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(54) Title: COSMETIC COMPOSITION COMPRISING A BRANCHED SULPHONIC POLYESTER AND A PARTICULAR THICKENER AND USES IN HAIR STYLING

(57) Abstract: The present application relates to a cosmetic composition comprising, in a cosmetically acceptable medium: (i) one or more branched sulphonc polyesters, and (ii) one or more polyvinyl alcohols. The present application also relates to the uses of this composition especially for the styling and the shaping of the hair.



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**COSMETIC COMPOSITION COMPRISING A BRANCHED
SULPHONIC POLYESTER AND A PARTICULAR THICKENER AND
USES IN HAIR STYLING**

5

The present invention relates to novel cosmetic compositions comprising one or more branched sulphonic polyesters and one or more polyvinyl alcohols as thickening polymers, and also to the uses of these compositions, especially in styling.

10

The present invention also relates to a method of styling keratin materials using these compositions.

The use of branched sulphonic polyesters in hair styling and fixing compositions is known and described, for example, in patent applications EP 0 966 946, WO 98/38969 and WO 99/63955.

15

Nevertheless, the use of branched sulphonic polyesters is not without drawbacks:

- the use of these polyesters in hair lacquers containing large quantities of alcohol generally gives good styling properties but does not make it possible to obtain sufficient lacquering power;

20

- the application of these polyesters in the form of lacquers with a high alcohol content gives the hair, after brushing, a dry feel; this undesirable phenomenon is particularly noticeable for dyed hair; and

25

- these polyesters are generally in semi-solid form, this property often makes their use difficult, in particular it is often difficult to ensure a homogeneous distribution of these polyesters over all the hair to be treated.

30

Unexpectedly and advantageously, the Applicant has demonstrated that the use of one or more branched sulphonic polyesters with one or more thickening polymers of polyvinyl alcohol type makes it possible to overcome the aforementioned drawbacks.

One subject of the present invention is thus a cosmetic composition comprising one or more branched sulphonic polyesters and

one or more polyvinyl alcohols.

The compositions obtained are in the form of gels, mousses, sprays, creams or pastes.

5 The compositions according to the present invention are easy to prepare and to apply. They remain satisfactorily localized, without runs, at the point of application. The compositions according to the present invention may be applied without a reduction in viscosity over time.

10 Moreover, the compositions according to the present invention make it possible to give the hairstyle a natural and long-lasting form retention.

Another subject of the present invention is a method for styling keratin materials, preferably human keratin materials and in particular the hair, which uses the compositions according to the invention.

15 Another subject of the present invention is the uses of the compositions according to the invention, especially for styling and shaping of keratin materials, preferably human keratin materials and in particular the hair.

20 Other features, aspects, subjects and advantages of the invention will appear even more clearly on reading the description and examples that follow.

The expression "polyvinyl alcohol" is understood within the present application to mean a polymer comprising $-\text{CH}_2\text{CH}(\text{OH})-$ groups.

25 The branched sulphonic polyesters used in the compositions of the present invention are known in the prior art. Their structure and synthesis are described in documents WO 95/18191, WO 97/08261 and WO 97/20899.

Preferred, in particular, are branched sulphonic polyesters obtained by polycondensation of:

30 (a) at least one dicarboxylic acid that does not bear a sulphonic functional group,

(b) at least one diol or a mixture of a diol and of a diamine,

(c) at least one monomer comprising two identical or different reactive functional groups chosen from hydroxyl, amino and carboxyl groups, and that bears, in addition, at least one sulphonic functional group, and

(d) at least one monomer comprising at least three identical or different reactive functional groups chosen from hydroxyl, amino and carboxyl groups.

The dicarboxylic acids that form the units (a) may be aliphatic dicarboxylic acids, alicyclic dicarboxylic acids, aromatic dicarboxylic acids and mixtures of such acids.

Mention may be made, by way of example, of 1,4-cyclohexanedioic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, fumaric acid, maleic acid, 1,3-cyclohexanedioic acid, phthalic acid, terephthalic acid and isophthalic acid and mixtures of such acids.

The diols that form the units (b) are chosen, for example, from alkanediols and polyalkylenediols, and mention may be made, by way of example, of ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol and polypropylene glycol.

The diamines capable of forming one part of the units (b) are preferably chosen from alkanediamines and polyoxyalkylene diamines.

The expression "sulphonic functional group" of the units (c) encompasses both the sulphonic acid functional group ($-\text{SO}_3\text{H}$) and the corresponding salified functional groups obtained by neutralization of the sulphonic acid functional group with a base, for example an alkali metal hydroxide.

The sulphonic functional groups are preferably in the form which is neutralized by an organic or inorganic base.

The units (c) are derived, for example, from dicarboxylic acids, dicarboxylic acid esters, glycols and hydroxy acids, all bearing at least one sulphonic group, in acid and/or neutralized form, preferably in

neutralized form.

The units (c) bearing at least one sulphonic functional group preferably represent from 2 to 15 mol% of the total amount of monomers.

5 The units (d) derived from multifunctional monomers are preferably present in an amount between 0.1 and 40 mol% relative to the total amount of monomers.

10 The multifunctional monomers forming the units (d) are chosen, for example, from trimethylolethane, trimethylolpropane, glycerol, pentaerythritol, sorbitol, trimellitic anhydride, erythritol, threitol, dipentaerythritol, pyromellitic dianhydride and dimethylpropionic acid.

15 The branched sulphonic polyesters may comprise, in addition to the four types of units (a) to (d) described above, units (e) derived from monomers comprising two different reactive functional groups, chosen for example from hydroxy carboxylic acids and amino carboxylic acids or mixtures thereof.

20 These units (e) may represent up to 40 mol% of the total amount of monomers (a), (b), (c), (d) and (e).

25 Of course, the branched sulphonic polymers used in the present invention are preferably obtained from a mixture of monomers in which the number of equivalents of carboxylic acid functional groups is substantially equal to the number of equivalents of hydroxyl functional groups and of amino functional groups which may be present.

30 The branched sulphonic polymers used in the styling compositions of the present invention are known and sold, for example, by Eastman. Mention may be made, as a preferred commercial product, of the product sold under the name AQ 1350[®] by Eastman.

The composition according to the present invention advantageously comprises from 0.2 to 15%, preferably from 0.5 to 10%

by weight of one or more branched sulphonic polyesters relative to the total weight of the composition.

5 The composition according to the present invention also contains one or more polyvinyl alcohols. The latter are present as thickening polymers.

10 For the purposes of the present invention, the expression "thickening polymer" means a polymer capable, by its presence, of increasing the viscosity of the medium by at least 50 centipoise at 25°C and at a shear rate of 1 s⁻¹. Preferably, the thickening polymer has, at 1% in water or a 50/50 water/alcohol mixture by weight at 25°C, a viscosity of greater than 100 centipoise at a shear rate of 1 s⁻¹. These viscosities may be measured in particular with viscometers or rheometers with cone-plate geometry.

15

The expression "polyvinyl alcohol" as indicated above is understood to mean a polymer comprising -CH₂CH(OH)- units.

The polyvinyl alcohols are generally produced by hydrolysis of polyvinyl acetate. Usually, the reaction takes place in the presence of methanol
20 (alcoholysis). The reaction is customarily acid-catalysed or base-catalysed. The degree of hydrolysis of commercial products is variable, often around 87% but there are also products with a degree of hydrolysis of 100. Copolymers with monomers other than vinyl acetate also exist, such as ethylene/vinyl alcohol copolymers.

25

The polyvinyl alcohol polymers as thickening polymers are preferably chosen from homopolymers or copolymers with vinyl acetate, the latter corresponding in particular to a partial hydrolysis of polyvinyl acetate. Use may be made, for example, of the products from the Celvol range sold
30 by the company CELANESE under the names Celvol 540, Celvol 350, Celvol 325, Celvol 165, Celvol 125 Celvol 540 S, Celvol 840, Celvol 443.

The composition according to the present invention advantageously comprises from 0.05 to 20%, preferably from 0.1 to 10% by weight of one or more polyvinyl alcohols relative to the total weight of the composition.

5 Advantageously, in the cosmetic composition according to the invention, the polyvinyl alcohol(s) are chosen from homopolymers or copolymers. More advantageously still, the copolymer(s) are copolymers with vinyl acetate.

Preferably, the cosmetically acceptable medium is aqueous.

10 The cosmetic composition according to the invention may also comprise one or more organic solvents, preferably in an amount between 0.05 and 40%, very preferably between 1 and 20% by weight, relative to the total weight of the composition.

15 This organic solvent may be a C₂ to C₄ lower alcohol, in particular ethanol, polyols and polyol ethers such as propylene glycol, polyethylene glycol or glycerol.

20 The compositions according to the invention may also contain other cosmetically acceptable adjuvants, such as for example ionic or nonionic surfactants, additional thickeners other than the polyvinyl alcohols used in the compositions according to the present application, ethoxylated or non-ethoxylated fatty alcohols, co-thickeners, penetrants, fragrances, dyes, plasticizers, buffers, and various customary adjuvants such as waxes, volatile or non-volatile silicones that are cyclic or linear or branched, and are organomodified especially alkoxylated or modified
25 by amine groups or are unmodified, for example silicone gums, ceramides, pseudoceramides, plant, mineral or synthetic oils, vitamins or provitamins such as panthenol, opacifiers, reducing agents, emulsifiers, preservatives, mineral fillers, pearlescent agents, flakes, sunscreens, proteins, anionic, nonionic, cationic or amphoteric fixing
30 polymers, moisturisers, emollients, demulcents, anti-foaming agents, antiperspirants, free-radical scavengers, bactericides, sequestrants, anti-dandruff agents, antioxidants, basifying agents, acidifying agents, and

any other additive conventionally used in cosmetic compositions intended to be applied to the hair.

5 The surfactants that can be used in the composition according to the present invention may be anionic, nonionic, amphoteric or cationic surfactants, or mixtures thereof.

10 The term "anionic surfactant" means a surfactant comprising, as ionic or ionizable groups, only anionic groups. These anionic groups are preferably chosen from the following groups: CO_2H , CO_2^- , SO_3H , SO_3^- , OSO_3H , OSO_3^- , H_2PO_3 , HPO_3^- , PO_3^{2-} , H_2PO_2 , HPO_2 , HPO_2^- , PO_2^- , POH , PO^- .

15 As examples of anionic surfactants that may be used in the composition according to the invention, mention may be made of alkyl sulphates, alkyl ether sulphates, alkylamido ether sulphates, alkylaryl polyether sulphates, monoglyceride sulphates, alkyl sulphonates, alkylamide sulphonates, alkylaryl sulphonates, alpha-olefin sulphonates, paraffin sulphonates, alkyl sulphosuccinates, alkyl ether sulphosuccinates, alkylamide sulphosuccinates, alkyl sulphoacetates, 20 acyl sarcosinates, acyl glutamates, alkyl sulphosuccinamates, acyl isethionates and N-acyltaurates, salts of alkyl monoesters of polyglycoside-polycarboxylic acids, acyl lactylates, D-galactoside-uronic acid salts, alkyl ether carboxylic acid salts, alkylaryl ether carboxylic acid salts, alkylamido ether carboxylic acid salts; and the 25 corresponding non-salified forms of all these compounds; the alkyl and acyl groups of all these compounds comprising from 6 to 24 carbon atoms and the aryl group denoting a phenyl group.

30 These compounds may be oxyethylenated and then preferably comprise from 1 to 50 ethylene oxide units.

The salts of C_{6-24} alkyl monoesters of polyglycoside-polycarboxylic acids may be chosen from C_{6-24} alkyl polyglycoside

citrates, C₆₋₂₄ alkyl polyglycoside tartrates and C₆₋₂₄ alkyl polyglycoside sulphosuccinates.

5 When the anionic surfactant(s) (ii) are in salt form, they may be chosen from alkali metal salts such as the sodium or potassium salt and preferably the sodium salt, the ammonium salts, the amine salts and in particular amino alcohol salts or the alkaline-earth metal salts such as the magnesium salt.

10 Examples of amino alcohol salts that may especially be mentioned include monoethanolamine, diethanolamine and triethanolamine salts, monoisopropanolamine, diisopropanolamine or triisopropanolamine salts, 2-amino-2-methyl-1-propanol salts, 2-amino-2-methyl-1,3-propanediol salts and tris(hydroxymethyl)aminomethane
15 salts.

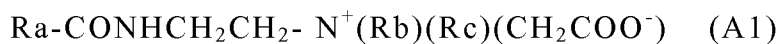
Alkali metal or alkaline-earth metal salts and in particular the sodium or magnesium salts are preferably used.

20 Among the anionic surfactants, it is preferred, according to the invention, to use alkyl sulphate salts and alkyl ether sulphate salts and mixtures thereof.

25 Nonionic surfactants are themselves also compounds that are well known *per se* (see especially in this regard the "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178). Thus, they may be chosen especially from (non-limiting list) alcohols, alpha-diols and alkylphenols, these
30 compounds being polyethoxylated, polypropoxylated or polyglycerolated and containing a fatty chain comprising, for example, 8 to 18 carbon atoms, it being possible for the number of ethylene oxide or propylene

oxide groups to range especially from 2 to 50 and it being possible for the number of glycerol groups to range especially from 2 to 30. Mention may also be made of copolymers of ethylene oxide and propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty
5 alcohols; polyethoxylated fatty amides preferably having from 2 to 30 mol of ethylene oxide, polyglycerolated fatty amides containing on average 1 to 5, and in particular 1.5 to 4 glycerol groups, ethoxylated fatty acid esters of sorbitan containing from 2 to 30 mol of ethylene
10 oxide, fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, amine oxides such as (C₁₀-C₁₄)alkylamine oxides or N-acylaminopropylmorpholine oxides. It will be noted that alkylpolyglycosides constitute nonionic surfactants that are particularly suitable within the context of the
15 present invention.

The amphoteric or zwitterionic surfactant(s) that can be used in the present invention may especially be optionally quaternized, secondary or tertiary aliphatic amine derivatives, in which the aliphatic group is a linear or branched chain containing from 8 to 22 carbon atoms, said amine derivatives containing at least one anionic group such as, for example, a carboxylate, sulphonate, sulphate, phosphate or phosphonate group. In particular, mention may be made of (C₈-C₂₀)alkylbetaines, sulphobetaines, (C₈-C₂₀ alkyl)amido(C₃₋₈ alkyl)betaines or (C₈-C₂₀ alkyl)amido(C₆-C₈ alkyl)sulphobetaines. Among the optionally quaternized, secondary or tertiary aliphatic amine derivatives that can be used, as defined above, mention may also be made of the compounds having the respective structures (A1) and (A2) below:



in which:

Ra represents a C₁₀-C₃₀ alkyl or alkenyl group derived from an acid

Ra-COOH, preferably present in hydrolysed coconut oil, a heptyl, nonyl or undecyl group,

Rb represents a beta-hydroxyethyl group, and

Rc represents a carboxymethyl group;

and



in which:

B represents -CH₂CH₂OX',

B' represents -(CH₂)_zY', with z = 1 or 2,

X' represents the group $-\text{CH}_2-\text{COOH}$, $\text{CH}_2-\text{COOZ}'$, $-\text{CH}_2\text{CH}_2-\text{COOH}$, $-\text{CH}_2\text{CH}_2-\text{COOZ}'$, or a hydrogen atom,

Y' represents $-\text{COOH}$, $-\text{COOZ}'$, the group $-\text{CH}_2-\text{CHOH}-\text{SO}_3\text{H}$ or $-\text{CH}_2-\text{CHOH}-\text{SO}_3\text{Z}'$,

5 Z' represents an ion derived from an alkali metal or alkaline-earth metal, such as sodium, an ammonium ion or an ion derived from an organic amine.

 Ra' represents a $\text{C}_{10}-\text{C}_{30}$ alkyl or alkenyl or alkenyl group of an acid Ra'-COOH preferably present in coconut oil or in hydrolysed
10 linseed oil, an alkyl group, especially a C_{17} alkyl group, and its iso form, or an unsaturated C_{17} group.

 These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium
15 capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, disodium capryloamphodipropionate, lauroamphodipropionic acid and cocoamphodipropionic acid.

 By way of example, mention may be made of the
20 cocoamphodiacetate sold by the company Rhodia under the trade name Miranol® C2M Concentrate.

 The composition according to the invention may also comprise one or more cationic surfactants that are well known *per se*, such as optionally polyoxyalkylenated, primary, secondary or tertiary fatty
25 amine salts; quaternary ammonium salts such as tetraalkylammonium, alkylamidoalkyltrialkylammonium, trialkylbenzylammonium, trialkylhydroxyalkylammonium or alkylpyridinium chlorides or bromides; imidazoline derivatives; or amine oxides of cationic nature.

 The nonionic, amphoteric and cationic surfactants described
30 above may be used alone or as mixtures and the amount thereof is between 0.01% and 30% by weight, preferably between 0.05% and 20% by weight and better still between 0.1% and 10% by weight, relative to

the total weight of the composition.

5 The additional gelling agents and/or thickeners other than the polyvinyl alcohols of the invention and that are suitable for the compositions of the invention are well known in the art and may be chosen from poly(oxyalkylene) glycols, poly(oxyalkylene) glycol esters, alginates, biosaccharides, starch derivatives, natural gums such as xanthan gum, guar gum, carob bean gum, scleroglucans, derivatives of chitin and of chitosan, carrageenans, clays, and mixtures thereof.

10 By way of example of gelling agents, especially that are in the aqueous phase, mention may be made of Fucogel[®] 1000 PP sold by the company Solabia, Satiagel[®] KSO sold by Degussa and Keltrol[®] sold by the company Kelco.

The additional gelling agents in general represent from 0.05 to 15%, preferably from 0.5 to 10% by weight of the composition.

15 The silicones that may be used as additives in the cosmetic compositions of the present invention are volatile or non-volatile, cyclic, linear or branched silicones, optionally modified with organic groups, having a viscosity from 5×10^{-6} to $2.5 \text{ m}^2/\text{s}$ at 25°C and preferably 1×10^{-5} to $1 \text{ m}^2/\text{s}$.

20 The silicones that can be used in accordance with the invention may be soluble or insoluble in the composition and in particular may be polyorganosiloxanes that are insoluble in the composition of the invention. They may be in the form of oils, waxes, resins or gums.

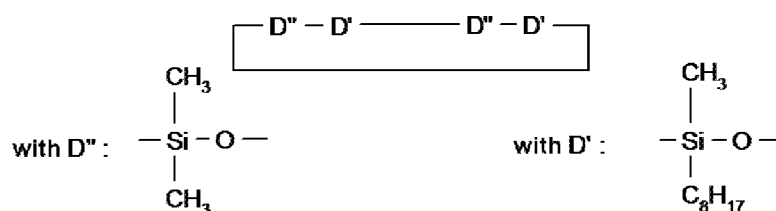
25 Organopolysiloxanes are defined in greater detail in Walter Noll's "Chemistry and Technology of Silicones" (1968), Academic Press. They may be volatile or non-volatile.

When they are volatile, the silicones are more particularly chosen from those having a boiling point of between 60°C and 260°C , and even more particularly from:

30 (i) cyclic silicones containing from 3 to 7 and preferably 4 to 5 silicon atoms. These are, for example, octamethylcyclotetrasiloxane sold in particular under the name

Volatile Silicone[®] 7207 by Union Carbide or Silbione[®] 70045 V2 by Rhodia, decamethylcyclotetrasiloxane sold under the name Volatile Silicone[®] 7158 by Union Carbide, and Silbione[®] 70045 V5 by Rhodia, and mixtures thereof.

- 5 Mention may also be made of cyclocopolymers of the dimethylsiloxane/methylalkylsiloxane type, such as Volatile Silicone[®] FZ 3109 sold by the company Union Carbide, of formula:



- 10 Mention may also be made of mixtures of cyclic silicones with organosilicon compounds, such as the mixture of octamethylcyclotetrasiloxane and tetratrimethylsilylpentaerythritol (50/50) and the mixture of octamethylcyclotetrasiloxane and oxy-1,1'-bis(2,2,2',2',3,3'-hexatrimethylsilyloxy)neopentane;

- 15 (ii) linear volatile silicones containing 2 to 9 silicon atoms and having a viscosity of less than or equal to 5×10^{-6} m²/s at 25°C. An example is decamethyltetrasiloxane sold in particular under the name SH 200 by the company Toray Silicone. Silicones belonging to this category are also described in the article published in Cosmetics and Toiletries, 20 Vol. 91, Jan. 76, pp. 27-32, Todd & Byers "Volatile Silicone Fluids for Cosmetics".

- 25 Non-volatile silicones, and more particularly polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, silicone gums and resins, polyorganosiloxanes modified with organofunctional groups, and mixtures thereof, are preferably used.

These silicones are more particularly chosen from polyalkylsiloxanes, among which mention may be made mainly of polydimethylsiloxanes containing trimethylsilyl end groups. The

viscosity of the silicones is measured at 25°C according to ASTM standard 445 Appendix C.

Among these polyalkylsiloxanes, mention may be made, in a non-limiting manner, of the following commercial products:

- 5 - the Silbione® oils of the 47 and 70 047 series or the Mirasil® oils sold by Rhodia, for instance the oil 70 047 V 500 000;
 - the oils of the Mirasil® series sold by the company Rhodia;
 - the oils of the 200 series from the company Dow Corning, such as DC200 with a viscosity of 60 000 mm²/s;
10 - the Viscasil® oils from General Electric and certain oils of the SF series (SF 96, SF 18) from General Electric.

Mention may also be made of polymethylsiloxanes containing dimethylsilanol end groups, known by the name dimethiconol (CTFA), such as the oils of the 48 series from the company Rhodia.

- 15 In this category of polyalkylsiloxanes, mention may also be made of the products sold under the names "Abil Wax® 9800 and 9801" by the company Goldschmidt, which are poly(C₁-C₂₀) alkylsiloxanes.

- The polyalkylarylsiloxanes are chosen particularly from linear and/or branched polydimethyl/methylphenylsiloxanes and
20 polydimethyl/diphenylsiloxanes with a viscosity of from 1×10⁻⁵ to 5×10⁻² m²/s at 25°C.

Among these polyalkylarylsiloxanes, examples that may be mentioned include the products sold under the following names:

- the Silbione® oils of the 70 641 series from Rhodia;
25 - the oils of the Rhodorsil® 70 633 and 763 series from Rhodia;
 - the Dow Corning 556 Cosmetic Grade Fluid oil from Dow Corning;
 - the silicones of the PK series from Bayer, such as the product PK20;
30 - the silicones of the PN and PH series from Bayer, such as the products PN1000 and PH1000;
 - certain oils of the SF series from General Electric, such as SF

1023, SF 1154, SF 1250 and SF 1265.

5 The silicone gums that can be used in accordance with the invention are, in particular, polyorganosiloxanes having high number-average molecular weights of between 200 000 and 1 000 000, used alone or as a mixture in a solvent. This solvent can be chosen from volatile silicones, polydimethylsiloxane (PDMS) oils, polyphenylmethylsiloxane (PPMS) oils, isoparaffins, polyisobutylenes, methylene chloride, pentane, dodecane and tridecane, or mixtures thereof.

10 Mention may be made more particularly of the following products:

- polydimethylsiloxane gums,
- polydimethylsiloxane/methylvinylsiloxane gums,
- polydimethylsiloxane/diphenylsiloxane gums,
- 15 - polydimethylsiloxane/phenylmethylsiloxane gums,
- polydimethylsiloxane/diphenylsiloxane/methylvinylsiloxane gums.

Products that can be used more particularly in accordance with the invention are mixtures such as:

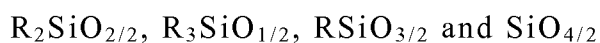
- 20 - mixtures formed from a polydimethylsiloxane hydroxylated at the end of the chain, or dimethiconol (CTFA) and from a cyclic polydimethylsiloxane also called cyclomethicone (CTFA), such as the product Q2 1401 sold by the company Dow Corning;

- 25 - mixtures formed from a polydimethylsiloxane gum with a cyclic silicone, such as the product SF 1214 Silicone Fluid from the company General Electric; this product is an SF 30 gum corresponding to a dimethicone, having a number-average molecular weight of 500 000, dissolved in the oil SF 1202 Silicone Fluid corresponding to decamethylcyclopentasiloxane;

- 30 - mixtures of two PDMSs with different viscosities, and more particularly of a PDMS gum and a PDMS oil, such as the product SF 1236 from the company General Electric. The product SF 1236 is a

mixture of a gum SE 30 defined above with a viscosity of 20 m²/s and of an oil SF 96 with a viscosity of 5×10⁻⁶ m²/s. This product preferably comprises 15% of gum SE 30 and 85% of an oil SF 96.

5 The organopolysiloxane resins that can be used in accordance with the invention are crosslinked siloxane systems containing the following units:



10 in which R represents a hydrocarbon-based group containing 1 to 16 carbon atoms or a phenyl group. Among these products, the ones that are particularly preferred are those in which R denotes a C₁-C₄ lower alkyl group, more particularly methyl, or a phenyl group.

15 Among these resins, mention may be made of the product sold under the name Dow Corning 593 or those sold under the names Silicone Fluid SS 4230 and SS 4267 by the company General Electric, which are silicones of dimethyl/trimethylsiloxane structure.

Mention may also be made of the trimethylsiloxysilicate type resins sold in particular under the names X22-4914, X21-5034 and X21-5037 by the company Shin-Etsu.

20 The organomodified silicones that can be used in accordance with the invention are silicones as defined above and comprising in their structure one or more organofunctional groups attached via a hydrocarbon-based group.

Among the organomodified silicones, mention may be made of polyorganosiloxanes comprising:

25 - polyethyleneoxy and/or polypropyleneoxy groups optionally containing C₆-C₂₄ alkyl groups, such as the products known as dimethicone copolyol sold by the company Dow Corning under the name DC 1248 or the oils Silwet® L 722, L 7500, L 77, L 711 from the company Union Carbide and the (C₁₂)alkylmethicone copolyol sold by
30 the company Dow Corning under the name Q2 5200;

- substituted or unsubstituted amine groups, such as the products sold under the name GP 4 Silicone Fluid and GP 7100 by the company

- Genesee, or the products sold under the names Q2 8220 and Dow Corning 929 or 939 or Dow Corning 2-8299 by the company Dow Corning or the product sold under the name Belsil ADM LOG 1 by the company Wacker. The substituted amine groups are, in particular, C₁-C₄ aminoalkyl groups;
- 5 - thiol groups such as the products sold under the names GP 72A and GP 71 from Genesee;
- alkoxyated groups such as the product sold under the name Silicone Copolymer F-755 by SWS Silicones and Abil Wax® 2428, 2434
- 10 and 2440 by the company Goldschmidt;
- hydroxylated groups such as the polyorganosiloxanes containing a hydroxyalkyl functional group, described in French patent application FR-A-8 516 334;
- alkoxyalkyl groups such as, for example, the
- 15 polyorganosiloxanes described in patent US-A-4 957 732;
- anionic groups of carboxylic type, such as, for example, in the products described in patent EP 186 507 from the company Chisso Corporation, or of alkylcarboxylic type, such as those present in the product X-22-3701E from the company Shin-Etsu; 2-hydroxyalkyl
- 20 sulphonate; 2-hydroxyalkyl thiosulphate such as the products sold by the company Goldschmidt under the names Abil® S201 and Abil® S255;
- hydroxyacrylamino groups, for instance the polyorganosiloxanes described in patent application EP 342 834. Mention may be made, for example, of the product Q2-8413 from the
- 25 company Dow Corning.
- The silicones as described above may be used, alone or as a mixture, in an amount of between 0.01% and 20% by weight and preferably between 0.1% and 5% by weight.
- The compositions of the invention may also comprise non-
- 30 silicone fatty substances such as mineral, plant, animal and synthetic oils, waxes, fatty esters, ethoxylated or non-ethoxylated fatty alcohols, and fatty acids.

As oils that may be used in the composition of the invention, examples that may be mentioned include:

- hydrocarbon-based oils of animal origin, such as perhydosqualene;
- 5 - hydrocarbon-based oils of plant origin, such as liquid fatty acid triglycerides containing from 4 to 10 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively, for example, sunflower oil, maize oil, soybean oil, marrow oil, grapeseed oil, sesame seed oil, hazelnut oil, apricot oil, macadamia oil, arara oil, castor oil, 10 avocado oil, caprylic/capric acid triglycerides, for instance those sold by the company Stéarineries Dubois or those sold under the names Miglyol[®] 810, 812 and 818 by the company Dynamit Nobel, jojoba oil and shea butter oil;
- 15 - linear or branched hydrocarbons of mineral or synthetic origin, such as volatile or non-volatile liquid paraffins, and derivatives thereof, petroleum jelly, polydecenes, hydrogenated polyisobutene such as Parleam[®]; isoparaffins, for instance isohexadecane and isodecane;
- 20 - partially hydrocarbon-based and/or silicone-based fluoro oils, for instance those described in document JP-A-2-295 912; fluoro oils that may also be mentioned include perfluoromethylcyclopentane and perfluoro-1,3-dimethylcyclohexane, sold under the names Flutec[®] PC1 and Flutec[®] PC3 by the company BNFL Fluorochemicals; perfluoro-1,2-dimethylcyclobutane; perfluoroalkanes such as dodecafluoropentane and tetradecafluorohexane, sold under the names PF 5050[®] and PF 5060[®] by 25 the company 3M, or bromoperfluorooctyl sold under the name Foralkyl[®] by the company Atochem; nonafluoromethoxybutane and nonafluoroethoxyisobutane; perfluoromorpholine derivatives such as 4-trifluoromethyl perfluoromorpholine sold under the name PF 5052[®] by the company 3M;
- 30 The wax(es) are selected in particular from carnauba wax, candelilla wax, esparto grass wax, paraffin wax, ozokerite, plant waxes such as olive wax, rice wax, hydrogenated jojoba wax or the absolute

waxes of flowers such as the essential wax of blackcurrant blossom sold by the company Bertin (France), animal waxes, for instance beeswaxes or modified beeswaxes (cerabellina); other waxes or waxy raw materials that may be used according to the invention are especially marine waxes
5 such as the product sold by the company Sophim under the reference M82, and polyethylene waxes or polyolefin waxes in general.

The saturated or unsaturated fatty acids are more particularly chosen from myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid and isostearic acid.

10 The fatty esters are especially carboxylic acid esters, in particular mono-, di-, tri-, or tetracarboxylic esters.

The carboxylic acid esters are especially esters of saturated or unsaturated, linear or branched C_1 - C_{26} aliphatic acids and of saturated or unsaturated, linear or branched C_1 - C_{26} aliphatic alcohols, the total
15 carbon number of the esters being greater than or equal to 10.

Among the monoesters, mention may be made of dihydroabietyl behenate; octyldodecyl behenate; isocetyl behenate; cetyl lactate; C_{12} - C_{15} alkyl lactate; isostearyl lactate; lauryl lactate; linoleyl lactate; oleyl lactate; (iso)stearyl octanoate; isocetyl octanoate; octyl octanoate; cetyl
20 octanoate; decyl oleate; isocetyl isostearate; isocetyl laurate; isocetyl stearate; isodecyl octanoate; isodecyl oleate; isononyl isononanoate; isostearyl palmitate; methylacetyl ricinoleate; myristyl stearate; octyl isononanoate; 2-ethylhexyl isononate; octyl palmitate; octyl pelargonate; octyl stearate; octyldodecyl erucate; oleyl erucate; ethyl
25 and isopropyl palmitates, 2-ethylhexyl palmitate, 2-octyldecyl palmitate, alkyl myristates such as isopropyl, butyl, cetyl or 2-octyldodecyl myristate, hexyl stearate, butyl stearate, isobutyl stearate; dioctyl malate, hexyl laurate, 2-hexyldecyl laurate.

Esters of C_4 - C_{22} dicarboxylic or tricarboxylic acids and of C_1 - C_{22} alcohols and esters of monocarboxylic, dicarboxylic or tricarboxylic
30 acids and of C_2 - C_{26} dihydroxy, trihydroxy, tetrahydroxy or pentahydroxy alcohols may also be used.

Mention may especially be made of: diethyl sebacate; diisopropyl sebacate; diisopropyl adipate; di-n-propyl adipate; dioctyl adipate; diisostearyl adipate; dioctyl maleate; glyceryl undecylenate; octyldodecyl stearyl stearate; pentaerythrityl monoricinoleate; 5 pentaerythrityl tetraisononanoate; pentaerythrityl tetrapelargonate; pentaerythrityl tetraisostearate; pentaerythrityl tetraoctanoate; propylene glycol dicaprylate; propylene glycol dicaprate; tridecyl erucate; triisopropyl citrate; triisostearyl citrate; glyceryl trilactate; glyceryl trioctanoate; trioctyldodecyl citrate; trioleyl citrate; propylene glycol dioctanoate and neopentyl glycol diheptanoate. The esters mentioned 10 above being different from the esters of formula (I).

Among the esters mentioned above, it is preferred to use ethyl and isopropyl palmitates, 2-ethylhexyl palmitate, 2-octyldecyl palmitate, alkyl myristates such as isopropyl, butyl, cetyl or 2-octyldodecyl 15 myristate, hexyl stearate, butyl stearate, isobutyl stearate; dioctyl malate, hexyl laurate, 2-hexyldecyl laurate, isononyl isononanoate or cetyl octanoate.

As fatty alcohols, mention may be made of linear or branched, saturated or unsaturated fatty alcohols containing from 8 to 26 carbon 20 atoms, for instance cetyl alcohol, stearyl alcohol and the mixture thereof (cetylstearyl alcohol), octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol, oleyl alcohol or linoleyl alcohol.

The fatty substances in general represent from 0.1 to 50%; preferably from 1 to 30%, and more preferably still from 2 to 20% by 25 weight of the total composition.

As indicated previously, the compositions may comprise fixing polymers other than the polymers used according to the invention. The expression "fixing polymer" is understood within the meaning of the present invention to mean any polymer that makes it possible to give a 30 shape to the hair or to hold the hair in a given shape.

All the anionic, cationic, amphoteric and nonionic fixing polymers and mixtures thereof used in the art may be used in the

compositions according to the present application.

The fixing polymers may be soluble in the cosmetically acceptable medium or insoluble in this same medium and used in this case in the form of dispersions of solid or liquid particles of polymer (latex or pseudolatex).

The anionic fixing polymers generally used are polymers containing groups derived from carboxylic, sulphonic or phosphoric acid, and have a number-average molecular mass of between approximately 500 and 5 000 000.

The anionic fixing containing carboxylic groups that are preferred according to the invention are:

A) copolymers of acrylic acid and of acrylamide sold in the form of their sodium salts under the names Reten 421, 423 or 425 by the company Hercules, the sodium salts of polyhydroxycarboxylic acids;

B) copolymers of acrylic or methacrylic acid with a monoethylenic monomer such as ethylene, styrene, vinyl esters, acrylic or methacrylic acid esters, optionally grafted onto a polyalkylene glycol such as polyethylene glycol and optionally crosslinked. Such polymers are described in particular in French patent 1 222 944 and German patent application 2 330 956, the copolymers of this type comprising an optionally N-alkylated and/or hydroxyalkylated acrylamide unit in their chain as described in particular in Luxembourg patent application 75370 and 75371 or sold under the name Quadramer by the company American Cyanamid. Mention may also be made of the acrylic acid/ethyl acrylate/N-*tert*-butylacrylamide terpolymers such as Ultrahold Strong sold by the company BASF. Mention may also be made of copolymers of acrylic acid and of C₁-C₄ alkyl methacrylate and terpolymers of vinylpyrrolidone, of acrylic acid and of methacrylate of C₁-C₂₀ alkyl, for example lauryl methacrylate, such as the product sold by the company ISP under the name Acrylidone[®] LM and methacrylic acid/ethyl acrylate/*tert*-butyl acrylate terpolymers such as the product sold under the name Luvimer[®] 100 P by the company BASF;

Mention may also be made of methacrylic acid/acrylic acid/ethyl acrylate/methyl methacrylate copolymers as an aqueous dispersion, sold under the name Amerhold® DR 25 by the company Amerchol.

5 C) crotonic acid copolymers, such as those comprising vinyl acetate or propionate units in their chain and optionally other monomers such as allyl esters or methallyl esters, vinyl ether or vinyl ester of a linear or branched saturated carboxylic acid with a long hydrocarbon chain such as those containing at least 5 carbon atoms, it being possible for these polymers optionally to be grafted or crosslinked, or
10 or alternatively another vinyl, allyl or methallyl ester monomer of an α - or β -cyclic carboxylic acid. Such polymers are described, *inter alia*, in French patents 1 222 944, 1 580 545, 2 265 782, 2 265 781, 1 564 110 and 2 439 798. Commercial products that come under this category are the resins 28-29-30, 26-13-14 and 28-13-10 sold by the company
15 National Starch;

D) copolymers of C₄-C₈ monounsaturated carboxylic acids or anhydrides chosen from:

- copolymers comprising (i) one or more maleic, fumaric or itaconic acids or anhydrides and (ii) at least one monomer selected from
20 vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, the anhydride functions of these copolymers optionally being monoesterified or monoamidated. Such polymers are described, in particular, in US patents 2 047 398, 2 723 248 and 2 102 113, and GB patent 839 805. Commercial products are especially
25 those sold under the names Gantrez® AN or ES by the company ISP;

- copolymers comprising (i) one or more maleic, citraconic or itaconic anhydride units and (ii) one or more monomers chosen from allyl or methallyl esters optionally comprising one or more acrylamide, methacrylamide, α -olefin, acrylic or methacrylic ester, acrylic or
30 methacrylic acid or vinylpyrrolidone groups in their chain,

the anhydride functions of these copolymers optionally being monoesterified or monoamidated.

These polymers are described, for example, in French patents 2 350 384 and 2 357 241 by the Applicant;

E) polyacrylamides comprising carboxylate groups.

5 F) homopolymers and copolymers comprising sulphonic groups such as polymers comprising vinylsulphonic, styrenesulphonic, naphthalenesulphonic or acrylamidoalkylsulphonic units, different from the branched sulphonic polyesters used according to the invention.

These polymers can be chosen in particular from:

10 - polyvinylsulphonic acid salts having a molecular weight of approximately between 1000 and 100 000, and also the copolymers with an unsaturated comonomer such as acrylic or methacrylic acids and their esters, and also acrylamide or its derivatives, vinyl ethers and vinylpyrrolidone;

15 - polystyrenesulphonic acid salts such as the sodium salts that are sold for example under the names Flexan[®] 500 and Flexan[®] 130 by National Starch. These compounds are described in patent FR 2 198 719;

20 - polyacrylamidesulphonic acid salts, such as those mentioned in patent US 4 128 631 and more particularly polyacrylamidoethylpropanesulphonic acid sold under the name Cosmedia Polymer HSP 1180 by Henkel.

As another anionic fixing polymer that can be used according to the invention, mention may be made of the branched block anionic polymer sold under the name Fixate G-100 by the company Lubrizol.

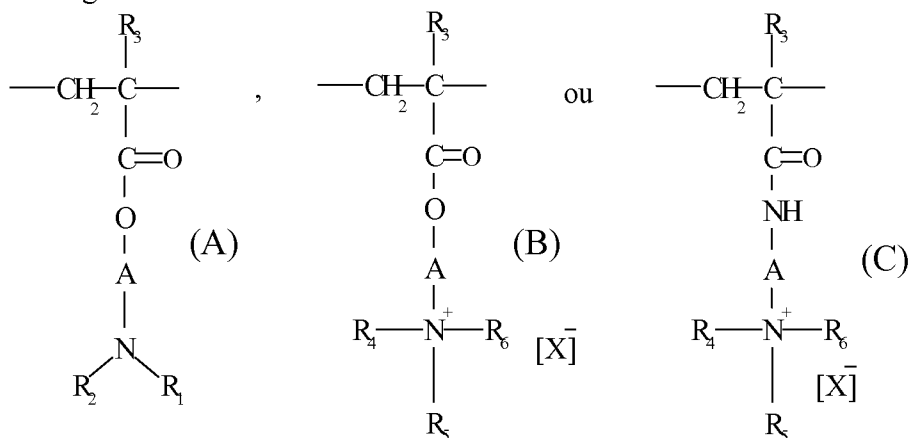
25 According to the invention, the anionic fixing polymers are preferably chosen from copolymers of acrylic acid or of acrylic esters, such as the acrylic acid/ethyl acrylate/*N-tert*-butylacrylamide terpolymers sold especially under the name Ultrahold[®] Strong by the company BASF, copolymers derived from crotonic acid, such as vinyl acetate/vinyl *tert*-butylbenzoate/crotonic acid terpolymers and the
30 crotonic acid/vinyl acetate/vinyl neododecanoate terpolymers sold especially under the name Resin 28-29-30 by the company National Starch, polymers derived from maleic, fumaric or itaconic acids or

anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives and acrylic acid and esters thereof, such as the methyl vinyl ether/monoesterified maleic anhydride copolymers sold, for example, under the name Gantrez[®] by the company ISP, the copolymers of methacrylic acid and of methyl methacrylate sold under the name Eudragit[®] L by the company Rohm Pharma, the copolymers of methacrylic acid and of ethyl acrylate sold under the name Luvimer[®] MAEX or MAE by the company BASF, the vinyl acetate/crotonic acid copolymers sold under the name Luviset CA 66 by the company BASF, the vinyl acetate/crotonic acid copolymers grafted with polyethylene glycol sold under the name Aristoflex[®] A by the company BASF, and the polymer sold under the name Fixate G-100 L by the company Lubrizol.

The cationic fixing film-forming polymers that can be used according to the present invention are preferably chosen from polymers comprising primary, secondary, tertiary and/or quaternary amine groups forming part of the polymer chain or directly attached thereto, and having a molecular weight of between 500 and about 5 000 000 and preferably between 1 000 and 3 000 000.

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

(1) homopolymers or copolymers derived from acrylic or methacrylic esters or amides and comprising at least one of the units of the following formulae:



in which:

R_3 denotes a hydrogen atom or a CH_3 radical;

A is a linear or branched alkyl group comprising 1 to 6 carbon atoms or a hydroxyalkyl group comprising 1 to 4 carbon atoms;

5 R_4 , R_5 and R_6 , which may be identical or different, represent an alkyl group having from 1 to 18 carbon atoms or a benzyl radical;

R_1 and R_2 , which may be identical or different, each represent a hydrogen atom or an alkyl group having from 1 to 6 carbon atoms;

10 X denotes a methosulphate anion or a halide such as chloride or bromide.

The copolymers of the family (1) also contain one or more units derived from comonomers that may be chosen from the family of acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides substituted on the nitrogen with lower (C_{1-4}) alkyl groups, groups derived from acrylic or methacrylic acids or esters thereof, vinyl lactams such as vinylpyrrolidone or vinylcaprolactam, and vinyl esters.

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

20 - copolymers of acrylamide and of dimethylaminoethyl methacrylate quaternized with dimethyl sulphate or with a dimethyl halide, such as the product sold under the name Hercofloc® by the company Hercules,

25 - copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium chloride, described, for example, in patent application EP-A-080 976 and sold under the name Bina Quat P 100 by the company Ciba Geigy,

30 - copolymers of acrylamide and of methacryloyloxyethyltrimethylammonium methosulphate, such as the product sold under the name Reten by the company Hercules,

- quaternized or non-quaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers, such as the

products sold under the name Gafquat® by the company ISP, such as, for example, Gafquat® 734 or Gafquat® 755, or alternatively the products known as Copolymer® 845, 958 and 937. These polymers are described in detail in French patents 2 077 143 and 2 393 573,

5 - fatty-chain polymers containing a vinylpyrrolidone unit, such as the products sold under the name Styleze W20 and Styleze W10 by the company ISP,

 - dimethylaminoethyl methacrylate/vinylcaprolactam/vinylpyrrolidone terpolymers, such as the product sold under the name Gaffix VC 713 by the company ISP, and

10 - quaternized vinylpyrrolidone/dimethylaminopropylmethacrylamide copolymers, such as the products sold under the name Gafquat® HS 100 by the company ISP;

 (2) non-cellulosic cationic polysaccharides, preferably containing quaternary ammonium, such as those described in US patents 3 589 578 and 4 031 307, such as guar gums containing trialkylammonium cationic groups. Such products are sold in particular under the trade names Jaguar C13 S, Jaguar C 15 and Jaguar C 17 by the company Meyhall.

20 (3) Quaternary copolymers of vinylpyrrolidone and of vinylimidazole.

 (4) Chitosans or salts thereof; the salts that can be used are, in particular, chitosan acetate, lactate, glutamate, gluconate or pyrrolidonecarboxylate.

25 Among these compounds, mention may be made of chitosan having a degree of deacetylation of 90.5% by weight, sold under the name Kytan Brut Standard by the company Aber Technologies, and chitosan pyrrolidonecarboxylate sold under the name Kytamer® PC by the company Amerchol.

30 (5) Cationic cellulose derivatives such as copolymers of cellulose or of cellulose derivatives grafted with a water-soluble monomer comprising a quaternary ammonium, and disclosed in

particular in patent US 4 131 576, such as hydroxyalkylcelluloses, for instance hydroxymethyl-, hydroxyethyl- or hydroxypropylcelluloses grafted in particular with a methacryloyloxyethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt.

The products sold corresponding to this definition are, more particularly, the products sold under the name Celquat L 200 and Celquat H 100 by the company National Starch.

The amphoteric fixing that can be used in accordance with the invention can be selected from polymers comprising units B and C distributed randomly in the polymer chain, where B denotes a unit derived from a monomer comprising at least one basic nitrogen atom and C denotes a unit derived from an acid monomer comprising one or more carboxylic or sulphonic groups, or alternatively B and C can denote groups derived from carboxybetaine or sulphobetaine zwitterionic monomers;

B and C can also denote a cationic polymer chain comprising primary, secondary, tertiary or quaternary amine groups, in which at least one of the amine groups bears a carboxylic or sulphonic group connected via a hydrocarbon group or alternatively B and C form part of a chain of a polymer containing an α,β -dicarboxylic ethylene unit in which one of the carboxylic groups has been made to react with a polyamine comprising one or more primary or secondary amine groups.

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

(1) copolymers having acidic vinyl units and basic vinyl units, such as those resulting from the copolymerization of a monomer derived from a vinyl compound bearing a carboxylic group such as, more particularly, acrylic acid, methacrylic acid, maleic acid, α -chloroacrylic acid, and a basic monomer derived from a substituted vinyl compound containing at least one basic atom, such as, more particularly,

dialkylaminoalkyl methacrylate and acrylate, dialkylaminoalkylmethacrylamides and acrylamides. Such compounds are described in patent US 3 836 537.

(2) Polymers comprising units derived from:

5 a) at least one monomer selected from acrylamides and methacrylamides substituted on the nitrogen atom by an alkyl group,

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

10 c) at least one basic comonomer such as esters containing primary, secondary, tertiary and quaternary amine substituents of acrylic and methacrylic acids and the product of quaternization of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

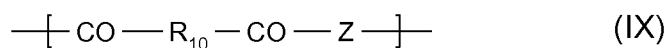
The N-substituted acrylamides or methacrylamides that are more particularly preferred according to the invention are compounds in
15 which the alkyl groups contain from 2 to 12 carbon atoms and more particularly N-ethylacrylamide, N-*tert*-butylacrylamide, N-*tert*-octylacrylamide, N-octylacrylamide,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

The acidic comonomers are chosen more particularly from
20 acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid and alkyl monoesters, having 1 to 4 carbon atoms, of maleic or fumaric acids or anhydrides.

The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-*tert*-butylamino-ethyl
25 methacrylates.

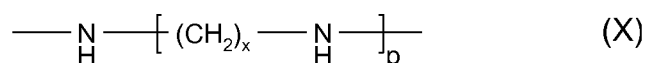
Use is made particularly of the copolymers whose CTFA (4th edition, 1991) name is octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer, such as the products sold under the name Amphomer[®] or Lovocryl[®] 47 by the company National Starch.

30 (3) Crosslinked and acylated polyaminoamides partially or totally deriving from polyaminoamides of general formula:



5 in which R₁₀ represents a divalent group derived from a saturated dicarboxylic acid, a mono- or dicarboxylic aliphatic acid containing an ethylenic double bond, an ester of a lower alkanol, having 1 to 6 carbon atoms, of these acids, or a group derived from the addition of any one of said acids to a bis(primary) or bis(secondary) amine, and Z denotes a group derived from a bis(primary), mono- or bis(secondary) polyalkylene-polyamine and preferably represents:

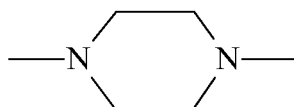
10 a) in proportions of from 60 to 100 mol%, the group:



where x = 2 and p = 2 or 3, or alternatively x = 3 and p = 2

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

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



20 c) in proportions of from 0 to 20 mol%, the —NH-(CH₂)₆-NH- group being derived from hexamethylenediamine,

these polyamino amides being crosslinked by addition reaction of a difunctional crosslinking agent chosen from epihalohydrins, diepoxides, dianhydrides and bis-unsaturated derivatives, using from 0.025 to 0.35 mol of crosslinking agent per amine group of the polyamino amide and acylated by the action of acrylic acid, chloroacetic acid or an alkane sultone, or salts thereof.

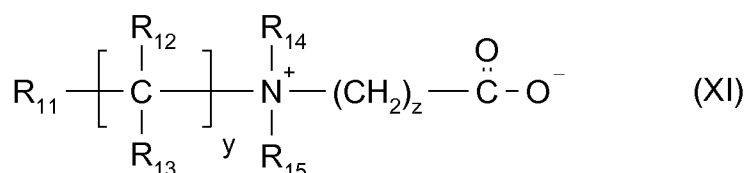
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The saturated carboxylic acids are preferably selected from acids having 6 to 10 carbon atoms, such as adipic acid, 2,2,4-trimethyladipic acid and 2,4,4-trimethyladipic acid, terephthalic acid, acids containing

an ethylenic double bond such as, for example, acrylic acid, methacrylic acid and itaconic acid.

5 The alkane sultones used in the acylation are preferably propane sultone or butane sultone; the salts of the acylating agents are preferably the sodium or potassium salts.

(4) Polymers comprising zwitterionic units of formula:



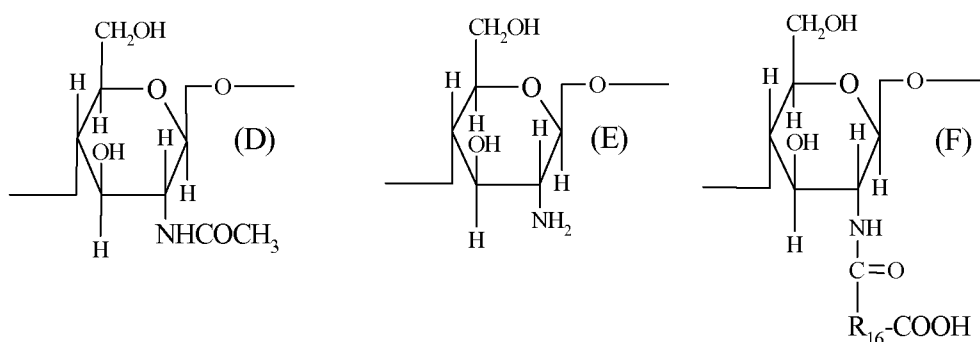
10 in which R_{11} denotes a polymerizable unsaturated group such as an acrylate, methacrylate, acrylamide or methacrylamide group, y and z represent an integer from 1 to 3, R_{12} and R_{13} represent a hydrogen atom, a methyl, ethyl or propyl group, R_{14} and R_{15} represent a hydrogen atom or an alkyl group such that the sum of the carbon atoms in R_{14} and R_{15} does not exceed 10.

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

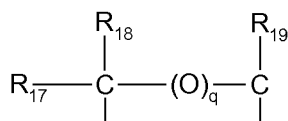
20 By way of example, mention may be made of the copolymers of methyl methacrylate/methyl dimethylcarboxymethylammonioethyl methacrylate such as the product sold under the name Diaformer Z301 by the company Sandoz.

(5) Polymers derived from chitosan comprising monomer units corresponding to the following formulae:

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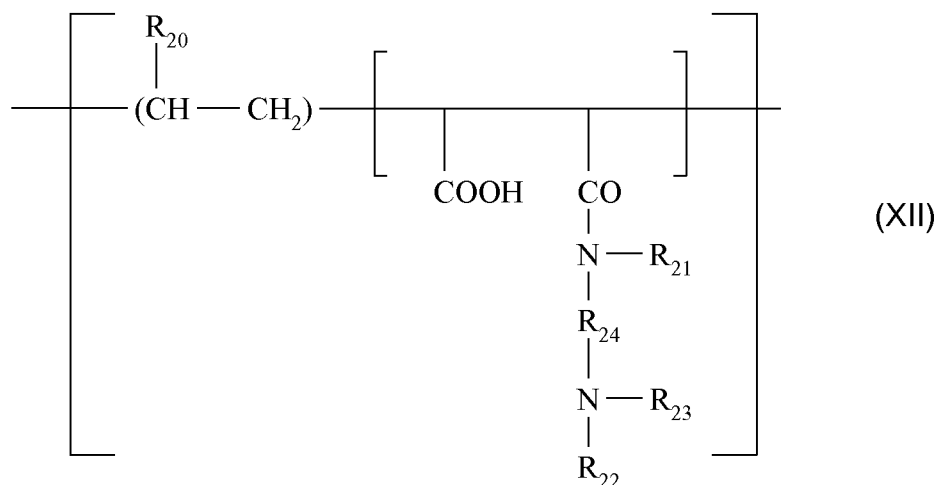
the unit (D) being present in proportions of between 0 and 30%, the unit (E) in proportions of between 5% and 50% and the unit (F) in proportions of between 30% and 90%, it being understood that, in this unit (F), R₁₆ represents a group of formula:



in which, if q=0, R₁₇, R₁₈ and R₁₉, which are identical or different, each represent a hydrogen atom, a methyl, hydroxyl, acetoxy or amino residue, a monoalkylamine residue or a dialkylamine residue that are optionally interrupted by one or more nitrogen atoms and/or optionally substituted by one or more amine, hydroxyl, carboxyl, alkylthio or sulphonic groups, an alkylthio residue in which the alkyl group bears an amino residue, at least one of the groups R₁₇, R₁₈ and R₁₉ being, in this case, a hydrogen atom;

or, if q=1, R₁₇, R₁₈ and R₁₉ each represent a hydrogen atom, as well as the salts formed by these compounds with bases or acids.

(6) Polymers with units corresponding to the general formula (XII) are described, for example, in French patent 1 400 366:

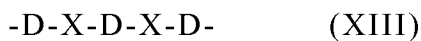


5 in which R_{20} represents a hydrogen atom, a CH_3O , $\text{CH}_3\text{CH}_2\text{O}$ or phenyl group, R_{21} denotes a hydrogen atom or a lower alkyl group such as methyl or ethyl, R_{22} denotes a hydrogen atom or a C_1 - C_6 lower alkyl group such as methyl or ethyl, R_{23} denotes a C_1 - C_6 lower alkyl group such as methyl or ethyl or a group corresponding to the formula: $-\text{R}_{24}-\text{N}(\text{R}_{22})_2$, R_{24} representing a $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ or $-\text{CH}_2-\text{CH}(\text{CH}_3)-$ group, and R_{22} having the abovementioned meanings.

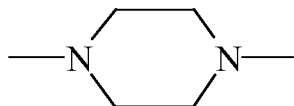
10 (7) Polymers derived from the N-carboxyalkylation of chitosan, such as N-carboxymethylchitosan or N-carboxybutylchitosan sold under the name "Evalsan" by the company Jan Dekker.

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

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



where D denotes a group



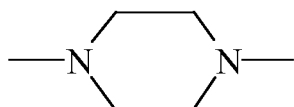
20 and X denotes the symbol E or E', E or E', which may be identical or different, denote a divalent group that is an alkylene group with a straight or branched chain containing up to 7 carbon atoms in the

main chain, which is unsubstituted or substituted by hydroxyl groups and which can comprise, in addition to the oxygen, nitrogen and sulphur atoms, 1 to 3 aromatic and/or heterocyclic rings; the oxygen, nitrogen and sulphur atoms being present in the form of ether, thioether, sulfoxide, sulphone, sulphonium, alkylamine or alkenylamine groups, hydroxyl, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester and/or urethane groups.

b) Polymers of formula:



where D denotes a group



and X denotes the symbol E or E' and at least once E'; E having the meaning given above and E' is a divalent group that is an alkylene group with a straight or branched chain having up to 7 carbon atoms in the main chain, which is unsubstituted or substituted with one or more hydroxyl groups and containing one or more nitrogen atoms, the nitrogen atom being substituted with an alkyl chain that is optionally interrupted by an oxygen atom and necessarily comprising one or more carboxyl functions or one or more hydroxyl functions and betainized by reaction with chloroacetic acid or sodium chloroacetate.

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

Among the amphoteric fixing polymers mentioned above, the ones that are most particularly preferred according to the invention are those of family (3), such as the copolymers whose CTFA name is octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer, such as the products sold under the names Amphomer[®], Amphomer[®] LV

71 or Lovocryl[®] 47 by the company National Starch and those of family (4) such as the methyl methacrylate/methyl dimethylcarboxymethylammonioethyl methacrylate copolymers, sold, for example, under the name Diaformer Z301 by the company Sandoz.

5 The nonionic fixing that may be used according to the present invention are selected, for example, from:

- polyalkyloxazolines;

- vinyl acetate homopolymers;

10 - vinyl acetate copolymers, for instance copolymers of vinyl acetate and of acrylic ester; copolymers of vinyl acetate and of ethylene, or copolymers of vinyl acetate and of maleic ester, for example of dibutyl maleate;

15 - homopolymers and copolymers of acrylic esters, for instance copolymers of alkyl acrylates and of alkyl methacrylates, such as the products sold by the company Rohm & Haas under the names Primal[®] AC-261 K and Eudragit[®] NE 30 D, by the company BASF under the name 8845, or by the company Hoechst under the name Appretan[®] N9212;

20 - acrylonitrile copolymers and copolymers of a nonionic monomer selected, for example, from butadiene and alkyl (meth)acrylates; mention may be made of the products sold under the name CJ 0601 B by the company Rohm & Haas;

- styrene homopolymers;

25 - styrene copolymers, for instance copolymers of styrene and of an alkyl (meth)acrylate, such as the products Mowilith[®] LDM 6911, Mowilith[®] DM 611 and Mowilith[®] LDM 6070 sold by the company Hoechst, and the products Rhodopas[®] SD 215 and Rhodopas[®] DS 910 sold by the company Rhône-Poulenc; copolymers of styrene, of alkyl methacrylate and of alkyl acrylate; copolymers of styrene and of butadiene; or copolymers of styrene, of butadiene and of vinylpyridine;

30 - polyamides;

- vinyl lactam homopolymers such as vinylpyrrolidone

homopolymers and such as the polyvinylcaprolactam sold under the name Luviskol[®] Plus by the company BASF; and

5 - vinyl lactam copolymers such as a
poly(vinylpyrrolidone/vinyl lactam) copolymer sold under the trade name
Luvitec[®] VPC 55K65W by the company BASF,
10 poly(vinylpyrrolidone/vinyl acetate) copolymers, such as those sold
under the name PVPVA[®] S630L by the company ISP, Luviskol[®] VA 73,
VA 64, VA 55, VA 37 and VA 28 by the company BASF; and
poly(vinylpyrrolidone/vinyl acetate/vinyl propionate) terpolymers, for
15 instance the product sold under the name Luviskol[®] VAP 343 by the
company BASF.

The alkyl groups of the nonionic polymers mentioned above preferably have from 1 to 6 carbon atoms.

15 According to the invention, it is also possible to use fixing
polymers of grafted silicone type comprising a polysiloxane portion and
a portion consisting of a non-silicone organic chain, one of the two
portions constituting the main chain of the polymer, and the other being
grafted onto said main chain.

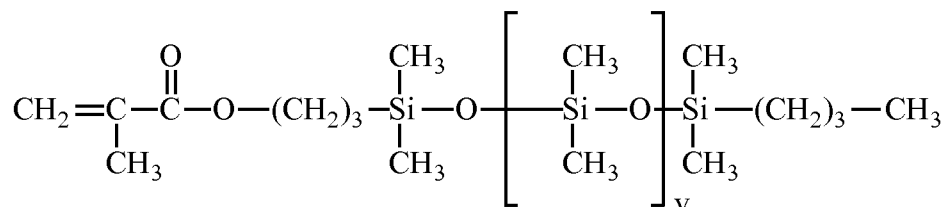
20 These polymers are described, for example, in patent
applications EP-A-0 412 704, EP-A-0 412 707, EP-A-0 640 105 and WO
95/00578, EP-A-0 582 152 and WO 93/23009 and patents US 4 693 935,
US 4 728 571 and US 4 972 037.

These polymers may be amphoteric, anionic or nonionic, and are preferably anionic or nonionic.

25 Such polymers are, for example, copolymers that can be obtained
by free radical polymerization from the monomer mixture formed from:

- a) 50 to 90 % by weight of *tert*-butyl acrylate;
- b) 0 to 40 % by weight of acrylic acid;
- c) 5 to 40 % by weight of a silicone macromer of formula:

30



in which v is a number ranging from 5 to 700, the weight percentages being calculated relative to the total weight of the monomers.

- 5 Other examples of grafted silicone polymers are, in particular, polydimethylsiloxanes (PDMSs) onto which are grafted, via a thiopropylene-type connecting chain, mixed polymer units of the poly(meth)acrylic acid type and of the polyalkyl (meth)acrylate type and
- 10 polydimethylsiloxanes (PDMSs) onto which are grafted, via a thiopropylene-type connecting chain, polymer units of the polyisobutyl (meth)acrylate type.

Another type of silicone fixing polymer that may be mentioned is the product Luviflex[®] Silk sold by the company BASF.

- 15 As fixing it is also possible to use functionalized or non-functionalized, cationic, nonionic, anionic or amphoteric, silicone or non-silicone polyurethanes, or mixtures thereof.

- 20 The polyurethanes particularly intended by the present invention are those disclosed in patent applications EP 0 751 162, EP 0 637 600, EP 0 648 485 and FR 2 743 297, of which the Applicant is the Proprietor, and patent applications EP 0 656 021 and WO 94/03510 from the company BASF and EP 0 619 111 from the company National Starch.

As polyurethanes that are particularly suitable for the present invention, mention may be made of the products sold under the names Luviset Pur[®] and Luviset[®] Si Pur by the company BASF.

- 25 The concentration of fixing polymer(s) used in the compositions according to the present invention is between 0.1% and 20% and preferably between 0.5% and 10% by weight relative to the total weight of the composition.

A person skilled in the art should know how to add the additives

without disturbing the properties of the compositions of the invention.

Preferably, the compositions are in the form of gels. Preferably, the compositions have a viscosity greater than 500 cps at a temperature of 25°C and at a shear rate of 1 s⁻¹.

5 When the composition according to the invention is packaged in an aerosol device, it comprises at least one propellant, which may be chosen from volatile hydrocarbons, such as N-butane, propane, isobutane, pentane, halogenated hydrocarbons and mixtures thereof. It is also possible to use carbon dioxide, nitrous oxide, dimethyl ether
10 (DME), nitrogen or compressed air as the propellant. Mixtures of propellants can also be used. Preferably, dimethyl ether is used.

Advantageously, the propellant is present at a concentration between 5 and 90% by weight relative to the total weight of the composition in the aerosol device and, more particularly, at a
15 concentration between 10 and 60%.

The composition according to the invention may especially be used as a leave-in application on the hair.

Another subject of the invention is a method for shaping the hair, comprising the application of a cosmetic composition according to the
20 invention. In particular, the invention relates to a styling method comprising the application of a composition according to the invention to the hair, optional rinsing of the hair, then the shaping and drying of the hair.

The examples that follow illustrate the invention without
25 limiting the scope thereof.

Examples

The following compositions were produced:

The concentrations are expressed as grams of active material
 5 per 100 g of composition.

Starting material	Supplier	A	B	C	D	E
POLYVINYL ALCOHOL (Celvol 540)	CELANESE CHEMICALS	8	3	10	1	5
POLYESTER-13 (Eastman AQ 10 D Polymer)	EASTMAN CHEMICAL	2	1	3.5	2.5	1.3
ACRYLATES/C10-30 ALKYL ACRYLATE CROSSPOLYMER (Carbopol 1382)	LUBRIZOL	0.5				
CARBOMER (Carbopol 980)	LUBRIZOL		0.8			
HYDROXYPROPYL GUAR (Jaguar HP120)	RHODIA			1.5		
ACRYLATES/STEARETH-20 METHACRYLATE COPOLYMER (Aculyn 22)	ROHM AND HAAS (DOW CHEMICAL)				0.6	
BENZOPHENONE-4 (Uvinul MS40)	BASF	0.1				
SORBITOL	ROQUETTE		1.4			
PROPYLENE GLYCOL	DOW CHEMICAL			3	3	
GLYCEROL	OLEON				5	
Ethanol	BP		2	20		
AMP-ACRYLATES/ALLYL METHACRYLATE COPOLYMER (Fixate G100-L Polymer)	NOVEON		2.7			
Polyvinylpyrrolidone	ISP			2		

VP/ACRYLATES/LAURYL METHACRYLATE COPOLYMER (Acrylidone LM)	ISP					3
(Cremophor RH410)	BASF	0.5		0.3		1.5
Fragrance		0.2		0.1		0.3
TRIETHANOLAMINE	BASF	0.8			0.3	1.3
2-AMINO-2-METHYL-1- PROPANOL	ANGUS (DOW CHEMICAL)		0.6			
PRESERVATIVES		0.3	0.3		0.3	0.3
WATER		qs 100 g	qs 100 g	qs 100 g	qs 100 g	qs 100 g

Examples of formulations (Styling mousses):

In % AM

Raw materials	Supplier	F	G	H	I
POLYVINYL ALCOHOL (Celvol 540)	CELANESE CHEMICALS	0.95	3.6	1.76	4.75
POLYESTER-13 (Eastman AQ 10 D Polymer)	EASTMAN CHEMICAL	0.95	1.8	2.2	1.43
PROPYLENE GLYCOL	DOW CHEMICAL	2.85	2.7	2.6	2.85
GLYCEROL	OLEON			4.4	
Ethanol	BP				2.85
AMP-ACRYLATES/ALLYL METHACRYLATE COPOLYMER (Fixate G100-L Polymer)	NOVEON	5.3			
VP/VA COPOLYMER (Luviskol VA64)	BASF			1.5	
POLYQUATERNIUM-4 (Celquat	AKZO NOBEL				0.48

LOR)					
AMODIMETHICONE (and) TRIDECETH-6 (and) CETRIMONIUM CHLORIDE (Dow Corning 2-8299)	DOW CORNING	0.54			
PEG/PPG-17/18 DIMETHICONE (Dow Corning Q2 5220)	DOW CORNING				0.95
LAURETH-4 (BRIJ L4)	CRODA	0.19			
DECYL GLUCOSIDE (Oramix NS 10)	SEPPIC			0.25	
Fragrance		0.1		0.18	
PHENOXYETHANOL	CLARIANT	0.48	0.8	0.62	0.48
PRESERVATIVES		0.1			
ISOBUTANE (and) BUTANE (and) PROPANE (Propel 45)	REPSOL	5	10	12	5
WATER		qs 100 g	qs 100 g	qs 100 g	qs 100 g

These compositions are easily distributed over the hair and fix said hair with good shape retention.

CLAIMS

1. Cosmetic composition characterized in that it comprises, in a cosmetically acceptable medium:
 - (i) one or more branched sulphonic polyesters; and
 - (ii) one or more polyvinyl alcohols.
- 5 2. Cosmetic composition according to Claim 1, in which the branched sulphonic polyester is obtained by polycondensation of:
 - (a) at least one dicarboxylic acid that does not bear a sulphonic functional group,
 - (b) at least one diol or a mixture of a diol and of a diamine,
 - 10 (c) at least one monomer comprising two identical or different reactive functional groups chosen from hydroxyl, amino and carboxyl groups, and that bears, in addition, at least one sulphonic functional group, and
 - (d) at least one monomer comprising at least three identical or
 - 15 different reactive functional groups chosen from hydroxyl, amino and carboxyl groups.
- 20 3. Cosmetic composition according to Claim 2, in which the branched sulphonic polyester comprises units (e) derived from monomers comprising two different reactive functional groups chosen from hydroxy carboxylic acids and amino carboxylic acids or mixtures thereof.
- 25 4. Cosmetic composition according to any one of the preceding claims, comprising from 0.2 to 15%, preferably from 0.5 to 10% by weight of one or more branched sulphonic polyesters relative to the total weight of the composition.
5. Cosmetic composition according to any one of the preceding claims in which the polyvinyl alcohol or alcohols are chosen from homopolymers or copolymers.
6. Cosmetic composition according to the preceding claim, in

which the copolymer or copolymers are copolymers with vinyl acetate.

7. Cosmetic composition according to any one of the preceding claims, comprising from 0.05 to 20%, preferably from 0.1 to 10% by weight of one or more polyvinyl alcohols relative to the total weight of the composition.

8. Cosmetic composition according to any one of the preceding claims, comprising one or more surfactants chosen from anionic, nonionic, amphoteric or cationic surfactants.

9. Cosmetic composition according to any one of the preceding claims, comprising one or more gelling agents and/or additional thickeners chosen from poly(oxyalkylene) glycols, poly(oxyalkylene) glycol esters, alginates, biosaccharides, starch derivatives, natural gums such as xanthan gum, guar gum, carob bean gum, scleroglucans, derivatives of chitin and of chitosan, carrageenans, clays, and mixtures thereof.

10. Cosmetic composition according to any one of the preceding claims, comprising one or more compounds chosen from silicones and non-silicone fatty substances chosen from mineral, plant, animal and synthetic oils, waxes, fatty esters, ethoxylated or non-ethoxylated fatty alcohols, and fatty acids.

11. Cosmetic composition according to any one of the preceding claims, comprising one or more fixing polymers chosen from anionic, nonionic, amphoteric or cationic fixing polymers.

12. Use of the cosmetic composition according to any one of the preceding claims, for styling, especially for styling or shaping keratin materials, preferably human keratin materials and in particular the hair.

13. Styling method that comprises the application of a composition according to any one of Claims 1 to 11 to the hair, optional rinsing of the hair, then shaping and drying of the hair.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/060037

A. CLASSIFICATION OF SUBJECT MATTER INV. A61K8/85 A61Q5/06 A61K8/81 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) A61K A61Q		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 320 836 A (SINGLETON ANDY H [US]) 14 June 1994 (1994-06-14) column 2, line 5 - line 50; examples -----	1-13
Y	FR 2 760 360 A1 (OREAL [FR]) 11 September 1998 (1998-09-11) cited in the application page 2, line 20 - line 25 page 3, line 26 - page 4, line 15 examples -----	1-13
Y	FR 2 687 932 A1 (OREAL [FR]) 3 September 1993 (1993-09-03) page 1, line 1 - line 15 page 2, line 11 - line 28 page 3, line 11 - line 39 examples ----- -/-	1-13
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 25 October 2011	Date of mailing of the international search report 04/11/2011	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ruckebusch, Virginie	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/060037

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/263342 A1 (GLENN JR ROBERT WAYNE [US] ET AL) 22 October 2009 (2009-10-22) paragraphs [0011], [0162] - [0169]; examples -----	1-13
Y	US 4 880 618 A (GROLLIER JEAN F [FR] ET AL) 14 November 1989 (1989-11-14) column 1, line 38 - column 2, line 4 column 2, line 51 - column 3, line 8 examples -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/060037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5320836	A	14-06-1994	AT 142869 T 15-10-1996
		CA 2152176 A1 21-07-1994	
		DE 69400573 D1 24-10-1996	
		DK 676946 T3 07-10-1996	
		EP 0676946 A1 18-10-1995	
		ES 2094644 T3 16-01-1997	
		GR 3021800 T3 28-02-1997	
		JP H08505394 A 11-06-1996	
		WO 9415575 A1 21-07-1994	
FR 2760360	A1	11-09-1998	AT 252882 T 15-11-2003
		AU 729706 B2 08-02-2001	
		AU 6736198 A 22-09-1998	
		BR 9808304 A 16-05-2000	
		CA 2281641 A1 11-09-1998	
		CN 1264282 A 23-08-2000	
		DE 69819354 D1 04-12-2003	
		DE 69819354 T2 22-07-2004	
		EP 1023033 A2 02-08-2000	
		ES 2210732 T3 01-07-2004	
		WO 9838969 A2 11-09-1998	
		HU 0003130 A2 28-02-2001	
		JP 3654911 B2 02-06-2005	
		JP 2000509735 A 02-08-2000	
		PL 335407 A1 25-04-2000	
		PT 1023033 E 31-03-2004	
		RU 2195924 C2 10-01-2003	
		US 6346234 B1 12-02-2002	
FR 2687932	A1	03-09-1993	AT 135564 T 15-04-1996
		CA 2109195 A1 28-08-1993	
		DE 69301877 D1 25-04-1996	
		DE 69301877 T2 10-10-1996	
		DK 0583459 T3 05-08-1996	
		EP 0583459 A1 23-02-1994	
		ES 2086935 T3 01-07-1996	
		WO 9316684 A1 02-09-1993	
		GR 3020205 T3 30-09-1996	
		JP H06507422 A 25-08-1994	
US 2009263342	A1	22-10-2009	AU 2009236166 A1 22-10-2009
		CA 2721640 A1 22-10-2009	
		CN 102006852 A 06-04-2011	
		EP 2262470 A2 22-12-2010	
		JP 2011516614 A 26-05-2011	
		WO 2009129358 A2 22-10-2009	
US 4880618	A	14-11-1989	AU 606867 B2 21-02-1991
		AU 7299887 A 19-11-1987	
		BE 1000998 A5 06-06-1989	
		CA 1283608 C 30-04-1991	
		CH 672593 A5 15-12-1989	
		DE 3716380 A1 19-11-1987	
		ES 2005575 A6 16-03-1989	
		FR 2598613 A1 20-11-1987	
		GB 2190393 A 18-11-1987	
		IT 1211335 B 18-10-1989	
		JP 1882679 C 10-11-1994	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/060037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		JP 6010128 B	09-02-1994
		JP 62277312 A	02-12-1987
		LU 86430 A1	16-12-1987
		NL 8701175 A	16-12-1987
