1-C4)alkylcelluloses such as methylcelluloses and ethylcelluloses (for example Ethocel Standard 100 Premium from Dow Chemical); (poly)hydroxy(C1-C4)alkylcelluloses such as hydroxymethylcelluloses, hydroxyethylcelluloses (for example Natrosol 250 HHR sold by Ashland) and hydroxypropylcelluloses (for example Klucel EF, Klucel H, Klucel LHF, Klucel MF and Klucel G from Aqualon and Cellosize Polymer PCG-10 from the company Amerchol); (poly)hydroxy(C1-C4)alkyl-(C1-C4)alkylcellulose mixed celluloses such as hydroxypropyl-methylcelluloses (for example Methocel E4M from Dow Chemical), hydroxyethyl-methylcelluloses, hydroxyethyl-ethylcelluloses (for example Bermocoll E 481 FQ from AkzoNobel) and hydroxybutyl-methylcelluloses.

Among the anionic cellulose ethers, mention may be made of (poly)carboxy(C1-C4)alkylcelluloses and salts thereof. Examples that may be mentioned include carboxymethylcelluloses, carboxymethylmethylcelluloses (for example Blanose 7M from the company Aqualon) and carboxymethylhydroxyethylcelluloses, and the sodium salts thereof.

Preferably, the composition according to the invention comprises one or more nonionic polysaccharides.

Nonionic polysaccharides that may notably be mentioned include those chosen from glucans, modified or unmodified starches (such as those resulting, for example, from cereals, such as wheat, corn or rice, from legumes, such as yellow pea, or from tubers, such as potato or cassava), amylose, amylopectin, glycogen, dextrans, celluloses and derivatives thereof (methylcelluloses, hydroxyalkylcelluloses, ethylhydroxyethylcelluloses), mannans, xylans, lignins, arabans, galactans, galacturonans, chitin, chitosans, glucuronoxylans, arabinoxylans, xyloglucans, glucomannans, pectic acids and pectins, arabinogalactans, carrageenans, agars, gums arabic, gums tragacanth, ghatti gums, karaya gums, locust bean gums, galactomannans, such as guar gums and nonionic derivatives thereof (hydroxypropyl guar), and mixtures thereof.

Preferably, the polysaccharide(s) according to the invention are chosen from guar gums and/or derivatives thereof which are nonionic, and/or mixtures thereof; more preferentially from nonionic guar gums modified with hydroxyalkyl groups.

Preferably, the total content of the polysaccharide(s) other than cationic polymers
 5 is between 0.01% and 20% by weight, preferentially between 0.1% and 10% by weight, even better still between 0.2% and 5% by weight, and better still between 0.5% and 3% by weight relative to the total weight of the composition.

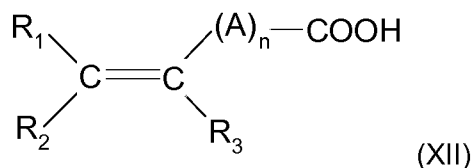
The composition according to the present invention may also comprise one or more
 10 **fixing polymers** other than the polyurethanes and other than the cationic polymers described previously.

The term "fixing polymer" refers to any polymer that is capable of giving a shape to a head of hair or of maintaining a head of hair in a given shape.

The fixing polymer(s) used may be chosen from anionic, cationic, amphoteric and
 15 nonionic fixing polymers, and mixtures thereof.

Anionic fixing polymers that may be mentioned include polymers including groups derived from carboxylic, sulfonic or phosphoric acids, and having a number-average molecular mass of between 500 and 5 000 000.

The carboxylic groups are provided by unsaturated monocarboxylic or dicarboxylic
 20 acid monomers, such as those corresponding to formula (XII):



in which

n is an integer from 0 to 10,

A denotes a methylene group, optionally connected to the carbon atom of the
 25 unsaturated group or to the adjacent methylene group, when n is greater than 1, via a heteroatom, such as oxygen or sulfur,

R1 denotes a hydrogen atom or a phenyl or benzyl group,

R2 denotes a hydrogen atom, an alkyl group including from 1 to 4 carbon atoms or
 a carboxyl group,

30 R3 denotes a hydrogen atom, an alkyl group including from 1 to 4 carbon atoms, a $-CH_2-COOH$ group, a phenyl group or a benzyl group.

In formula (XII) above, the alkyl group including from 1 to 4 carbon atoms may in particular denote methyl and ethyl groups.

The anionic fixing polymers bearing carboxylic or sulfonic groups that are preferred are:

A) copolymers of acrylic or methacrylic acid or salts thereof, including copolymers of acrylic acid and acrylamide, and methacrylic acid/acrylic acid/ethyl acrylate/methyl methacrylate copolymers, particularly Amerhold DR 25 sold by the company Amerchol, and sodium salts of polyhydroxycarboxylic acids. Mention may also be made of methacrylic acid/ethyl acrylate copolymers, in particular in aqueous dispersion, such as Luviflex Soft and Luvimer MAE, which are sold by the company BASF.

B) copolymers of acrylic or methacrylic acids with a monoethylenic monomer such as ethylene, styrene, vinyl esters and acrylic or methacrylic acid esters, optionally grafted onto a polyalkylene glycol such as polyethylene glycol and optionally crosslinked. Such polymers are described in particular in French patent 1 222 944 and German application No. 2 330 956, the copolymers of this type including an optionally N-alkylated and/or hydroxyalkylated acrylamide unit in their chain as described notably in Luxembourg patent applications 75370 and 75371. Mention may also be made of copolymers of acrylic acid and C1-C4 alkyl methacrylate.

As another anionic fixing polymer from this class, mention may also be made of the butyl acrylate/acrylic acid/methacrylic acid branched block anionic polymer sold under the name Fixate G-100 L by the company Lubrizol (INCI name AMP-Acrylates/Allyl Methacrylate Copolymer).

C) copolymers derived from crotonic acid, such as those of which the chain includes vinyl acetate or propionate units and optionally other monomers such as allyl or methallyl esters, vinyl ether or vinyl ester of a saturated, linear or branched carboxylic acid bearing a long hydrocarbon-based chain such as those including at least 5 carbon atoms, it being possible for these polymers to be optionally grafted and crosslinked, or alternatively a vinyl, allyl or methallyl ester of an α - or β -cyclic carboxylic acid. Such polymers are described, *inter alia*, in French patents Nos. 1 222 944, 1 580 545, 2 265 782, 2 265 781, 1 564 110 and 2 439 798. Commercial products that fall within this category are the resins 282930, 261314 and 281310 sold by the company National Starch.

Mention may also be made, as copolymer derived from crotonic acid, of crotonic acid/vinyl acetate/vinyl tert-butylbenzoate terpolymers, and particularly Mexomer PW supplied by the company Chimex.

D) polymers derived from maleic, fumaric or itaconic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives or acrylic acid and esters thereof; these polymers may be esterified. Such polymers are described in particular in

US patents 2 047 398, 2 723 248 and 2 102 113 and GB patent 839 805, and notably those sold under the names Gantrez® AN or ES by the company ISP.

Polymers also falling within this category are the copolymers of maleic, citraconic or itaconic anhydrides and of an allylic or methallylic ester optionally including an acrylamide or methacrylamide group, an α -olefin, acrylic or methacrylic esters, acrylic or methacrylic acids or vinylpyrrolidone in their chain, the anhydride functions being monoesterified or monoamidated. These polymers are described, for example, in French patents 2 350 384 and 2 357 241 by the Applicant.

E) polyacrylamides including carboxylate groups.

F) polymers comprising sulfonic groups. These polymers may be polymers including vinylsulfonic, styrenesulfonic, naphthalenesulfonic, acrylamidoalkylsulfonic or sulfoisophthalate units.

These polymers may be notably chosen from:

- polyvinylsulfonic acid salts with a molecular mass of between 1000 and 100 000 approximately, and also the copolymers with an unsaturated comonomer such as acrylic or methacrylic acids and esters thereof, and also acrylamide or derivatives thereof, vinyl ethers and vinylpyrrolidone;

- polystyrenesulfonic acid salts and sodium salts, with a molecular mass of about 500 000 and of about 100 000. These compounds are described in patent FR 2198719;

- polyacrylamidesulfonic acid salts such as those mentioned in patent US 4 128 631;

G) grafted anionic silicone polymers.

The grafted silicone polymers used are preferentially chosen from polymers bearing a non-silicone organic backbone grafted with monomers containing a polysiloxane, polymers bearing a polysiloxane backbone grafted with non-silicone organic monomers, and mixtures thereof.

Polymers containing sulfoisophthalate groups, such as the polymers AQ55 and AQ48 sold by the company Eastman, may also be used.

According to the invention, the anionic fixing polymers are preferably chosen from acrylic acid copolymers, such as the acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymer sold under the name Ultrahold Strong® by the company BASF, methacrylic acid/ethyl acrylate copolymers, notably in aqueous dispersion, such as Luviflex Soft and Luvimer MAE sold by the company BASF, crotonic acid-based copolymers, such as the vinyl acetate/vinyl tert-butylbenzoate/crotonic acid terpolymers and the crotonic acid/vinyl acetate/vinyl neododecanoate terpolymers sold under the name Resin 28-29-30 by the company National Starch, polymers derived from maleic, fumaric or itaconic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives,

acrylic acid and its esters, such as the monoesterified methyl vinyl ether/maleic anhydride copolymer sold under the name Gantrez® ES 425 by the company ISP, Mexomer PW, polymers comprising sulfoisophthalate groups, and anionic fixing polymers of the B) class; and even more particularly, use is preferably made of the butyl acrylate/acrylic acid/methacrylic acid branched block anionic polymer sold under the name Fixate G-100 L by the company Lubrizol (INCI name: AMP-Acrylates/Allyl Methacrylate Copolymer).

The amphoteric fixing polymers that may be used in accordance with the invention may be chosen from polymers including units B and C distributed randomly in the polymer chain, in which B denotes a unit derived from a monomer including at least one basic nitrogen atom and C denotes a unit derived from an acid monomer including one or more carboxylic or sulfonic groups, or alternatively B and C may denote groups derived from carboxybetaine or sulfobetaine zwitterionic monomers; B and C may also denote a cationic polymer chain including primary, secondary, tertiary or quaternary amine groups, in which at least one of the amine groups bears a carboxylic or sulfonic group connected via a hydrocarbon-based group, or alternatively B and C form part of a chain of a polymer bearing an ethylenedicarboxylic unit in which one of the carboxylic groups has been made to react with a polyamine including one or more primary or secondary amine groups.

The amphoteric fixing polymers corresponding to the definition given above that are more particularly preferred are chosen from the following polymers:

1) Polymers resulting from the copolymerization of a monomer derived from a vinyl compound bearing a carboxylic group, such as, more particularly, acrylic acid, methacrylic acid, maleic acid, α -chloroacrylic acid, and a basic monomer derived from a substituted vinyl compound containing at least one basic atom, such as, more particularly, dialkylaminoalkyl methacrylate and acrylate, dialkylaminoalkyl methacrylamide and acrylamide. Such compounds are described in US patent 3 836 537.

The vinyl compound may also be a dialkyldiallylammonium salt such as diethyldiallylammonium chloride.

2) Polymers including units derived:

a) from at least one monomer chosen from acrylamides and methacrylamides substituted on the nitrogen with an alkyl group,

b) from at least one acidic comonomer containing one or more reactive carboxylic groups, and

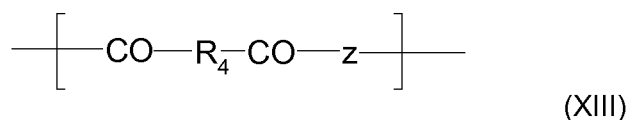
c) from at least one basic comonomer such as acrylic and methacrylic acid esters containing primary, secondary, tertiary and quaternary amine substituents, and the

product of quaternization of dimethylaminoethyl methacrylate with dimethyl or diethyl sulfate.

The N-substituted acrylamides or methacrylamides that are more particularly preferred according to the invention are groups in which the alkyl groups contain from 2 to 12 carbon atoms and more particularly N-ethylacrylamide, N-tert-butylacrylamide, N-tert-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide, and the corresponding methacrylamides.

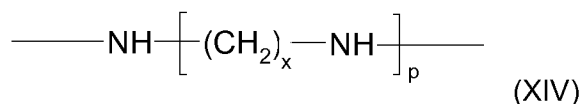
The acidic comonomers are more particularly chosen from acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid and alkyl monoesters, containing 1 to 4 carbon atoms, of maleic or fumaric acids or anhydrides. The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert-butylaminoethyl methacrylates. The copolymers of which the CTFA (4th edition, 1991) name is octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer, such as the products sold under the name Amphomer® or Lovocryl® 47 by the company National Starch, are particularly used.

3) Crosslinked and alkylated polyaminoamides partially or totally derived from polyaminoamides of general formula (XIII):



in which R₄ represents a divalent group derived from a saturated dicarboxylic acid, from a mono- or dicarboxylic aliphatic acid with an ethylenic double bond, from an ester of an alcohol containing 1 to 6 carbon atoms with these acids, or from a group derived from the addition of any one of said acids with a bis-primary amine or bis-secondary-derived amine, and Z denotes a group of a bis-primary or mono- or bis-secondary polyalkylene-polyamine, and preferably represents:

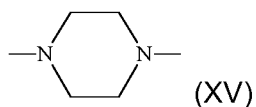
a) in proportions of from 60 mol% to 100 mol%, the group (XIV)



in which x = 2 and p = 2 or 3, or else x = 3 and p = 2,

this group being derived from diethylenetriamine, from triethylenetetramine or from dipropylenetriamine;

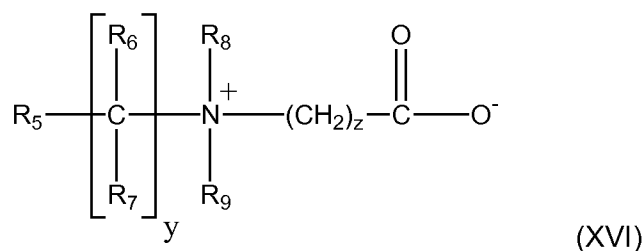
b) in proportions of from 0 mol% to 40 mol%, the group (XIV) above, in which x = 2 and p = 1, which derives from ethylenediamine, or the group derived from piperazine



c) in proportions of from 0 mol% to 20 mol%, the -NH-(CH₂)₆-NH- group being derived from hexamethylenediamine, these polyamino amines being crosslinked by addition of a difunctional crosslinking agent chosen from epihalohydrins, diepoxides, dianhydrides and bis-unsaturated derivatives, using from 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino amide and alkylated by the action of acrylic acid, chloroacetic acid or an alkane sultone, or salts thereof.

The saturated carboxylic acids are preferably chosen from acids containing 6 to 10 carbon atoms, such as adipic acid, 2,2,4-trimethyladipic acid, 2,4,4-trimethyladipic acid and terephthalic acid, and acids bearing an ethylenic double bond, for instance acrylic, methacrylic and itaconic acids. The alkane sultones used in the alkylation are preferably propane sultone or butane sultone, the salts of the alkylating agents are preferably the sodium or potassium salts.

(4) Polymers including zwitterionic units of formula (XVI):



in which

R₅ denotes a polymerizable unsaturated group such as an acrylate, methacrylate, acrylamide or methacrylamide group,

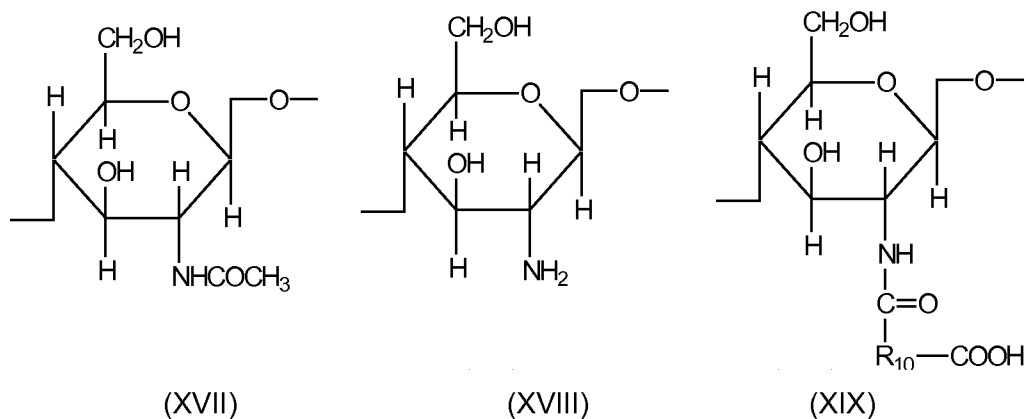
y and z each represent an integer from 1 to 3,

R₆ and R₇ represent a hydrogen atom or a methyl, ethyl or propyl group,

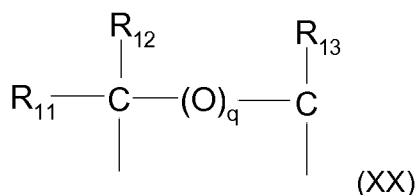
R₈ and R₉ represent a hydrogen atom or an alkyl group such that the sum of the carbon atoms in R₁₀ and R₁₁ does not exceed 10.

The polymers comprising such units may also include units derived from non-zwitterionic monomers such as dimethyl- or diethylaminoethyl acrylate or methacrylate or alkyl acrylates or methacrylates, acrylamides or methacrylamides or vinyl acetate.

5) Polymers derived from chitosan including monomer units corresponding to the following formulae (XVII), (XVIII) and (XIX) below:



the unit (XVII) being present in proportions of between 0% and 30%, the unit (XVIII) in proportions of between 5% and 50% and the unit (XIX) in proportions of between 30% and 90%, it being understood that, in this unit (XIX), R₁₀ represents a group of formula (XX):

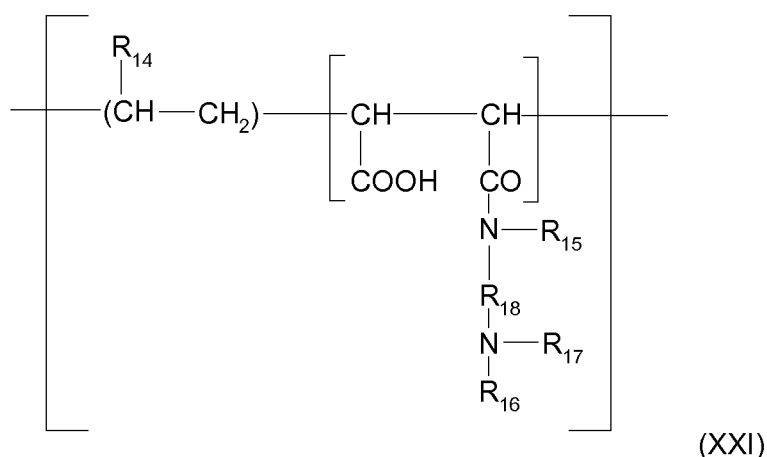


in which, if q = 0, R₁₁, R₁₂ and R₁₃, which may be identical or different, each represent a hydrogen atom, a methyl, hydroxyl, acetoxy or amino residue, a monoalkylamine residue or a dialkylamine residue that are optionally interrupted with one or more nitrogen atoms and/or optionally substituted with one or more amine, hydroxyl, carboxyl, alkylthio or sulfonic groups, an alkylthio residue in which the alkyl group bears an amino residue, at least one of the groups R₁₁, R₁₂ and R₁₃ being, in this case, a hydrogen atom;

or, if q = 1, R₁₁, R₁₂ and R₁₃ each represent a hydrogen atom, and also the salts formed by these compounds with bases or acids.

6) Polymers derived from N-carboxyalkylation of chitosan.

7) Polymers of units corresponding to general formula (XXI), described, for example, in French patent 1 400 366:



in which R₁₄ represents a hydrogen atom, a CH₃O, CH₃CH₂O or phenyl group, R₁₅ denotes hydrogen or a C1-C4 alkyl group such as methyl or ethyl, R₁₆ denotes hydrogen or a C1-C4 alkyl group such as methyl or ethyl, R₁₇ denotes a C1-C4 alkyl group such as methyl or ethyl or a group corresponding to the formula: -R₁₈-N(R₁₆)₂, R₁₈ representing a -CH₂-CH₂-, -CH₂-CH₂-CH₂- or -CH₂-CH(CH₃)- group, R₁₆ having the meanings mentioned above,

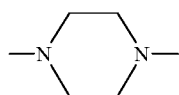
and also the higher homologues of these groups, containing up to six carbon atoms.

8) Amphoteric polymers of the type -D-X-D-X-, chosen from:

a) polymers obtained by the action of chloroacetic acid or sodium chloroacetate on compounds including at least one unit of formula:



in which D denotes a group

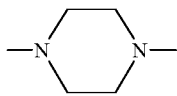


and X denotes the symbol E or E', where E and E', which may be identical or different, denote a divalent group that is an alkylene group with a straight or branched chain including up to seven carbon atoms in the main chain, which is unsubstituted or substituted with hydroxyl groups and which may include, in addition to oxygen, nitrogen and sulfur atoms, one to three aromatic and/or heterocyclic rings; the oxygen, nitrogen and sulfur atoms being present in the form of ether, thioether, sulfoxide, sulfone, sulfonium, alkylamine or alkenylamine groups, hydroxyl, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester and/or urethane groups;

b) polymers of formula:



in which D denotes a group



and X denotes the symbol E or E' and at least once E'; E having the meaning given above and E' is a divalent group that is an alkylene group with a straight or branched chain containing up to six carbon atoms in the main chain, which is unsubstituted or substituted with one or more hydroxyl groups and which includes one or more nitrogen atoms, the nitrogen atom being substituted with an alkyl chain that is optionally interrupted with an oxygen atom and necessarily includes one or more carboxyl functions or one or more hydroxyl functions, betainized by reaction with chloroacetic acid or sodium chloroacetate.

9) (C1-C5)Alkyl vinyl ether/maleic anhydride copolymers partially modified by semiamidation with an N,N-dialkylaminoalkylamine such as N,N-dimethylaminopropylamine or by semiesterification with an N,N-dialkanolamine. These copolymers may also include other vinyl comonomers such as vinylcaprolactam.

According to a preferred embodiment, the amphoteric fixing polymers that may be used in the invention may be chosen from branched block copolymers comprising:

(a) nonionic units derived from at least one monomer chosen from C1-C20 alkyl (meth)acrylates, N-mono-(C2-C12 alkyl)(meth)acrylamides and N,N-di(C2-C12 alkyl)(meth)acrylamides,

(b) anionic units derived from at least one monomer chosen from acrylic acid and methacrylic acid, and

(c) polyfunctional units derived from at least one monomer including at least two polymerizable unsaturated functional groups,

and preferably having a structure constituted of hydrophobic blocks onto which are fixed, via polyfunctional units (c), several blocks that are more hydrophilic.

Preferably, the amphoteric polymers have at least two glass transition temperatures (T_g), at least one of which is greater than 20°C and the other of which is less than 20°C.

The preferred amphoteric polymers are polymers including units derived:

a) from at least one monomer chosen from acrylamides and methacrylamides substituted on the nitrogen with an alkyl group,

b) from at least one acidic comonomer containing one or more reactive carboxylic groups, and

c) from at least one basic comonomer such as acrylic and methacrylic acid esters bearing primary, secondary, tertiary and quaternary amine substituents, and the product of quaternization of dimethylaminoethyl methacrylate with dimethyl or diethyl sulfate.

Mention may be made in particular of the polymers sold under the name Amphomer by the company National Starch.

- The nonionic fixing polymers that may be used according to the present invention are chosen, for example, from:
- polyalkyloxazolines,
 - vinyl acetate homopolymers,
 - vinyl acetate copolymers, for instance copolymers of vinyl acetate and of acrylic ester, copolymers of vinyl acetate and of ethylene, or copolymers of vinyl acetate and of maleic ester, for example of dibutyl maleate,
 - acrylic ester homopolymers and copolymers, for instance copolymers of alkyl acrylates and of alkyl methacrylates, such as the products sold by the company Röhm & Haas under the names Primal® AC-261 K and Eudragit® NE 30 D, by the company BASF under the name 8845, or by the company Hoechst under the name Appretan® N9212,
 - copolymers of acrylonitrile and of a nonionic monomer chosen, for example, from butadiene and alkyl (meth)acrylates, such as the products sold under the name CJ 0601 B by the company Röhm & Haas,
 - styrene homopolymers,
 - styrene copolymers, for instance copolymers of styrene and of alkyl (meth)acrylate, such as the products Mowilith® LDM 6911, Mowilith® DM 611 and Mowilith® LDM 6070 sold by the company Hoechst, and the products Rhodopas® SD 215 and Rhodopas® DS 910 sold by the company Rhône-Poulenc; copolymers of styrene, of alkyl methacrylate and of alkyl acrylate; copolymers of styrene and of butadiene; or copolymers of styrene, of butadiene and of vinylpyridine,
 - polyamides,
 - vinyl lactam homopolymers such as vinylpyrrolidone homopolymers and the polyvinylcaprolactam sold under the name Luviskol® Plus by the company BASF,
 - vinyl lactam copolymers such as a poly(vinylpyrrolidone/vinyl lactam) copolymer sold under the trade name Luvitec® VPC 55K65W by the company BASF, poly(vinylpyrrolidone/vinyl acetate) copolymers, such as those sold under the name PVPVA® S630L by the company ISP, Luviskol® VA 73, VA 64, VA 55, VA 37 and VA 28 by the company BASF; and poly(vinylpyrrolidone/vinyl acetate/vinyl propionate) terpolymers, for instance the product sold under the name Luviskol® VAP 343 by the company BASF, and
 - poly(vinyl alcohols).

The alkyl groups of the nonionic polymers mentioned above preferably contain from one to six carbon atoms.

Preferably, the fixing polymer(s) are chosen from nonionic fixing polymers and anionic fixing polymers, and mixtures thereof. More preferentially, the fixing polymer(s) are chosen from nonionic fixing polymers such as those described above, and even more preferentially from vinyl lactam homopolymers and/or copolymers, such as vinyl pyrrolidone homopolymers, poly(vinyl pyrrolidone/vinyl lactam) copolymers, poly(vinyl pyrrolidone/vinyl acetate) copolymers, poly(vinyl pyrrolidone/vinyl acetate/vinyl propionate) terpolymers and mixtures thereof.

When present in the composition, the total content of the fixing polymer(s) other than the polyurethanes and the cationic polymers, preferably nonionic polymers, present in the composition is preferably between 0.01% and 10% by weight, preferably between 0.1% and 5% by weight, and more preferentially between 0.2% and 2% by weight, relative to the total weight of the composition.

Preferably, the composition according to the invention comprises one or more fixing polymers other than the polyurethanes and other than the cationic polymers and other than the polysaccharides, more preferentially chosen from anionic fixing polymers, nonionic fixing polymers, amphoteric fixing polymers, and mixtures thereof; even more preferentially from anionic fixing polymers, nonionic fixing polymers, and mixtures thereof; more better still nonionic fixing polymers and even better still from vinyl lactam homopolymers and/or copolymers, such as vinyl pyrrolidone homopolymers, poly(vinyl pyrrolidone/vinyl lactam) copolymers, poly(vinyl pyrrolidone/vinyl acetate) copolymers, poly(vinyl pyrrolidone/vinyl acetate/vinyl propionate) terpolymers, and mixtures thereof.

When present in the composition, the total content of the fixing polymer(s) is between 0.01% and 10% by weight, preferably between 0.1% and 5% by weight, and more preferentially between 0.2% and 3% by weight, relative to the total weight of the composition.

The composition according to the invention may also comprise one or more additional compounds chosen from surfactants, preferably chosen from nonionic, anionic, cationic and amphoteric surfactants, silicones other than organosilanes, natural or synthetic thickeners or viscosity regulators other than the compounds described above; UV filters, fillers such as nacre, titanium dioxide, resins and clays, fragrances, peptizers, vitamins, preserving agents, acidic agents, alkaline agents.

A person skilled in the art will take care to select the optional additives and the amount thereof such that they do not harm the properties of the composition of the present invention.

These additives may be present in the composition according to the invention in
5 an amount ranging from 0% to 20% by weight relative to the total weight of the composition.

The pH of the composition according to the invention generally ranges from 2 to 12, preferably from 2.5 to 7, preferentially from 3 to 6 and better still from 3.5 to 5.5.

The pH of the composition may be adjusted to the desired value by means of
10 basifying agents or acidifying agents that are customarily used. Among the basifying agents, examples that may be mentioned include aqueous ammonia, alkanolamines, and mineral or organic hydroxides. Among the acidifying agents, examples that may be mentioned include mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid or sulfuric acid, carboxylic acids, for instance acetic acid, tartaric
15 acid, citric acid and lactic acid, and sulfonic acids.

A subject of the present invention is also a process for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres a composition as described previously.

20 This or these steps of applying the composition according to the invention may optionally be preceded by at least one step of washing said fibres using a shampoo.

Moreover, this or these steps of applying the composition according to the invention may optionally be followed by a step of leaving the composition on, for example a leave-on time of 1 to 15 minutes, in particular 2 to 5 minutes; then followed by an
25 optional rinsing step, for example with water; and/or a drying step.

Preferably, the keratin fibres are not rinsed after the step(s) of applying the composition according to the invention. The expression "are not rinsed" means that no step of rinsing the keratin fibres is performed for at least 30 minutes, preferentially 1 hour, after the step of applying the composition according to the invention.

30

A subject of the present invention is also a use of the composition as described previously for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair and notably for defining the hair curls.

Preferably, the composition as described previously is used on curly hair, to define
35 the curls.

The examples that follow serve to illustrate the invention without, however, being limiting in nature.

Example 1

5

A composition 1 according to the invention and a comparative composition 2 were prepared using the following ingredients, the contents of which are indicated in the tables below (as g of starting material in unmodified form).

Ingredients	1 (invention)	2 (comparative)
Ethyltrimethylammonium methacrylate chloride homopolymer (PQ-37) ⁽¹⁾	2.6 (1.3 AM)	2.6 (1.3 AM)
Guar gum, 2-hydroxypropyl ether ⁽²⁾	1.0	1.0
3-Aminopropyltriethoxysilane ⁽³⁾	3.0	3.0
Polydimethyldiallylammonium chloride at 40% in water (PQ-6) ⁽⁴⁾	2.0 (0.8 AM)	2.0 (0.8 AM)
Vinylpyrrolidone/vinyl acetate copolymer (60/40) as an aqueous 50% solution ⁽⁵⁾	1.0 (0.5 AM)	1.0 (0.5 AM)
Lactic acid	1.8	1.8
Aqueous dispersion of polyurethane Polyurethane-34 ⁽⁶⁾	2.5 (0.8 AM)	-
Crosslinked ethyl acrylate/methyl methacrylate copolymer (80/20), as an aqueous 50% dispersion ⁽⁷⁾	-	1.6 (0.8 AM)
Oxyethylenated (40 EO) hydrogenated castor oil	0.9	0.9
Preserving agents, fragrances	qs	qs
Water	qs 100	qs 100

10

AM: Active material

⁽¹⁾: Salcare SC 96 sold by BASF

⁽²⁾: Jaguar HP 105 sold by Rhodia

⁽³⁾: Silsoft A-1100 sold by Momentive Performance Materials

⁽⁴⁾: Merquat 100 Polymer sold by Nalco

15

⁽⁵⁾: Luviskol VA 64W sold by BASF

⁽⁶⁾: Baycusan C 1001 sold by Bayer

⁽⁷⁾: Daitosol 5000 AD sold by Daito Kasei Kogyo

Control of the volume and frizziness

5 The control of the volume and frizziness was evaluated on locks of natural Caucasian hair of frizziness type IV, each weighing 2.7 g and measuring 26 cm.

Each of the protocols described below was performed on a group of six locks.

Protocol 1: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water. They were then disentangled and left to dry naturally.

10 Protocol 2: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water. They were then disentangled. Composition 1 according to the invention was then applied to the wet hair, at a rate of 0.4 g per gram of hair. The locks were then disentangled and left to dry naturally.

15 Protocol 3: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water. They were then disentangled. Composition 1 according to the invention was then applied to the wet hair, at a rate of 0.4 g per gram of hair. The locks were then disentangled and left to dry naturally. The locks were then washed using a standard shampoo, rinsed with water and left to dry naturally.

20 Protocol 4: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water. They were then disentangled. Composition 1 according to the invention was then applied to the wet hair, at a rate of 0.4 g per gram of hair. The locks were then disentangled and left to dry naturally. The locks were then washed with four successive standard shampoos, each shampoo washing step being followed by rinsing and drying naturally.

25 On conclusion of each protocol, the area occupied by each lock of hair, the global volume of each lock, was measured at T0 and then after 48 hours placed in a chamber with a relative humidity of 80%, at 25°C.

The smaller the area occupied by the lock, the more the volume and frizziness are controlled.

30 The averages of the measurements (on six locks in each case) are reported in the table below.

Area occupied by the lock (cm ²)	Protocol 1 (control)	Protocol 2 (composition 1)	Protocol 3 (composition 1 and then one shampoo wash)	Protocol 4 (composition 1 and then four shampoo washes)
T0	119.2 ± 14.7	22.9 ± 2.7	41.3 ± 4.6	64.7 ± 14.6
T 48 h	138.4 ± 15.3	40.3 ± 10.5	69.0 ± 9.6	80.2 ± 19.4

5 Better control of the volume of the hair is observed, in particular there is no frizziness, for the hair treated with the composition of the invention relative to the control, even after 48 hours at a relative humidity of 80%. It is observed that the superiority of performance level in terms of control of the volume and frizziness persists after one and four shampoo washes.

Conditioning

10 Each of the protocols described below was performed on a group of six locks of moderately sensitized hair each weighing 1 g.

Protocol 1b: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water (35°C, flow rate 300 l/h). They were then disentangled.

15 Protocol 2b: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water (35°C, flow rate 300 l/h). They were then disentangled. Composition 1 according to the invention was then applied to the wet hair, at a rate of 0.45 g per gram of hair. The locks were then disentangled.

20 Protocol 3b: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water (35°C, flow rate 300 l/h). They were then disentangled. Composition 1 according to the invention was then applied to the wet hair, at a rate of 0.45 g per gram of hair. The locks were then disentangled. The locks were then washed using a standard shampoo and rinsed with water (35°C, flow rate 300 l/h).

25 Protocol 4b: the locks were washed using a standard shampoo at a rate of 0.4 g per gram of hair and then rinsed with water (35°C, flow rate 300 l/h). They were then disentangled. Composition 1 according to the invention was then applied to the wet hair, at a rate of 0.45 g per gram of hair. The locks were then disentangled. Next, the locks were washed with four successive standard shampoos, rinsing with water (35°C, flow rate 300 l/h) and drying with a hairdryer (50-55°C) between each shampoo wash.

30 The surface state of the hair thus treated was evaluated by means of a sliding test.

The sliding test measures the force required to move a lock sandwiched between two other locks placed in the opposite direction. This test, performed on wet hair, reveals the surface quality of the fibre. Specifically, the ease of sliding of the hair depends on its surface quality.

5 Locks of hair are superimposed head-to-tail and kept in perfect contact. A device drives the central lock in a rectilinear movement. A dynamometer measures the force developed to effect this movement. The smoother and more homogeneous the surface of the hair, the weaker the sliding force.

10 The sliding test is performed on each lock (per group of three locks) treated according to each of the protocols: the average force recorded throughout the movement of the lock is then retained.

The average forces obtained for each of the protocols are given below:

	Average force (N) on wet hair
Protocol 1b (control)	1.47 ± 0.10
Protocol 2b (composition 1)	0.55 ± 0.06
Protocol 3b (composition 1 and then one shampoo wash)	0.43 ± 0.04
Protocol 4b (composition 1 and then four shampoo washes)	0.17 ± 0.08

15

The average force obtained with protocols 2b, 3b and 4b is markedly lower than that obtained with protocol 1b: the surface state of the locks treated with the composition of the invention according to protocols 2b, 3b and 4b is smoother and more homogeneous than that of the locks treated according to protocol 1b, even after
20 shampoo washing several times.

Curl definition and volume control

25 Three locks of natural curly hair A, B and C, weighing 2.7 g and measuring 26 cm, were washed beforehand with a standard shampoo at a rate of 0.4 g of shampoo per gram of hair.

After rinsing, lock A is disentangled with a comb and then left to dry naturally. The lock was then subjected to a standard shampoo wash, and was then rinsed and left to dry naturally. (Control lock)

After rinsing, locks B and C are treated, respectively, with compositions 1 and 2 described above, at a rate of 0.4 g of composition per gram of hair, and are then disentangled with a comb and then left to dry naturally. The locks were then subjected to a standard shampoo wash, and were then rinsed and left to dry naturally.

- 5 Better curl definition and better control of the volume of the hair is observed, in particular there is no frizziness, after a shampoo wash for lock B treated with a composition 1 according to the invention, relative to lock C treated with a comparative composition 2. In addition, lock B has a more beautiful visual effect, in terms of sheen, than lock C.

10

Exemple 2

A composition A according to the invention and a comparative composition B were prepared using the following ingredients, the contents of which are indicated in the tables below

15

Compositions (in grams of active material per 100 g of composition)

	A (invention)	B (comparative)
Ethyltrimethylammonium methacrylate chloride homopolymer (PQ-37)	1.3 AM	1.3 AM
Guar gum, 2-hydroxypropyl ether	1.0	1.0
3-Aminopropyltriethoxysilane	3.0	-
Polydimethyldiallylammonium chloride (Polyquaternium-6)	0.8 AM	0.8 AM
Vinylpyrrolidone/vinyl acetate copolymer (60/40)	0.5 AM	0.5 AM
Lactic acid	1.8	1.8
Polyurethane-34	0.8 AM	0.8 AM
hydrogenated castor oil oxyethylenated with 40 moles of ethylene oxide	0.9	0.9
Preserving agents, fragrances	qs	qs
Water	qs 100	qs 100

Application

20

Compositions A and B were applied comparatively on a malleable head with curly hair, which had been washed and wrung dry beforehand, at a rate of 2 g per half-head. The hair was then dried with a diffuser.

5 “curl definition and regularity” and “frizziness control” evaluation

The “curl definition and regularity” and “frizziness control” were evaluated in a blind test by five experts: each of the five experts gave his opinion regarding which side of the head had the better curl definition and the better frizziness control.

10 The evaluation of the curl definition and regularity is visual: the expert states whether the curl is well shaped, geometrical, with a regular pitch. A well-defined curl is formed by hair strands that are grouped together.

15 For the frizziness control, the expert observes whether the hair strands are grouped together well, or if there are isolated strands which give the hairstyle a “vague” and poorly shaped look.

The results obtained are presented below:

	Curl definition		Frizziness control	
	A invention	B Prior art	A invention	B Prior art
Expert 1	+	-	+	-
Expert 2	+	-	+	-
Expert 3	+	-	+	-
Expert 4	+	-	+	-
Expert 5	+	-	+	-
% in favour of A	100%		100%	

20

5 experts out of 5 (100%) judged that the fibres treated with composition (A) according to the invention had better curl definition and regularity and better frizziness control than the fibres treated with composition (B) which does not contain silane of formule (X).

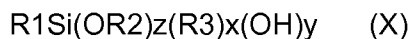
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CLAIMS

1. Cosmetic composition, comprising:

- 5 - one or more polyurethanes,
 - one or more cationic polymers other than polyurethanes,
 - one or more organosilanes, and
 - one or more polysaccharides other than cationic polymers,

10 the organosilane(s) being chosen from the compounds of formula (X), oligomers thereof, hydrolysis products thereof and/or mixtures thereof:



in which

- R₁ is a cyclic or acyclic, linear or branched, saturated or unsaturated C₁ to C₂₂,
15 notably C₂ to C₂₀, hydrocarbon-based chain, which may be substituted with one or more groups chosen from amine groups NH₂ or NHR (R being a linear or branched C₁ to C₂₀, notably C₁ to C₆, alkyl, or a C₃ to C₄₀ cycloalkyl or a C₆ to C₃₀ aromatic radical); a hydroxyl group (OH); a thiol group; an aryl group (more particularly benzyl) which is unsubstituted or substituted with an NH₂ or NHR group; it being possible for R₁ to be
20 interrupted with one or more oxygen, sulfur or nitrogen heteroatoms and/or with one or more carbonyl groups (CO);

 - R₂ and R₃, which may be identical or different, represent a linear or branched alkyl group comprising from 1 to 6 carbon atoms,

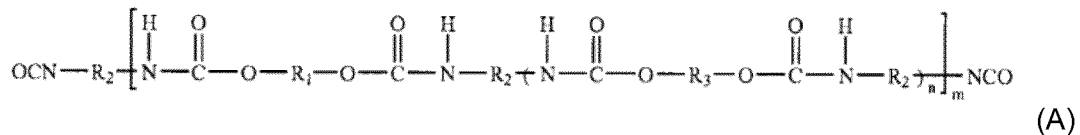
- y denotes an integer ranging from 0 to 3,
25 - z denotes an integer ranging from 0 to 3, and
 - x denotes an integer ranging from 0 to 2,
 - with $z + x + y = 3$.

30 2. Composition according to Claim 1, characterized in that the polyurethane(s) are chosen from non-associative polyurethanes.

3. Composition according to either of the preceding claims, characterized in that the polyurethane is in the form of an aqueous dispersion of polyurethane particles.

35 4. Composition according to any one of the preceding claims, characterized in that the polyurethanes are derived from the reaction of:

- a prepolymer of formula (A) below:



in which:

R_1 represents a divalent radical of a dihydroxylated compound,

5 R_2 represents a radical of an aliphatic or cycloaliphatic polyisocyanate,

R_3 represents a radical of a low molecular weight diol, optionally substituted with one or more ionic groups,

n represents an integer ranging from 1 to 5, and

m is greater than 1;

10 - at least one chain extender according to the formula $\text{H}_2\text{N}-\text{R}_4-\text{NH}_2$ (B), in which R_4 represents an alkylene or alkylene oxide radical which is not substituted with one or more ionic or potentially ionic groups; and

- at least one chain extender according to the formula $\text{H}_2\text{N}-\text{R}_5-\text{NH}_2$ (C), in which R_5 represents an alkylene radical substituted with one or more ionic or potentially ionic

15 groups.

5. Composition according to the preceding claim, characterized in that R_2 represents an organic diisocyanate, preferably chosen from tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,3-
 20 diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,5,5-trimethylcyclohexane isocyanate (isophorone diisocyanate or IPDI), bis(4-isocyanatocyclohexyl)methane, 1,3-bis(isocyanatomethyl)cyclohexane, 1,4-bis(isocyanatomethyl)cyclohexane, bis(4-isocyanato-3-methyl-cyclohexyl)methane, isomers of toluene diisocyanate (TDI) such as toluene 2,4-diisocyanate, toluene 2,6-
 25 diisocyanate and mixtures thereof, hydrogenated toluene diisocyanate, diphenylmethane 4,4'-diisocyanate and mixtures with its diphenylmethane 2,4-diisocyanate isomers and optionally diphenylmethane 2,2'-diisocyanate isomers, naphthalene 1,5-diisocyanate, and mixtures thereof, and more preferentially from 1,6-hexamethylene diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexane
 30 isocyanate, and mixtures thereof.

6. Composition according to either of Claims 4 and 5, characterized in that R_3 represents a low molecular weight diol containing more than 20 carbon atoms, preferably chosen from ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol,

1,3-butylene glycol, neopentyl glycol, butyl ethyl propanediol, cyclohexanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, bisphenol A (2,2-bis(4-hydroxyphenyl)propane), hydrogenated bisphenol A (2,2-bis(4-hydroxycyclohexyl)propane), and mixtures thereof.

5

7. Composition according to any one of Claims 4 to 6, characterized in that the chain extender(s) of formula (B) are chosen from hydrazine, ethylenediamine, propylenediamine, 1,4-butylenediamine, piperazine, 3-{2-[2-(3-aminopropoxy)ethoxy]ethoxy}propylamine, 2-methyl-1,5-pentanediamine,

10

hexanediamine, isophoronediamine, 4,4-methylenedi(cyclohexylamine), dipropylamine propylene glycol, dipropylamine dipropylene glycol, dipropylamine tripropylene glycol, dipropylamine poly(propylene glycol), dipropylamine ethylene glycol, dipropylamine poly(ethylene glycol), dipropylamine 1,3-propanediol, dipropylamine 2-methyl-1,3-propanediol, dipropylamine 1,4-butanediol, dipropylamine 1,3-butanediol, dipropylamine

15

1,6-hexanediol, dipropylamine cyclohexane-1,4-dimethanol, and mixtures thereof.

8. Composition according to any one of Claims 4 to 6, characterized in that the chain extender(s) of formula (C) are chosen from diaminosulfonates, and preferably from the sodium salt of N-(2-aminoethyl)-2-aminoethanesulfonic acid, the sodium salt of N-(2-aminoethyl)-2-aminopropionic acid, and mixtures thereof.

20

9. Composition according to any one of the preceding claims, characterized in that the polyurethane is the compound whose INCI name is Polyurethane-34, preferably in the form of an aqueous dispersion of polyurethane particles.

25

10. Composition according to any one of the preceding claims, characterized in that the total content of the polyurethane(s) is between 0.01% and 20% by weight, preferably between 0.1% and 10% by weight, more preferentially between 0.2% and 5% by weight and better still between 0.3% and 2% by weight relative to the total weight of the composition.

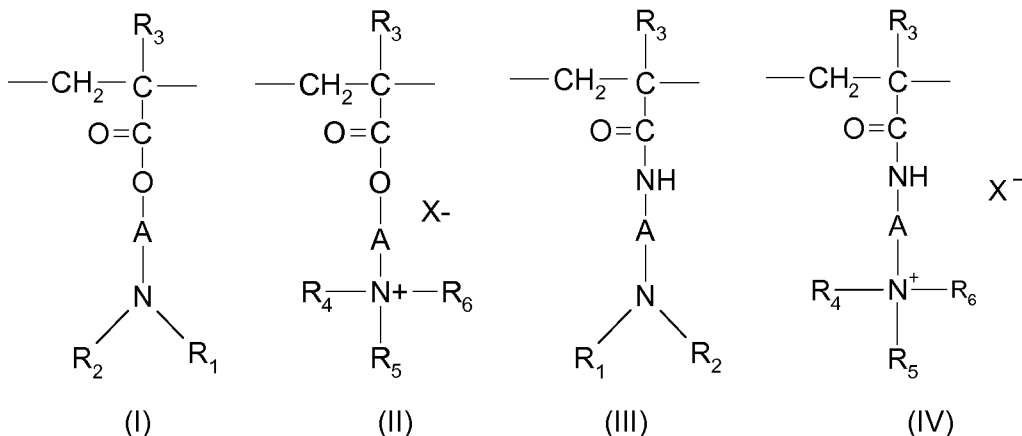
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11. Composition according to any one of the preceding claims, characterized in that it comprises at least two distinct cationic polymers other than polyurethanes.

35

12. Composition according to any one of the preceding claims, characterized in that the cationic polymer(s) are chosen from:

(1) homopolymers or copolymers derived from acrylic or methacrylic esters or amides and including at least one of the units of formula (I), (II), (III) or (IV) below:

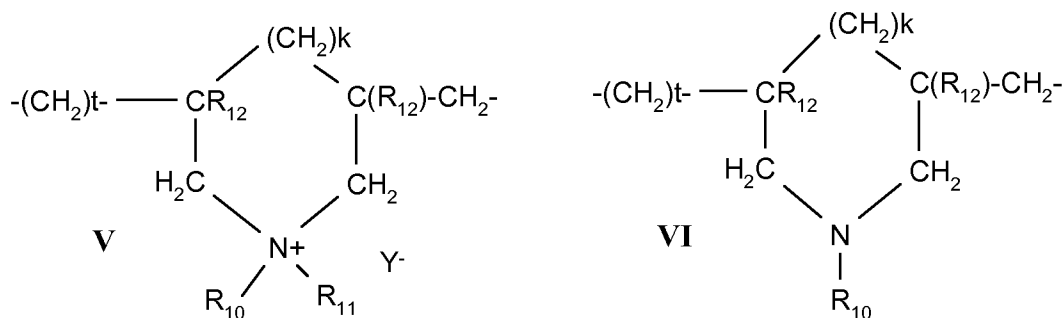


5 in which:

- R₃, which may be identical or different, denote a hydrogen atom or a CH₃ radical;
 - A, which may be identical or different, represent a linear or branched divalent alkyl group of 1 to 6 carbon atoms, preferably 2 or 3 carbon atoms, or a hydroxyalkyl group of 1 to 4 carbon atoms;
 - 10 - R₄, R₅ and R₆, which may be identical or different, represent an alkyl group containing from 1 to 18 carbon atoms or a benzyl radical, preferably an alkyl group containing from 1 to 6 carbon atoms;
 - R₁ and R₂, which may be identical or different, represent a hydrogen atom or an alkyl group containing from 1 to 6 carbon atoms, preferably methyl or ethyl;
 - 15 - X⁻ denotes an anion derived from a mineral or organic acid, such as a methosulfate anion or a halide such as chloride or bromide;
- (2) cationic polysaccharides, notably cellulose ether derivatives including quaternary ammonium groups, cationic cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer and cationic galactomannan gums;
- 20 (3) polymers constituted of piperazinyl units and divalent alkylene or hydroxyalkylene radicals containing linear or branched chains, optionally interrupted with oxygen, sulfur or nitrogen atoms or with aromatic or heterocyclic rings, and also the oxidation and/or quaternization products of these polymers;
- (4) water-soluble polyaminoamides prepared in particular by polycondensation of an
- 25 acidic compound with a polyamine; these polyaminoamides can be crosslinked with an epihalohydrin, a diepoxide, a dianhydride, an unsaturated dianhydride, a bis-unsaturated derivative, a bis-halohydrin, a bis-azetidinium, a bis-haloacyldiamine, a bis-alkyl halide or alternatively with an oligomer resulting from the reaction of a difunctional compound which is reactive with a bis-halohydrin, a bis-azetidinium, a bis-haloacyldiamine, a bis-
- 30 alkyl halide, an epihalohydrin, a diepoxide or a bis-unsaturated derivative; the

crosslinking agent being used in proportions ranging from 0.025 to 0.35 mol per amine group of the polyaminoamide; these polyaminoamides can be alkylated or, if they include one or more tertiary amine functions, they can be quaternized;

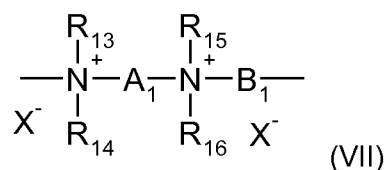
- (5) polyamino amide derivatives resulting from the condensation of polyalkylene polyamines with polycarboxylic acids followed by alkylation with difunctional agents;
- (6) polymers obtained by reacting a polyalkylene polyamine including two primary amine groups and at least one secondary amine group with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids containing from 3 to 8 carbon atoms;
- (7) cyclopolymers of alkyldiallylamine or of dialkyldiallylammonium, such as the homopolymers or copolymers including, as main constituent of the chain, units corresponding to formula (V) or (VI):



in which

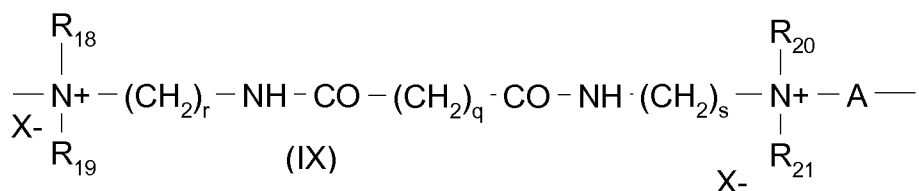
- k and t are equal to 0 or 1, the sum k + t being equal to 1;
- R₁₂ denotes a hydrogen atom or a methyl radical;
- R₁₀ and R₁₁, independently of each other, denote a C1-C6 alkyl group, a C1-C5 hydroxyalkyl group, a C1-C4 amidoalkyl group; or alternatively R₁₀ and R₁₁ may denote, together with the nitrogen atom to which they are attached, a heterocyclic group such as piperidyl or morpholinyl; R₁₀ and R₁₁, independently of each other, preferably denote a C1-C4 alkyl group;
- Y⁻ is an anion such as bromide, chloride, acetate, borate, citrate, tartrate, bisulfate, bisulfite, sulfate or phosphate;

(8) quaternary diammonium polymers comprising repeating units of formula (VII) below:



in which:

- R₁₃, R₁₄, R₁₅ and R₁₆, which may be identical or different, represent aliphatic, alicyclic or arylaliphatic radicals comprising from 1 to 20 carbon atoms or C₁-C₁₂ hydroxyalkyl aliphatic radicals,
- or else R₁₃, R₁₄, R₁₅ and R₁₆, together or separately, form, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second non-nitrogen heteroatom;
- or else R₁₃, R₁₄, R₁₅ and R₁₆ represent a linear or branched C₁-C₆ alkyl radical substituted with a nitrile, ester, acyl, amide or -CO-O-R₁₇-D or -CO-NH-R₁₇-D group, where R₁₇ is an alkylene and D is a quaternary ammonium group;
- A1 and B1 represent linear or branched, saturated or unsaturated, divalent polymethylene groups comprising from 2 to 20 carbon atoms, which may contain, linked to or intercalated in the main chain, one or more aromatic rings or one or more oxygen or sulfur atoms or sulfoxide, sulfone, disulfide, amino, alkylamino, hydroxyl, quaternary ammonium, ureido, amide or ester groups; and
- X- denotes an anion derived from a mineral or organic acid;
- it being understood that A1, R₁₃ and R₁₅ can form, with the two nitrogen atoms to which they are attached, a piperazine ring;
- in addition, if A1 denotes a linear or branched, saturated or unsaturated alkylene or hydroxyalkylene radical, B1 may also denote a group (CH₂)_n-CO-D-OC-(CH₂)_p- with n and p, which may be identical or different, being integers ranging from 2 to 20, and D denoting:
- a glycol residue of formula -O-Z-O-, in which Z denotes a linear or branched hydrocarbon-based radical or a group corresponding to one of the following formulae: - (CH₂CH₂O)_x-CH₂CH₂- and -[CH₂CH(CH₃)O]_y-CH₂CH(CH₃)-, in which x and y denote an integer from 1 to 4, representing a defined and unique degree of polymerization or any number from 1 to 4 representing an average degree of polymerization;
 - a bis-secondary diamine residue, such as a piperazine derivative;
 - a bis-primary diamine residue of formula -NH-Y-NH-, in which Y denotes a linear or branched hydrocarbon-based radical, or else the divalent radical -CH₂-CH₂-S-S-CH₂-CH₂-;
 - an ureylene group of formula -NH-CO-NH-;
- (9) polyquaternary ammonium polymers comprising units of formula (IX):



in which:

- R_{18} , R_{19} , R_{20} and R_{21} , which may be identical or different, represent a hydrogen atom or a methyl, ethyl, propyl, β -hydroxyethyl, β -hydroxypropyl or $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_p\text{OH}$ radical, in which p is equal to 0 or to an integer between 1 and 6, with the proviso that

5 R_{18} , R_{19} , R_{20} do not simultaneously represent a hydrogen atom and

- r and s , which may be identical or different, are integers between 1 and 6,

- q is equal to 0 or to an integer between 1 and 34,

- X^- denotes an anion such as a halide,

- A denotes a divalent dihalide radical or preferably represents $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$;

10 (10) polyamines; and

(11) mixtures of the above polymers.

13. Composition according to the preceding claim, characterized in that the cationic polymer(s) are chosen from those of families (1), (7) and (8), and mixtures thereof; and

15 preferably chosen from:

- alkyldiallylamine or dialkyldiallylammonium cyclopolymers,

- homopolymers or copolymers derived from acrylic or methacrylic esters or amides and including units as defined in family (1),

- and mixtures thereof.

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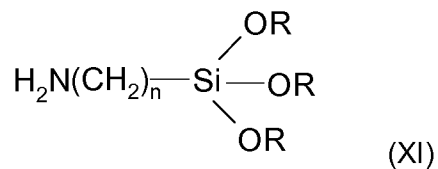
14. Composition according to any one of the preceding claims, characterized in that the cationic polymer(s) are chosen from 2-methacryloyloxyethyltrimethylammonium chloride homopolymers or copolymers, dimethyldiallylammonium chloride homopolymers, and mixtures thereof.

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15. Composition according to any one of the preceding claims, characterized in that the total content of the cationic polymer(s) other than polyurethanes is between 0.01% and 15% by weight, preferably between 0.05% and 10% by weight, more preferentially between 0.1% and 5% by weight and better still between 1% and 3% by weight relative

30 to the total weight of the composition.

16. Composition according to any one of the preceding claims, characterized in that the organosilane(s) are chosen from the compounds of formula (XI), oligomers thereof, hydrolysis products thereof and/or mixtures thereof:



in which the radicals R, which may be identical or different, are chosen from linear or branched C1-C6, more preferentially C2 to C4, alkyl radicals; and n is an integer ranging from 1 to 6, more preferentially from 2 to 4.

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17. Composition according to any one of the preceding claims, characterized in that the organosilane(s) are chosen from methyltriethoxysilane, octyltriethoxysilane (OTES), dodecyltriethoxysilane, octadecyltriethoxysilane, hexadecyltriethoxysilane, 3-aminopropyltriethoxysilane (APTES), 2-aminoethyltriethoxysilane (AETES), 3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, 3-(m-aminophenoxy)propyltrimethoxysilane, p-aminophenyltrimethoxysilane, N-(2-aminoethylaminomethyl)phenethyltrimethoxysilane, oligomers thereof, hydrolysis products thereof, and mixtures thereof; and preferably the organosilane(s) are chosen from methyltriethoxysilane, octyltriethoxysilane (OTES) and 3-aminopropyltriethoxysilane (APTES), oligomers thereof, hydrolysis products thereof, and mixtures thereof; and even more preferentially from 3-aminopropyltriethoxysilane (APTES), oligomers thereof, hydrolysis products thereof, and mixtures thereof.

18. Composition according to any one of the preceding claims, characterized in that the total content of the organosilane(s) is between 0.1% and 15% by weight, preferably between 1% and 10% by weight, and more preferentially between 2% and 8% by weight, relative to the total weight of the composition.

19. Composition according to any one of the preceding claims, characterized in that the polysaccharide(s) are chosen from:

- a) tree or shrub exudates, preferably gum arabic, ghatti gum, karaya gum and tragacanth;
- b) gums derived from algae, preferably agar, alginates, carrageenans and furcellerans;
- c) gums derived from seeds or tubers, preferably guar gum, locust bean gum, fenugreek gum, tamarind gum and konjac gum;
- d) microbial gums, preferably xanthan gum, gellan gum and scleroglucan gum;
- e) polymers extracted from plants, preferably chosen from celluloses, starches and inulin;
- f) mixtures of these compounds,

these polysaccharides being optionally modified by a heat treatment, an esterification reaction, an etherification reaction, an amidation reaction or an oxidation reaction.

20. Composition according to the preceding claim, characterized in that said
5 polysaccharide(s) are chosen from starches, guar gums, celluloses and derivatives thereof, and mixtures thereof; preferably from guar gums and/or derivatives thereof which are nonionic, and mixtures thereof; more preferentially from nonionic guar gums modified with hydroxyalkyl groups.

10 21. Composition according to any one of the preceding claims, characterized in that the total content of the polysaccharide(s) is between 0.01% and 20% by weight, preferably between 0.1% and 10% by weight, more preferentially between 0.2% and 5% by weight and better still between 0.5% and 3% by weight relative to the total weight of the composition.

15 22. Composition according to any one of the preceding claims, characterized in that it comprises one or more fixing polymers other than the polyurethanes and other than the cationic polymers and other than the polysaccharides, preferably chosen from anionic fixing polymers, nonionic fixing polymers, amphoteric fixing polymers, and mixtures
20 thereof; even more preferably from anionic fixing polymers, nonionic fixing polymers, and mixtures thereof; more preferentially nonionic fixing polymers and even more preferentially from vinyl lactam homopolymers and/or copolymers, such as vinylpyrrolidone homopolymers, poly(vinylpyrrolidone/vinyl lactam) copolymers, poly(vinylpyrrolidone/vinyl acetate) copolymers, poly(vinylpyrrolidone/vinyl acetate/vinyl
25 propionate) terpolymers, and mixtures thereof.

23. Composition according to the preceding claim, characterized in that the total content of the fixing polymer(s) is between 0.01% and 10% by weight, preferably between 0.1% and 5% by weight, and more preferentially between 0.2% and 3% by weight, relative to
30 the total weight of the composition.

24. Process for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres a composition as defined in any one of Claims 1 to 24.

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25. Use of the composition as defined according to any one of Claims 1 to 23, for shaping and/or conditioning keratin fibres, in particular human keratin fibres such as the hair, and notably for defining the hair curls.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/067014

A. CLASSIFICATION OF SUBJECT MATTER				
INV.	A61K8/04	A61Q5/06	A61K8/365	A61K8/58
	A61K8/81	A61K8/87	A61K8/92	C08G18/66
	C08G18/08	C08G18/32	C08G18/38	C08G18/42
				C08L39/00
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols)				
A61Q A61K C08L C08G C09J C08K				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)				
EPO-Internal, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages			Relevant to claim No.
A	US 2007/275927 A1 (PHILIPPE MICHEL [FR]) 29 November 2007 (2007-11-29) paragraphs [0001], [0004], [0010], [0011]; claims 1-20 example 8 paragraphs [0046], [0063]			1-25
X	FR 3 009 679 A1 (OREAL [FR]) 20 February 2015 (2015-02-20) claims 1-16 page 1, line 3 - line 6 page 20, line 9 - line 14 examples C, D page 8, line 15 - line 26 ----- -/-			1-25
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.				
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family				
Date of the actual completion of the international search			Date of mailing of the international search report	
26 August 2019			09/09/2019	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Paulus, Florian	

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/067014

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 924 339 A1 (OREAL [FR]) 5 June 2009 (2009-06-05)	1-25
Y	claims 1-44 page 1, line 4 - line 18 page 41, line 30 - page 42, line 8 composition B page 42, line 31 - page 43, line 8 -----	1-25
Y	FR 2 910 276 A1 (OREAL [FR]) 27 June 2008 (2008-06-27) page 1, line 1 - line 15; claims 1-42 examples -----	1-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/067014

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