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(74) Agent: FEVRIER, Murielle; L'Oréal, D.I.P.I., 25-29
Quai Aulagnier, F-92665 Asnières-sur-Seine (FR).

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(71) Applicant (for all designated States except US): L'OREAL [FR/FR]; 14, rue Royale, F-75008 Paris (FR).

(72) Inventor; and

(75) Inventor/Applicant (for US only): SAUNIER, Jean-Baptiste [FR/FR]; 144 rue Auguste Blanqui, F-69400 Villefranche-sur-Saône (FR).

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(54) Title: DYEING COMPOSITION COMPRISING A SECONDARY PARA-PHENYLENEDIAMINE OXIDATION BASE AND A THICKENING POLYMER

(57) Abstract: A subject-matter of the invention is a dyeing composition comprising at least one specific secondary para-phenylenediamine oxidation base and a specific thickening polymer. Another subject-matter of the invention is the use of this composition for dyeing keratinous fibres and the dyeing method employing this composition. Finally, a subject-matter of the invention is a multicompartiment device. The composition of the present invention makes it possible in particular to obtain a colouring with varied, intense and/or chromatic, attractive and not very selective shades which is highly resistant to the various attacks which hair may be subjected to.



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**DYEING COMPOSITION COMPRISING A SECONDARY PARA-
PHENYLENEDIAMINE OXIDATION BASE AND A THICKENING
POLYMER**

5 A subject-matter of the invention is a dyeing composition comprising at least one specific secondary para-phenylenediamine oxidation base and a thickening polymer chosen from i) noncationic nonassociative polymers comprising a sugar unit, ii) nonionic, anionic
10 or cationic associative polymers, iii) nonsilicone cationic polymers without a fatty chain and iv) anionic nonassociative acrylic polymers. Another subject-matter of the invention is the use of this composition for dyeing keratinous fibres and the dyeing method
15 employing this composition. Finally, a subject-matter of the invention is a multicompartment device.

 It is known to dye keratinous fibres, in particular human hair, with dyeing compositions comprising oxidation dye precursors, generally known as
20 oxidation bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are colourless or weakly coloured compounds which, in combination with oxidizing products, can give rise, by an oxidative
25 coupling process, to coloured compounds.

 It is also known that it is possible to vary the shades obtained with these oxidation bases by combining them with couplers or colouring modifiers, the latter being chosen in particular from aromatic meta-diamines,
30 meta-aminophenols, meta-diphenols and certain heterocyclic compounds, such as indole compounds.

 The variety of the molecules employed as oxidation bases and couplers makes it possible to obtain a rich palette of colours.

35 The "permanent" colouring obtained by virtue of these oxidation dyes furthermore has to satisfy a certain number of requirements. Thus, it must be without disadvantage toxicologically, it must make it possible to obtain shades within the desired intensity

and it must behave well in the face of external agents, such as light, bad weather, washing, permanent waving, perspiration and rubbing.

The dyes must also make it possible to cover white hair and, finally, be as unselective as possible, that is to say make it possible to obtain the smallest possible differences in colouring along the same keratinous fibre, which is generally sensitized (i.e., damaged) to different extents between its tip and its root.

It is already known to use oxidation bases of the secondary para-phenylenediamine type of formula (I) below for dyeing keratinous fibres, in particular the hair. Such a base is disclosed in particular in the documents EP 1 580 184 and EP 0 055 386. This base exhibits the disadvantages of resulting in colourings which are insufficiently intense or chromatic and/or excessively selective.

Furthermore, it is known to use, in the field of hair dyeing, compositions employing thickening polymers i) to v) as defined above.

For example, as regards i), noncationic polymers comprising sugar unit(s) have been used in combination with cationic direct dyes (EP 0 970 686, EP 0 970 687) or oxidation dyes (EP 1 149 576); as regards ii), nonionic, anionic or cationic associative polymers have been used in combination with oxidation dyes derived from para-phenylenediamines (EP 1 263 398); as regards iii), nonsilicone cationic polymers without a fatty chain have been used in combination with oxidation dyes (FR 2 923 339); and, as regards iv), it is known, in hair dyeing, to combine associative polymers formed of acrylic acids with oxidation dyes in the presence of laccase (EP 1 041 957).

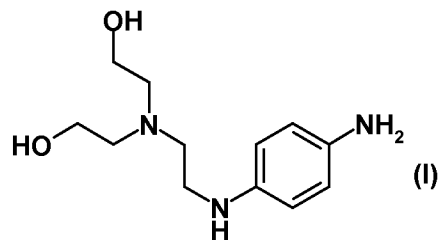
However, the colourings obtained are not entirely satisfactory, in particular in terms of chromaticity, of power, of selectivity and/or of resistance to external agents.

The aim of the present invention is to obtain a

composition for dyeing the hair which exhibits dyeing properties which are improved in terms of intensity or of chromaticity, and/or of selectivity and/or of resistance to external agents.

5 This aim is achieved with the present invention, a subject-matter of which is a composition for dyeing keratinous fibres comprising, in an appropriate dyeing medium:

- 10 - one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid:



and

- 15 - one or more thickening polymer(s) chosen from
 - i) noncationic nonassociative polymers comprising sugar unit(s),
 - ii) nonionic, anionic or cationic associative polymers,
 - iii) non-silicone cationic polymers without a fatty
 - 20 chain,
 - iv) anionic nonassociative acrylic polymers, and
 - v) their mixtures.

Another subject-matter of the invention is a dyeing method employing this composition.

25 Another subject-matter of the invention is the use of the composition of the present invention for dyeing keratinous fibres, in particular human keratinous fibres, such as the hair.

Finally, subject-matters of the invention are multicompartiment devices employing the compound of formula (I) or its addition salts with an acid and one or more thickening polymer(s) chosen from i) to v) as defined above.

35 The composition of the present invention makes it possible in particular to obtain a composition for dyeing keratinous fibres which is suitable for use in

oxidation dyeing and which makes it possible to obtain a colouring with varied, intense or chromatic, attractive and not very selective shades which is highly resistant to the various attacks which hair may be subjected to, such as shampoos, sweat, permanent deformations and light.

It should be noted that, in that which will follow and unless otherwise indicated, the limits of a range of values are included within this range.

The compound of formula (I) can be in the form of cosmetically acceptable addition salts chosen in particular from the addition salts with an acid, such as hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, tosylates, benzene-sulphonates, phosphates and acetates.

The compound of formula (I) or its salts are generally present each in an amount of between 0.001 and 10% by weight approximately of the total weight of the dyeing composition, preferably between 0.005 and 6%.

The polymers according to the invention are thickeners. The term "thickening polymer" is understood to mean, within the meaning of the present invention, a polymer exhibiting, as a 1% by weight solution or dispersion of active material in water or in ethanol at 25°C, a viscosity of greater than 0.2 poise at a shear rate of 1 s^{-1} . The viscosity is measured with a Haake RS600 viscometer from Thermo Electron. This viscometer is a controlled-stress viscometer in cone-plate geometry (for example with a diameter of 60 mm).

*** According to a specific embodiment of the invention, the thickening polymer is i) a noncationic non-associative polymer comprising sugar unit(s).**

In this case, the compositions of the invention comprise at least one noncationic nonassociative polymer comprising sugar unit(s).

The expression "nonassociative polymer" is understood to mean, according to the invention, a non-

amphiphilic polymer, i.e. which does not simultaneously comprise at least one hydrophilic unit and at least one hydrophobic unit composed of at least one C₈-C₃₀ alkyl or alkenyl fatty chain.

5 The term "sugar unit" is understood to mean, within the meaning of the present invention, a unit resulting from a carbohydrate of formula C_n(H₂O)_{n-1} or (CH₂O)_n which can be optionally modified by substitution and/or by oxidation and/or by dehydration. More
10 particularly, sugar unit denotes a monosaccharide portion (i.e., monosaccharide or glycoside or simple sugar) or an oligosaccharide portion (short chains formed by the linking of optionally different monosaccharide units) or a polysaccharide portion [long
15 chains composed of optionally different monosaccharide units, i.e. polysaccharides (homopolysaccharides or heteropolysaccharides)]. The saccharide units can in addition be substituted by linear or branched (C₁-C₆)alkyl or linear or branched hydroxy(C₁-C₆)alkyl or
20 linear or branched (C₁-C₆)alkoxy or linear or branched (C₁-C₆)acyloxy or carboxyl groups.

According to one embodiment of the invention, the sugar units which can participate in the composition of the thickening polymers i) result from the sugars
25 chosen from 1) glucose, 2) galactose, 3) arabinose, 4) rhamnose, 5) mannose, 6) xylose, 7) fucose, 8) anhydrogalactose, 9) galacturonic acid, 10) glucuronic acid, 11) mannuronic acid, 12) galactose sulphate, 13) fructose and 14) anhydrogalactose sulphate.

30 Mention may in particular be made, as thickening polymers i) comprising sugar unit(s) according to the invention, of:

i) native gums chosen from:

a) exudates of trees or shrubs, including:

- 35 o gums arabic (branched polymer of galactose, arabinose, rhamnose and glucuronic acid);
o gums ghatti (polymer resulting from arabinose, galactose, mannose, xylose and glucuronic acid);

- o gums karaya (polymer resulting from galacturonic acid, galactose, rhamnose and glucuronic acid);
- o gums tragacanth (polymer of galacturonic acid, galactose, fucose, xylose and arabinose);
- b) gums resulting from algae, including:
 - o agar (polymer resulting from galactose and anhydrogalactose);
 - o alginates (polymers of mannuronic acid and glucuronic acid);
 - o carrageenans and furcellerans (polymers of galactose sulphate and anhydrogalactose sulphate);
- c) gums resulting from seeds or tubers, including:
 - o guar gums (polymers of mannose and galactose);
 - o locust bean gums (polymers of mannose and galactose);
 - o fenugreek gums (polymers of mannose and galactose);
 - o tamarind gums (polymers of galactose, xylose and glucose);
 - o konjac gums (polymers of glucose and mannose);
- d) microbial gums, including:
 - o xanthan gums (polymers of glucose, mannose acetate, mannose/pyruvic acid and glucuronic acid);
 - o gellan gums (polymers of glucose, which is partially acylated, rhamnose and glucuronic acid);
 - o scleroglucan gums (polymers of glucose);
- ii) extracts of plants or trees, including:
 - o celluloses (polymers of glucose);
 - o starches (polymers of glucose);
 - o inulins (polymers of fructose);
 - o pectins (polymers of galacturonic acid and neutral sugars, such as arabinose, galactose and rhamnose).

These thickening polymers i) can be modified

physically or chemically. Mention may in particular be made, as physical treatment, of temperature.

Mention may be made, as chemical treatments, of esterification, etherification, amidation or oxidation reactions. These treatments make it possible to result in polymers which can be nonionic, anionic or amphoteric.

Biopolysaccharide gums of microbial origin, such as scleroglucan or xanthan gums, gums resulting from plant exudates, such as gum arabic, gum ghatti, gum karaya or gum tragacanth, carrageenan, agar, locust bean gum, hydroxy(C₁-C₆)alkylcelluloses and carboxymethylcelluloses, pectins, alginates and starches are well known to a person skilled in the art and are described in particular in the work by Robert L. Davidson entitled "Handbook of Water-Soluble Gums and Resins", published by McGraw-Hill Book Company (1980).

Among these gums, the scleroglucans more particularly used according to the present invention are represented by the products sold under the Actigum CS name by Sanofi Bio Industries, in particular Actigum CS 11, and under the Amigel name by Alban Muller International. Other scleroglucans, such as those treated with glyoxal in French Patent Application No. 2 633 940, can also be used.

The xanthan gums more particularly used according to the present invention are represented by the products sold under the names Keltrol, Keltrol T, Keltrol TF, Keltrol BT, Keltrol CG-BT [xanthan gum: polysaccharides glucose/mannose/glucuronic acid (40/30/30)], Keltrol RD and Keltrol CG by Nutrasweet Kelco, or under the names Rhodicare S, Rhodicare H and Rhodicare XC (xanthan gum) by Rhodia Chimie, or under the name Nomcort Z [modified xanthan gum (glucose/mannose/glucuronic acid) (Apparent MW: 20 000 000)].

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

The nonionic guar gums may be modified or unmodified.

a) The unmodified guar gums are, for example, the products sold under the name Vidogum GH 175 by Unipeptine and under the name Jaguar C by Meyhall.

b) The modified nonionic guar gums can be modified by linear or branched C₁-C₆-hydroxyalkyl groups. Mention may be made, among the hydroxyalkyl groups, by way of example, of the hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl groups.

These guar gums are well known in the state of the art and can, for example, be prepared by reacting the corresponding alkene oxides, such as, for example, propylene oxide, with a guar gum, so as to obtain a guar gum modified by hydroxypropyl groups.

The degree of hydroxyalkylation preferably varies from 0.4 to 1.2 and corresponds to the number of molecules of alkylene oxide consumed by the number of free hydroxyl functional groups present on the guar gum. Such nonionic guar gums optionally modified by hydroxyalkyl groups are sold, for example, under the trade names Jaguar HP8, Jaguar HP60 (hydroxypropylguar) and Jaguar HP120 by Rhodia Chimie and Jaguar HP105 (guar gum 2-hydroxypropyl ether) by Rhône-Poulenc (Meyhall), or under the name Galactasol 4H4FD2 by Aqualon, or under the name Guargel D15 (Cyamopsis tetragonolobus gum).

The inulins can be obtained from chicory, dahlia or Jerusalem artichoke. They comprise fructans. The fructans are oligosaccharides or polysaccharides comprising a sequence of anhydrofructose units. The fructans can be linear or branched. The fructans can be products obtained directly from a plant or microbial source or else products having a chain length which has been modified (increased or reduced) by fractionation, synthesis or hydrolysis, in particular by enzymes. The fructans generally have a degree of polymerization of 2 to approximately 1000 and preferably of 3 to approximately 60.

The starch molecules used in the present invention can have, of botanical origin, cereals or tubers. Thus, the starches are, for example, chosen from maize, rice, manioc, barley, potato, wheat, sorghum or pea starches.

5 The starches may be modified chemically or physically, in particular by one or more of the following reactions: pregelatinization, oxidation, crosslinking, esterification, etherification, amidation or heat treatments.

10 More particularly, these reactions can be carried out in the following way:

- pregelatinization, by causing the starch granules to burst (for example drying and cooking in a drum-type dryer);
- 15 - oxidation by strong oxidizing agents, resulting in the introduction of carboxyl groups into the starch molecule and in the depolymerization of the starch molecule (for example by treating an aqueous starch solution with sodium hypochlorite);
- 20 - crosslinking by functional agents capable of reacting with the hydroxyl groups of the starch molecules, which will thus be bonded to one another (for example with glyceryl and/or phosphate groups);
- 25 - esterification in an alkaline medium for the grafting of functional groups, in particular C₁-C₆ acyl (acetyl), C₁-C₆ hydroxyalkylated (hydroxyethyl, hydroxypropyl), carboxymethyl or octenylsuccinic functional groups.

30

In particular, it is possible to obtain, by crosslinking with phosphorus compounds:

- i) monostarch phosphates (of the St-O-P(O)(OX)₂ type),
- 35 ii) distarch phosphates (of the St-O-P(O)(OX)-O-St type) or even tristarch phosphates (of the St-O-P(O)(O-St)₂ type) or their mixtures (St indicating starch) with X denoting a cationic counterion, such as that chosen from alkali

metals (for example sodium or potassium), alkaline earth metals (for example calcium or magnesium), the ammonium ions, ions formed from amines, such as those of monoethanolamine, diethanolamine, triethanolamine or 3-amino-1,2-propanediol, and ammonium ions resulting from basic amino acids, such as lysine, arginine, sarcosine, ornithine or citruline.

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

Use will preferably be made of distarch phosphates or compounds rich in distarch phosphate, such as the product provided under the references Prejel VA-70-T AGGL (gelatinized hydroxypropylated manioc distarch phosphate) or Prejel TK1 (gelatinized manioc distarch phosphate) or Prejel 200 (gelatinized acetylated manioc distarch phosphate) by Avebe or Structure ZEA by National Starch (gelatinized maize distarch phosphate).

A preferred starch is a starch which has been subjected to at least one modification by the chemical route, such as at least one esterification. According to the invention, use may also be made of amphoteric starches, these amphoteric starches comprising one or more anionic groups and one or more cationic groups. The anionic groups can be bonded to the same reactive site of the starch molecule or to different reactive sites; preferably, they are bonded to the same reactive site. The anionic groups can be of carboxylic, phosphate or sulphate type and preferably carboxylic type. The cationic groups can be of primary, secondary, tertiary or quaternary amine type.

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

$ \begin{array}{c} \text{R}' \quad \text{R} \\ \quad \\ \text{CH} - \text{CH} - \text{COOM} \\ / \quad \backslash \\ \text{St-O}-(\text{CH}_2)_n-\text{N} \\ \backslash \quad / \\ \text{CH} - \text{CH} - \text{COOM} \\ \quad \\ \text{R}' \quad \text{R} \end{array} $	$ \begin{array}{c} \text{COOM} \quad \text{R} \\ \quad \\ \text{CH} - \text{CH} - \text{COOM} \\ / \quad \backslash \\ \text{St-O}-(\text{CH}_2)_n-\text{N} \\ \backslash \\ \text{R}'' \end{array} $
(II)	(III)
$ \begin{array}{c} \text{R}' \quad \text{R}'' \\ \backslash \quad / \\ \text{N} \\ \\ \text{St-O}-\text{CH}_2-\text{CH}-\text{COOM} \end{array} $	$ \begin{array}{c} \text{R}' \quad \text{R}'' \\ \backslash \quad / \\ \text{N} \\ \\ \text{St-O}-\text{CH}-\text{CH}_2-\text{COOM} \end{array} $
(IV)	(V)

in which formulae (II) to (V):

- St-O represents a starch molecule,
- R, which are identical or different, represent a hydrogen atom or a methyl radical,
- R', which are identical or different, represent a hydrogen atom, a linear or branched (C₁-C₆)alkyl radical such as a methyl radical, or a -COOH group,
- n is an integer equal to 2 or 3,
- M, which are identical or different, denote a hydrogen atom or a cationic counterion, such as an alkali metal or alkaline earth metal, such as Na, K or Li, NH₄, a quaternary ammonium or an organic amine, and
- R'' represents a hydrogen atom or a linear or branched (C₁-C₆)alkyl radical.

These compounds are described in particular in Patents US 5 455 340 and US 4 017 460, which are included by way of reference.

The starch molecules can result from all plant starch sources, such as, in particular, maize, potato, oats, rice, tapioca, sorghum, barley or wheat. Use may also be made of the hydrolysates of the abovementioned starches. The starch preferably results from potato or maize B.

Use is particularly made of the starches of formula (II) or (III). Use is more particularly made of the starches modified by 2-chloroethylaminodipropionic acid, that is to say the starches of formula (II) or (III) in which R, R', R'' and M represent a hydrogen atom and n is equal to 2. The preferred amphoteric starch is a starch chloroethylamidodipropionate. More particularly, the preferred starches are of solonaceae structure, which corresponds to potato starch modified by 2-chloroethylaminodipropionic acid neutralized with a base, such as sodium hydroxide. Mention may also be made of Primojel (carboxymethyl starch = potato starch, sodium salt, slightly crosslinked).

Mention may be made, among the native celluloses, of wood flours.

As indicated above, the cellulose derivatives according to the invention may be anionic, amphoteric or nonionic.

A distinction is made, among these derivatives, between cellulose ethers, cellulose esters and cellulose ester ethers.

The cellulose esters include inorganic cellulose esters (cellulose nitrates, sulphates, phosphates, and the like), organic cellulose esters (cellulose monoacetates, triacetates, amidopropionates, acetate butyrates, acetate propionates, acetate trimellitates, and the like) and mixed organic/inorganic cellulose esters, such as cellulose acetate butyrate sulphates and cellulose acetate propionate sulphates. Mention may be made, among the cellulose ester ethers, of hydroxypropylmethylcellulose phthalates and ethylcellulose sulphates.

Mention may be made, among the nonionic cellulose ethers, of (C₁-C₆)alkylcelluloses, such as methylcelluloses and ethylcelluloses (for example Ethocel Standard 100 Premium from Dow Chemical); hydroxy(C₁-C₆)alkylcelluloses, such as hydroxymethylcelluloses, hydroxyethylcelluloses (for example Cellosize QP3L, Cellosize QP4400H, Cellosize QP30000H, Cellosize

HEC30000A or Cellisize Polymer PCG10 from Amerchol, or Natrosol 250HHR, Natrosol 250MR, Natrosol 250M, Natrosol 250HHXR, Natrosol 250HHX, Natrosol 250HR, Natrosol 250HHR or Natrosol HX from Hercules and
5 Aqualon, or Tylose H1000 from Hoechst) and hydroxypropylcelluloses (for example sold under the names Klucel EF, Klucel H, Klucel LHF, Klucel MF and Klucel G by Aqualon); or mixed hydroxy(C₁-C₆)alkyl (C₁-C₆)alkyl
10 celluloses, such as hydroxypropyl methyl celluloses (for example Methocel E4M from Dow Chemical and Methocel F4M), hydroxyethyl methyl celluloses, hydroxyethyl ethyl celluloses (for example Bermocoll E 481 FQ from Akzo Nobel) and hydroxybutyl methyl celluloses.

Mention may be made, among the anionic cellulose
15 ethers, of carboxy(C₁-C₆)alkylcelluloses and their salts. Mention may be made, by way of example, of carboxymethylcelluloses, carboxymethylmethylcelluloses (for example carboxy(C₁-C₆)alkylcelluloses; use is preferably made of carboxymethylcellulose, for which
20 mention may be made of the products sold under the names Blanose 7M8/SF, Blanose Refined 7M, Blanose 7LF, Blanose 7MF, Blanose 9M31F, Blanose 12M31XP, Blanose 12M31P, Blanose 9M31XF, Blanose 7H, Blanose 7M31 and Blanose 7H3SXF (cellulose gums = sodium carboxymethyl-
25 cellulose) by Aqualon, or Aquasorb A500 and Ambergum 1221 by Hercules, or Cellogen HP810A and Cellogen HP6HS9 by Montello, or Primellose by Avebe) and carboxymethylhydroxyethylcelluloses, and their sodium salts.

30 The pectins can have various origins, such as apple, lemon, beet or sunflower. They may be esterified or amidated.

According to a specific embodiment of the invention, the thickening polymer i) comprising at
35 least one sugar unit which can be used according to the present invention is chosen from the group consisting of:

- i) - nonionic and chemically modified or unmodified guar gum;

- ii) - biopolysaccharide gums of microbial origin,
such as scleroglucan or xanthan gum;
iii) - gums resulting from plant exudates, such as
gums arabic, ghatti, karaya or tragacanth,
5 carrageenan, agar and locust bean gum;
iv) - pectins;
v) - alginates;
vi) - starches;
vii) - chemically unmodified celluloses;
10 viii)- hydroxy(C₁-C₆)alkylcelluloses and carboxy-
(C₁-C₆)alkylcelluloses and particularly
hydroxy(C₁-C₆)alkylcelluloses.

The thickening polymer or polymers i) of the
15 invention are preferably chosen from guar gums, xanthan
gums, starches or modified or unmodified celluloses.

The thickening polymer or polymers i) comprising
sugar unit(s) in accordance with the invention
preferably represent from 0.01 to 10% by weight and
20 more preferably still from 0.1 to 5% by weight, with
respect to the total weight of the composition.

Preferably, the ratio by weight of the compound or
compounds of formula (I) to the thickening polymer(s)
i) comprising sugar unit(s) in accordance with the
25 invention is between 0.01 and 20 and more preferably
still between 0.1 and 5.

**** According to another specific embodiment of the
invention, the thickening polymer is ii) a nonionic,
30 anionic or cationic associative polymer.**

The term "associative polymers" is understood to
mean water-soluble polymers capable, in an aqueous
medium, of reversibly associating with one another or
with other molecules. Their chemical structure
35 comprises hydrophilic regions and hydrophobic regions
characterized by at least one fatty chain.

The associative polymers according to the
invention can be of anionic, cationic, amphoteric or

nonionic type. Preferably, the associative polymers are cationic or nonionic.

According to a preferred embodiment of the invention, the associative thickening polymer ii) is of anionic type:

Mention may be made, among them, of:

- (A) those comprising at least one hydrophilic unit and at least one allyl ether unit comprising a fatty chain, more particularly those for which the hydrophilic unit is composed of an ethylenic unsaturated anionic monomer, more particularly still of a vinylcarboxylic acid and very particularly of an acrylic acid or a methacrylic acid or the mixtures of these, and for which the allyl ether unit comprising a fatty chain corresponds to the monomer of following formula (II'):



in which R' denotes H or CH₃, B denotes the ethyleneoxy radical, n is zero or denotes an integer ranging from 1 to 100, and R denotes a hydrocarbon radical chosen from alkyl, arylalkyl, aryl, alkylaryl or cycloalkyl radicals comprising from 8 to 30 carbon atoms, preferably from 10 to 24 carbon atoms, and more particularly still from 12 to 18 carbon atoms. A more particularly preferred unit of formula (II') is a unit in which R' denotes H, n is equal to 10 and R denotes a stearyl (C₁₈) radical.

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

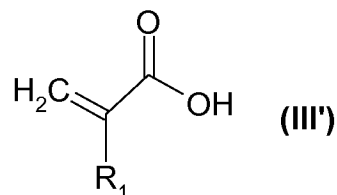
Preference is particularly given according to the invention, among these anionic associative polymers, to the polymers formed from 20 to 60% by weight of acrylic acid and/or methacrylic acid, from 5 to 60% by weight of lower alkyl (meth)acrylates, from 2 to 50% by weight of allyl ether comprising a fatty chain of formula (I), and from 0 to 1% by weight of a crosslinking agent which is a well-known copolymerizable polyethylenic unsaturated monomer,

such as diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide.

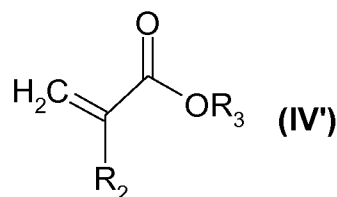
Among the latter, preference is very particularly given to crosslinked terpolymers of methacrylic acid, of ethyl acrylate and of polyethylene glycol (10 EO) ether of stearyl alcohol (Steareth 10), in particular those sold by Allied Colloids under the names Salcare SC 80® and Salcare SC90®, which are 30% aqueous emulsions of a crosslinked terpolymer of methacrylic acid, of ethyl acrylate and of steareth-10 allyl ether (40/50/10).

-(B) those comprising at least one hydrophilic unit of olefinic unsaturated carboxylic acid type and at least one hydrophobic unit of alkyl (C₁₀-C₃₀) ester of unsaturated carboxylic acid type.

Preferably, these polymers are chosen from those for which the hydrophilic unit of olefinic unsaturated carboxylic acid type corresponds to the monomer of following formula (III'):



in which formula (III') R₁ denotes H or CH₃ or C₂H₅, that is to say acrylic acid, methacrylic acid or ethacrylic acid units, and for which the hydrophobic unit of alkyl (C₁₀-C₃₀) ester of unsaturated carboxylic acid type corresponds to the monomer of following formula (IV'):



in which formula (**IV'**) R_2 denotes H or CH_3 or C_2H_5 (that is to say, acrylate, methacrylate or ethacrylate units) and preferably H (acrylate units) or CH_3 (methacrylate units), R_3 denoting a C_{10} - C_{30} and preferably C_{12} - C_{22} alkyl radical.

Alkyl (C_{10} - C_{30}) esters of unsaturated carboxylic acids in accordance with the invention comprise, for example, lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate, dodecyl acrylate, and the corresponding methacrylates, lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate.

Anionic polymers of this type are, for example, described and prepared according to Patents US-3 915 921 and 4 509 949.

Use will more particularly be made, among anionic associative thickening polymers ii) of this type, of polymers formed from a mixture of monomers comprising:

- (i) essentially acrylic acid,
- (ii) an ester of formula (**III'**) described above and in which R_2 denotes H or CH_3 , R_3 denoting an alkyl radical having from 12 to 22 carbon atoms, and
- (iii) a crosslinking agent which is a well-known copolymerizable polyethylenic unsaturated monomer, such as diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide.

Use will more particularly be made, among anionic associative thickening polymers ii) of this type, of those composed of 95 to 60% by weight of acrylic acid (hydrophilic unit), 4 to 40% by weight of C_{10} - C_{30} alkyl acrylate (hydrophobic unit) and 0 to 6% by weight of crosslinking polymerizable monomer or else those composed of 98 to 96% by weight of acrylic acid (hydrophilic unit), 1 to 4% by weight of C_{10} - C_{30} alkyl acrylate (hydrophobic unit) and 0.1 to 0.6% by weight of crosslinking polymerizable monomer such as those described above.

Preference is very particularly given according to the present invention, among the said polymers above, to the products sold by Goodrich under the trade names Pemulen TR1®, Pemulen TR2® or Carbopol 1382® and more preferably still to Pemulen TR1® and the product sold by S.E.P.P.I.C. under the name Coatex SX®.

5 - (C) maleic anhydride/C₃₀-C₃₈ α -olefin/alkyl maleate terpolymers, such as the product (maleic anhydride/C₃₀-C₃₈ α -olefin/isopropyl maleate copolymer)
10 sold under the name Performa V 1608® by Newphase Technologies.

 - (D) acrylic terpolymers comprising:

 (a) approximately 20% to 70% by weight of a
15 carboxylic acid comprising α,β -monoethylenic unsaturation,

 (b) approximately 20 to 80% by weight of a non-surface-active monomer comprising α,β -monoethylenic unsaturation other than (a),

20 (c) approximately 0.5 to 60% by weight of a nonionic monourethane which is the reaction product of a monohydric surfactant with a monoisocyanate comprising monoethylenic unsaturation,

 such as those described in Patent Application
25 EP-A-0 173 109 and more particularly that described in Example 3, namely a methacrylic acid/methyl acrylate/dimethyl(meta-isopropenyl)benzyl isocyanate of ethoxylated behenyl alcohol (40 EO) terpolymer as a 25% aqueous dispersion.

30 - (E) copolymers comprising, among their monomers, a carboxylic acid comprising α,β -monoethylenic unsaturation and an ester of a carboxylic acid comprising α,β -monoethylenic unsaturation and of an oxyalkylenated fatty alcohol.

35 Preferably, these compounds also comprise, as monomer, an ester of a carboxylic acid comprising α,β -monoethylenic unsaturation and of a C₁-C₄ alcohol.

 Mention may be made, as an example of this type of compound, of Aculyn 22®, sold by Rohm & Haas,

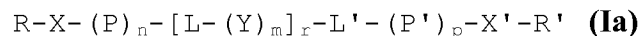
which is a methacrylic acid/ethyl acrylate/oxyalkylenated stearyl methacrylate terpolymer.

In these anionic associative polymers, use will preferably be made of the compounds of the families (B) and (E).

According to another preferred embodiment of the invention, the associative thickening polymer ii) is of cationic type:

Mention may be made, among them, of:

-(A') associative cationic polyurethanes, the family of which was described by the Applicant Company in French Patent Application No. 00/09609; it can be represented by the following general formula (Ia):



in which formula (Ia):

- o R and R', which are identical or different, represent a hydrophobic group or a hydrogen atom;
- o X and X', which are identical or different, represent a group comprising an amine functional group which may or may not carry a hydrophobic group, or alternatively the L" group;
- o L, L' and L", which are identical or different, represent a group derived from a diisocyanate;
- o P and P', which are identical or different, represent a group comprising an amine functional group which may or may not carry a hydrophobic group;
- o Y represents a hydrophilic group;
- o r is an integer between 1 and 100 inclusive, preferably between 1 and 50 inclusive and in particular between 1 and 25 inclusive,
- o n, m, and p have values, each independently of the others, between 0 and 1000 inclusive;

the molecule comprising at least one protonated or quaternized amine functional group and at least one hydrophobic group.

5 In a preferred embodiment of these polyurethanes, the sole hydrophobic groups are the R and R' groups at the chain ends.

A preferred family of cationic associative polyurethanes is that corresponding to the formula (**Ia**) described above in which:

- 10
- o R and R' both independently represent a hydrophobic group,
 - o X and X' each represent an L'' group,
 - o n and p are integers which have values between 1 and 1000 inclusive, and
 - 15 o L, L', L'', P, P', Y and m have the meanings indicated above.

Another preferred family of cationic associative polyurethanes is that corresponding to the formula (**Ia**) above in which:

- 20
- o The fact that n and p have the value 0 means that these polymers do not comprise units derived from a monomer comprising an amine functional group incorporated in a polymer during the polycondensation.
 - 25 o The protonated amine functional groups of these polyurethanes result from the hydrolysis of isocyanate functional groups, in excess, at the chain end, followed by the alkylation of the primary amine functional groups formed by
 - 30 alkylating agents comprising a hydrophobic group, that is to say compounds of RQ or R'Q type in which R and R' are as defined above and Q denotes a leaving group, such as a halide, a sulphate, and the like.

35 Yet another preferred family of cationic associative polyurethanes is that corresponding to the formula (**Ia**) above in which:

- o R and R' both independently represent a hydrophobic group,

- o X and X' both independently represent a group comprising a quaternary amine,
- o n and p have the value zero, and
- o L, L', Y and m have the meanings indicated above.

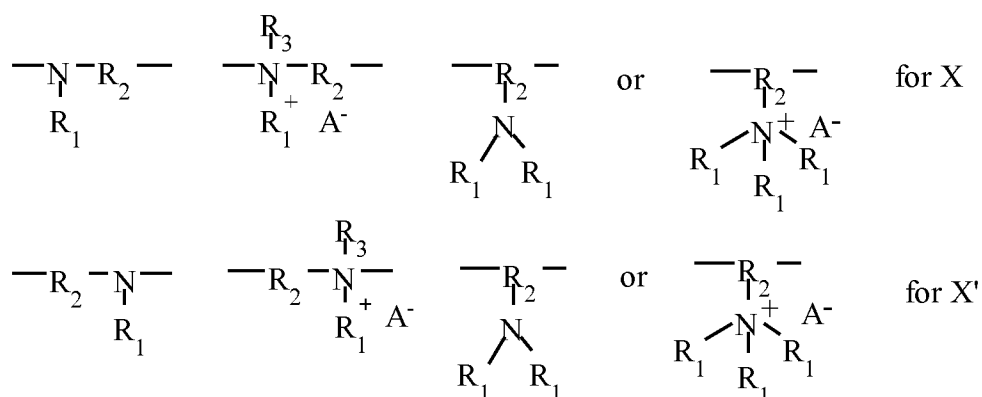
5 The number-average molecular weight of the cationic associative polyurethanes is preferably between 400 and 500 000 inclusive, in particular between 1000 and 400 000 inclusive and ideally between 1000 and 300 000 inclusive.

10 The term "hydrophobic group" is understood to mean a radical or polymer comprising a saturated or unsaturated and linear or branched hydrocarbon chain, which can comprise one or more heteroatoms, such as P, O, N, or S, or a radical comprising a
15 perfluorinated or silicone chain. When it denotes a hydrocarbon radical, the hydrophobic group comprises at least 10 carbon atoms, preferably from 10 to 30 carbon atoms, in particular from 12 to 30 carbon atoms and more preferably from 18 to 30 carbon
20 atoms.

 Preferably, the hydrocarbon group originates from a monofunctional compound.

 By way of example, the hydrophobic group can result from a fatty alcohol, such as stearyl
25 alcohol, dodecyl alcohol or decyl alcohol. It can also denote a hydrocarbon polymer, such as, for example, polybutadiene.

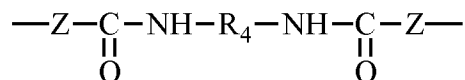
 When X and/or X' denote a group comprising a tertiary or quaternary amine, X and/or X' can
30 represent one of the following formulae:



in which:

- o R₂ represents a linear or branched alkylene radical having from 1 to 20 carbon atoms, which may or may not comprise a saturated or unsaturated ring, or an arylene radical, it being possible for one or more of the carbon atoms to be replaced by a heteroatom chosen from N, S, O or P;
- o R₁ and R₃, which are identical or different, denote a linear or branched C₁-C₃₀ alkyl or alkenyl radical or an aryl radical, it being possible for at least one of the carbon atoms to be replaced by a heteroatom chosen from N, S, O or P;
- o A⁻ is a physiologically acceptable anionic counterion, such as halide, for example chloride or bromide, or mesylate,

The L, L' and L'' groups represent a group of formula:

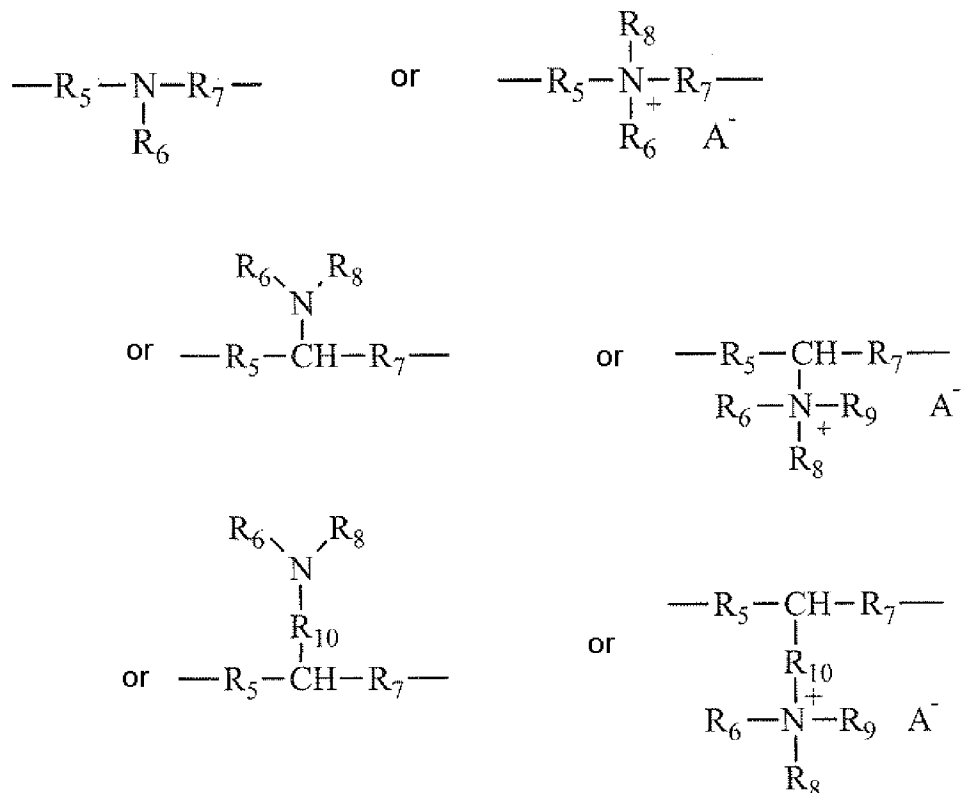


in which:

- o Z represents -O-, -S- or -NH-; and
- o R₄ represents a linear or branched alkylene radical having from 1 to 20 carbon atoms, which may or may not comprise a saturated or unsaturated ring, or an arylene radical, it being possible for one or

more of the carbon atoms to be replaced by a heteroatom chosen from N, S, O and P.

The P and P' groups, comprising an amine functional group, can represent at least one of the following formulae:



in which:

- o R₅ and R₇ have the same meanings as R₂ defined above;
- o R₆, R₈ and R₉ have the same meanings as R₁ and R₃ defined above;
- o R₁₀ represents a linear or branched alkylene group which is optionally unsaturated and which can comprise one or more heteroatoms chosen from N, O, S and P,
- o and A⁻ is a physiologically acceptable anionic counterion, such as halide, for example chloride or bromide, or mesylate.

As regards the meaning for Y, the term "hydrophilic group" is understood to mean a water-soluble polymeric or nonpolymeric group.

Mention may be made, by way of example, when polymers are not concerned, of ethylene glycol, diethylene glycol and propylene glycol.

When, in accordance with a preferred embodiment, a hydrophilic polymer is concerned, mention may be made, by way of example, of polyethers, sulphonated polyesters, sulphonated polyamides or a mixture of these polymers. Preferably, the hydrophilic compound is a polyether and in particular a poly(ethylene oxide) or poly(propylene oxide).

The cationic associative polyurethanes of formula (**Ia**) according to the invention are formed from diisocyanates and from various compounds having functional groups comprising a labile hydrogen. The functional groups comprising a labile hydrogen can be alcohol, primary or secondary amine or thiol functional groups which give, after reaction with the diisocyanate functional groups, polyurethanes, polyureas and polythioureas respectively. The term "polyurethanes" of the present invention encompasses these three types of polymers, namely polyurethanes proper, polyureas and polythioureas, and copolymers of these.

A first type of compound participating in the preparation of the polyurethane of formula (**Ia**) is a compound comprising at least one unit comprising an amine functional group. This compound can be polyfunctional but, preferably, the compound is difunctional, that is to say that, according to a preferred embodiment, this compound comprises two labile hydrogen atoms carried, for example, by a hydroxyl, primary amine, secondary amine or thiol functional group. Use may also be made of a mixture of polyfunctional and difunctional compounds in which the percentage of polyfunctional compounds is low.

As indicated above, this compound can comprise more than one unit comprising an amine functional group. It is then a polymer carrying a repetition of the unit comprising an amine functional group.

Compounds of this type can be represented by one of the following formulae:



in which Z, P, P', n and p are as defined above.

Mention may be made, as an example of a compound comprising an amine functional group, of N-methyldiethanolamine, N-tert-butyldiethanolamine or N-sulphoethyldiethanolamine.

The second compound participating in the preparation of the polyurethane of formula (**Ia**) is a diisocyanate corresponding to the formula:



in which R₄ is defined above.

Mention may be made, by way of example, of methylenediphenyl diisocyanate, methylenecyclohexane diisocyanate, isophorone diisocyanate, toluene diisocyanate, naphthalene diisocyanate, butane diisocyanate or hexane diisocyanate.

A third compound which participates in the preparation of the polyurethane of formula (**Ia**) is a hydrophobic compound intended to form the end hydrophobic groups of the polymer of formula (**Ia**).

This compound is composed of a hydrophobic group and of a functional group comprising a labile hydrogen, for example a hydroxyl, primary or secondary amine or thiol functional group.

By way of example, this compound can be a fatty alcohol, such as in particular stearyl alcohol, dodecyl alcohol or decyl alcohol. When this compound comprises a polymer chain, it can, for example, be α -hydroxyl hydrogenated polybutadiene.

The hydrophobic group of the polyurethane of formula (**Ia**) can also result from the quaternization reaction of the tertiary amine of the compound comprising at least one tertiary amine unit. Thus, the hydrophobic group is introduced by the quaternizing agent. This quaternizing agent is a compound of RQ or R'Q type in which R and R' are as defined above and Q denotes a leaving group, such as a halide, a sulphate, and the like.

The cationic associative polyurethane can additionally comprise a hydrophilic sequence. This sequence is contributed by a fourth type of compound participating in the preparation of the polymer. This compound can be polyfunctional. It is preferably difunctional. It is also possible to have a mixture where the percentage of polyfunctional compound is low.

The functional groups comprising a labile hydrogen are alcohol, primary or secondary amine or thiol functional groups. This compound can be a polymer terminated at the ends of the chains by one of these functional groups comprising a labile hydrogen.

Mention may be made, by way of example, when polymers are not concerned, of ethylene glycol, diethylene glycol and propylene glycol.

When a hydrophilic polymer is concerned, mention may be made, by way of example, of polyethers, sulphonated polyesters, sulphonated polyamides or a mixture of these polymers. Preferably, the hydrophilic compound is a polyether and in particular a poly(ethylene oxide) or poly(propylene oxide).

The hydrophilic group recorded as Y in the formula (**Ia**) is optional. This is because the units comprising a quaternary or protonated amine functional group may be sufficient to contribute the solubility or water-dispersibility necessary for this type of polymer in an aqueous solution.

Although the presence of a hydrophilic Y group is optional, preference is given, however, to cationic

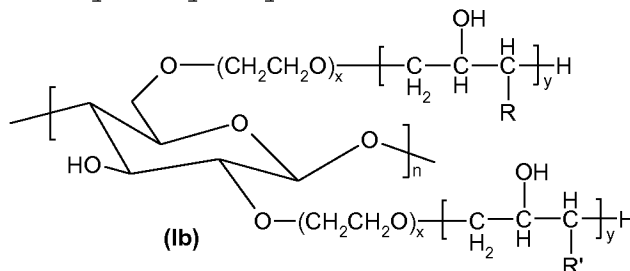
associative polyurethanes comprising such a group.

-(B') quaternized cellulose derivatives. The quaternized cellulose derivatives are in particular,

- i) quaternized celluloses modified by groups comprising at least one fatty chain, such as linear or branched alkyl, linear or branched arylalkyl or linear or branched alkylaryl groups comprising at least 8 carbon atoms, or mixtures of these;

- ii) quaternized hydroxyethylcelluloses modified by groups comprising at least one fatty chain, such as linear or branched alkyl, linear or branched arylalkyl or linear or branched alkylaryl groups comprising at least 8 carbon atoms, or mixtures of these;

- iii) hydroxyethylcelluloses of formula (Ib):



in which formula (Ib):

o R and R', which are identical or different, represent an ammonium group, such as $-N^+R_aR_bR_c Q^-$, in which R_a , R_b and R_c , which are identical or different, represent a hydrogen atom or a linear or branched C_1 - C_{30} , preferably C_1 - C_{20} , alkyl group, such as methyl or dodecyl, and Q^- represents an anionic counterion, such as halide, for example a chloride or bromide;

o n, x and y, which are identical or different, represent an integer between 1 and 10 000.

The alkyl radicals carried by the above quaternized celluloses i) or hydroxyethylcelluloses ii) preferably comprise from 8 to 30 carbon atoms. The aryl radicals preferably denote the phenyl, benzyl, naphthyl or anthryl groups.

Examples of quaternized alkylhydroxyethylcelluloses comprising C_8 - C_{30} fatty chains which may be

indicated are the products Quatrisoft LM 200®, Quatrisoft LM-X 529-18-A®, Quatrisoft LM-X 529-18B® (C₁₂ alkyl) and Quatrisoft LM-X 529-8® (C₁₈ alkyl) sold by Amerchol and the products Crodacel QM®, Crodacel QL® (C₁₂ alkyl) and Crodacel QS® (C₁₈ alkyl) sold by Croda.

Mention may also be made of hydroxyethylcelluloses of formula (**Ib**) in which R represents trimethylammonium halide and R' represents dimethyldodecylammonium halide; more preferably, R represents a trimethylammonium chloride- $\text{N}^+(\text{CH}_3)_3 \text{Cl}^-$ and R' represents dimethyldodecylammonium chloride- $\text{N}^+(\text{CH}_3)_2(\text{C}_{12}\text{H}_{25}) \text{Cl}^-$. Polymers of this type are known under the SoftCAT Polymer SL[®] trade names, such as SL-100 and SL-60.

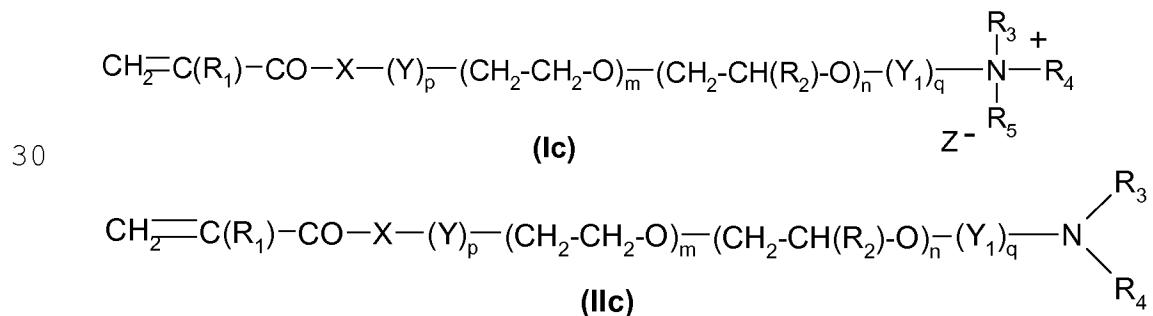
More particularly, the polymers of formula (Ib) are those having a viscosity of between 2000 and 3000 cPs inclusive. Preferably, the viscosity is between 2700 and 2800 cPs inclusive. Typically, the softCAT Polymer SL-5 has a viscosity of 2500 cPs, the softCAT Polymer SL-30 has a viscosity of 2700 cPs, the softCAT Polymer SL-60 has a viscosity of 2700 cPs and the softCAT Polymer SL-100 has a viscosity of 2800 cPs.

-**(C')** Cationic polyvinyl lactams, the family of which was described by the Applicant Company in French Patent Application No. 0 101 106.

25 The said polymers comprise:

-a) at least one monomer of vinyl lactam or alkyl-vinyl lactam type;

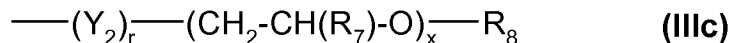
-b) at least one monomer with the following structure (**Ic**) or (**IIc**):



in which formulae **(Ic)** and **(IIc)**:

o X denotes an oxygen atom or an NR_6 radical,

- o R_1 and R_6 denote, independently of one another, a hydrogen atom or a linear or branched C_1 - C_5 alkyl radical,
- o R_2 denotes a linear or branched C_1 - C_4 alkyl radical,
- 5 o R_3 , R_4 and R_5 denote, independently of one another, a hydrogen atom, a linear or branched C_1 - C_{30} alkyl radical or a radical of formula (**IIIc**):



- 10 - Y , Y_1 and Y_2 denote, independently of one another, a linear or branched C_2 - C_{16} alkylene radical,
- R_7 denotes a hydrogen atom or a linear or branched C_1 - C_4 alkyl radical or a linear or branched C_1 - C_4 hydroxyalkyl radical,
- 15 - R_8 denotes a hydrogen atom or a linear or branched C_1 - C_{30} alkyl radical,
- o p , q and r denote, independently of one another, either the value 0 or the value 1,
- o m and n denote, independently of one another, an integer ranging from 0 to 100 inclusive,
- 20 o x denotes an integer ranging from 1 to 100 inclusive,
- o Z denotes an organic or inorganic acid anionic counterion, such as halide, for example chloride or bromide, or mesylate;
- 25 with the proviso that:
 - at least one of the substituents R_3 , R_4 , R_5 or R_8 denotes a linear or branched C_9 - C_{30} alkyl radical,
 - if m or n is other than zero, then q is equal to 1,
 - 30 - if m or n are equal to zero, then p or q is equal to 0.

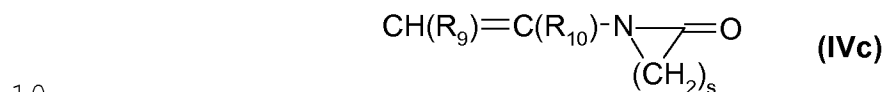
The cationic poly(vinyl lactam) polymers according to the invention may or may not be crosslinked and may also be block polymers.

- 35 Preferably, the Z^- counterion or the monomers of formula (**Ic**) is chosen from halide ions, phosphate ions, the methosulphate ion or the tosylate ion.

Preferably, R_3 , R_4 and R_5 denote, independently of one another, a hydrogen atom or a linear or branched C_1 - C_{30} alkyl radical.

More preferably, the monomer b) is a monomer of formula (**Ic**) for which, more preferably still, m and n are equal to zero.

The vinyl lactam or alkylvinyl lactam monomer is preferably a compound with the structure (**IVc**):



in which:

- o s denotes an integer ranging from 3 to 6,
 - o R_9 denotes a hydrogen atom or a linear or branched C_1 - C_5 alkyl radical,
 - o R_{10} denotes a hydrogen atom or a linear or branched C_1 - C_5 alkyl radical,
- with the proviso that at least one of the R_9 and R_{10} radicals denotes a hydrogen atom.

More preferably still, the monomer (**IVc**) is vinylpyrrolidone.

The cationic poly(vinyl lactam) polymers according to the invention can also comprise one or more additional monomers, preferably cationic or nonionic monomers.

Mention may be made, as thickening polymers ii) more particularly preferred according to the invention, of the following terpolymers comprising at least:

- a)- one monomer of formula (**IVc**),
- b)- one monomer of formula (**Ic**) in which $p = 1$, $q = 0$, R_3 and R_4 denote, independently of one another, a hydrogen atom or a C_1 - C_5 alkyl radical and R_5 denotes a linear or branched C_9 - C_{24} alkyl radical and
- c)- one monomer of formula (**IIc**) in which R_3 and R_4 denote, independently of one another, a hydrogen atom or a linear or branched C_1 - C_5 alkyl radical.

More preferably still, use will be made of the terpolymers comprising, by weight, from 40 to 95% of monomer (a), from 0.1 to 55% of monomer (c) and from 0.25 to 50% of monomer (b).

5 Such polymers are described in Patent Application WO-00/68282, the content of which forms an integral part of the invention.

Use is made in particular, as cationic poly(vinyl-lactam) polymers according to the invention, of vinyl-
10 pyrrolidone/dimethylaminopropylmethacrylamide/dodecyl-dimethylmethacrylamidopropylammonium tosylate terpolymers, vinylpyrrolidone/dimethylaminopropyl-methacrylamide/cocoyldimethylmethacrylamidopropyl-ammonium tosylate terpolymers or vinylpyrrolidone/di-
15 methylaminopropylmethacrylamide/lauryldimethylmeth-acrylamidopropylammonium tosylate or chloride terpolymers.

The weight-average molecular weight of the cationic poly(vinyl-lactam) polymers according to the
20 present invention is preferably between 500 and 20 000 000. It is more particularly between 200 000 and 2 000 000 and more preferably still between 400 000 and 800 000.

*According to another preferred embodiment of the
25 invention, the associative thickening polymer ii) is of nonionic type:*

According to the invention, they are preferably chosen from:

- (1) celluloses modified by groups comprising at
30 least one fatty chain;

mention may be made, by way of example, of:

- hydroxyethylcelluloses modified by groups comprising at least one fatty chain, such as linear or branched alkyl, linear or branched arylalkyl or linear
35 or branched alkylaryl groups, or their mixtures, and in which the linear or branched alkyl groups are preferably C₈-C₂₂ alkyl groups, such as the product Natrosol Plus Grade 330 CS® (C₁₆ alkyl) sold by Aqualon or the product Bermocoll EHM 100® sold by Berol Nobel,

- those modified by alkylphenol polyalkylene glycol ether groups, such as the product Amercell Polymer HM-1500® (nonylphenol polyethylene glycol (15) ether) sold by Amerchol.

5 -(2) hydroxypropyl guar modified by groups comprising at least one fatty chain, such as the product Esaflor HM 22® (C₂₂ alkyl chain) sold by Lamberti or the products RE210-18® (C₁₄ alkyl chain) and RE205-1® (C₂₀ alkyl chain) sold by Rhône-Poulenc.

10 -(3) copolymers of vinylpyrrolidone and of hydrophobic monomers comprising a fatty chain, of which may be mentioned, by way of example:

- the products Antaron V216® or Ganex V216® (vinylpyrrolidone/hexadecene copolymer) sold by I.S.P.,

15 - the products Antaron V220® or Ganex V220® (vinylpyrrolidone/eicosene copolymer) sold by I.S.P.

- (4) copolymers of C₁-C₆ alkyl methacrylates or acrylates and of amphiphilic monomers comprising at least one fatty chain, such as, for example, the methyl
20 acrylate/oxyethylenated stearyl acrylate copolymer sold by Goldschmidt under the name Antil 208®.

- (5) copolymers of hydrophilic methacrylates or acrylates and of hydrophobic monomers comprising at least one fatty chain, such as, for example, the
25 polyethylene glycol methacrylate/lauryl methacrylate copolymer.

- (6) polyether polyurethanes comprising, in their chain, both hydrophilic sequences of generally polyoxyethylene nature and hydrophobic sequences which
30 can be aliphatic strings only and/or cycloaliphatic and/or aromatic strings.

- (7) polymers comprising an aminoplast ether backbone having at least one fatty chain, such as the compounds Pure Thix® provided by Sud-Chemie.

35 Preferably, the polyether polyurethanes comprise at least two lipophilic hydrocarbon chains having from 6 to 30 carbon atoms which are separated by a hydrophilic sequence, it being possible for the hydrocarbon chains to be pendant chains or chains at the end of the

hydrophilic sequence. In particular, it is possible for one or more pendant chains to be provided. In addition, the polymer can comprise a hydrocarbon chain at one end or at both ends of a hydrophilic sequence.

5 The polyether polyurethanes can be polysequential, in particular in the triblock form. The hydrophobic sequences can be at each end of the chain (for example: triblock copolymer comprising a central hydrophilic sequence) or distributed both at the ends and in the
10 chain (polysequential copolymer, for example). These same polymers can also be graft polymers or star polymers.

 The nonionic polyether polyurethanes comprising a fatty chain can be triblock copolymers, the hydrophilic
15 sequence of which is a polyoxyethylene chain comprising from 50 to 1000 oxyethylene groups. The nonionic polyether polyurethanes comprise a urethane bond between the hydrophilic sequences, hence the origin of the name.

 By extension, the nonionic polyether polyurethanes
20 comprising a fatty chain optionally include those of which the hydrophilic sequences are bonded to the lipophilic sequences via other chemical bonds.

 Use may also be made, as examples of nonionic polyether polyurethanes comprising a fatty chain which
25 can be used in the invention, of Rhéolate 205® comprising a urea functional group sold by Rheox or Rhéolates® 208, 204 or 212, and also Acrysol RM 184®.

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

 The product DW 1206B® from Rohm & Haas comprising a C₂₀ alkyl chain and comprising a urethane bond, provided at a dry matter content of 20% in water, can also be used.

35 Use may also be made of solutions or dispersions of these polymers, in particular in water or in an aqueous/alcoholic medium. Mention may be made, as examples of such polymers, of Rhéolate® 255, Rhéolate®

278 and Rhéolate® 244, sold by Rheox. Use may also be made of the products DW 1206F and DW 1206J provided by Rohm & Haas.

5 The polyether polyurethanes which can be used according to the invention are in particular those described in the paper by G. Fonnum, J. Bakke and Fk. Hansen, Colloid Polym. Sci., 271, 380-389 (1993).

More particularly still, it is preferable, according to the invention, to use a thickening polymer
10 iii) which is a polyether polyurethane capable of being obtained by polycondensation of at least three compounds comprising

- (i) at least one polyethylene glycol comprising from 150 to 180 mol of ethylene oxide,
- 15 (ii) stearyl alcohol or decyl alcohol and
- (iii) at least one diisocyanate.

Such polyether polyurethanes are sold in particular by Rohm & Haas under the names Aculyn 46® and Aculyn 44® [Aculyn 46® is a polycondensate of
20 polyethylene glycol comprising 150 or 180 mol of ethylene oxide, of stearyl alcohol and of methylenebis(4-cyclohexyl isocyanate) (SMDI), at 15% by weight in a matrix of maltodextrin (4%) and of water (81%); Aculyn 44® is a polycondensate of
25 polyethylene glycol comprising 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 of water (26%)].

30 In a first preferred alternative form of the invention, the thickening polymers ii) are the associative thickening polymers chosen from those of the families **(1)**, **(6)**, **(E)**, **(B)** and **(B')**.

In a preferred composition according to the
35 present invention, the associative polymers are chosen from those of nonionic or cationic type and more particularly still from polyether urethanes comprising

hydrophilic and hydrophobic sequences, nonionic cellulose derivatives comprising at least one fatty chain and quaternized cellulose derivatives comprising at least one fatty chain.

5 Mention may particularly be made, as preferred polymers according to the invention, of the nonionic polyurethanes Aculyn 44[®] and Aculyn 46[®], the cetyl hydroxyethyl cellulose Natrosol Plus Grade 330 CS[®] and the cationic celluloses SoftCAT Polymer SL-100[®] e,
10 SoftCAT Polymer SL-60[®] or Quatrisoft LM200.

 In an even more particularly preferred composition according to the invention, the associative thickening polymer ii) is chosen from nonionic or cationic cellulose derivatives comprising
15 at least one fatty chain.

 The nonionic, anionic or cationic associative thickening polymer or polymers ii) used in the composition according to the invention can be present in an amount varying from 0.01 to 20% by weight, preferably in an amount varying from 0.1 to 15% by weight and more preferably still in an amount varying from 0.1 to 10% by weight, with respect to the total weight of the composition.
20

 Preferably, the ratio by weight of the compound of formula (I) or its salts to the nonionic, anionic or cationic associative thickening polymer or polymers ii) in accordance with the invention is between 0.005 and 20 and more preferably still between 0.001 and 10, better still between 0.05 and 1.
25

30

***** According to another preferred alternative form of the invention, the thickening polymer is iii) a non-silicone cationic polymer without a fatty chain.**

 In this case, the compositions of the invention
35 comprise at least one non-silicone cationic thickening polymer iii) without a fatty chain.

 Generally, within the meaning of the present invention, the expression "cationic polymer" denotes

any polymer comprising cationic groups and/or groups which can be ionized to give cationic groups.

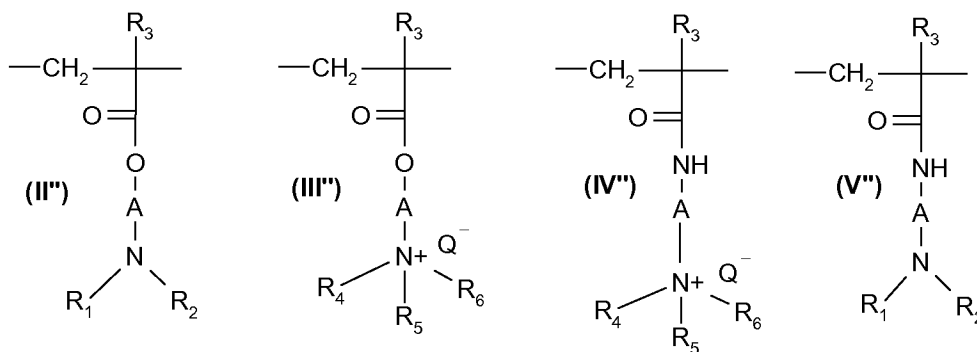
The non-silicone cationic polymers without a fatty chain which are preferred are chosen from those which
 5 comprise units comprising primary, secondary, tertiary and/or quaternary amine groups which can either form part of the main polymer chain or be contributed by a side substituent directly connected to the latter.

The non-silicone cationic polymers without a fatty
 10 chain used preferably have a number-average or weight-average molar mass of between 500 and 5×10^6 approximately and preferably of between 10^3 and 3×10^6 .

Mention may more particularly be made, among non-silicone cationic polymers without a fatty chain, of
 15 polymers of the polyamine, polyaminoamide and polyquaternary ammonium type, in particular those described in French Patents FR 2 505 348 and FR 2 542 997.

According to a specific embodiment of the invention, the cationic polymers are chosen from:

20 (1') Homopolymers or copolymers derived from acrylic or methacrylic esters or amides and comprising at least one of the units of following formulae (II''), (III''), (IV'') or (V''):



25 in which formulae (II'') to (V''):

- **R₃**, which are identical or different, denote a hydrogen atom or a CH₃ radical;
- **A**, which are identical or different, represent a
 30 linear or branched C₁-C₆, preferably C₂-C₃, alkyl group or a C₁-C₄ hydroxyalkyl group;

- R_4 , R_5 and R_6 , which are identical or different, represent a C_1 - C_6 alkyl group or a benzyl radical and preferably a C_1 - C_4 alkyl group;
- R_1 and R_2 , which are identical or different, represent hydrogen or a C_1 - C_6 alkyl group, and preferably methyl or ethyl;
- Q^- denotes an anionic counterion derived from an inorganic or organic acid, such as a methosulphate anion or a halide, such as chloride or bromide.

According to a specific embodiment of the invention, in the case of the formulae with the structures (II'') and (V''), at least one of the radicals R_3 or A comprises or carries an $-N^+R_4R_5R_6$ Q^- cationic group with R_4 , R_5 and R_6 as defined above.

The polymers of the family (1') can additionally comprise one or more units deriving from comonomers which can be chosen from the family of the acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides substituted under nitrogen with lower (C_1 - C_4) alkyls, acrylic or methacrylic acids or their esters, vinyl lactams, such as vinylpyrrolidone or vinylcaprolactam, or vinyl esters.

Thus, mention may be made, among these polymers of the family (1'), of:

- copolymers of acrylamide and of dimethylaminoethyl methacrylate quaternized with dimethylsulphate or with a methyl halide, such as that sold under the name Hercofloc by Hercules,
- copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium chloride described, for example, in EP 80976 and sold under the name Bina Quat P 100 by Ciba Geigy,
- the copolymer of acrylamide and of methacryloyloxyethyltrimethylammonium methosulphate sold under the name Reten by Hercules,
- quaternized or nonquaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers, such as the products sold under the name "Gafquat" by ISP, such as, for example,

"Gafquat 734" or "Gafquat 755", or else the products known as "Copolymer 845, 958 and 937". These polymers are described in FR 2 077 143 and FR 2 393 573,

- 5 - dimethylaminoethyl methacrylate/vinylcaprolactam/vinylpyrrolidone terpolymers, such as the product sold under the name Gaffix VC 713 by ISP,
- vinylpyrrolidone/methacrylamidopropyl dimethylamine copolymers, sold in particular under the name
- 10 Styleze CC 10 by ISP,
- quaternized vinylpyrrolidone/dimethylaminopropylmethacrylamide copolymers, such as the product sold under the name "Gafquat HS 100" by ISP;
- and crosslinked polymers of methacryloyloxy(C₁-C₄)alkyltri(C₁-C₄)alkylammonium salts, such as
- 15 polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride or by copolymerization of acrylamide with dimethylaminoethyl methacrylate
- 20 quaternized with methyl chloride, the homo- or the copolymerization being followed by a crosslinking with a compound possessing olefinic unsaturation, in particular methylenebisacrylamide. Use may more particularly be made of a crosslinked acrylamide/
- 25 methacryloyloxyethyltrimethylammonium chloride copolymer (20/80 by weight) in the form of a dispersion comprising 50% by weight of the said copolymer in mineral oil. This dispersion is sold under the name of "Salcare® SC 92" by Ciba. Use may
- 30 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 of
- 35 "Salcare® SC 95" and "Salcare® SC 96" by Ciba.

(2') The cellulose ether derivatives comprising quaternary ammonium groups described in FR 1 492 597 and in particular the polymers sold under the "JR" names (JR 400, JR 125, JR 30M) or "LR" names (LR 400,

LR 30M) by Union Carbide Corporation. These polymers are also defined in the CTFA dictionary as quaternary ammoniums of hydroxyethylcellulose which has reacted with an epoxide substituted with a trimethylammonium group.

(3') Cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer, and described in particular in US 4 131 576, such as hydroxyalkylcelluloses, such as hydroxymethyl-, hydroxyethyl- or hydroxypropylcelluloses, grafted in particular with a methacryloyloxyethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt.

The products sold according to this definition are more particularly the products sold under the names "Celquat L 200" and "Celquat H 100" by National Starch.

(4') The cationic non-cellulose polysaccharides described in Patents US 3 589 578 and 4 031 307, such as guar gums comprising cationic trialkylammonium groups. Use is made, for example, of guar gums modified with a 2,3-epoxypropyltrimethylammonium salt (for example chloride).

Such products are sold in particular under the trade names of Jaguar C13S, Jaguar C15, Jaguar C17 or Jaguar C162 by Meyhall.

(5') Polymers composed of piperazinyl units and of divalent alkylene or hydroxyalkylene radicals possessing straight or branched chains, optionally interrupted by oxygen, sulphur or nitrogen atoms or by aromatic or heterocyclic rings, and the oxidation and/or quaternization products of these polymers. Such polymers are described in particular in FR 2 162 025 and FR 2 280 361.

(6') Water-soluble polyaminoamides prepared in particular by polycondensation of an acid compound with a polyamine; these polyaminoamides can be crosslinked with an epihalohydrin, a diepoxide, a dianhydride, an unsaturated dianhydride, a bisunsaturated derivative, a bishalohydrin, a bisazetadinium, a bishaloacyldiamine

or a bis(alkyl halide) or also with an oligomer resulting from the reaction of a bifunctional compound which is reactive with respect to a bishalohydrin, a bisazetadinium, a bishaloacyldiamine, a bis(alkyl
5 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 comprise
10 one or more tertiary amine functional groups, quaternized. Such polymers are described in particular in FR 2 252 840 and FR 2 368 508.

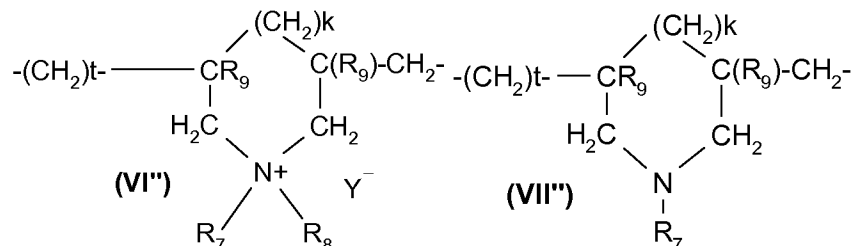
Polyaminoamide derivatives resulting from the condensation of polyalkylenepolyamines with poly-
15 carboxylic acids, followed by an alkylation with bifunctional agents. Mention may be made, for example, of adipic acid/dialkylaminohydroxyalkyldialkylenetriamine polymers in which the alkyl radical is a C₁-C₄ alkyl radical and preferably denotes methyl, ethyl or
20 propyl. Such polymers are described in particular in FR 1 583 363.

Mention may more particularly be made, among these derivatives, of the adipic acid/dimethylaminohydroxypropyl/diethylenetriamine polymers sold under the name
25 "Cartaretine F, F4 or F8" by Sandoz.

(7') Polymers obtained by reaction of a polyalkylenepolyamine comprising two primary amine groups and at least one secondary amine group with a dicarboxylic acid chosen from diglycolic acid and saturated C₃-C₈,
30 preferably C₃-C₆, aliphatic dicarboxylic acids, the molar ratio of the polyalkylenepolyamine to the dicarboxylic acid being between 0.8:1 and 1.4:1; the polyaminoamide resulting therefrom being reacted with epichlorohydrin in a molar ratio of epichlorohydrin
35 with respect to the secondary amine group of the polyaminoamide of between 0.5:1 and 1.8:1. Such polymers are described in particular in US 3 227 615 and US 2 961 347.

Polymers of this type are sold in particular under the name "Hercosett 57", "PD 170" or "Delsette 101" by Hercules.

(8') Alkyldiallylamine or dialkyldiallylammonium cyclopolymers, such as homopolymers or copolymers comprising, as main constituent of the chain, units corresponding to the formulae (VI'') and (VII''):



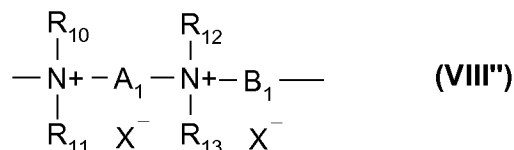
in which formulae (VI'') and (VII''):

- **k** and **t** are equal to 0 or 1, the sum $k + t$ being equal to 1;
- **R₉** denotes a hydrogen atom or a methyl radical;
- **R₇** and **R₈** denote, independently of one another, a linear or branched C₁-C₈, preferably C₁-C₆, alkyl group, a hydroxyalkyl group in which the alkyl group is a linear or branched C₁-C₅ alkyl group, or an amidoalkyl group, the alkyl of which is a linear or branched C₁-C₄ alkyl group;
- **R₇** and **R₈** can also denote, jointly with the nitrogen atom to which they are attached, a heterocyclic group, such as piperidinyl or morpholinyl;
- **R₇** and **R₈** preferably denote, independently of one another, a linear or branched C₁-C₄ alkyl group;
- **Y⁻** is an organic or inorganic anionic counterion, such as halide, for example bromide or chloride, or acetate, borate, citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate. These polymers are described in particular in FR 2 080 759 and FR 2 190 406.

Mention may more particularly be made, among the thickening polymers iii) defined above, of the dimethyldiallylammonium chloride homopolymer sold under

the name "Merquat 100" or "Polyquaternium-6" by Nalco (and its homologues of low weight-average molecular weight) and the copolymers of diallyldimethylammonium chloride and of acrylamide sold under the name "Merquat 5 550".

(9') Diquaternary ammonium polymers comprising repeat units corresponding to the following formula:



10 in which formula (VIII'):

- **R₁₀**, **R₁₁**, **R₁₂** and **R₁₃**, which are identical or different, represent C₁-C₆ aliphatic, alicyclic or arylaliphatic radicals or represent aliphatic hydroxyalkyl radicals, the alkyl radical of which is a linear or branched C₁-C₄ alkyl radical, or else R₁₀, R₁₁, R₁₂ and R₁₃, together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second heteroatom other than nitrogen, or else R₁₀, R₁₁, R₁₂ and R₁₃ represent a linear or branched C₁-C₆ alkyl radical substituted by a nitrile, ester, acyl, amide or -CO-O-R₁₄-D or -CO-NH-R₁₄-D group where R₁₄ is a linear or branched, preferably C₁-C₆, alkylene and D is a quaternary ammonium group of -N⁺R₄R₅R₆ Q⁻ type, where R₄, R₅, R₆ and Q⁻ are as defined above;
- **A₁** and **B₁**, which are identical or different, represent saturated or unsaturated, linear or branched, C₂-C₆ polymethylene groups which can comprise, bonded to or intercalated in the main chain, one or more aromatic rings or one or more oxygen or sulphur atoms or sulfoxide, sulphone, disulphide, amino, alkylamino, hydroxyl, quaternary ammonium, ureido, amide or ester groups, and

- X^- , which are identical or different, denote an anionic counterion derived from an inorganic or organic acid, such as a halide;
- A_1 , R_{10} and R_{12} can form, with the two nitrogen atoms to which they are attached, a piperazine ring;

in addition, if A_1 denotes a linear or branched alkylene radical or a linear or branched hydroxyalkylene radical which is saturated or unsaturated, B_1 can also denote a group: $-(CH_2)_n-CO-D-OC-(CH_2)_n-$, in which n is an integer ranging from 1 to 6 inclusive and D denotes a quaternary ammonium group:

- a) a glycol residue of formula: $-O-Z-O-$, where Z denotes a linear or branched hydrocarbon radical or a group corresponding to one of the following formulae:

$-(CH_2-CH_2-O)_x-CH_2-CH_2-$; $-[CH_2-CH(CH_3)-O]_y-CH_2-CH(CH_3)-$, where 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 a mean degree of polymerization;

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

- c) a bisprimary diamine residue of formula: $-NH-Y-NH-$, where Y denotes a linear or branched hydrocarbon radical, or else the $-CH_2-CH_2-S-S-CH_2-CH_2-$ radical;

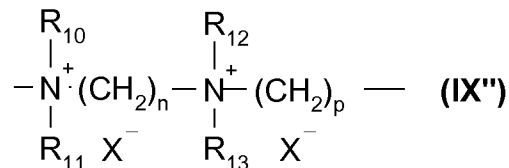
- d) a ureylene group of formula: $-NH-CO-NH-$.

Preferably, X^- is an anionic counterion, such as a halide, for example chloride or bromide.

These polymers have a number-average molecular weight generally between 1000 and 100 000.

Polymers of this type are described in particular in FR 2 320 330, FR 2 270 846, FR 2 316 271, FR 2 336 434, FR 2 413 907, US 2 273 780, US 2 375 853, US 2 388 614, US 2 454 547, US 3 206 462, US 2 261 002, US 2 271 378, US 3 874 870, US 4 001 432, US 3 929 990, US 3 966 904, US 4 005 193, US 4 025 617, US 4 025 627, US 4 025 653, US 4 026 945 and US 4 027 020.

Use may more particularly be made of thickening polymers which are composed of repeat units corresponding to the following formula (IX''):



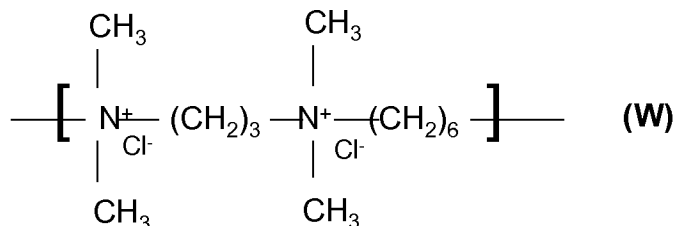
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in which formula (IX''):

- R_{10} , R_{11} , R_{12} and R_{13} , which are identical or different, denote a linear or branched C_1 - C_4 alkyl radical or a linear or branched C_1 - C_4 hydroxyalkyl radical;
- n and p are integers varying from 2 to 6 approximately inclusive and;
- X^- , which are identical or different, are an anionic counterion derived from an inorganic or organic acid, such as a halide.

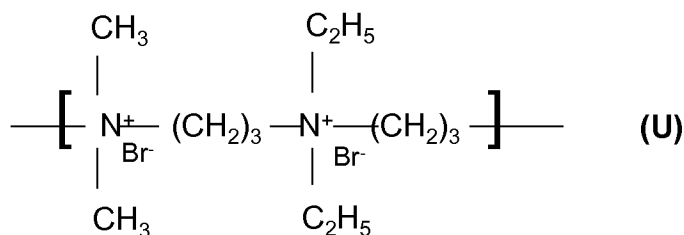
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More advantageously still, the cationic polymers corresponding to this family comprise the repeat units of following formulae (W) and (U):



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and in particular those having a molecular weight, determined by gel permeation chromatography, of between 9500 and 9900;

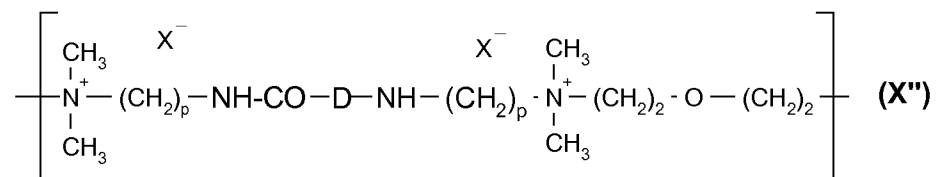


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and in particular those having a molecular weight, determined by gel permeation chromatography, of approximately 1200.

Mention may be made of the tetramethylhexa-
methylenediamine/1,3-propylene dichloride poly-
condensate. Mention may also be made of the
diethyldimethylethylenediamine/1,3-propylene dibromide
5 polycondensate (Polyquaternium-34).

(10') Polyquaternary ammonium polymers composed of
repeat units of formula (X''):



10 in which formula (X'') p denotes an integer varying from
1 to 6 approximately inclusive, D can be zero, i.e. can
correspond to a σ bond, or can represent a $\text{---}(\text{CH}_2)_r\text{---CO---}$
group in which r denotes a number equal to 4 or to 7,
and X^- is an anionic counterion as defined above.

15 Such polymers can be prepared according to the
processes described in US 4 157 388, US 4 702 906 and
US 4 719 282. They are described in particular in
Patent Application EP 122 324.

Mention may be made among them, for example, of
20 the products "Mirapol A 15", "Mirapol AD1", "Mirapol
AZ1" and "Mirapol 175", sold by Miranol.

(11') Quaternary polymers of vinylpyrrolidone and of
vinylimidazole, such as, for example, the products sold
under the names Luviquat FC 905, FC 550 and FC 370 by
25 BASF.

(12') Polylysines, which correspond more particularly
to the condensation of several lysine amino acids.

Mention may be made, as examples of polylysine,
of:

- 30 - the poly(ϵ -L-lysine) (N=5) sold by Chisso
Corporation, which is a 5% solution of polylysine
in water;
- the product polylysine 10% solution M grade from
Chisso Corporation, which is a 10% solution of
35 polylysine in water;

- the product polylysine 25% solution from Chisso Corporation, which is a 25% solution of polylysine in water;
- the product polylysine 50% from Chisso Corporation, which is a 50/50 mixture of polylysine (N=25 to 30) with dextrin.

According to a specific embodiment, the polylysine can be a modified polylysine, a polylysine comprising a guanidine or biguanidine functional group, as described in Application FR 2 851 465, or a thiolated polylysine, as described in Application FR 2 853 533.

The polylysine can be in the form of organic or inorganic salts.

The addition salts with an acid are, for example, the salts of hydrochloric or hydrobromic or sulphuric or citric or succinic or tartaric or lactic or para-toluenesulphonic or phosphoric or acetic acid or the salts of fatty acids, such as linoleic, oleic, palmitic, stearic, behenic and 18-methyleicosanoic acids.

The addition salts with a base are, for example, the salts of sodium or calcium and the salts of hydroxyalkylamines, such as, for example, N-methyl-glucamine, aminopropanediol or triethanolamine.

(13') Polyethyleneimines and

(14') Partially hydrolysed polyvinylformamides.

Use is more advantageously made, among the cationic thickening polymers iii) capable of being used in the context of the present invention, of the polymers of the families (1'), (2'), (3'), (4'), (8'), (9') or their mixtures.

Preferably, the cationic thickening polymers iii) employed are chosen from the families (1'), (8') and (9') and more preferably still those of the families (8') and (9'), in particular those corresponding to the dimethyldiallylammonium halide, particularly chloride, homopolymer and/or to a polymer of abovementioned formula (U) or abovementioned formula (W) or to

crosslinked homo- or copolymers of methacryloyloxy(C₁-C₄)alkyltri(C₁-C₄)alkylammonium salts.

Mention may particularly be made, as preferred thickening polymers according to the invention, of
5 Polyquaternium-6, Polyquaternium-34 and the tetramethylhexamethylenediamine/1,3-propylene dichloride polycondensate.

The cationic polymers iii) of the invention are non-silicone polymers without a fatty chain.

10 The term "non-silicone cationic polymer without a fatty chain" is understood to mean a polymer which comprises one or more cationic charges, which does not comprise a polysiloxane bond (which preferably does not comprise a silicon atom) and which does not comprise a
15 fatty chain, that is to say a hydrocarbon chain comprising more than 8 carbon atoms, preferably comprising more than 10 carbon atoms.

The cationic thickening polymer or polymers iii) used in the composition according to the invention can
20 be present in an amount varying from 0.01 to 20% by weight, preferably in an amount varying from 0.1 to 15% by weight and more preferably still in an amount varying from 0.1 to 10% by weight, with respect to the total weight of the composition.

25 Preferably, the ratio by weight of the compound of formula (I) or its salts to the cationic thickening polymer or polymers iii) in accordance with the invention is between 0.005 and 20 and more preferably still between 0.01 and 10, better still between 0.05
30 and 1.

****** According to another specific alternative form of the invention, the thickening polymer is iv) an anionic nonassociative acrylic polymer.**

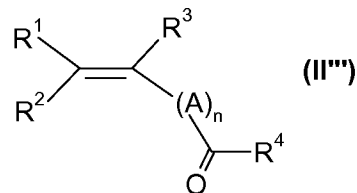
35 The compositions of the invention comprise at least one anionic nonassociative acrylic thickening polymer.

The expression "nonassociative thickener" is understood to mean, according to the invention, a non-

amphiphilic thickener, i.e. which does not simultaneously comprise at least one hydrophilic unit and at least one hydrophobic unit composed of at least one C₈-C₃₀ alkyl or alkenyl fatty chain.

5 The term "thickening polymer" is understood to mean, within the meaning of the present invention, a polymer exhibiting, as a 1% by weight solution or dispersion of active material in water or in ethanol at 25°C, a viscosity of greater than 0.2 poise at a shear
10 rate of 1 s^{-1} . The viscosity is measured with a Haake RS600 viscometer from Thermo Electron. This viscometer is a controlled-stress viscometer in cone-plate geometry (for example with a diameter of 60 mm).

The anionic nonassociative acrylic thickening
15 polymers iv) can be chosen from those resulting from at
least one monomer of formula (**II'**):



in which formula (II''') :

- 20 o **n** represents an integer between 0 and 10 inclusive,
 o **A** denotes a $-\text{CH}_2-$ or $-\text{CH}_2=\text{CH}_2-$ group,
 o **R¹** denotes a hydrogen atom or a C₁-C₆ alkyl, phenyl or
 benzyl group,
 o **R²** denotes a hydrogen atom or a C₁-C₆ alkyl or
25 carboxyl group,
 o **R³** denotes a hydrogen atom, a C₁-C₆ alkyl group or a
 $-(\text{CH}_2)_p\text{-X}$, phenyl or benzyl group, with p being an
 integer between 1 and 6 inclusive and X representing
 a carboxyl (COOH), sulpho (SO₃H) or phospho (PO₄H₂)
30 group,
 o **Z** denotes a linear or branched alkylene group
 comprising from 1 to 6 carbon atoms,
 o **R⁴** denotes a hydroxyl or linear or branched C₁-C₆
 alkoxy group or an NH-Z-R^5 radical, and
35 o **R⁵** denotes a carboxyl, sulpho or phospho group,

it being understood that the carboxylic, sulphonic or phosphoric acid groups can be partially or completely neutralized with an organic or inorganic base or can be esterified with lower alcohols R-OH with R
5 corresponding to a linear or branched C₁-C₆ alkyl group.

According to a specific embodiment of the invention, the carboxylic, sulphonic or phosphoric acid groups are not esterified.

Preferably, in the formula (**II'''**), n has the value
10 0.

According to a specific embodiment of the invention, the compounds of formula (**II'''**) are such that R¹ represents a hydrogen atom or a C₁-C₄ alkyl radical, such as methyl, and R² and R³ represent a hydrogen atom
15 or R¹, R² and R³ represent a C₁-C₄ alkyl radical, such as methyl. According to another preferred embodiment, the compounds of formula (**II'''**) are such that R⁴ represents a hydroxyl or C₁-C₆ alkoxy group.

The preferred anionic thickening polymers iv)
20 according to the invention are:

A₁) Acrylic or methacrylic acid homo- or copolymers.

Mention may be made, among crosslinked copolymers of (meth)acrylic acid and of C₁-C₆ alkyl acrylate, of the product sold under the name Viscoatex 538C by
25 Coatex, which is a crosslinked copolymer of methacrylic acid and of ethyl acrylate as a 38% aqueous dispersion of active material, or the product sold under the name Aculyn 33 by Rohm & Haas, which is a crosslinked copolymer of acrylic acid and of ethyl acrylate as a
30 28% aqueous dispersion of active material. Mention may more particularly be made of the crosslinked methacrylic acid/ethyl acrylate copolymer in the form of a 30% aqueous dispersion manufactured and sold under the name Carbopol Aqua SF-1 by Noveon.

35 Mention may be made, among acrylic acid homopolymers, of those of the family of the Carbopols, including in particular Carbopol 980 (homopolymer of acrylic acid crosslinked with a pentaerythritol allyl ether, a sucrose allyl ether or a propylene allyl

ether). Mention may also be made, among crosslinked homopolymers of acrylic acid, for example, of the products sold under the names Carbopol 981, Carbopol 954, Carbopol 2984 and Carbopol 5984 by Goodrich or the products sold under the names Synthalen M and Synthalen K by 3 VSA.

Mention may be made, among ammonium acrylate homopolymers, of the product sold under the name Microsap PAS 5193 by Hoechst. Mention may be made, among copolymers of ammonium acrylate and of acrylamide, of the product sold under the name Bozepol C Nouveau or the product PAS 5193 sold by Hoechst (they are described and prepared in the documents FR 2 416 723, USP 2 798 053 and USP 2 923 692).

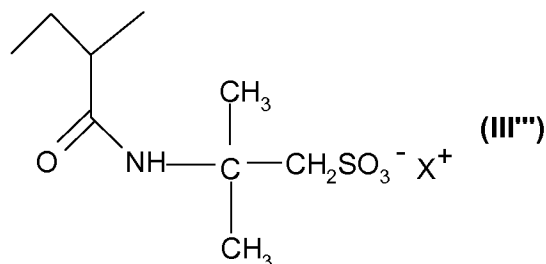
B₁) Polyacrylamides comprising sulphonic groups.

The polymers comprising sulphonic groups are polymers comprising vinylsulphonic, styrenesulphonic, naphthalenesulphonic or acrylamidoalkylsulphonic units.

These polymers can in particular be chosen from:

- salts of polyvinylsulphonic acid having a weight-average molecular weight of between approximately 1000 and 100 000, as well as their copolymers with an unsaturated comonomer, such as acrylic or methacrylic acids and their esters, acrylamide or its derivatives, vinyl ethers and vinylpyrrolidone;
- salts of polystyrenesulphonic acid, the sodium salts having a weight-average molecular weight of approximately 500 000 and of approximately 100 000 being sold respectively under the names "Flexan 500" and "Flexan 130" by National Starch. These compounds are described in Patent FR 2 198 719;
- homopolymers of acrylamidomethylpropanesulphonic acid of formula (**III'**) (AMPS), such as salts of polyacrylamido(C₁-C₆)alkylsulphonic acids, such as those mentioned in Patent US 4 128 631, more particularly the polyacrylamidomethylpropanesulphonic acid sold under the name "Cosmedia Polymer HSP 11 80" by Henkel and the crosslinked polyacrylamidomethylpropanesulphonic acid

partially neutralized to 50% with aqueous ammonia sold under the name "Hostacerin AMPS" by Hoechst;



- 5 - copolymers, which may or may not be crosslinked and which may or may not be neutralized, comprising from 15 to 60% by weight of AMPS units and from 40 to 85% by weight of (C₁-C₆)alkyl(meth)acrylamide units or of (C₁-C₆)alkyl
 10 (meth)acrylate units with respect to the polymer, such as those described in Application EP-750 899;
 - terpolymers comprising from 10 to 90 mol% of acrylamide units, from 0.1 to 10 mol% of AMPS units and from 5 to 80 mol% of n-(C₁-C₆)alkyl-
 15 acrylamide units, such as those described in Patent US-5 089 578.

Mention may in particular be made, among copolymers of 2-acrylamido-2-methylpropanesulphonic acid which are partially or completely neutralized (by
 20 a base, such as sodium hydroxide, potassium hydroxide or an amine), of the product described in Example 1 of the document EP-A-503 853 (forming an integral part of the content of the description) and in particular the product sold by SEPPIC under the name Sepigel 305.

25 According to the invention, use may also be made of anionic thickening polymers iv) in the latex or pseudolatex form, that is to say in the form of an aqueous dispersion of insoluble particles of polymers.

The anionic nonassociative acrylic thickening
 30 polymer or polymers iv) of the invention preferably have a molecular weight of between 500 and 5 000 000.

The anionic nonassociative acrylic thickening polymers iv) are used in the compositions of the invention in proportions of between 0.01 and 20% by

weight and preferably between 0.1 and 8% by weight, with respect to the total weight of the composition.

******* According to another specific embodiment of the invention, the thickening polymers are composed of a mixture of thickening polymers i), ii), iii) and iv) as defined above.**

The mixture v) is, for example, composed of a "binary" mixture, i.e. comprising two polymers chosen from i) to (iv) as defined above but of different categories, such as polymers i) + ii), or i) + iii), or i) + iv), or ii) + iii), or iii) + iv). It is also possible for the mixture to be composed of polymers of the same category i) to iv) but of different types, such as: the combination of polymer iii) of type (9') and of type (8').

In particular, the mixture v) is "binary" and comprises:
either a mixture of:
- thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; or a gum, such as xanthan gum; and of
- thickening polymers iii), such as those of type (9'), for example the polymer (W), or of type (8');

or a mixture of:
- thickening polymers iv), such as those which are anionic, such as those of type (A₁); and of
- thickening polymers iii), such as those of type (9').

According to another alternative form, the mixture v) is a "ternary" mixture, i.e. comprising three polymers of different categories, such as polymers i) + ii) + iii), or i) + iii) + iv), or i) + ii) + iv), or ii) + iii) + iv). It is also possible for the mixture to be composed of polymers of the same category i) to iv) but of different types, such as: the combination of

polymers iii) of type (9'), of type (8') and of type (A').

It is also preferred for the mixture v) to be composed of polymers of different categories and of different types, such as the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; or a gum, such as xanthan gum; and of thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8').

According to another particularly advantageous form, the mixture is a "ternary" mixture and comprises a mixture of:

- thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of nonionic cellulose ether type; or of gum, such as xanthan gum; and of
- thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8');

or alternatively the ternary mixture comprises a mixture of:

- thickening polymers ii), such as cetyl hydroxyethylcellulose (Natrosol Plus Grade 330CS); and of
- thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8').

According to a particularly advantageous form of the invention, the mixture v) comprises the combination of polymers iii) of type (9') and of type (8').

According to another alternative form, the mixture v) is a "quaternary" mixture, i.e. comprising four polymers of different categories i) + ii) + iii) + iv). It is also possible for the mixture to be composed of polymers of the same category i) to iv) but of different types.

It is preferred for the mixture v) to be composed of polymers of different categories and of different types, such as:

- 5 - the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; and of thickening polymers iii), such as those of type (9'), for example the polymer (W), of type (8') and of type (A'), or alternatively
- 10 - the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8'); and of thickening polymers ii),
15 such as cetyl hydroxyethylcellulose (Natrosol Plus Grade 330CS), or alternatively
- 20 - the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8'); and of thickening polymers ii),
25 such as those of type (7), or alternatively
- 30 - the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8'); and of thickening polymers ii),
35 such as those of type (D).

According to another alternative form, the mixture v) comprises five or more polymers of different categories and of different types. Preferably, the mixture v) is a "quintuple" mixture and comprises five different polymers chosen from i) to iv) as defined above.

It is preferred for the mixture v) to be composed of:

- the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; and of thickening polymers iii), such as those of type (9'), for example the polymer (W), of type (8') and of type (A'); and of anionic thickening polymers iv), such as those of type (A₁);
or alternatively
- the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8'); of thickening polymers ii), such as cetyl hydroxyethylcellulose (Natrosol Plus Grade 330CS); and of anionic thickening polymers iv), such as those of type (A₁);
or alternatively
- the combination of thickening polymers i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymers iii), such as those of type (9'), for example the polymer (W), and of type (8'); of thickening polymers ii), such as those of type (D); and of anionic thickening polymers iv), such as those of type (A₁).

The dyeing composition according to the invention can comprise one or more couplers conventionally used for dyeing keratinous fibres. Mention may in particular be made, among these couplers, of metapenylenediamines, meta-aminophenols, meta-diphenols, naphthalene couplers, heterocyclic couplers and their addition salts.

35

Mention may be made, as example of coupler, of 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 6-chloro-2-methyl-5-aminophenol, 3-aminophenol, 2,4-dichloro-3-aminophenol, 5-amino-4-

chloro-o-cresol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethyloxy)benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diamino-
 5 benzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-(dimethylamino)benzene, sesamol, 1-(β -hydroxyethylamino)-3,4-methylenedioxybenzene, α -naphthol, 2-methyl-1-naphthol, 1,5-dihydroxynaphthalene, 2,7-naphthalenediol, 1-acetoxy-2-
 10 methylnaphthalene, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 3-amino-2-methylamino-6-methoxypyridine, 1-N-(β -
 15 hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-bis(β -hydroxyethylamino)toluene, 3-methyl-1-phenyl-5-pyrazolone and their addition salts with an acid.

In the composition of the present invention, the coupler or couplers, if they are present, generally
 20 represent an amount of between 0.001 and 10% by weight approximately of the total weight of the dyeing composition, preferably between 0.005 and 6%.

The dyeing composition of the invention can optionally comprise one or more additional oxidation
 25 bases conventionally used for dyeing keratinous fibres other than the compound of formula (I) or its salts.

By way of example, these additional oxidation bases are chosen from para-phenylenediamines, bisphenylalkylenediamines, para-aminophenols, bis-para-
 30 aminophenols, ortho-aminophenols, heterocyclic bases other than the oxidation bases of formula (I), and their addition salts.

Mention may be made, among para-phenylenediamines, by way of example, of para-phenylenediamine, para-
 35 toluediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine,

N,N-dipropyl-para-phenylenediamine, 4-amino-
 N,N-diethyl-3-methylaniline, N,N-bis(β -hydroxyethyl)-
 para-phenylenediamine, 4-N,N-bis(β -hydroxyethyl)amino-
 2-methylaniline, 4-N,N-bis(β -hydroxyethyl)amino-
 5 2-chloroaniline, 2-(β -hydroxyethyl)-para-phenylene-
 diamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-
 para-phenylenediamine, N-(β -hydroxypropyl)-para-
 phenylenediamine, 2-hydroxymethyl-para-
 phenylenediamine, N,N-dimethyl-3-methyl-para-
 10 phenylenediamine, N,N-(ethyl, β -hydroxyethyl)-para-
 phenylenediamine, N-(β,γ -dihydroxypropyl)-para-
 phenylenediamine, N-(4'-aminophenyl)-para-
 phenylenediamine, N-phenyl-para-phenylenediamine,
 2-(β -hydroxyethyloxy)-para-phenylenediamine,
 15 2-(β -acetylaminoethyloxy)-para-phenylenediamine,
 N-(β -methoxyethyl)-para-phenylenediamine, 4-amino-
 phenylpyrrolidine, 2-thienyl-para-phenylenediamine,
 2-(β -hydroxyethylamino)-5-aminotoluene, 3-hydroxy-1-
 (4'-aminophenyl)pyrrolidine and their addition salts
 20 with an acid.

Among the para-phenylenediamines mentioned above,
 para-phenylenediamine, para-toluenediamine,
 2-isopropyl-para-phenylenediamine, 2-(β -hydroxyethyl)-
 para-phenylenediamine, 2-(β -hydroxyethyloxy)-para-
 25 phenylenediamine, 2,6-dimethyl-para-phenylenediamine,
 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-
 phenylenediamine, N,N-bis(β -hydroxyethyl)-para-
 phenylenediamine, 2-chloro-para-phenylenediamine,
 2-(β -acetylaminoethyloxy)-para-phenylenediamine and
 30 their addition salts with an acid are particularly
 preferred.

Mention may be made, among bisphenylalkylene-
 diamines, by way of example, of N,N'-bis(β -hydroxy-
 ethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol,
 35 N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-
 ethylenediamine, N,N'-bis(4-aminophenyl)tetra-
 methylenediamine, N,N'-bis(β -hydroxyethyl)-
 N,N'-bis(4-aminophenyl)tetramethylenediamine,
 N,N'-bis(4-methylaminophenyl)tetramethylenediamine,

N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine, 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane and their addition salts with an acid.

Mention may be made, among para-aminophenols, by way of example, of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-2-methylphenol, 4-amino-2-(hydroxymethyl)phenol, 4-amino-2-(methoxymethyl)phenol, 4-amino-2-(aminomethyl)phenol, 4-amino-2-((β -hydroxyethyl)aminomethyl)phenol, 4-amino-2-fluorophenol, 1-hydroxy-4-(methylamino)benzene, 2,2'-methylenebis-(4-aminophenol) and their addition salts with an acid.

Mention may be made, among ortho-aminophenols, by way of example, of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol and their addition salts with an acid.

Mention may be made, among heterocyclic bases, by way of example, of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Mention may be made, among pyridine derivatives, of the compounds described, for example, in Patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-[(4-methoxyphenyl)amino]-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-[(β -methoxyethyl)amino]-3-amino-6-methoxypyridine, 3,4-diaminopyridine and their addition salts with an acid.

Mention may be made, among pyrimidine derivatives, of the compounds described, for example, in Patents DE 2 359 399; JP 88-169571; JP 05-63124; EP 0 770 375 or Patent Application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine or 2,5,6-triaminopyrimidine, and pyrazolopyrimidine derivatives, such as those mentioned in Patent Application FR-A-2 750 048 and among which may be mentioned pyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,5-dimethylpyrazolo[1,5-a]-

pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-7-ol; 3-aminopyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-amino-
 5 pyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-amino-pyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxyethyl)amino]ethanol,
 10 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 3-amino-5-methyl-7-(imidazolylpropylamino)pyrazolo[1,5-a]pyrimidine and their addition
 15 salts with an acid and their tautomeric forms, when a tautomeric equilibrium exists.

Mention may be made, among pyrazole derivatives, of the compounds described in Patents DE 3 843 892 and DE 4 133 957 and Patent Applications WO 94/08969, WO
 20 94/08970, FR-A-2 733 749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(β -hydroxyethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-
 25 1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-(tert-butyl)-1-methylpyrazole, 4,5-diamino-1-(tert-butyl)-3-methylpyrazole, 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole,
 30 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-(hydroxymethyl)pyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole,
 35 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-(methylanino)pyrazole,

3,5-diamino-4-(β -hydroxyethyl)amino-1-methylpyrazole
and their addition salts with an acid.

Mention may also be made of the diaminopyrazolinones
described in Patent Application FR 2 886 137 and in
5 particular 2,3-diamino-6,7-dihydro-1H,5H-pyrazol-1-one
and its salts.

Generally, the addition salts of the oxidation bases
and couplers which can be used in the context of the
invention are chosen in particular from the addition
10 salts with an acid, such as hydrochlorides,
hydrobromides, sulphates, citrates, succinates,
tartrates, lactates, tosylates, benzenesulphonates,
phosphates and acetates, and the addition salts with a
base, such as sodium hydroxide, potassium hydroxide,
15 aqueous ammonia, amines or alkanolamines.

The dyeing composition in accordance with the
invention can additionally comprise one or more direct
dyes which can in particular be chosen from
nitrobenzene dyes, azo direct dyes or methine direct
20 dyes. These direct dyes can be nonionic, anionic or
cationic in nature.

The medium appropriate for dyeing, also referred
to as dyeing vehicle, generally comprises water or a
mixture of water and of one or more solvents, such as,
25 for example, lower C₁-C₄ alkanols, such as ethanol and
isopropanol, polyols, such as propylene glycol,
dipropylene glycol or glycerol, and polyol ethers, such
as the monomethyl ether of dipropylene glycol.

The solvent or solvents are generally present in
30 proportions which can be between 1 and 40% by weight
approximately, with respect to the total weight of the
dyeing composition, and more preferably still between 3
and 30% by weight approximately.

The dyeing composition in accordance with the
35 invention can also include various adjuvants
conventionally used in compositions for dyeing the hair,
such as anionic, cationic, nonionic, amphoteric or
zwitterionic surfactants or their mixtures, cationic
polymers, anionic, nonionic, amphoteric or zwitterionic

polymers, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, inorganic thickening agents, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioning agents, such as, for example, volatile or non-volatile and modified or unmodified silicones, film-forming agents, ceramides, preservatives or opacifying agents.

The above adjuvants are generally present in an amount, for each of them, of between 0.01 and 20% by weight, with respect to the weight of the composition.

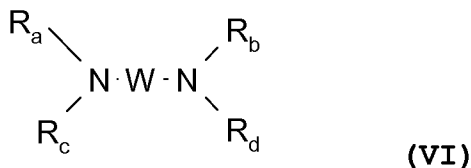
Of course, a person skilled in the art will take care to choose this or these optional additional compounds so that the advantageous properties intrinsically attached to the oxidation dyeing composition in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

The pH of the dyeing composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 11 approximately. It can be adjusted to the desired value using acidifying or basifying agents commonly used in the dyeing of keratinous fibres or else by means of conventional buffering systems.

Mention may be made, among acidifying agents, by way of example, of inorganic or organic acids, such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, such as acetic acid, tartaric acid, citric acid or lactic acid, or sulphonc acids.

Mention may be made, among basifying agents, by way of example, of aqueous ammonia, alkaline carbonates, alkanolamines, such as mono-, di- and triethanolamines and their derivatives, sodium hydroxide, potassium hydroxide and the compounds of following formula (VI):

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in which formula (VI) W is a propylene residue optionally substituted by a hydroxyl group or a C₁-C₄ alkyl radical and R_a, R_b, R_c and R_d, which are identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical.

The composition according to the invention can comprise one or more oxidizing agents.

The oxidizing agents are those conventionally used for the oxidation dyeing of keratinous fibres and are, for example, hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, such as perborates and persulphates, peracids and oxidase enzymes, among which may be mentioned peroxidases, 2-electron oxidoreductases, such as uricases, and 4-electron oxygenases, such as laccases. Hydrogen peroxide is particularly preferred.

The dyeing composition according to the invention can be provided in various forms, such as in the form of liquids, of creams or of gels or in any other form appropriate for carrying out dyeing of keratinous fibres and in particular of human hair.

It can result from the mixing, at the time of use, of several compositions.

In a first specific alternative form, it results from the mixing of at least two compositions, one comprising one or more oxidation bases chosen from the compounds of formula (I) or their addition salts with an acid, optionally one or more additional oxidation bases other than the compounds of formula (I) or their salts and optionally one or more couplers, a second composition comprising the specific thickening polymer or polymers i) to v) described above and optionally a third composition comprising one or more oxidizing agents as described above.

In a second specific alternative form, it results from the mixing of two compositions, one comprising one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid, the
5 specific thickening polymer or polymers i) to v) described above, optionally one or more additional oxidation bases other than the compounds of formula (I) or their salts and optionally one or more couplers, and another composition comprising one or more oxidizing
10 agents as described above.

The composition of the invention, devoid of oxidizing agent, is applied to the hair for the dyeing of the keratinous fibres, either as is or in the presence of one or more oxidizing agents for the dyeing
15 of keratinous fibres.

The method of the present invention is a method in which the composition, devoid of oxidizing agent, according to the present invention as defined above is applied to the fibres, either alone or in the presence
20 of one or more oxidizing agents, for a time sufficient to develop the desired colouring. The colour can be developed at acidic, neutral or alkaline pH and the oxidizing agent can be added to the composition of the invention only at the time of use or it can be employed
25 starting from an oxidizing composition comprising it, applied simultaneously with or sequentially to the composition of the invention.

According to a specific embodiment, the composition devoid of oxidizing agent according to the
30 present invention is mixed, preferably at the time of use, with a composition comprising, in a medium appropriate for dyeing, one or more oxidizing agents. The mixture obtained is subsequently applied to the keratinous fibres.

35 The oxidizing agents are those indicated above.

The temperature during the application of the composition is conventionally between ambient temperature (between 15 and 25°C) and 80°C, preferably between ambient temperature and 60°C.

Whether with or without an oxidizing agent, after a leave-in time of 3 to 50 minutes approximately, preferably of 5 to 30 minutes approximately, the keratinous fibres are rinsed, washed with a shampoo, rinsed again and then dried.

The oxidizing composition can also include various adjuvants conventionally used in compositions for dyeing the hair and as defined above.

The pH of the oxidizing composition including the oxidizing agent is such that, after mixing with the dyeing composition, the pH of the resulting composition applied to the keratinous fibres preferably varies between 3 and 12 approximately and more preferably still between 5 and 11. It can be adjusted to the desired value using acidifying or basifying agents commonly used in the dyeing of keratinous fibres and as defined above.

The ready-for-use composition, with or without oxidizing agent, which is finally applied to the keratinous fibres can be provided in various forms, such as in the form of liquids, of creams or of gels or in any other form appropriate for carrying out dyeing of keratinous fibres and in particular of human hair.

Another subject-matter of the invention is a dyeing kit or multicompartiment device in which a first compartment includes the dyeing composition devoid of oxidizing agent of the present invention as defined above and a second compartment includes one or more oxidizing agents.

A second device is composed of a first compartment, comprising a composition comprising one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid and optionally one or more couplers, and a second compartment, comprising a composition comprising one or more thickening polymers i) to v) as defined above.

A third device can optionally comprise the two compartments of the second device plus a third

compartment including a composition comprising one or more oxidizing agents.

These devices can be equipped with a means allowing the desired product to be deposited on the hair, such as the devices described in Patent FR-2 586 913 on behalf of the Applicant Company.

It is possible, starting from these devices, to dye keratinous fibres starting from a method which comprises mixing the compositions present in each of the compartments of the said devices and applying the mixture obtained to the keratinous fibres for a time sufficient to develop the desired colouring.

The examples which follow serve to illustrate the invention without, however, exhibiting a limiting nature.

EXAMPLES**EXAMPLE 1**

The following composition 1 is produced:

Composition 1	g
2- [{2- [(4-Aminophenyl) amino] ethyl} (2-hydroxyethyl) amino] ethanol as a 50% aqueous solution	2.4 (A.M.) (0.01 mol)
2-Methylresorcinol	0.99 (0.08 mol)
2-Amino-3-hydroxypyridine	0.22 (0.002 mol)
Mixture of linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C _{22/24} -7/58/30/6 - alcohol content > 95%)	3.0 g
Oxyethylenated stearyl alcohol (2 EO)	5 g
Oxyethylenated stearyl alcohol (21 EO)	3.8 g
Oleic acid	3 g
Polyglycerolated oleyl alcohol comprising 2 mol of glycerol	1.5 g
Stearic acid monoethanolamide	2.5 g
C ₁₂ alkyl ether of glycerol (1.5 mole)	2 g
Hydroxyethylcellulose (MW : 1 300 000) Natrosol 250 HHR [Thickening polymer i) nonionic cellulose ether type]	0.4 g A.M.
Cationic polymer of formula (W) [Thickening polymer iii) - Type (9')]	1.2 g A.M.
Merquat 100 , sold by Calgon [Thickening polymer iii) - Type (8')]	1.6 g A.M.
Desmodur W - N,N-dimethylethanolamine - stearyl bromide - polyethylene oxide di-OH m = 10 000	0.1 g
Titanium oxide (untreated anatase) coated with polydimethylsiloxane (98/2) (CI: 77891)	0.15 g
Reducing agents	0.7 g
Sequestering agents	0.2 g
Monoethanolamine	4.0 g
Aqueous ammonia (comprising 20.5% of NH ₃)	6 g

Demineralized water	q.s. for 100 g
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Method of application

Composition 1 is diluted at the time of use with 1.5 times its weight of 20 volume aqueous hydrogen peroxide solution.

The mixture thus prepared is applied at ambient temperature to natural grey hair comprising 90% white hairs, at the rate of 10 g per 1 g of hair, for 30 min.

The hair is subsequently rinsed, washed with a standard shampoo and dried.

Result

The hair colouring was evaluated visually.

Composition	Height of tone	Highlight
Composition 1	Light chestnut	Mahogany golden

EXAMPLE 2

The following composition 2 is prepared:

Composition 2	g
2- [{2- [(4-Aminophenyl) amino] ethyl} (2-hydroxyethyl) amino] ethanol	2.2 (A.M.) (0.0092 mol)
6-Hydroxybenzomorpholine	0.18 (0.0012 mol)
2-Amino-3-hydroxypyridine	0.88 (0.008 mol)
Cetearyl alcohol (C ₁₆ /C ₁₈ 50/50)	16.2 g
Oxyethylenated oleocetyl alcohol (30 EO)	3.6 g
Oleyl alcohol	2.7 g
Oleic acid	3.5 g
N-Oleyldihydrosphingosine	0.01 g
Cationic polymer of formula (W)	3.0 g A.M.

[Thickening polymer iii) - Type (9')]	
Titanium oxide (untreated anatase) coated with polydimethylsiloxane (98/2) (CI: 77891)	0.15 g
Xanthan gum [Thickening polymer i)]	0.2 g A.M.
Reducing agents	0.7 g
Sequestering agents	0.2 g
Monoethanolamine	4.0 g
Demineralized water	q.s. for 100 g

Method of application

Composition 2 is diluted at the time of use with 1.5 times its weight of 20 volume aqueous hydrogen peroxide solution.

5

The mixture thus prepared is applied at ambient temperature to natural grey hair comprising 90% white hairs, at a rate of 10 g per 1 g of hair, for 30 min.

The hair is subsequently rinsed, washed with a standard shampoo and dried.

10

Result

The hair colouring was evaluated visually.

Composition	Height of tone	Highlight
Composition 2	Chestnut	Mahogany

15 **EXAMPLE 3**

The following composition 3 is prepared:

Composition 3	g
2-[(2-[(4-Aminophenyl)amino]ethyl)(2-hydroxyethyl)amino]ethanol trihydrochloride	1.8 g (A.M.) (0.0052 mol)
meta-Aminophenol	0.562 g (0.0052 mol)
Mixture of linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C ₂₂ /C ₂₄ : 7/57/30/6 - alcohol content > 95%)	3.0 g

Oxyethylenated stearyl alcohol (2 EO)	4.5 g
Oxyethylenated stearyl alcohol (21 EO)	1.75 g
Oleic acid	2.6 g
Polyurethane comprising a fatty chain obtained from the condensation of 1,3-bis(isocyanatomethyl)cyclohexane, of N,N-dimethylethanolamine and of polyoxyethylene with a molecular weight of 10 000 and quaternization with bromodecane [Thickening polymer iii) - Type (A')]	1g MA
Crosslinked polyacrylic acid (Carbopol 980 from Goodrich) [Anionic thickening polymer iv) - Type (A ₁)]	0.4 g
Hydroxypropylmethylcellulose [Thickening polymer i) type viii) - hydroxy(C ₁ -C ₆)alkylcellulose]	0.2 g
Stearic acid monoethanolamide	3.0 g
Merquat 100 as a 40% aqueous solution [Thickening polymer iii) - Type (8')]	4.0 g
Cationic polymer of formula (W) [Thickening polymer iii) - Type (9')]	2.0 g
Propylene glycol	2.0 g
Sodium metabisulphite	0.71 g
EDTA (ethylenediaminetetraacetic acid)	0.2 g
tert-Butylhydroquinone	0.3 g
Monoethanolamine	1.0 g
Aqueous ammonia comprising 20% of NH ₃	11 g
Fragrance	q.s.
Demineralized water	q.s. for 100 g

EXAMPLE 4

The following composition 4 is prepared:

Composition 4	g
2- [{2- [(4-Aminophenyl) amino] ethyl} (2-hydroxyethyl) amino] ethanol trihydrochloride	2.5 g (A.M. (0.0072 mol))
2-Methyl-5- [(2-hydroxyethyl) amino] phenol	0.6 g (0.0036 mol)
6-Hydroxybenzomorpholine	0.55 g (0.0036 mol)
Mixture of linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C ₂₂ /C ₂₄ : 7/57/30/6 - alcohol content > 95%)	3.0 g
Oxyethylenated stearyl alcohol (2 EO)	4.5 g
Oxyethylenated stearyl alcohol (21 EO)	1.75 g
Oleic acid	2.6 g
Natrosol Plus Grade 330CS , sold by Aqualon [Thickening polymer ii)]	1.0 g
Crosslinked polyacrylic acid (Carbopol 980 from Goodrich) [Anionic thickening polymer iv) - Type (A ₁)]	0.4 g
Hydroxypropylmethylcellulose [Thickening polymer i) type viii) - hydroxy (C ₁ -C ₆) alkylcellulose]	0.2 g
Stearic acid monoethanolamide	3.0 g
Merquat 100 as a 40% aqueous solution [Thickening polymer iii) - Type (8')]	4 g
Cationic polymer of formula (W) [Thickening polymer iii) - Type (9')]	2 g (A.M.)
Propylene glycol	2 g
Sodium metabisulphite	0.71 g
EDTA (ethylenediaminetetraacetic acid)	0.2 g
tert-Butylhydroquinone	0.3 g
Monoethanolamine	1 g
Aqueous ammonia comprising 20% of NH ₃	11 g
Fragrance	q.s.
Demineralized water	q.s. for 100 g

EXAMPLE 5

The following composition 5 is prepared:

Composition 5	g
2- [{2- [(4-Aminophenyl) amino] ethyl} (2-hydroxyethyl) amino] ethanol trihydrochloride	1.2 g (A.M.) (0.0034 mol)
Resorcinol	0.374 g (0.0034 mol)
Mixture of linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C ₂₂ /C ₂₄ : 7/57/30/6 - alcohol content > 95%)	3.0 g
Oxyethylenated stearyl alcohol (2 EO)	4.5 g
Oxyethylenated stearyl alcohol (21 EO)	1.75 g
Oleic acid	2.6 g
Acrylic copolymer soluble in an alkaline medium as a 30% aqueous dispersion which is not stabilized (Aculyn 22) [Anionic thickening polymer ii)]	0.67 g
Crosslinked polyacrylic acid (Carbopol 980 from Goodrich) [Anionic thickening polymer iv) - Type (A ₁)]	0.4 g
Hydroxypropylmethylcellulose [Thickening polymer i) type viii) - hydroxy(C ₁ -C ₆)alkylcellulose]	0.2 g
Stearic acid monoethanolamide	3.0 g
Merquat 100 as a 40% aqueous solution [Thickening polymer iii) - Type (8')]	4 g
Cationic polymer of formula (W) [Thickening polymer iii) - Type (9')]	2 g
Propylene glycol	2 g
Sodium metabisulphite	0.71 g
EDTA (ethylenediaminetetraacetic acid)	0.2 g
tert-Butylhydroquinone	0.3 g
Monoethanolamine	1 g
Aqueous ammonia comprising 20% of NH ₃	11 g
Fragrance	q.s.
Demineralized water	q.s. for 100 g

EXAMPLE 6

The following composition 6 is prepared:

Composition 6	g
2-[[2-[(4-Aminophenyl)amino]ethyl](2-hydroxyethyl)amino]ethanol trihydrochloride	2.8 g (A.M. (0.008 mol)
1-Methyl-2-hydroxy-4-aminobenzene	0.5 g (0.004 mol)
6-Chloro-2-methyl-5-aminophenol	0.63 g (0.004 mol)
Mixture of linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C ₂₂ /C ₂₄ : 7/57/30/6 - alcohol content > 95%)	3.0 g
Oxyethylenated stearyl alcohol (2 EO)	4.5 g
Oxyethylenated stearyl alcohol (21 EO)	1.75 g
Oleic acid	2.6 g
Copolymer of SMDI and of polyethylene glycol comprising an alkyl (methyl/C₁₈) ending at 15% in a maltodextrin/water matrix (Aculyn 46) [Nonionic thickening polymer ii) - Type (7)]	1.34 g
Crosslinked polyacrylic acid	0.4 g
Hydroxypropylmethylcellulose [Thickening polymer i) type viii) - hydroxy(C ₁ -C ₆)alkylcellulose]	0.2 g
Stearic acid monoethanolamide	3.0 g
Merquat 100 as a 40% aqueous solution [Thickening polymer iii) - Type (8')]	4 g
Cationic polymer of formula (W) [Thickening polymer iii) - Type (9')]	2 g (A.M.)
Propylene glycol	2 g
Sodium metabisulphite	0.71 g
EDTA (ethylenediaminetetraacetic acid)	0.2 g
tert-Butylhydroquinone	0.3 g
Monoethanolamine	1 g
Aqueous ammonia comprising 20% of NH ₃	11 g
Fragrance	q.s.
Demineralized water	q.s. for 100 g

EXAMPLE 7

The following composition 7 is prepared:

Composition 7	g
2- [{2- [(4-Aminophenyl) amino] ethyl} (2-hydroxyethyl) amino] ethanol trihydrochloride	3.75 g (A.M.) (0.0108 mol)
6-Hydroxybenzomorpholine	0.9 g (0.006 mol)
2-Methylresorcinol	0.6 g (0.0048 mol)
Mixture of linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C ₂₂ /C ₂₄ : 7/57/30/6 - alcohol content > 95%)	3.0 g
Oxyethylenated stearyl alcohol (2 EO)	4.5 g
Oxyethylenated stearyl alcohol (21 EO)	1.75 g
Oleic acid	2.6 g
Oxyethylenated (25 EO) methacrylic acid/ethyl acrylate/beheryl methacrylate terpolymer as a 20% aqueous emulsion (Aculyn 28) [Anionic thickening polymer ii) - Type (D)]	1 g
Crosslinked polyacrylic acid (Carbopol 980 from Goodrich) [Anionic thickening polymer iv) - Type (A ₁)]	0.4 g
Hydroxypropylmethylcellulose [Thickening polymer i) type viii) - hydroxy(C ₁ -C ₆)alkylcellulose]	0.2 g
Stearic acid monoethanolamide	3.0 g
Merquat 100 as a 40% aqueous solution [Thickening polymer iii) - Type (8')]	4 g
Cationic polymer of formula (W) [Thickening polymer iii) - Type (9')]	2 g
Propylene glycol	2 g
Sodium metabisulphite	0.71 g
EDTA (ethylenediaminetetraacetic acid)	0.2 g

tert-Butylhydroquinone	0.3 g
Monoethanolamine	1 g
Aqueous ammonia comprising 20% of NH ₃	11 g
Fragrance	q.s.
Demineralized water	q.s. for 100 g

Method of application

Each of the compositions 3 to 7 is diluted at the time of use with 1.5 times its weight of 25 volume aqueous hydrogen peroxide solution, the pH of which is 3.

The mixture thus prepared is applied at ambient temperature to natural grey hair comprising 90% white hairs, at a rate of 10 g per 1 g of hair, for 15 min for composition 6, 20 min for composition 3 and 30 min for the other compositions.

The hair is subsequently rinsed, washed with a standard shampoo and dried.

Results

The hair colourings were evaluated visually.

Composition	Height of tone	Highlight
Composition 3	Blond	Iridescent deep purple
Composition 4	Light chestnut	Iridescent brown
Composition 5	Dark blond	Matt natural
Composition 6	Dark blond	Red iridescent
Composition 7	Light chestnut	Iridescent natural

EXAMPLE 8

The following composition 8 is prepared:

Composition 8	G
2-[[2-[(4-Aminophenyl)amino]ethyl](2-hydroxyethyl)amino]ethanol trihydrochloride	0.9 g (A.M.) (0.0026 mol)
Resorcinol	0.23 g (0.0021 mol)
meta-Aminophenol	0.045 g (0.0042 mol)
1- β -Hydroxyethyloxy-2,4-diaminobenzene dihydrochloride	0.016 g (0.000066 mol)
Oxyethylenated sodium lauryl ether sulphate comprising 2.2 mol of ethylene oxide as a 70% aqueous solution, sold under the name Texapon N702 by Cognis	6.44 g (A.M.)
Oxyethylenated alkyl(C ₁₃ /C ₁₅ 70/30 50% linear) ether carboxylic acid monoethanolamide comprising 2 mol of ethylene oxide	5.0 g
Tetramethylhexamethylenediamine/1,3-propylene dichloride polycondensate as a 60% aqueous solution [Thickening polymer iii) - Type (9')]	2 g A.M.
Pentasodium salt of diethylenetriamine-pentaacetic acid as a 40% aqueous solution, sold under the name Dissolvine D-40 [®] by Akzo	0.80 g A.M.*
Ammonium thiolactate as a 58% aqueous solution	0.46 g A.M.*
Aqueous ammonia comprising 20.5% of NH ₃	12.0 g
Demineralized water	q.s. for 100 g

Method of application

Composition 8 is diluted at the time of use with 1 times its weight of 20 volume aqueous hydrogen peroxide solution.

5 The mixture thus prepared is applied at ambient temperature to natural grey hair comprising 90% white hairs, at the rate of 10 g per 1 g of hair, for 30 min.

The hair is subsequently rinsed, washed with a standard shampoo and dried.

10

EXAMPLE 9

The following composition 9 is prepared:

Composition 9	g
2-[[2-[(4-Aminophenyl)amino]ethyl](2-hydroxyethyl)amino]ethanol trihydrochloride	3.25 g (A.M.) (0.0093 mol)
1-(2-Hydroxyethyl)-1H-indol-4-ol	1.65 g (0.0093 mol)
Oxyethylenated sodium lauryl ether sulphate comprising 2.2 mol of ethylene oxide as a 70% aqueous solution, sold under the name Texapon N702 by Cognis	6.44 g (A.M.)
Oxyethylenated alkyl(C ₁₃ /C ₁₅ 70/30 50% linear) ether carboxylic acid monoethanolamide comprising 2 mol of ethylene oxide	5.0 g
Poly(dimethyldiallylammonium chloride) at 40% in water which is not stabilized [Thickening polymer iii) - Type (8')]	0.8 g
Pentasodium salt of diethylenetriamine-pentaacetic acid as a 40% aqueous solution, sold under the name Dissolvine D-40® by Akzo	0.80 g (A.M.*)
Ammonium thiolactate as a 58% aqueous solution	0.46 g (A.M.*)
Aqueous ammonia comprising 20.5% of NH ₃	6 g

Pure monoethanolamine	6 g
Demineralized water	q.s. for 100 g

Method of application

Composition 9 is diluted at the time of use with 1 times its weight of 15 volume aqueous hydrogen peroxide solution.

The mixture thus prepared is applied at ambient temperature to natural grey hair comprising 90% white hairs, at the rate of 10 g per 1 g of hair, for 30 min.

The hair is subsequently rinsed, washed with a standard shampoo and dried.

Results

The hair colourings were evaluated visually.

Composition	Height of tone	Highlight
Composition 8	Blond	Natural
Composition 9	Light chestnut	Purplish ash

EXAMPLE 10

The following composition 10 is prepared:

Composition 10	G
2-[[2-[(4-Aminophenyl)amino]ethyl](2-hydroxyethyl)amino]ethanol as a 50% aqueous solution	2.87 g (A.M.)
2-Methyl-5-[(2-hydroxyethyl)amino]phenol	2 g
Mixture of linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C _{22/24} - 7/58/30/6 - alcohol content > 95%)	3.0 g
Mixture of oxyethylenated linear C ₁₈ to C ₂₄ alcohols (C ₁₈ /C ₂₀ /C _{22/24} - 7/58/30/6 - alcohol content > 95%) (30 EO)	1.0 g
Oxyethylenated stearyl alcohol (2 EO)	4.0 g
Oxyethylenated stearyl alcohol (21 EO)	1.75 g

Oleic acid	2.6 g
Hexylene glycol	6.0 g
Coconut acid monoisopropanolamide	3.0 g
Crosslinked polyacrylic acid (Carbopol 980 from Goodrich) [Anionic thickening polymer iv) - Type (A ₁)]	0.6 g A.M.
Tetramethylhexamethylenediamine/1,3-propylene dichloride polycondensate as a 60% aqueous solution [Thickening polymer iii) - Type (9')]	6.66 g
Sodium metabisulphite	0.71 g
Sequestering agents	0.2 g
Ascorbic acid	0.25 g
Monoethanolamine	1.0 g
Aqueous ammonia comprising 20% of NH ₃	11.0 g
Demineralized water	q.s. for 100 g

Method of application

Composition 10 is diluted at the time of use with 1.5 times its weight of 25 volume aqueous hydrogen peroxide solution, the pH of which is 3.

- 5 The mixture thus prepared is applied to natural grey hair comprising 90% white hairs, at the rate of 10 g per 1 g of hair, for 30 min.

The hair is subsequently rinsed, washed with a standard shampoo and dried.

10 **Result**

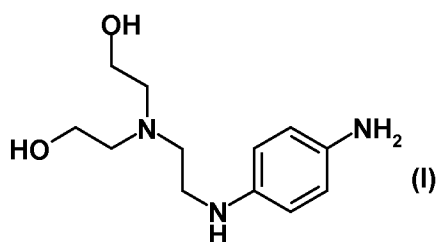
The hair colouring was evaluated visually.

Composition	Height of tone 90% NW	Hightlight 90% NW
Composition 10	Light chestnut	Iridescent

CLAIMS

1. Composition for dyeing keratinous fibres comprising, in a medium appropriate for dyeing
5 keratinous fibres:

- one or more oxidation bases chosen from the compound of formula (I) or its addition salts with an acid:



10

and

- one or more thickening polymer(s) chosen from
i) noncationic nonassociative polymers comprising sugar unit(s), ii) nonionic, anionic
15 or cationic associative polymers, iii) non-silicone cationic polymers without a fatty chain, iv) anionic nonassociative acrylic polymers, and v) their mixtures.

20 2. Composition according to the preceding claim, characterized in that the content of compound of formula (I) is between 0.001 and 10% by weight approximately of the total weight of the dyeing composition.

25

3. Composition according to either one of the preceding claims, characterized in that the thickening polymer(s) is (are) chosen from i) noncationic non-associative polymers comprising sugar unit(s);
30 particularly those comprising sugar units resulting from the sugars chosen from 1) glucose, 2) galactose, 3) arabinose, 4) rhamnose, 5) mannose, 6) xylose, 7) fucose, 8) anhydrogalactose, 9) galacturonic acid, 10) glucuronic acid, 11) mannuronic acid, 12) galactose

sulphate, 13) fructose and 14) anhydrogalactose sulphate.

4. Composition according to any one of the preceding
5 claims, characterized in that the noncationic non-associative thickening polymer or polymers i) comprising sugar unit(s) are chosen from:

i) native gums chosen from:

a) exudates of trees or shrubs, including:

- 10 o gums arabic;
- o gums ghatti;
- o gums karaya;
- o gums tragacanth;

b) gums resulting from algae, including:

- 15 o agar;
- o alginates;
- o carrageenans and furcellerans;

c) gums resulting from seeds or tubers, including:

- o guar gums;
- 20 o locust bean gums;
- o fenugreek gums;
- o tamarind gums;
- o konjac gums;

d) microbial gums, including:

- 25 o xanthan gums;
- o gellan gums;
- o scleroglucan gums;

ii) extracts of plants or trees, including:

- o celluloses;
- 30 o starches;
- o inulins;
- o pectins;

which may or may not be modified;

and in particular the noncationic nonassociative
35 thickening polymer or polymers i) comprising sugar unit(s) are chosen from:

i) - nonionic and chemically modified or unmodified guar gum;

- ii) - biopolysaccharide gums of microbial origin, such as scleroglucan or xanthan gum;
- iii) - gums resulting from plant exudates, such as gums arabic, ghatti, karaya or tragacanth,
- 5 carrageenan, agar and locust bean gum;
- iv) - pectins;
- v) - alginates;
- vi) - starches;
- vii) - chemically unmodified celluloses;
- 10 viii)- hydroxy(C₁-C₆)alkylcelluloses and carboxy-(C₁-C₆)alkylcelluloses.

5. Composition according to either one of Claims 1 and 2, characterized in that the thickening polymer(s)

15 is (are) chosen from ii) nonionic, anionic or cationic associative polymers; chosen in particular from:

i) anionic polymers **(A)** to **(E)**:

-**(A)** which comprise at least one hydrophilic unit and at least one allyl ether unit comprising a fatty chain, more particularly those for which the

20 hydrophilic unit is composed of an ethylenic unsaturated anionic monomer, more particularly still of a vinylcarboxylic acid and very particularly of an acrylic acid or a methacrylic acid or the mixtures of

25 these, and for which the allyl ether unit comprising a fatty chain corresponds to the monomer of following formula **(II')**:

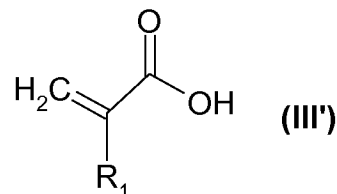


in which formula **(II')** R' denotes H or CH₃, B denotes the ethyleneoxy radical, n is zero or denotes an integer ranging from 1 to 100, and R denotes a hydrocarbon radical chosen from alkyl, arylalkyl, aryl, alkylaryl or cycloalkyl radicals comprising from 8 to 30 carbon atoms preferably from 10 to 24 carbon atoms,

35 and more particularly still from 12 to 18 carbon atoms;

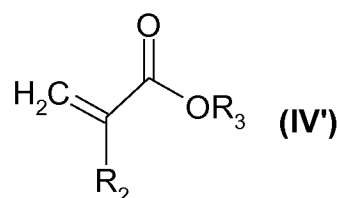
-**(B)** which comprise at least one hydrophilic unit of olefinic unsaturated carboxylic acid type and at least one hydrophobic unit of alkyl (C₁₀-C₃₀) ester of unsaturated carboxylic acid type, particularly those

for which the hydrophilic unit of olefinic unsaturated carboxylic acid type corresponds to the monomer of following formula (**III'**):



5

in which formula (**III'**) R_1 denotes H or CH_3 or C_2H_5 , that is to say acrylic acid, methacrylic acid or ethacrylic acid units, and for which the hydrophobic unit of alkyl (C_{10} - C_{30}) ester of unsaturated carboxylic acid type corresponds to the monomer of following formula (**IV'**):



15

in which formula (**IV'**) R_2 denotes H or CH_3 or C_2H_5 ;

-(C) maleic anhydride/ $\text{C}_{30}\text{C}_{38}$ α -olefin/alkyl maleate terpolymers;

-(D) acrylic terpolymers comprising:

20 (a) approximately 20% to 70% by weight of a carboxylic acid comprising α,β -monoethylenic unsaturation,

(b) approximately 20 to 80% by weight of a non-surface-active monomer comprising α,β -monoethylenic unsaturation other than (a),

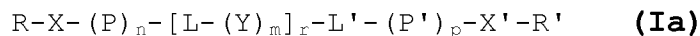
25 (c) approximately 0.5 to 60% by weight of a nonionic monourethane which is the reaction product of a monohydric surfactant with a monoisocyanate comprising monoethylenic unsaturation,

30 -(E) copolymers comprising, among their monomers, a carboxylic acid comprising α,β -monoethylenic unsaturation and an ester of a carboxylic acid

comprising α,β -monoethylenic unsaturation and of an oxyalkylenated fatty alcohol;

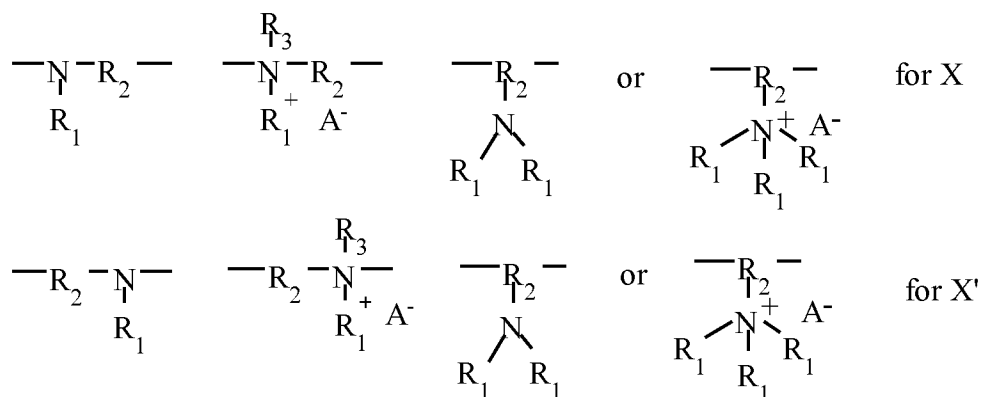
ii) cationic polymers (**A'**) to (**C'**):

- (**A'**) associative cationic polyurethanes
5 represented by the following general formula (**Ia**):



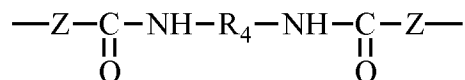
in which:

- 10 o R and R', which are identical or different, represent a hydrophobic group or a hydrogen atom;
- o X and X', which are identical or different, represent a group comprising an amine functional group which may or may not carry a hydrophobic
- 15 group, or alternatively the L" group;
- o L, L' and L", which are identical or different, represent a group derived from a diisocyanate;
- o P and P', which are identical or different, represent a group comprising an amine functional
- 20 group which may or may not carry a hydrophobic group;
- o Y represents a hydrophilic group;
- o r is an integer between 1 and 100 inclusive;
- o n, m, and p have values, each independently of
- 25 the others, between 0 and 1000 inclusive;
- o the molecule comprising at least one protonated or quaternized amine functional group and at least one hydrophobic group;
- o when X and/or X' denote a group comprising a
- 30 tertiary or quaternary amine, X and/or X' can represent one of the following formulae:



in which:

- R₂ represents a linear or branched alkylene radical having from 1 to 20 carbon atoms, which may or may not comprise a saturated or unsaturated ring, or an arylene radical, it being possible for one or more of the carbon atoms to be replaced by a heteroatom chosen from N, S, O or P;
- 5 - R₁ and R₃, which are identical or different, denote a linear or branched C₁-C₃₀ alkyl or alkenyl radical or an aryl radical, it being possible for at least one of the carbon atoms to be replaced by a heteroatom chosen from N, S, O or P;
- 10 - A⁻ is a physiologically acceptable anionic counterion, such as halide, for example chloride or bromide, or mesylate;
- 15 - the L, L' and L'' groups represent a group of formula:
- 20

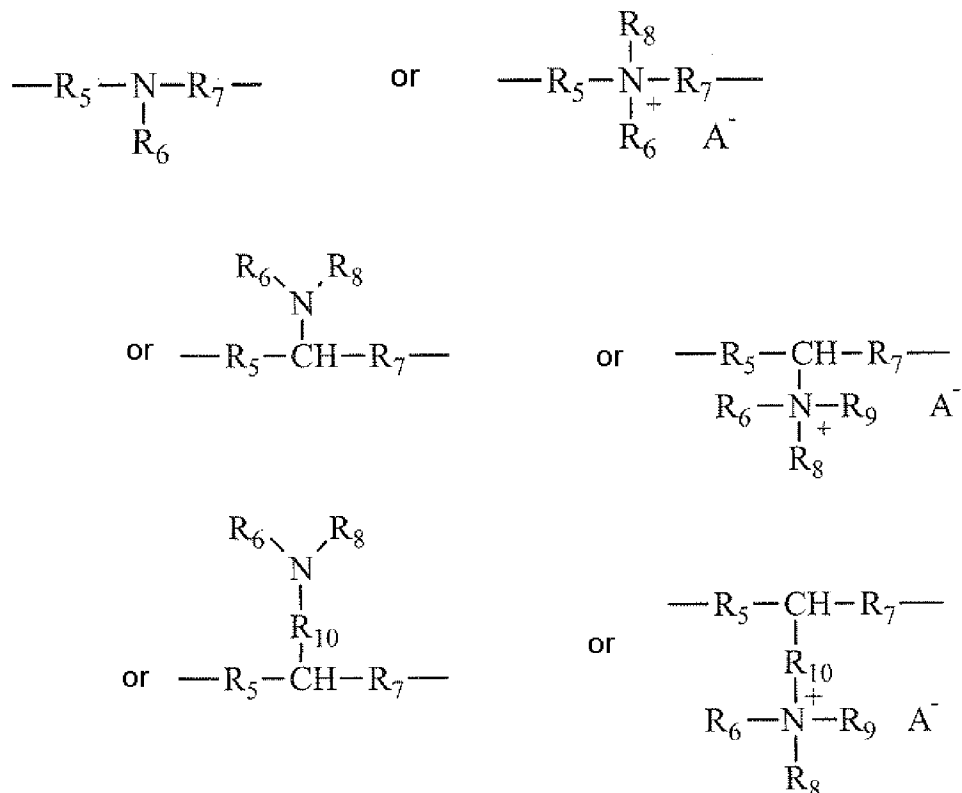


in which:

- Z represents -O-, -S- or -NH-; and
- 25 - R₄ represents a linear or branched alkylene radical having from 1 to 20 carbon atoms, which may or may not comprise a saturated or unsaturated ring, or an arylene radical, it being possible for one or

more of the carbon atoms to be replaced by a heteroatom chosen from N, S, O and P;

- o the P and P' groups, comprising an amine functional group, can represent at least one of the following formulae:

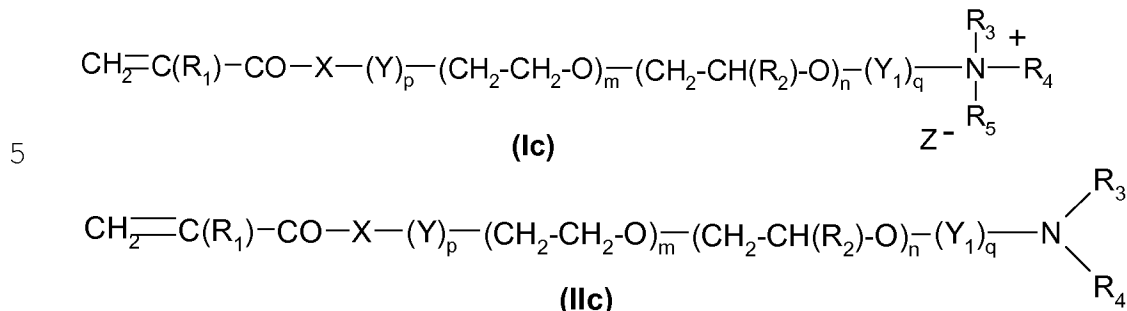


in which:

- R₅ and R₇ have the same meanings as R₂ defined above;
- R₆, R₈ and R₉ have the same meanings as R₁ and R₃ defined above;
- 15 - R₁₀ represents a linear or branched alkylene group which is optionally unsaturated and which can comprise one or more heteroatoms chosen from N, O, S and P,
- and A⁻ is a physiologically acceptable anionic counterion, such as halide, for example chloride or bromide, or mesylate;
- 20 - (B') quaternized cellulose derivatives;
- (C') cationic polyvinyl lactams which comprise:

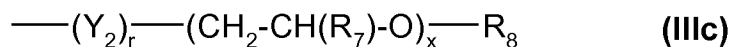
-a) at least one monomer of vinyl lactam or alkyl-vinyl lactam type;

-b) at least one monomer with the following structure (**Ic**) or (**IIc**):



in which formulae (**Ic**) and (**IIc**):

- o X denotes an oxygen atom or an NR₆ radical,
- o R₁ and R₆ denote, independently of one another, a
10 hydrogen atom or a linear or branched C₁-C₅ alkyl radical,
- o R₂ denotes a linear or branched C₁-C₄ alkyl radical,
- o R₃, R₄ and R₅ denote, independently of one another, a
hydrogen atom, a linear or branched C₁-C₃₀ alkyl
15 radical or a radical of formula (**IIIc**):



- Y, Y₁ and Y₂ denote, independently of one another, a linear or branched C₂-C₁₆ alkylene radical,
 - 20 - R₇ denotes a hydrogen atom or a linear or branched C₁-C₄ alkyl radical or a linear or branched C₁-C₄ hydroxyalkyl radical,
 - R₈ denotes a hydrogen atom or a linear or branched C₁-C₃₀ alkyl radical,
 - 25 o p, q and r denote, independently of one another, either the value 0 or the value 1,
 - o m and n denote, independently of one another, an integer ranging from 0 to 100 inclusive,
 - o x denotes an integer ranging from 1 to 100 inclusive,
 - 30 o Z denotes an organic or inorganic acid anionic counterion, such as halide, for example chloride or bromide, or mesylate;
- with the proviso that:

- at least one of the substituents R_3 , R_4 , R_5 or R_8 denotes a linear or branched C_9 - C_{30} alkyl radical,
- if m or n is other than zero, then q is equal to 1,
- 5 - if m or n are equal to zero, then p or q is equal to 0;

and

iii) nonionic polymers (1) to (7):

- (1) celluloses modified by groups comprising at least
10 one fatty chain;
- (2) hydroxypropyl guar modified by groups comprising at least one fatty chain;
- (3) copolymers of vinylpyrrolidone and of hydrophobic monomers comprising a fatty chain;
- 15 - (4) copolymers of C_1 - C_6 alkyl methacrylates or acrylates and of aliphatic monomers comprising at least one fatty chain;
- (5) copolymers of hydrophilic methacrylates or acrylates and of hydrophobic monomers comprising at
20 least one fatty chain;
- (6) polyether polyurethanes comprising, in their chain, both hydrophilic sequences of generally polyoxyethylene nature and hydrophobic sequences which can be aliphatic strings only and/or cycloaliphatic
25 and/or aromatic strings;
- (7) polymers comprising an aminoplast ether backbone having at least one fatty chain.

6. Composition according to the preceding claim,
30 characterized in that the nonionic, anionic or cationic associative polymer or polymers are chosen from those of the families (1), (6), (E), (B) and (B') chosen in particular from:

- those of the following family (1):
35 - hydroxyethylcelluloses modified by groups comprising at least one fatty chain, such as linear or branched alkyl, linear or branched arylalkyl or linear or branched alkylaryl groups, or their mixtures, and in which the linear or

branched alkyl groups are preferably C₈-C₂₂ alkyl groups;

- those modified by alkylphenol polyalkylene glycol ether groups;

- 5 • those of the family (6) of polyether polyurethanes capable of being obtained by polycondensation of at least three compounds comprising:

i) at least one polyethylene glycol comprising from 150 to 180 mol of ethylene oxide,

10 ii) stearyl alcohol or decyl alcohol and

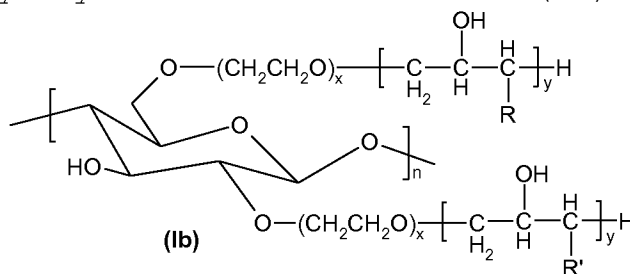
iii) at least one diisocyanate;

- those of the family (B') of quaternized cellulose derivatives:

15 i) quaternized celluloses modified by groups comprising at least one fatty chain, such as linear or branched alkyl, linear or branched arylalkyl or linear or branched alkylaryl groups comprising at least 8 carbon atoms, or mixtures of these;

20 ii) quaternized hydroxyethylcelluloses modified by groups comprising at least one fatty chain, such as linear or branched alkyl, linear or branched arylalkyl or linear or branched alkylaryl groups comprising at least 8 carbon atoms, or mixtures of these;

25 iii) hydroxyethylcelluloses of formula (Ib):

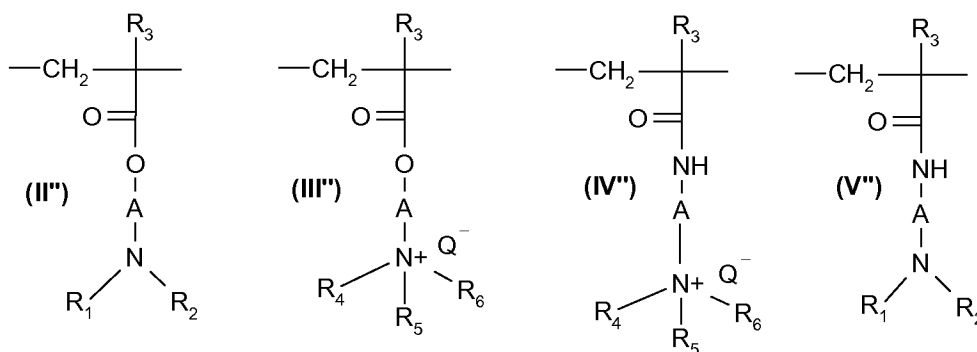


in which formula (Ib):

- 30 o R and R', which are identical or different, represent an ammonium group, such as -N⁺R_aR_bR_c Q⁻, in which R_a, R_b and R_c, which are identical or different, represent a hydrogen atom or a linear or branched C₁-C₃₀ alkyl group; and Q⁻ represents an anionic counterion;

- o n , x and y , which are identical or different, represent an integer between 1 and 10 000.

7. Composition according to either one of Claims 1 and 2, characterized in that the thickening polymer(s) is (are) chosen from iii); in particular chosen from:
 (1') Homopolymers or copolymers derived from acrylic or methacrylic esters or amides and comprising at least one of the units of following formulae (II''), (III''), (IV'') or (V''):



in which formulae (II'') to (V''):

- R_3 , which are identical or different, denote a hydrogen atom or a CH_3 radical;
 - A , which are identical or different, represent a linear or branched C_1 - C_6 , preferably C_2 - C_3 , alkyl group or a C_1 - C_4 hydroxyalkyl group;
 - R_4 , R_5 and R_6 , which are identical or different, represent a C_1 - C_6 alkyl group or a benzyl radical;
 - R_1 and R_2 , which are identical or different, represent hydrogen or a C_1 - C_6 alkyl group;
 - Q^- denotes an anionic counterion derived from an inorganic or organic acid;
- it being possible for the polymers of the family (1') to additionally comprise one or more units deriving from comonomers chosen from the family of the acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides substituted under nitrogen with lower (C_1 - C_4) alkyls, acrylic or methacrylic acids or their

esters, vinyl lactams, such as vinylpyrrolidone or vinylcaprolactam, or vinyl esters;

(2') cellulose ether derivatives comprising quaternary ammonium groups of hydroxyethylcellulose which has reacted with an epoxide substituted with a trimethylammonium group;

(3') cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer;

(4') cationic non-cellulose polysaccharides;

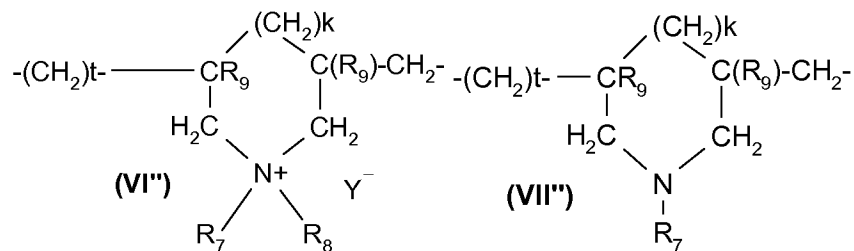
(5') polymers composed of piperazinyl units and of divalent alkylene or hydroxyalkylene radicals possessing straight or branched chains, optionally interrupted by oxygen, sulphur or nitrogen atoms or by aromatic or heterocyclic rings, and the oxidation and/or quaternization products of these polymers;

(6') water-soluble polyaminoamides prepared in particular by polycondensation of an acid compound with a polyamine; these polyaminoamides can be crosslinked with an epihalohydrin, a diepoxide, a dianhydride, an unsaturated dianhydride, a bisunsaturated derivative, a bishalohydrin, a bisazetadinium, a bishaloacyldiamine or a bis(alkyl halide) or also with an oligomer resulting from the reaction of a bifunctional compound which is reactive with respect to a bishalohydrin, a bisazetadinium, a bishaloacyldiamine, a bis(alkyl halide), an epihalohydrin, a diepoxide or a bisunsaturated 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 comprise one or more tertiary amine functional groups, quaternized.

(7') polymers obtained by reaction of a polyalkylene-polyamine comprising two primary amine groups and at least one secondary amine group with a

dicarboxylic acid chosen from diglycolic acid and saturated C₃-C₈ aliphatic dicarboxylic acids, the molar ratio of the polyalkylenepolyamine to the dicarboxylic acid being between 0.8:1 and 1.4:1; the polyaminoamide resulting therefrom being reacted with epichlorohydrin in a molar ratio of epichlorohydrin with respect to the secondary amine group of the polyaminoamide of between 0.5:1 and 1.8:1;

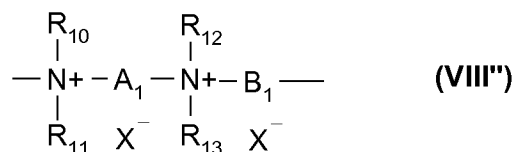
(8') alkyldiallylamine or dialkyldiallylammonium cyclopolymers, such as homopolymers or copolymers comprising, as main constituent of the chain, units corresponding to the formulae (VI'') and (VII''):



in which formulae (VI'') and (VII''):

- **k** and **t** are equal to 0 or 1, the sum **k** + **t** being equal to 1;
- **R₉** denotes a hydrogen atom or a methyl radical;
- **R₇** and **R₈** denote, independently of one another, a linear or branched C₁-C₈ alkyl group, a hydroxyalkyl group in which the alkyl group is a linear or branched C₁-C₅ alkyl group, or an amidoalkyl group, the alkyl of which is a linear or branched C₁-C₄ alkyl group;
- **R₇** and **R₈** can also denote, jointly with the nitrogen atom to which they are attached, a heterocyclic group;
- **Y⁻** is an organic or inorganic anionic counterion;

(9') diquaternary ammonium polymers comprising repeat units corresponding to the following formula:



in which formula (VIII'):

- **R₁₀**, **R₁₁**, **R₁₂** and **R₁₃**, which are identical or different, represent C₁-C₆ aliphatic, alicyclic or arylaliphatic radicals or represent aliphatic hydroxyalkyl radicals, the alkyl radical of which is a linear or branched C₁-C₄ alkyl radical, or else **R₁₀**, **R₁₁**, **R₁₂** and **R₁₃**, together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second heteroatom other than nitrogen, or else **R₁₀**, **R₁₁**, **R₁₂** and **R₁₃** represent a linear or branched C₁-C₆ alkyl radical substituted by a nitrile, ester, acyl, amide or -CO-O-R₁₄-D or -CO-NH-R₁₄-D group where **R₁₄** is a linear or branched alkylene and D is a quaternary ammonium group of -N⁺R₄R₅R₆ Q⁻ type, where **R₄**, **R₅**, **R₆** and Q⁻ are as defined above;
- **A₁** and **B₁**, which are identical or different, represent saturated or unsaturated, linear or branched, C₂-C₆ polymethylene groups which can comprise, bonded to or intercalated in the main chain, one or more aromatic rings or one or more oxygen or sulphur atoms or sulphoxide, sulphone, disulphide, amino, alkylamino, hydroxyl, quaternary ammonium, ureido, amide or ester groups, and
- **X⁻**, which are identical or different, denote an anionic counterion derived from an inorganic or organic acid, such as a halide;
- **A₁**, **R₁₀** and **R₁₂** can form, with the two nitrogen atoms to which they are attached, a piperazine ring;

in addition, if **A₁** denotes a linear or branched alkylene radical or a linear or branched hydroxyalkylene radical which is saturated or unsaturated, **B₁** can also denote a group: -(CH₂)_n-CO-D-OC-(CH₂)_n-, in which **n** is an integer

ranging from 1 to 6 inclusive and D denotes a quaternary ammonium group:

a) a glycol residue of formula: $-O-Z-O-$, where Z denotes a linear or branched hydrocarbon radical or a group corresponding to one of the following formulae:

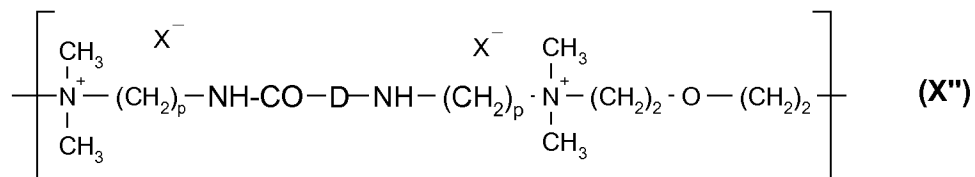
$-(CH_2-CH_2-O)_x-CH_2-CH_2-$; $-[CH_2-CH(CH_3)-O]_y-CH_2-CH(CH_3)-$,
where x and y denote an integer from 1 to 4, representing a defined and unique degree of polymerization, or any number from 1 to 4, representing a mean degree of polymerization;

b) a bissecondary diamine residue, such as a piperazine derivative;

c) a bisprimary diamine residue of formula: $-NH-Y-NH-$, where Y denotes a linear or branched hydrocarbon radical, or else the $-CH_2-CH_2-S-S-CH_2-CH_2-$ radical;

d) a ureylene group of formula: $-NH-CO-NH-$;

(10') polyquaternary ammonium polymers composed of repeat units of formula (X''):



in which formula (X'') p denotes an integer varying from 1 to 6 approximately inclusive, D corresponds to a σ bond or represents a $-(CH_2)_r\text{-CO-}$ group in which r denotes a number equal to 4 or to 7, and X^- is an anionic counterion as defined above;

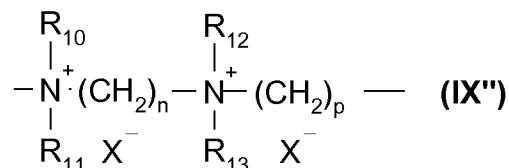
(11') quaternary polymers of vinylpyrrolidone and of vinylimidazole;

(12') polylysines, which correspond more particularly to the condensation of several salified or cationic lysine amino acids;

(13') cationic polyethyleneimines; and

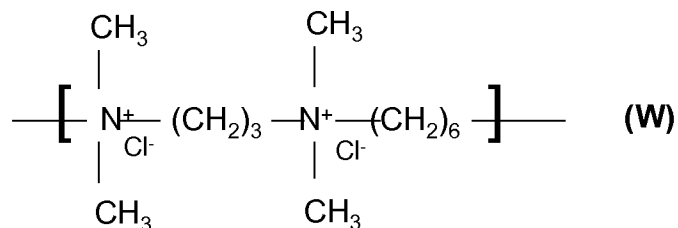
(14') cationic partially hydrolyzed polyvinyl-formamides.

8. Composition according to the preceding claim, characterized in that the thickening polymer(s) iii) is (are) chosen from those of the families **(1')**, **(8')** and
 5 **(9')**; in particular from the polymers composed of repeat units corresponding to the following formula **(IX'')**:

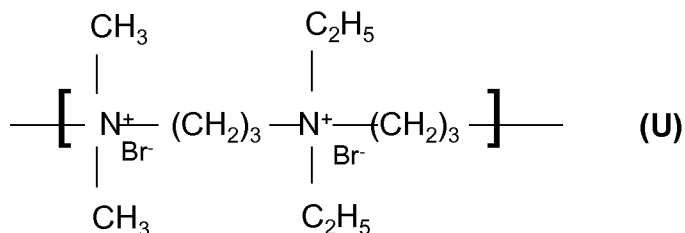


10 in which formula **(IX'')**:

- **R₁₀**, **R₁₁**, **R₁₂** and **R₁₃**, which are identical or different, denote a linear or branched C₁-C₄ alkyl radical or a linear or branched C₁-C₄ hydroxyalkyl radical;
- 15 - **n** and **p** are integers varying from 2 to 6 approximately inclusive and;
- **X⁻**, which are identical or different, are an anionic counterion derived from an inorganic or organic acid, such as a halide;
- 20 such as the cationic thickening polymers comprising the repeat units of following formula **(W)** and following formula **(U)**:



25 and in particular those having a molecular weight, determined by gel permeation chromatography, of between 9500 and 9900;

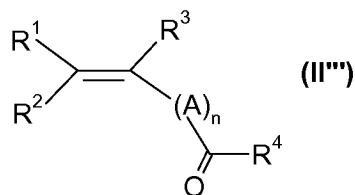


and in particular those having a molecular weight, determined by gel permeation chromatography, of approximately 1200.

5

9. Composition according to either one of Claims 1 and 2, characterized in that the thickening polymer(s) is (are) chosen from iv); in particular result(s) from at least one monomer of formula (**II'**):

10



in which formula (II''') :

- o **n** represents an integer between 0 and 10 inclusive,
- o **A** denotes a $-\text{CH}_2-$ or $-\text{CH}_2=\text{CH}_2-$ group,
- 15 o **R¹** denotes a hydrogen atom or a C_1 - C_6 alkyl, phenyl or benzyl group,
- o **R²** denotes a hydrogen atom or a C_1 - C_6 alkyl or carboxyl group,
- o **R³** denotes a hydrogen atom, a C_1 - C_6 alkyl group or a
20 $-(\text{CH}_2)_p\text{-X}$, phenyl or benzyl group, with p being an integer between 1 and 6 inclusive and X representing a carboxyl, sulpho or phospho group,
- o **Z** denotes a linear or branched alkylene group comprising from 1 to 6 carbon atoms,
- 25 o **R⁴** denotes a hydroxyl or linear or branched C_1 - C_6 alkoxy group or an NH-Z-R^5 radical, and
- o **R⁵** denotes a carboxylic, sulphonic or phosphoric group,

it being understood that the carboxylic, sulphonic or
30 phosphoric acid groups can be partially or completely
neutralized with an organic or inorganic base or can be

esterified with lower alcohols R-OH with R corresponding to a linear or branched C₁-C₆ alkyl group; in particular, in the formula (**II'''**), n has the value 0 and R¹ represents a hydrogen atom or a C₁-C₄ alkyl radical and R² and R³ represent a hydrogen atom or R¹, R² and R³ represent a C₁-C₄ alkyl radical.

10. Composition according to the preceding claim, characterized in that the anionic nonassociative acrylic thickening polymer(s) iv) is (are) chosen from:

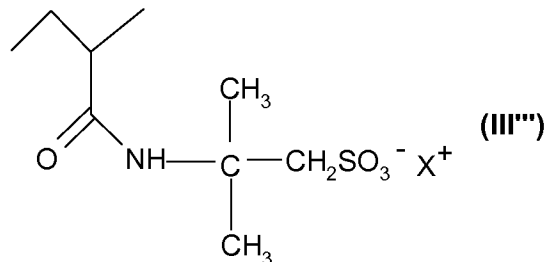
A₁) acrylic or methacrylic acid homo- or copolymers or their salts, such as crosslinked copolymers of (meth)acrylic acid and of C₁-C₆ alkyl acrylate, such as i) crosslinked copolymer of methacrylic acid and of ethyl acrylate as a 38% aqueous dispersion of active material, ii) crosslinked copolymer of acrylic acid and of ethyl acrylate as a 28% aqueous dispersion of active material, iii) crosslinked methacrylic acid/ethyl acrylate copolymer in the form of a 30% aqueous dispersion, iv) homopolymer of acrylic acid crosslinked with a pentaerythritol allyl ether, a sucrose allyl ether or a propylene allyl ether; and ammonium acrylate homopolymers; and

B₁) polyacrylamides comprising sulpho groups and in particular homo- or copolymers of 2-acrylamido-2-methylpropanesulphonic acid or their salts; especially the polymers comprising sulpho groups comprising vinylsulphonic, styrenesulphonic, naphthalenesulphonic or acrylamidoalkylsulphonic units, such as:

i) salts of polyvinylsulphonic acid having a weight-average molecular weight of between approximately 1000 and 100 000, and their copolymers with an unsaturated comonomer chosen from acrylic or methacrylic acids and their esters, acrylamide or its derivatives, vinyl ethers and vinylpyrrolidone;

ii) salts of polystyrenesulphonic acid, the sodium salts having a weight-average molecular weight of approximately 500 000 and of approximately 100 000;

5 iii) homopolymers of acrylamidomethylpropane-
sulphonic acid of formula (**III'''**) (AMPS):



chosen from salts of polyacrylamido(C₁-C₆)alkyl-
sulphonic acids, such as polyacrylamidomethyl-
propanesulphonic acid and crosslinked
polyacrylamidomethylpropanesulphonic acid
partially neutralized to 50% with aqueous ammonia;

iv) copolymers, which may or may not be
crosslinked and which may or may not be
neutralized, comprising from 15 to 60% by weight
of the AMPS units and from 40 to 85% by weight of
(C₁-C₆)alkyl(meth)acrylamide units or of (C₁-
C₆)alkyl(meth)acrylate units, with respect to the
polymer; and

v) terpolymers comprising from 10 to 90 mol% of acrylamide units, from 0.1 to 10 mol% of AMPS units and from 5 to 80 mol% of n-(C₁-C₆)alkyl-acrylamide units.

25 11. Composition according to either one of Claims 1 and 2, characterized in that the thickening polymer(s) is (are) composed of a mixture of thickening polymers chosen from the polymers i) to iv) as defined in any
30 one of the preceding claims; in particular, the mixture v) is:

- "binary" and comprises a mixture of:
 - thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxy-

propylmethylcellulose; or a gum, such as xanthan gum; and of

- thickening polymer iii), such as those of type (9') or of type (8'); or alternatively a mixture of:
- 5 - thickening polymer iv), such as those which are anionic, for example those of type (A₁); and of
- thickening polymer iii), such as those of type (9');
- "ternary" and comprises a mixture of:
- 10 - thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of nonionic cellulose ether type; or a gum, such as xanthan gum; and of
- thickening polymer iii), such as those of type (9') or of type (8'); or alternatively a mixture of:
- 15 - thickening polymer ii), such as cetyl hydroxyethylcellulose; and of
- thickening polymer iii), such as those of type (9') and of type (8');
- 20 • "quaternary" and comprises a mixture of:
- thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; and of thickening polymer iii), such as those of type (9'), of type (8') and of
- 25 type (A');

or alternatively a mixture of:

- thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymer iii),
- 30 such as those of type (9') and of type (8'); and of thickening polymer ii), such as cetyl hydroxyethylcellulose;

or alternatively a mixture of:

- thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymer iii),
- 35 such as those of type (9') and of type (8'); and of thickening polymer ii), such as those of type (7); or alternatively

- of thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymer iii), such as those of type (9') and of type (8'); and of thickening polymer ii), such as those of type (D);

- or "quintuple" and comprises a mixture of:
 - thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; and of thickening polymer iii), such as those of type (9'), of type (8') and of type (A'); and of anionic thickening polymer iv), such as those of type (A₁);

or alternatively a mixture of:

- thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymer iii), such as those of type (9') and of type (8'); and of thickening polymer ii), such as cetyl hydroxyethylcellulose; and of anionic thickening polymer iv), such as those of type (A₁);

or alternatively a mixture of:

- thickening polymer i), such as those of type viii), for example hydroxyethylcellulose or hydroxypropylmethylcellulose; of thickening polymer iii), such as those of type (9') and of type (8'); and of thickening polymer ii), such as those of type (D); and of anionic thickening polymer iv), such as those of type (A₁).

12. Composition according to any one of the preceding claims, characterized in that the thickening polymer or polymers i) to v) are used in the compositions of the invention in proportions of between 0.01 and 20% by weight and particularly of 0.1 to 5% by weight.

13. Composition according to any one of the preceding claims, characterized in that it comprises one or more couplers chosen in particular from meta-phenylenediamines, meta-aminophenols, meta-diphenols,

naphthalene couplers, heterocyclic couplers and their addition salts.

14. Composition according to the preceding claim,
5 characterized in that the coupler or couplers represent an amount of between 0.001 and 10% by weight approximately of the total weight of the dyeing composition, preferably between 0.005 and 6%.

10 15. Composition according to any one of the preceding claims, characterized in that it comprises one or more additional oxidation bases other than the compounds of formula (I) or their salts, in particular those chosen from ortho- or para-phenylenediamines, double bases,
15 ortho- or para-aminophenols and heterocyclic bases, and the addition salts of these compounds with an acid.

16. Composition according to any one of the preceding claims, characterized in that it comprises one or more
20 oxidizing agents.

17. Method for dyeing keratinous fibres, characterized in that a composition as defined in any one of Claims 1 to 15 is applied to the keratinous fibres without an
25 oxidizing agent.

18. Method for dyeing keratinous fibres, characterized in that a composition as defined in any one of Claims 1 to 15 is applied to the keratinous fibres in the
30 presence of one or more oxidizing agents.

19. Multicompartment device, in which:
- a first compartment comprises one or more
oxidation bases chosen from the compound of
35 formula (I) or one of its salts with an acid and one or more thickening polymers chosen from i) to v), such as described in any one of Claims 1 and 3 to 11, and optionally one or more couplers, such as described in either one of Claims 13 and 14,

- and optionally one or more additional oxidation bases other than the compound of formula (I) or its salts, such as described in Claim 15, and
- a second compartment comprising a composition comprising one or more oxidizing agents;
- 5 or alternatively
- a first compartment comprises one or more oxidation bases chosen from the compound of formula (I) or its salts with an acid according to Claim 1 and optionally one or more oxidation bases
- 10 other than the compound of formula (I), such as described in Claim 15, or their salts, and optionally one or more couplers, such as described in either one of Claims 13 and 14;
- 15 - a second compartment includes a composition comprising one or more thickening polymers i) to v), such as described in any one of Claims 1 and 3 to 11; and optionally
 - a third compartment includes a composition
- 20 comprising one or more oxidizing agents.

20. Use for colouring keratinous fibres of a composition according to any one of Claims 1 to 16.