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(54) Title: COMPOSITION FOR DYEING KERATIN FIBRES COMPRISING A DIRECT DYE BEARING A DISULFIDE/THIOL FUNCTION, A FATTY SUBSTANCE, AN ALKALINE AGENT AND A REDUCING AGENT

(57) Abstract: The invention relates to a process for dyeing and/or lightening keratin fibres such as the hair, using *i*) at least one direct dye bearing a disulfide, thiol or protected-thiol function and *ii*) at least 25% of one or more fatty substances, *iii*) at least one alkaline agent, and *iv*) at least one reducing agent. The invention also relates to a composition comprising the ingredients *i*) to *iv*), to the use of the combination of *i*), *ii*), *iii*) and *iv*) for the dyeing and/or lightening of keratin fibres, and to a multi-compartment kit comprising the ingredients *i*) to *iv*). The dyeing process and the composition according to the invention especially afford a long-lasting coloration on keratin fibres, which is strong, chromatic and/or homogeneous, with or without the use of an oxidizing agent.



**COMPOSITION FOR DYEING KERATIN FIBRES COMPRISING A DIRECT DYE  
BEARING A DISULFIDE/THIOL FUNCTION, A FATTY SUBSTANCE, AN ALKALINE  
AGENT AND A REDUCING AGENT**

5 The invention relates to a process for dyeing and/or lightening keratin fibres using direct dyes.

It is known practice to dye keratin fibres by direct dyeing or semi-permanent dyeing. Direct dyeing or semi-permanent dyeing consists in introducing colour via a coloured molecule that becomes adsorbed onto the surface of the hair or that penetrates into the  
10 hair. Thus, the process conventionally used in direct dyeing consists in applying to keratin fibres direct dyes, which are coloured, and colouring molecules that have affinity for the fibres, leaving the fibres in contact with the colouring molecules and then optionally rinsing the fibres. Generally, this technique leads to chromatic colorations.

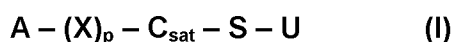
Scientific research has been conducted for several years to modify the colour of keratin  
15 materials, especially keratin fibres, and in particular to mask white fibres, to modify the colour of the fibres permanently or temporarily, and to satisfy new desires and needs in terms of colours and durability.

Patent applications EP 1 647 580, WO 2005/097 051, EP 2 004 759, EP 2 075 289, WO 2007/110 541, WO 2007/110 540, WO 2007/110 539, WO 2007/110 538, WO  
20 2007/110 537, WO 2007/110 536, WO 2007/110 535, WO 2007/110 534, WO 2007/110 533, WO 2007/110 532, WO 2007/110 531, EP 2 070 988, WO 2009/040 354 and WO 2009/034 059 disclose direct dyes bearing a disulfide, thiol or protected-thiol function, for dyeing the hair. The colours obtained are not sufficiently satisfactory, especially in terms of coloration intensity, colour selectivity between the root and the end, and chromaticity of the  
25 colour.

The aim of the present invention is to provide novel systems for dyeing the hair, even without the use of a chemical oxidizing agent, which make it possible to obtain improved colorations, especially in terms of fastness with respect to external agents, homogeneity of the coloration (little selectivity between the root and the end of the keratin fibres), and  
30 intensity, and/or which do not impair the cosmetic properties of the keratin fibres.

This aim is achieved with the present invention, a first subject of which is a cosmetic composition comprising:

*i)* at least one direct dye bearing a disulfide function, a thiol function or a protected-thiol  
35 function, especially of formula (I):



salts thereof with an organic or mineral acid, optical or geometric isomers thereof, tautomers thereof, and solvates thereof such as the hydrates,

in which formula (I):

40 • U represents a radical chosen from:

a) – S – C'<sub>sat</sub> – (X')<sub>p</sub> – A'; and

b) – Y;

- A and A', which may be identical or different, represent a radical containing at least one quaternized cationic chromophore or at least one chromophore bearing a quaternized or quaternizable cationic group;
- Y represents i) a hydrogen atom; or ii) a thiol-function protecting group;
- X and X', which may be identical or different, represent a linear or branched, saturated or unsaturated divalent C<sub>1</sub>-C<sub>30</sub> hydrocarbon-based chain, optionally interrupted and/or optionally terminated at one or both of its ends with one or more divalent groups or combinations thereof chosen from:
  - –N(R)-, –N<sup>+</sup>(R)(R)-, –O-, –S-, –CO-, –SO<sub>2</sub>- with R, which may be identical or different, chosen from a hydrogen and a C<sub>1</sub>-C<sub>4</sub> alkyl, hydroxyalkyl or aminoalkyl radical;
  - an aromatic or non-aromatic, saturated or unsaturated, fused or non-fused (hetero)cyclic radical optionally comprising one or more identical or different, optionally substituted heteroatoms;
- p and p', which may be identical or different, are equal to 0 or 1;
- C<sub>sat</sub> and C'<sub>sat</sub>, which may be identical or different, represent an optionally substituted linear or branched, or cyclic, C<sub>1</sub>-C<sub>18</sub> alkylene chain;

*ii)* at least 25% of one or more fatty substances;

*iii)* at least one alkaline agent; and

*iv)* at least one reducing agent.

Another subject of the invention is a process for dyeing and/or lightening keratin fibres, especially dark keratin fibres, by applying to the said fibres the ingredients *i)* to *iv)* as defined previously, the said ingredients being applied together or separately.

Another subject of the invention is the use of the composition comprising *i)*, *ii)*, *iii)* and *iv)* as defined previously, for the dyeing and/or lightening of keratin fibres.

Another subject of the invention is a multi-compartment kit comprising *i)*, *ii)*, *iii)* and *iv)* as defined previously.

The colorations obtained are attractive, aesthetic, intense, strong, chromatic and very fast or persistent with respect to common attacking factors or everyday assaults such as sun, sebum and especially with respect to perspiration, and other hair treatments such as successive shampooing, while at the same time respecting the keratin fibres. The intensity obtained is particularly noteworthy. The same is true for the colour homogeneity or selectivity of the colour.

For the purposes of the present invention, and unless otherwise indicated:

- 5     ▪ a "direct dye bearing a disulfide function" is a direct dye comprising one or more cationic chromophores that absorb light in the visible spectrum, and comprising a disulfide bond: -S-S- between two carbon atoms and is preferably indirectly bonded to the chromophore(s) of the dye, i.e. between the chromophores and the -S-S- function there is at least one methylene group;
- 10    ▪ a "direct dye bearing a protected-thiol function" is a direct dye comprising a chromophore, comprising a protected-thiol function -SY in which Y is a protecting group known to those skilled in the art, for instance those described in the publications *Protective Groups in Organic Synthesis*, T.W. Greene, John Wiley & Sons ed., NY, 1981, pp. 193-217; *Protecting Groups*, P. Kocienski, Thieme, 3<sup>rd</sup> ed., 2005, chap. 5; and Ullmann's Encyclopedia, *Peptide Synthesis*, pp. 4-5, 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a19 157; it being understood that the said protected-thiol function is preferably indirectly bonded to the chromophore of the dye, i.e. between the chromophore and the function -SY there is at least one methylene group;
- 15    ▪ a "direct dye bearing a thiol function" is a direct dye comprising a chromophore, and comprising a thiol function -SY' in which Y' is i) a hydrogen atom; ii) an alkali metal; iii) an alkaline-earth metal; iv) an ammonium group:  $N^+R^\alpha R^\beta R^\gamma R^\delta$  or a phosphonium group:  $P^+R^\alpha R^\beta R^\gamma R^\delta$  with  $R^\alpha$ ,  $R^\beta$ ,  $R^\gamma$  and  $R^\delta$ , which may be identical or different, representing a hydrogen atom or a group (C<sub>1</sub>-C<sub>4</sub>)alkyl, preferentially comprising a thiol function -SH, it being understood that the said thiol function is preferably indirectly bonded to the chromophore of the dye, i.e. between the chromophore and the function -SY' there is at least one methylene group;
- 20    ▪ a "chromophore" is a radical derived from a dye, i.e. a radical derived from the molecule that absorbs light in the visible radiation range that is visually perceptible by man, i.e. an absorption wavelength  $\lambda_{abs}$  inclusively between 400 and 800 nm; the chromophore may be fluorescent, i.e. it is capable of absorbing in the UV and visible radiation range at a wavelength  $\lambda_{abs}$  inclusively between 250 and 800 nm and capable of re-emitting in the visible range at an emission wavelength  $\lambda_{em}$  inclusively between 400 and 800 nm;
- 25    ▪ a "chromophore" is said to be "quaternized cationic" or "bearing a quaternized cationic group" if it comprises in its structure at least one permanent cationic charge formed from at least one quaternized nitrogen atom (ammonium) or quaternized phosphorus atom (phosphonium), preferably nitrogen;
- 30    ▪ a group is said to be "bearing a quaternizable cationic group" when it comprises in its structure at least one tertiary amine or tertiary phosphine at the end of a
- 35

hydrocarbon-based chain, preferably C<sub>1</sub>-C<sub>10</sub> alkyl, such as  $-(CR'R'')_p-N(R_a)-R_b$  with R' and R'', which may be identical or different, representing a hydrogen atom or a (C<sub>1</sub>-C<sub>6</sub>)alkyl group; R<sub>a</sub> and R<sub>b</sub>, which may be identical or different, representing a (C<sub>1</sub>-C<sub>6</sub>)alkyl group, a monohydroxy(C<sub>1</sub>-C<sub>6</sub>)alkyl group, a (poly)(hydroxy)(C<sub>1</sub>-C<sub>6</sub>)alkyl group or R<sub>a</sub> and R<sub>b</sub> forming, together with the nitrogen atom that bears them, a heterocycloalkyl group such as morpholino, which, once quaternized, will become morpholinium, piperidino, which, once quaternized, will become piperidinium, or piperazino, which, once quaternized, will become piperazinium; and p representing an integer between 1 and 10 inclusive; preferably, R' and R'' represent a hydrogen atom, R<sub>a</sub> and R<sub>b</sub> represent a (C<sub>1</sub>-C<sub>4</sub>)alkyl group and p is between 2 and 5;

- the dyes according to the invention contain one or more chromophores, and these dyes are capable of absorbing light at a wavelength  $\lambda_{abs}$  particularly of between 400 and 700 nm inclusive;
- the "*fluorescent*" dyes according to the invention are dyes containing at least one fluorescent chromophore, and these dyes are capable of absorbing in the visible range at a wavelength  $\lambda_{abs}$  particularly inclusively between 400 and 800 nm and of re-emitting in the visible range at a longer wavelength  $\lambda_{em}$  than that absorbed, inclusively between 400 and 800 nm. The difference between the absorption and emission wavelengths, also known as the Stoke's shift, is inclusively between 1 nm and 100 nm. More preferentially, fluorescent dyes are dyes that are capable of absorbing at a wavelength  $\lambda_{abs}$  inclusively between 420 and 550 nm and of re-emitting in the visible range at a wavelength  $\lambda_{em}$  inclusively between 470 and 600 nm;
- chromophores are said to be "*different*" when they differ in their chemical structure and may be chromophores derived from different families or from the same family on condition that they have different chemical structures: for example, the chromophores may be chosen from the family of azo dyes but differ in the chemical structure of the radicals constituting them or in the respective position of these radicals;
- an "alkylene chain" represents a divalent acyclic C<sub>1</sub>-C<sub>20</sub> hydrocarbon-based chain; particularly C<sub>1</sub>-C<sub>8</sub> and more particularly C<sub>1</sub>-C<sub>2</sub> when the chain is linear; optionally substituted with one or more groups, which may be identical or different, chosen from i) hydroxyl, ii) (C<sub>1</sub>-C<sub>2</sub>)alkoxy, iii) (poly)hydroxy(C<sub>2</sub>-C<sub>4</sub>)alkoxy(di)(C<sub>1</sub>-C<sub>2</sub>)(alkyl)amino, iv) R<sup>a</sup>-Z<sup>a</sup>-C(Z<sup>b</sup>)-Z<sup>c</sup>-, and v) R<sup>a</sup>-Z<sup>a</sup>-S(O)<sub>t</sub>-Z<sup>c</sup>- with Z<sup>a</sup> and Z<sup>b</sup>, which may be identical or different, representing an oxygen or sulfur atom, or a group NR<sup>a</sup>, Z<sup>c</sup>, representing a bond, an oxygen or sulfur atom, or a group NR<sup>a</sup>; R<sup>a</sup>,

representing an alkali metal, a hydrogen atom, an alkyl group, or alternatively is absent if another part of the cationic molecule and  $R^{a'}$  representing a hydrogen atom or an alkyl group and t is equal to 1 or 2; more particularly, the groups iv) are chosen from carboxylate  $-C(O)O^-$  or  $-C(O)OMetal$  (metal = alkali metal), carboxyl  $-C(O)-OH$ , guanidino  $H_2H-C(NH_2)-NH-$ , amidino  $H_2H-C(NH_2)-$ , (thio)ureo  $H_2N-C(O)-NH-$  and  $H_2N-C(S)-NH-$ , aminocarbonyl  $-C(O)-NRa'_2$  or aminothiocarbonyl  $-C(S)-NRa'_2$ ; carbamoyl  $Ra'-C(O)-NRa'-$  or thiocarbamoyl  $Ra'-C(S)-NRa'-$  with  $Ra'$ , which may be identical or different, representing a hydrogen atom or a  $(C_1-C_4)$ alkyl group;

- an "optionally substituted, saturated or unsaturated  $C_1-C_{30}$  divalent hydrocarbon-based chain" represents a hydrocarbon-based chain, particularly of  $C_1-C_8$ , optionally comprising one or more conjugated or unconjugated double bonds, and in particular the hydrocarbon-based chain is saturated; the said chain is optionally substituted with one or more groups, which may be identical or different, chosen from i) hydroxyl, ii)  $(C_1-C_2)$ alkoxy, iii) (poly)hydroxy $(C_2-C_4)$ alkoxy(di) $(C_1-C_2)$ (alkyl)amino, iv)  $R^a-Z^a-C(Z^b)-Z^c-$ , and v)  $R^a-Z^a-S(O)_t-Z^c-$  with  $Z^a$  and  $Z^b$ , which may be identical or different, representing an oxygen or sulfur atom, or a group  $NR^{a'}$ ,  $Z^c$ , representing a bond, an oxygen or sulfur atom, or a group  $NR^{a'}$ ;  $R^a$ , representing an alkali metal, a hydrogen atom, an alkyl group, or alternatively is absent if another part of the cationic molecule and  $R^{a'}$  representing a hydrogen atom or an alkyl group and t is equal to 1 or 2; more particularly, the groups iv) are chosen from carboxylate  $-C(O)O^-$  or  $-C(O)OMetal$  (metal = alkali metal), carboxyl  $-C(O)-OH$ , guanidino  $H_2H-C(NH_2)-NH-$ , amidino  $H_2H-C(NH_2)-$ , (thio)ureo  $H_2N-C(O)-NH-$  and  $H_2N-C(S)-NH-$ , aminocarbonyl  $-C(O)-NRa'_2$  or aminothiocarbonyl  $-C(S)-NRa'_2$ ; carbamoyl  $Ra'-C(O)-NRa'-$  or thiocarbamoyl  $Ra'-C(S)-NRa'-$  with  $Ra'$ , which may be identical or different, representing a hydrogen atom or a  $(C_1-C_4)$ alkyl group;
- the "aryl" or "heteroaryl" radicals or the aryl or heteroaryl part of a radical may be substituted with at least one substituent borne by a carbon atom, chosen from:

  - a  $C_1-C_{16}$  and preferably  $C_1-C_8$  alkyl radical optionally substituted with one or more radicals chosen from hydroxyl,  $C_1-C_2$  alkoxy,  $C_2-C_4$  (poly)hydroxyalkoxy, acylamino, amino substituted with two  $C_1-C_4$  alkyl radicals, which may be identical or different, optionally bearing at least one hydroxyl group, or the two radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered and preferably 5- or 6-membered heterocycle optionally comprising another heteroatom identical to or different from nitrogen;

- a halogen atom;
- a hydroxyl group;
- a C<sub>1</sub>-C<sub>2</sub> alkoxy radical;
- a C<sub>2</sub>-C<sub>4</sub> (poly)hydroxyalkoxy radical;
- 5 - an amino radical;
- a 5- or 6-membered heterocycloalkyl radical;
- an optionally cationic 5- or 6-membered heteroaryl radical, preferentially imidazolium, optionally substituted with a (C<sub>1</sub>-C<sub>4</sub>)alkyl radical, preferentially methyl;
- 10 - an amino radical substituted with one or two identical or different C<sub>1</sub>-C<sub>6</sub> alkyl radicals, optionally bearing at least:
  - i) a hydroxyl group,
  - ii) an amino group optionally substituted with one or two optionally substituted C<sub>1</sub>-C<sub>3</sub> alkyl radicals, the said alkyl radicals possibly forming with the nitrogen atom to which they are attached a saturated or  
15 unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other heteroatom identical to or different from nitrogen,
  - iii) a quaternary ammonium group -N<sup>+</sup>R'R''R''', M<sup>-</sup> for which R', R'' and R''' , which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group; and M<sup>-</sup> represents the counterion of the organic or  
20 mineral acid or of the corresponding halide;
  - iv) an optionally cationic 5- or 6-membered heteroaryl radical, preferentially imidazolium, optionally substituted with a (C<sub>1</sub>-C<sub>4</sub>)alkyl radical, preferentially methyl;
  - 25 - an acylamino radical (-NR-C(O)-R') in which the radical R is a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group and the radical R' is a C<sub>1</sub>-C<sub>2</sub> alkyl radical;
  - a carbamoyl radical ((R)<sub>2</sub>N-C(O)-) in which the radicals R, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group;
  - 30 - an alkylsulfonylamino radical (R'-S(O)<sub>2</sub>-N(R)-) in which the radical R represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group and the radical R' represents a C<sub>1</sub>-C<sub>4</sub> alkyl radical, or a phenyl radical;
  - 35 - an aminosulfonyl radical ((R)<sub>2</sub>N-S(O)<sub>2</sub>-) in which the radicals R, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical

optionally bearing at least one hydroxyl group;

- a carboxylic radical in acid or salified form (preferably with an alkali metal or a substituted or unsubstituted ammonium);
- a cyano group;
- a nitro or nitroso group;
- a polyhaloalkyl group, preferentially trifluoromethyl;

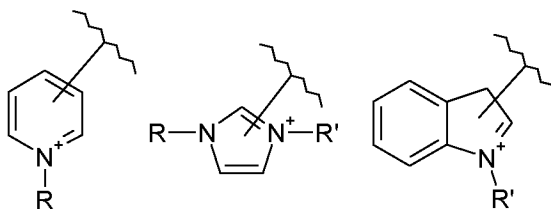
the cyclic or heterocyclic part of a non-aromatic radical may be substituted with at least one substituent chosen from the following groups:

- hydroxyl;
- C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>2</sub>-C<sub>4</sub> (poly)hydroxyalkoxy,
- (C<sub>1</sub>-C<sub>4</sub>)alkyl;
- alkylcarbonylamino (R-C(O)-N(R')-) in which the radical R' is a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group, and the radical R is a C<sub>1</sub>-C<sub>2</sub> alkyl radical or an amino radical optionally substituted with one or two C<sub>1</sub>-C<sub>4</sub> alkyl groups, which may be identical or different, themselves optionally bearing at least one hydroxyl group, the said alkyl radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle optionally comprising at least one other nitrogen or non-nitrogen heteroatom;
- alkylcarbonyloxy (R-C(O)-O-) in which the radical R is a C<sub>1</sub>-C<sub>4</sub> alkyl radical or an amino radical substituted with one or two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl groups, themselves optionally bearing at least one hydroxyl group, the said alkyl radicals possibly forming with the nitrogen atom to which it is attached a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom;
- alkoxy carbonyl (R-G-C(O)-) in which the radical R is a C<sub>1</sub>-C<sub>4</sub> alkoxy radical, G is an oxygen atom or an amino group optionally substituted with a C<sub>1</sub>-C<sub>4</sub> alkyl group optionally bearing at least one hydroxyl group, the said alkyl radical possibly forming, with the nitrogen atom to which it is attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom;

- a cyclic or heterocyclic radical, or a non-aromatic portion of an aryl or heteroaryl radical, may also be substituted with one or more oxo groups;
- a hydrocarbon-based chain is unsaturated when it comprises one or more double

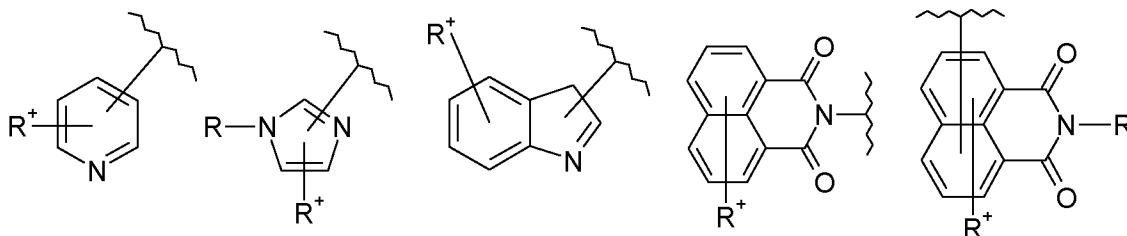
bonds and/or one or more triple bonds;

- an "aryl" radical represents a fused or non-fused monocyclic or polycyclic carbon-based group containing from 6 to 22 carbon atoms, and in which at least one ring is aromatic; preferentially, the aryl radical is a phenyl, biphenyl, naphthyl, indenyl, anthracenyl or tetrahydronaphthyl;
- a "heteroaryl radical" represents a fused or non-fused, optionally cationic, 5- to 22-membered monocyclic or polycyclic group, comprising from 1 to 6 heteroatoms chosen from nitrogen, oxygen, sulfur and selenium, and at least one ring of which is aromatic; preferentially, a heteroaryl radical is chosen from acridinyl, benzimidazolyl, benzobistriazolyl, benzopyrazolyl, benzopyridazinyl, benzoquinolyl, benzothiazolyl, benzotriazolyl, benzoxazolyl, pyridyl, tetrazolyl, dihydrothiazolyl, imidazopyridyl, imidazolyl, indolyl, isoquinolyl, naphthoimidazolyl, naphthoxazolyl, naphthopyrazolyl, oxadiazolyl, oxazolyl, oxazolopyridyl, phenazinyl, phenoxazolyl, pyrazinyl, pyrazolyl, pyrylyl, pyrazoyltriazyl, pyridyl, pyridinoimidazolyl, pyrrolyl, quinolyl, tetrazolyl, thiadiazolyl, thiazolyl, thiazolopyridyl, thiazoylimidazolyl, thiopyrylyl, triazolyl, xanthyl and the ammonium salt thereof;
- a "heterocyclic radical" or "heterocycle" is a fused or non-fused, 5- to 22-membered monocyclic or polycyclic non-aromatic radical, comprising from 1 to 6 heteroatoms chosen from nitrogen, oxygen, sulfur and selenium;
- a "heterocycloalkyl radical" is a heterocyclic radical comprising at least one saturated ring;
- a "cationic heteroaryl radical" is a heteroaryl group as defined previously, which comprises a quaternized endocyclic or exocyclic cationic group,
  - when the cationic charge is endocyclic, it is included in the electron delocalization via the mesomeric effect, for example it is a pyridinium, imidazolium or indolinium group:



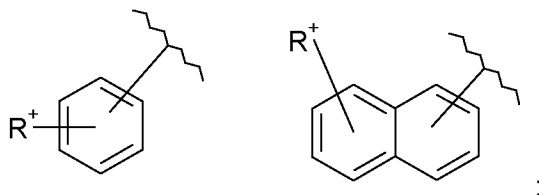
with R and R' being a heteroaryl substituent as defined previously and particularly a (hydroxy)(C<sub>1</sub>-C<sub>8</sub>)alkyl group such as methyl;

- when the cationic charge is exocyclic, for example, it is an ammonium or phosphonium substituent R<sup>+</sup> such as trimethylammonium, which is outside the heteroaryl such as pyridyl, indolyl, imidazolyl or naphthalimidyl in question:



with R being a heteroaryl substituent as defined previously and R<sup>+</sup> an ammonium R<sub>a</sub>R<sub>b</sub>R<sub>c</sub>N<sup>+</sup>-, phosphonium R<sub>a</sub>R<sub>b</sub>R<sub>c</sub>P<sup>+</sup>- or ammonium R<sub>a</sub>R<sub>b</sub>R<sub>c</sub>N<sup>+</sup>-(C<sub>1</sub>-C<sub>6</sub>)alkylamino group with R<sub>a</sub>, R<sub>b</sub> and R<sub>c</sub>, which may be identical or different, representing a hydrogen atom or a (C<sub>1</sub>-C<sub>8</sub>) alkyl group such as methyl;

- the term "*cationic aryl bearing an exocyclic charge*" means an aryl ring whose quaternized cationic group is outside the said ring; it is especially an ammonium or phosphonium substituent R<sup>+</sup> such as trimethylammonium, outside the aryl such as phenyl or naphthyl:



- an "*alkyl radical*" is a linear or branched C<sub>1</sub>-C<sub>20</sub> and preferably C<sub>1</sub>-C<sub>8</sub> hydrocarbon-based radical;
- an "*alkenylene radical*" is an unsaturated hydrocarbon-based divalent radical as defined previously, which may contain from 1 to 4 conjugated or unconjugated double bonds -C=C-; the alkenylene group particularly contains 1 or 2 unsaturations;
- the term "*optionally substituted*" attributed to the alkyl radical means that the said alkyl radical may be substituted with one or more radicals chosen from the following radicals: i) hydroxyl, ii) C<sub>1</sub>-C<sub>4</sub> alkoxy, iii) acylamino, iv) amino optionally substituted with one or two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl radicals, the said alkyl radicals possibly forming with the nitrogen atom that bears them a 5- to 7-membered heterocycle, optionally comprising another heteroatom identical to or different from nitrogen; v) or a quaternary ammonium group -N<sup>+</sup>R'R''R''', M<sup>-</sup> for which R', R'' and R''', which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group, or else -N<sup>+</sup>R'R''R''' forms a heteroaryl such as imidazolium optionally substituted with a C<sub>1</sub>-C<sub>4</sub> alkyl group, and M<sup>-</sup> represents the counterion of the organic or mineral acid or of the corresponding halide;
- an "*alkoxy*" radical is an alkyloxy radical for which the alkyl radical is a linear or branched C<sub>1</sub>-C<sub>16</sub> and preferentially C<sub>1</sub>-C<sub>8</sub> hydrocarbon-based radical;
- when the alkoxy group is optionally substituted, this implies that the alkyl group is optionally substituted as defined hereinabove;

- 5       ▪ the "*tone depth*" is the unit known to hairstyling professionals, published in the book *Science des traitements capillaires* [Hair treatment sciences] by Charles Zviak, 1988, published by Masson, pp. 215 and 278; the tone depths range from 1 (black) to 10 (very light blond), one unit corresponding to one tone; the higher the figure, the lighter the shade;
- 10       ▪ a "*dark*" keratin fibre is a keratin fibre whose lightness  $L^*$  measured in the CIE  $L^*a^*b^*$  system is less than or equal to 45 and preferably less than or equal to 40, given that  $L^*=0$  is equivalent to black and  $L^*=100$  is equivalent to white;
- 15       ▪ "*naturally or artificially dark hair*" means hair whose tone depth is less than or equal to 6 (dark blond) and preferably less than or equal to 4 (chestnut-brown). Artificially dyed hair is hair whose colour has been modified by a coloration treatment, for example a coloration with direct dyes or oxidation dyes;
- 20       ▪ the term "*thickening polymer*" means a polymer which, when introduced at 1% by weight in an aqueous solution or an aqueous-alcoholic solution containing 30% ethanol, and at pH 7, or in an oil chosen from liquid petroleum jelly, isopropyl myristate or cyclopentadimethylsiloxane, makes it possible to achieve a viscosity of at least 100 cps and preferably of at least 500 cps, at 25°C and at a shear rate of 1 s<sup>-1</sup>. This viscosity may be measured using a cone/plate viscometer (Haake R600 rheometer or the like). The thickening polymers may thicken the aqueous phase and/or the fatty phase, preferentially the aqueous phase;
- 25       ▪ the term "*organic*" thickening polymer means a thickening polymer as defined previously, which is formed from carbon and hydrogen, and possibly nitrogen, oxygen, sulfur, halogens such as fluorine, chlorine or bromine, and also phosphorus, alkali metals such as sodium or potassium, or alkaline-earth metals such as magnesium or calcium. The organic polymers according to the invention do not comprise silicon;
- 30       ▪ For the purposes of the present invention, the term "*fatty substance*" means an organic compound that is insoluble in water at ordinary temperature (25°C) and at atmospheric pressure (760 mmHg) (solubility of less than 5%, preferably less than 1% and even more preferentially less than 0.1%); in addition, the fatty substances are soluble in organic solvents under the same temperature and pressure conditions, for instance in halogenated solvents such as chloroform or dichloromethane, lower alcohols such as ethanol or aromatic solvents such as benzene or toluene;
- 35       ▪ an "*organic or mineral acid salt*" is more particularly chosen from salts chosen from a salt derived from i) hydrochloric acid HCl, ii) hydrobromic acid HBr, iii) sulfuric acid H<sub>2</sub>SO<sub>4</sub>, iv) alkylsulfonic acids: Alk-S(O)<sub>2</sub>OH such as methanesulfonic acid and ethanesulfonic acid; v) arylsulfonic acids: Ar-S(O)<sub>2</sub>OH such as benzenesulfonic acid and toluenesulfonic acid; vi) citric acid; vii) succinic acid; viii) tartaric acid; ix) lactic acid;
- 40       x) alkoxyulfonic acids: Alk-O-S(O)OH such as methoxyulfonic acid and ethoxyulfonic acid; xi) aryloxyulfonic acids such as tolueneoxyulfonic acid and

phenoxysulfinic acid; xii) phosphoric acid  $H_3PO_4$ ; xiii) acetic acid  $CH_3C(O)OH$ ; xiv) triflic acid  $CF_3SO_3H$ ; and xv) tetrafluoroboric acid  $HF_4$ ;

- an "*anionic counterion*" means an anion or an anionic group derived from an organic or mineral acid salt which counterbalances the cationic charge of the dye; more particularly, the anionic counterion is chosen from: i) halides such as chloride or bromide; ii) nitrates; iii) sulfonates, including  $C_1$ - $C_6$  alkylsulfonates:  $Alk-S(O)_2O^-$  such as methanesulfonate or mesylate and ethanesulfonate; iv) arylsulfonates:  $Ar-S(O)_2O^-$  such as benzenesulfonate and toluenesulfonate or tosylate; v) citrate; vi) succinate; vii) tartrate; viii) lactate; ix) alkyl sulfates:  $Alk-O-S(O)O^-$  such as methyl sulfate and ethyl sulfate; x) aryl sulfates:  $Ar-O-S(O)O^-$  such as benzene sulfate and toluene sulfate; xi) alkoxy sulfates:  $Alk-O-S(O)_2O^-$  such as methoxy sulfate and ethoxy sulfate; xii) aryloxy sulfates:  $Ar-O-S(O)_2O^-$ , xiii) phosphates  $O=P(OH)_2O^-$ ,  $O=P(O^-)_2-OH$ ,  $O=P(O^-)_3$ ,  $HO-[P(O)(O^-)]_w-P(O)(O^-)_2$  with  $w$  being an integer; xiv) acetate; xv) triflate; and xvi) borates such as tetrafluoroborate, xvii) disulfate  $(O=)_2S(O^-)_2$  or  $SO_4^{2-}$  and monosulfate  $HSO_4^-$ ;
- the anionic counterion, derived from the organic or mineral acid salt, ensures the electrical neutrality of the molecule; thus, it is understood that when the anion comprises several anionic charges, then the same anion may serve for the electrical neutrality of several cationic groups in the same molecule or else may serve for the electrical neutrality of several molecules; for example, a disulfide dye of formula **(I)** which contains two cationic chromophores may contain either two "*singly charged*" anionic counterions or a "*doubly charged*" anionic counterion such as  $(O=)_2S(O^-)_2$  or  $O=P(O^-)_2-OH$ ;
- moreover, the addition salts that may be used in the context of the invention are especially chosen from addition salts with a cosmetically acceptable base such as basifying agents as defined below, for instance alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, aqueous ammonia, amines or alkanolamines;
  - the term "*at least one*" is equivalent to the term "*one or more*"; and
  - the term "*inclusive*" for a range of concentrations means that the limits of that range are included in the defined range.

### 1). The composition of the invention

The composition according to the invention is cosmetic, i.e. it is in a cosmetic medium and comprises:

- i)* at least one cationic direct dye bearing a disulfide function, a thiol function or a protected-thiol function;
- ii)* at least one fatty alcohol, which is preferably non-ethoxylated;
- iii)* at least one cationic surfactant;
- iv)* at least one alkaline agent; and

v) at least one reducing agent.

*The cosmetic medium:*

5 The term "*cosmetic medium*" means a medium that is suitable for dyeing keratin fibres, also known as a dye support, which is a cosmetic medium generally formed from water or a mixture of water and one or more organic solvents or a mixture of organic solvents. Preferably, the composition comprises water in a content especially inclusively between 5% and 95% relative to the total weight of the composition.

10 The term "organic solvent" means an organic substance that is capable of dissolving another substance without chemically modifying it.

*Organic solvents:*

15 Examples of organic solvents that may be mentioned include C<sub>1</sub>-C<sub>4</sub> lower alkanols, such as ethanol and isopropanol; polyols and polyol ethers, for instance 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, and also aromatic alcohols, for instance benzyl alcohol or phenoxyethanol, and mixtures thereof.

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The organic solvents are preferably present in proportions preferably inclusively between 0.1% and 40% by weight approximately relative to the total weight of the dye composition, more preferentially between 1% and 30% by weight approximately and even more particularly inclusively between 5% and 25% by weight relative to the total weight of the composition.

25

*j) Direct dyes bearing a disulfide or thiol function of the invention:*

30 The direct dye(s) bearing a disulfide, thiol or protected-thiol function used in the invention are of formula (I) as defined previously.

According to one particular mode of the invention, the dyes (I) are disulfide dyes, i.e. for which U represents the following radical a)  $-\text{S}-\text{C}'_{\text{sat}}-(\text{X}')_{\text{p}}-\text{A}'$ , and more particularly the dyes of formula (I) are symmetrical, i.e. they are such that  $\text{A} = \text{A}'$ ,  $\text{C}_{\text{sat}} = \text{C}'_{\text{sat}}$ ,  $\text{X} = \text{X}'$  and  $\text{p} = \text{p}'$ .

35

According to another particular mode of the invention, the dyes of formula (I) bearing a thiol function are as defined previously, i.e. U representing the radical b) Y.

Another particular embodiment of the invention relates to fluorescent dyes bearing a disulfide, thiol or protected-thiol function.

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*i). 1) Y:*

According to one particular embodiment of the invention, the direct dye of formula (I) is a thiol dye, i.e. Y represents i) a hydrogen atom.

In accordance with another particular embodiment of the invention, in the abovementioned formula (I), Y is a protecting group known to those skilled in the art, for instance those described in the publications "*Protective Groups in Organic Synthesis*", T. W. Greene, published by John Wiley & Sons, NY, 1981, pp. 193-217; "*Protecting Groups*", P. Kocienski, Thieme, 3rd edition, 2005, chapter 5, and Ullmann's Encyclopedia, "*Peptide Synthesis*", pp. 4-5, 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 10.1002/14356007.a19 157;

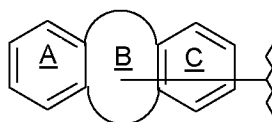
In particular, Y represents a thiol-function protecting group chosen from the following radicals:

- (C<sub>1</sub>-C<sub>4</sub>)alkylcarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkylthiocarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkoxythiocarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkylthio-thiocarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminocarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminothiocarbonyl;
- arylcarbonyl, for instance phenylcarbonyl;
- aryloxycarbonyl;
- aryl(C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminocarbonyl, for instance dimethylaminocarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)(alkyl)arylaminocarbonyl;
- carboxyl;
- SO<sub>3</sub><sup>-</sup>; M<sup>+</sup> with M<sup>+</sup> representing an alkali metal such as sodium or potassium, or alternatively a counterion of the cationic chromophore A and M<sup>+</sup> are absent;
- optionally substituted aryl such as phenyl, dibenzosuberyl or 1,3,5-cycloheptatrienyl;
- optionally substituted heteroaryl; especially including the following cationic or non-cationic heteroaryl radicals comprising from 1 to 4 heteroatoms:
  - i) 5-, 6- or 7-membered monocyclic radicals such as furanyl or furyl, pyrrolyl or pyrrol, thiophenyl or thienyl, pyrazolyl, oxazolyl, oxazolium, isoxazolyl, isoxazolium, thiazolyl, thiazolium, isothiazolyl, isothiazolium, 1,2,4-triazolyl, 1,2,4-triazolium, 1,2,3-triazolyl, 1,2,3-triazolium, 1,2,4-oxazolyl, 1,2,4-oxazolium, 1,2,4-thiadiazolyl, 1,2,4-thiadiazolium, pyrylium, thiopyridyl, pyridinium, pyrimidinyl, pyrimidinium, pyrazinyl, pyrazinium, pyridazinyl,

pyridazinium, triazinyl, triazinium, tetrazinyl, tetrazinium, azepine, azepinium, oxazepinyl, oxazepinium, thiepinyl, thiepinium, imidazolyl, imidazolium;

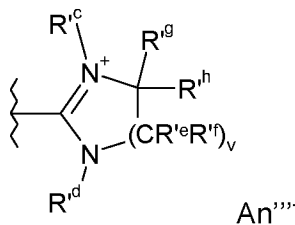
ii) 8- to 11-membered bicyclic radicals such as indolyl, indolinium, benzimidazolyl, benzimidazolium, benzoxazolyl, benzoxazolium, dihydrobenzoxazolyl, benzothiazolyl, benzothiazolium, pyridoimidazolyl, pyridoimidazolium, thienocycloheptadienyl, these monocyclic or bicyclic groups being optionally substituted with one or more groups such as (C<sub>1</sub>-C<sub>4</sub>)alkyl, for instance methyl, or polyhalo(C<sub>1</sub>-C<sub>4</sub>)alkyl, for instance trifluoromethyl;

iii) or the following tricyclic ABC radical:



in which the two rings A and C optionally comprise a heteroatom, and ring B is a 5-, 6- or 7-membered ring, particularly a 6-membered ring, and contains at least one heteroatom, for instance piperidyl or pyranyl;

➤ optionally cationic, optionally substituted heterocycloalkyl, the heterocycloalkyl group especially represents a saturated or partially saturated 5-, 6- or 7-membered monocyclic group comprising from 1 to 4 heteroatoms chosen from oxygen, sulfur and nitrogen, such as di/tetrahydrofuryl, di/tetrahydrothiophenyl, di/tetrahydropyrrolyl, di/tetrahydropyranyl, di/tetra/hexahydrothiopyranyl, dihydropyridyl, piperazinyl, piperidinyl, tetramethylpiperidyl, morpholinyl, di/tetra/hexahydroazepinyl, di/tetrahydropyrimidinyl, these groups being optionally substituted with one or more groups such as (C<sub>1</sub>-C<sub>4</sub>) alkyl, oxo or thioxo; or the heterocycle represents the following group:



in which R<sup>c</sup>, R<sup>d</sup>, R<sup>e</sup>, R<sup>f</sup>, R<sup>g</sup> and R<sup>h</sup>, which may be identical or different, represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>) alkyl group, or alternatively two groups R<sup>g</sup> with R<sup>h</sup>, and/or R<sup>e</sup> with R<sup>f</sup>, form an oxo or thioxo group, or alternatively R<sup>g</sup> with R<sup>e</sup> together form a cycloalkyl; and v represents an

integer between 1 and 3 inclusive; preferentially,  $R^c$  to  $R^h$  represent a hydrogen atom; and  $An^{m-}$  represents a counterion;

➤  $-C(NR^cR^d)=N^+R^eR^f$ ;  $An^{m-}$  with  $R^c$ ,  $R^d$ ,  $R^e$  and  $R^f$ , which may be identical or different, representing a hydrogen atom or a  $(C_1-C_4)$ alkyl group; preferentially,  $R^c$  to  $R^f$  represent a hydrogen atom; and  $An^{m-}$  represents a counterion;

➤  $-C(NR^cR^d)=NR^e$ ; with  $R^c$ ,  $R^d$  and  $R^e$  as defined previously;

➤ optionally substituted (di)aryl $(C_1-C_4)$ alkyl such as 9-anthracenylmethyl, phenylmethyl or diphenylmethyl optionally substituted with one or more groups especially chosen from  $(C_1-C_4)$  alkyl,  $(C_1-C_4)$  alkoxy such as methoxy, hydroxyl, alkylcarbonyl or (di) $(C_1-C_4)$ (alkyl)amino such as dimethylamino;

➤ optionally substituted (di)heteroaryl $(C_1-C_4)$ alkyl, the heteroaryl group especially being a cationic or noncationic, 5- or 6-membered monocyclic radical comprising from 1 to 4 heteroatoms chosen from nitrogen, oxygen and sulfur, such as pyrrolyl, furanyl, thiophenyl, pyridyl, pyridyl N-oxide such as 4-pyridyl or 2-pyridyl-N-oxide, pyrylium, pyridinium or triazinyl groups, optionally substituted with one or more groups such as alkyl, particularly methyl; advantageously, the (di)heteroaryl $(C_1-C_4)$ alkyl is (di)heteroarylmethyl or (di)heteroarylethyl;

➤  $CR^1R^2R^3$  with  $R^1$ ,  $R^2$  and  $R^3$ , which may be identical or different, representing a halogen atom or a group chosen from:

-  $(C_1-C_4)$ alkyl;

-  $(C_1-C_4)$ alkoxy;

- optionally substituted aryl such as phenyl optionally substituted with one or more groups, for instance  $(C_1-C_4)$ alkyl,  $(C_1-C_4)$ alkoxy or hydroxyl;

- optionally substituted heteroaryl such as thiophenyl, furanyl, pyrrolyl, pyranal or pyridyl, optionally substituted with a  $(C_1-C_4)$ alkyl group;

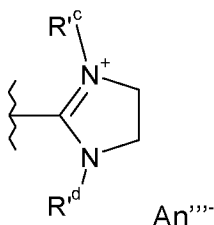
-  $P(Z^1)R^1R^2R^3$  with  $R^1$  and  $R^2$ , which may be identical or different, representing a hydroxyl,  $(C_1-C_4)$ alkoxy or alkyl group,  $R^3$  representing a hydroxyl or  $(C_1-C_4)$ alkoxy group, and  $Z^1$  representing an oxygen or sulfur atom;

▪ a sterically hindered ring; and

▪ optionally substituted alkoxyalkyl, such as methoxymethyl (MOM), ethoxyethyl (EOM) and isobutoxymethyl.

According to one particular embodiment, the thiol-protected dyes of formula (I) comprise

a group Y chosen from i) aromatic cationic 5- or 6-membered monocyclic heteroaryl comprising from 1 to 4 heteroatoms chosen from oxygen, sulfur and nitrogen, such as oxazolium, isoxazolium, thiazolium, isothiazolium, 1,2,4-triazolium, 1,2,3-triazolium, 1,2,4-oxazolium, 1,2,4-thiadiazolium, pyrylium, pyridinium, pyrimidinium, pyrazinyl, pyrazinium, pyridazinium, triazinium, tetrazinium, oxazepinium, thiepinyl, thiepinium, imidazolium; ii) cationic 8- to 11-membered bicyclic heteroaryl such as indolinium, benzimidazolium, benzoxazolium, benzothiazolium, these monocyclic or bicyclic heteroaryl groups optionally being substituted with one or more groups such as alkyls, for instance methyl, or polyhalo(C<sub>1</sub>-C<sub>4</sub>)alkyl such as trifluoromethyl; iii) or the following heterocyclic:



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in which R<sup>c</sup> and R<sup>d</sup>, which may be identical or different, represent a hydrogen atom or a group (C<sub>1</sub>-C<sub>4</sub>)alkyl; preferentially R<sup>c</sup> to R<sup>d</sup> represent a group (C<sub>1</sub>-C<sub>4</sub>)alkyl such as methyl; and An<sup>'''</sup> represents a counterion.

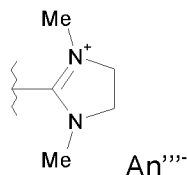
In particular, Y represents a group chosen from oxazolium, isoxazolium, thiazolium, isothiazolium, 1,2,4-triazolium, 1,2,3-triazolium, 1,2,4-oxazolium, 1,2,4-thiadiazolium, pyrylium, pyridinium, pyrimidinium, pyrazinium, pyridazinium, triazinium and imidazolium, benzimidazolium, benzoxazolium, benzothiazolium, these groups being optionally substituted with one or more (C<sub>1</sub>-C<sub>4</sub>)alkyl groups, especially methyl.

In particular, Y represents a protecting group such as:

- (C<sub>1</sub>-C<sub>4</sub>)alkylcarbonyl, for instance methylcarbonyl or ethylcarbonyl;
- arylcarbonyl, for instance phenylcarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- aryloxycarbonyl;
- aryl(C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminocarbonyl, for instance dimethylaminocarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)(alkyl)arylaminocarbonyl;
- optionally substituted aryl such as phenyl;
- 5- or 6-membered monocyclic heteroaryl such as imidazolyl or pyridyl;
- cationic 5- or 6-membered monocyclic heteroaryl such as pyrylium, pyridinium, pyrimidinium, pyrazinium, pyridazinium, triazinium, imidazolium; these groups being optionally substituted with one or more identical or different (C<sub>1</sub>-C<sub>4</sub>)alkyl groups such as methyl;

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- cationic 8- to 11-membered bicyclic heteroaryl such as benzimidazolium or benzoxazolium; these groups being optionally substituted with one or more identical or different (C<sub>1</sub>-C<sub>4</sub>)alkyl groups such as methyl;
- cationic heterocycle having the following formula:



5

- -C(NH<sub>2</sub>)=N<sup>+</sup>H<sub>2</sub>; An'''-; with An'''- being an anionic counterion as defined previously;
- -C(NH<sub>2</sub>)=NH;
- SO<sub>3</sub><sup>-</sup>, M<sup>+</sup> with M<sup>+</sup> representing an alkali metal such as sodium or potassium.

10

*i). 2) C<sub>sat</sub> and C'<sub>sat</sub>:*

As indicated previously, in formula (I), C<sub>sat</sub> and C'<sub>sat</sub>, independently of each other, represent a linear or branched or cyclic, optionally substituted C<sub>1</sub>-C<sub>18</sub> alkylene chain.

15

Substituents that may be mentioned include the following groups: i) amino, ii) (C<sub>1</sub>-C<sub>4</sub>)alkylamino, iii) (C<sub>1</sub>-C<sub>4</sub>)dialkylamino, or the group iv) R<sup>a</sup>-Z<sup>a</sup>-C(Z<sup>b</sup>)-Z<sup>c</sup>-, in which Z<sup>a</sup>, Z<sup>b</sup>, which may be identical or different, represent an oxygen or sulfur atom, or a group NR<sup>av</sup>, Z<sup>c</sup> represents a bond, an oxygen or sulfur atom or a group NR<sup>a</sup>, and R<sup>a</sup> represents an alkali metal, a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group and R<sup>av</sup> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group; more particularly, the groups iv) are chosen from carboxylate -C(O)O<sup>-</sup> or -C(O)OMetal (Metal = alkali metal), carboxyl -C(O)-OH, guanidino H<sub>2</sub>H-C(NH<sub>2</sub>)-NH-, amidino H<sub>2</sub>H-C(NH<sub>2</sub>)-, (thio)ureo H<sub>2</sub>N-C(O)-NH- and H<sub>2</sub>N-C(S)-NH-, aminocarbonyl-C(O)-NRA'<sub>2</sub> or aminothiocarbonyl -C(S)-NRA'<sub>2</sub>; carbamoyl Ra'-C(O)-NRA'- or thiocarbamoyl Ra'-C(S)-NRA'- with Ra', which may be identical or different, representing a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>) alkyl group; the said substituent(s) are preferably present on the carbon in the beta or gamma position relative to the sulfur atoms of the disulfide, thiol or protected-thiol group.

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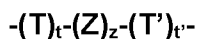
Preferably, in the case of formula (I), C<sub>sat</sub> and C'<sub>sat</sub> represent a chain -(CH<sub>2</sub>)<sub>k</sub>- with k being an integer between 1 and 8 inclusive.

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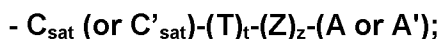
*i). 3) X and X':*

In accordance with one particular embodiment of the invention, in the abovementioned formula (I), when p and p' is equal to 1, the radicals X and X', which may be identical or different, represent the following sequence:

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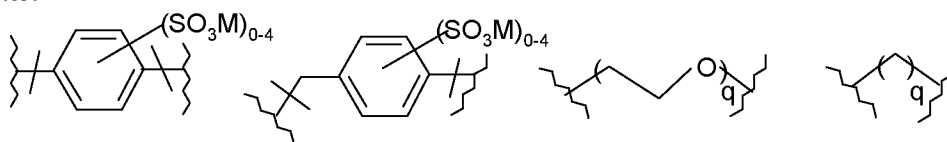
the said sequence being linked in formula (I) symmetrically as follows:



in which:

- T and T', which may be identical or different, represent one or more radicals or combinations thereof chosen from: -O-; -S-; -N(R)-; -N+(R)(R°)-; -S(O)-; -S(O)<sub>2</sub>-; -C(O)-; with R, R°, which may be identical or different, representing a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical or an aryl(C<sub>1</sub>-C<sub>4</sub>)alkyl radical; and a cationic or non-cationic, preferentially monocyclic heterocycloalkyl or heteroaryl radical, preferentially containing two heteroatoms (more preferentially two nitrogen atoms) and preferentially being 5- to 7-membered, more preferentially imidazolium;
- the indices t and t', which may be identical or different, are equal to 0 or 1;
- Z represents:
  - -(CH<sub>2</sub>)<sub>m</sub>- radical with m being an integer between 1 and 8;
  - -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>q</sub>- or -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>q</sub>- in which q is an integer between 1 and 5 inclusive;
  - an aryl, alkylaryl or arylalkyl radical in which the alkyl radical is C<sub>1</sub>-C<sub>4</sub> and the aryl radical is preferably C<sub>6</sub>, being optionally substituted with at least one group SO<sub>3</sub>M with M representing a hydrogen atom, an alkali metal or an ammonium group substituted with one or more identical or different, linear or branched C<sub>1</sub>-C<sub>18</sub> alkyl radicals optionally bearing at least one hydroxyl;
- z is 0 or 1.

Moreover, according to one particular embodiment of the invention, Z represents:



in which M represents a hydrogen atom, an alkali metal or an ammonium group or an ammonium group substituted with one or more identical or different, linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl radicals optionally bearing at least one hydroxyl; 0-4 represents an integer between 0 and 4 inclusive, and q represents an integer inclusively between 1 and 6.

i).4). A and A':

The radicals A and/or A' of formula (I) contain at least one quaternized cationic chromophore or at least one chromophore bearing a quaternized or quaternizable cationic group.

According to one preferred embodiment of the invention, the dyes (I) according to the invention are disulfides and comprise identical quaternized cationic chromophores A and

A'.

More particularly, the dyes of formula (I) according to the invention are symmetrical disulfides, i.e. they contain a C<sub>2</sub> axis of symmetry, i.e. formula (I) is such that:



5 As chromophores that are useful, mention may be made of those derived from the following dyes: acridines; acridones; anthranthrones; anthrapyrimidines; anthraquinones; azines; (poly)azos, hydrazono or hydrazones, in particular arylhydrazones; azomethines; benzanthrones; benzimidazoles; benzimidazolones; benzindoles; benzoxazoles; benzopyrans; benzothiazoles; benzoquinones; bisazines; bis-isindolines; carboxanilides; 10 coumarins; cyanins such as azacarbocyanins, diazocarbocyanins, diazahemicyanins, hemicyanin, or tetraazacarbocyanins; diazines; diketopyrrolopyrroles; dioxazines; diphenylamines; diphenylmethanes; dithiazines; flavonoids such as flavantrones and flavones; fluorindines; formazans; indamines; indantrones; indigoids and pseudo-indigoids; indophenols; indoanilines; isindolines; isindolinones; isoviolantrones; 15 lactones; (poly)methines such as dimethines of the type such as stilbene or styryl; naphthalimides; naphthanilides; naphtholactams; naphthoquinones; nitro, especially nitro(hetero)aromatics; oxadiazoles; oxazines; perilones; perinones; perylenes; phenazines; phenoxazine; phenothiazines; phthalocyanin; polyenes/carotenoids; porphyrins; pyranthrones; pyrazolantrones; pyrazolones; pyrimidinoanthrones; pyronines; 20 quinacridones; quinolines; quinophthalones; squaranes; tetrazoliums; thiazines, thioindigo; thiopyronines; triarylmethanes, or xanthenes.

Among the cationic azo chromophores, mention may be made particularly of those derived from the cationic dyes described in the *Kirk Othmer Encyclopedia of Chemical Technology*, "Dyes, Azo", J. Wiley & Sons, updated on 19/04/2010.

25 Among the azo chromophores A and/or A' that may be used according to the invention, mention may be made of the cationic azo dyes described in patent applications WO 95/15144, WO 95/01772 and EP-714954.

30 According to one preferred embodiment of the invention, the coloured chromophore A and/or A' is chosen from cationic chromophores, preferentially those derived from dyes known as "basic dyes".

Among the azo chromophores, mention may be made of those described in the Colour Index International 3rd edition, and especially the following compounds:

- Basic Red 22
- 35 -Basic Red 76
- Basic Yellow 57
- Basic Brown 16

-Basic Brown 17

Among the cationic quinone chromophores **A** and/or **A'**, those mentioned in the abovementioned Colour Index International are suitable for use, and among those, mention may be made, inter alia, of the radicals derived from the following dyes:

5 -Basic Blue 22

-Basic Blue 99

Among the cationic azine chromophores **A** and/or **A'**, those listed in the Colour Index International are suitable for use, and among those, for example the radicals derived from the following dyes:

10 -Basic Blue 17

-Basic Red 2.

Among the cationic triarylmethane chromophores **A** and/or **A'** that may be used according to the invention, mention may be made, besides those listed in the Colour Index, of the radicals derived from the following dyes:

15 -Basic Green 1

-Basic Violet 3

-Basic Violet 14

-Basic Blue 7

-Basic Blue 26.

20 Mention may also be made of the cationic chromophores derived from the dyes described in documents US 5 888 252, EP 1 133 975, WO 03/029 359, EP 860 636, WO 95/01772, WO 95/15144 and EP 714 954. Mention may also be made of those listed in the encyclopaedia "The chemistry of synthetic dye" by K. Venkataraman, 1952, Academic press vol. 1 to 7, in Kirk Othmer's encyclopaedia "Chemical technology", in the chapter  
25 "Dyes and dye intermediates", 1993, Wiley and Sons, and in various chapters of "Ullmann's encyclopedia of Industrial chemistry" 7th edition, Wiley and Sons.

Preferably, the chromophores **A** and/or **A'** are chosen from those derived from dyes of the type such as azo and hydrazono.

30 According to one particular embodiment, the cationic radicals **A** and/or **A'** in formula (I) comprise at least one cationic azo chromophore derived from a dye described in EP 850 636, FR 2 788 433, EP 920 856, WO 99/48465, FR 2 757 385, EP 85/0637, EP 91/8053, WO 97/44004, FR 2 570 946, FR 2 285 851, DE 2 538 363, FR 2 189 006, FR 1 560 664, FR 1 540 423, FR 1 567 219, FR 1 516 943, FR 1 221 122, DE 4 220 388, DE 4 137 005, WO 01/66646, US 5 708 151, WO 95/01772, WO 515 144, GB 1 195 386, US 3 524 842,  
35 US 5 879 413, EP 1 062 940, EP 1 133 976, GB 738 585, DE 2 527 638, FR 2 275 462, GB 1974-27645, *Acta Histochem.* (1978), 61(1), 48-52; *Tsitologiya* (1968), 10(3), 403-5; *Zh. Obshch. Khim.* (1970), 40(1), 195-202; *Ann. Chim. (Rome)* (1975), 65(5-6), 305-14;

Journal of the Chinese Chemical Society (Taipei) (1998), 45(1), 209-211; Rev. Roum. Chim. (1988), 33(4), 377-83; Text. Res. J. (1984), 54(2), 105-7; Chim. Ind. (Milan) (1974), 56(9), 600-3; Khim. Tekhnol. (1979), 22(5), 548-53; Ger. Monatsh. Chem. (1975), 106(3), 643-8; MRL Bull. Res. Dev. (1992), 6(2), 21-7; Lihua Jianyan, Huaxue Fence (1993), 29(4), 233-4; Dyes Pigm. (1992), 19(1), 69-79; Dyes Pigm. (1989), 11(3), 163-72.

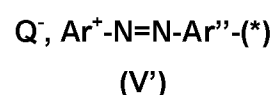
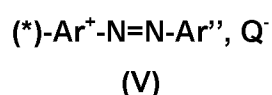
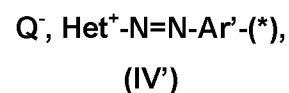
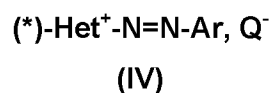
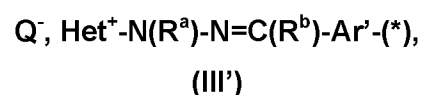
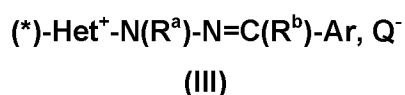
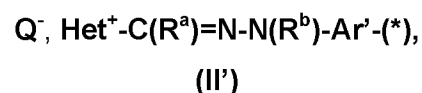
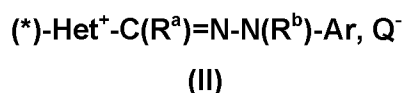
According to one variant, **A** and/or **A'** of formula **(I)** contain at least one cationic radical borne by, or included in, at least one of the chromophores.

Preferably, the cationic radical is a quaternary ammonium; more preferentially, the cationic charge is endocyclic.

10 These cationic radicals are, for example, a cationic radical:

- bearing an exocyclic (di/tri)(C<sub>1</sub>-C<sub>8</sub>)alkylammonium charge, or
- bearing an endocyclic charge, such as the following cationic heteroaryl groups: acridinium, benzimidazolium, benzobistriazolium, benzopyrazolium, benzopyridinium, benzoquinolium, benzothiazolium, benzotriazolium, benzoxazolium, bipyridinium, bis-tetrazolium, dihydrothiazolium, imidazopyridinium, imidazolium, indolium, isoquinolium, naphthoimidazolium, naphthoxazolium, naphthopyrazolium, oxadiazolium, oxazolium, oxazolopyridinium, oxonium, phenazinium, phenoxazolium, pyrazinium, pyrazolium, pyrazoyltriazolium, pyridinium, pyridinoimidazolium, pyrrolium, pyrylium, quinolium, tetrazolium, thiadiazolium, thiazolium, thiazolopyridinium, thiazoylimidazolium, thiopyrylium, triazolium or xanthylium.

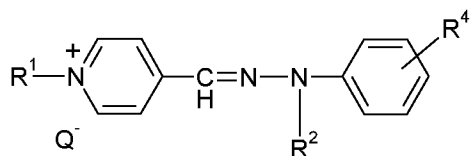
Mention may be made of the hydrazono cationic chromophores of formulae **(II)** and **(III')**, and the azo cationic chromophores **(IV)**, **(IV')**, **(V)** and **(V')** below:



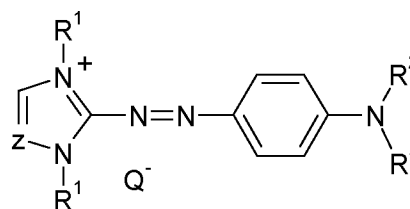
25 formulae **(II)** to **(V')** with:

- **Het<sup>+</sup>** representing a cationic heteroaryl radical, preferentially bearing an endocyclic cationic charge, such as imidazolium, indolium or pyridinium, optionally substituted, preferentially with one or more (C<sub>1</sub>-C<sub>8</sub>) alkyl groups such as methyl;
- **Ar<sup>+</sup>** represents an aralkyl radical, such as phenyl or naphthyl, bearing an exocyclic cationic charge, particularly tri(C<sub>1</sub>-C<sub>8</sub>)alkylammonium such as trimethylammonium;
- **Ar** represents an aryl group, especially phenyl, optionally substituted, preferentially with one or more electron-donating groups such as i) optionally substituted (C<sub>1</sub>-C<sub>8</sub>)alkyl, ii) optionally substituted (C<sub>1</sub>-C<sub>8</sub>)alkoxy, iii) (di)(C<sub>1</sub>-C<sub>8</sub>)(alkyl)amino optionally substituted on the alkyl group(s) with a hydroxyl group, iv) aryl(C<sub>1</sub>-C<sub>8</sub>)alkylamino, v) optionally substituted *N*-(C<sub>1</sub>-C<sub>8</sub>)alkyl-*N*-aryl(C<sub>1</sub>-C<sub>8</sub>)alkylamino or alternatively **Ar** represents a julolidine group;
- **Ar'** is an optionally substituted divalent (hetero)alkylene group such as phenylene, particularly para-phenylene, or naphthalene, which are optionally substituted, preferentially with one or more groups (C<sub>1</sub>-C<sub>8</sub>)alkyl, hydroxyl or (C<sub>1</sub>-C<sub>8</sub>)alkoxy;
- **Ar''** is an optionally substituted (hetero)aryl group such as phenyl or pyrazolyl, which is optionally substituted, preferentially with one or more groups (C<sub>1</sub>-C<sub>8</sub>)alkyl, hydroxyl, (di)(C<sub>1</sub>-C<sub>8</sub>)(alkyl)amino, (C<sub>1</sub>-C<sub>8</sub>)alkoxy or phenyl;
- **R<sup>a</sup>** and **R<sup>b</sup>**, which may be identical or different, represent a hydrogen atom or a group (C<sub>1</sub>-C<sub>8</sub>)alkyl, which is optionally substituted, preferentially with a hydroxyl group; or alternatively the substituent **R<sup>a</sup>** with a substituent of **Het<sup>+</sup>** and/or **R<sup>b</sup>** with a substituent of **Ar** form, together with the atoms that bear them, a (hetero)cycloalkyl; particularly, **R<sup>a</sup>** and **R<sup>b</sup>** represent a hydrogen atom or a group (C<sub>1</sub>-C<sub>4</sub>)alkyl, which is optionally substituted with a hydroxyl group;
- **Q<sup>-</sup>** represents an organic or mineral anionic counterion such as a halide or an alkyl sulfate;
- (\*) represents the part of the chromophore linked to the rest of the molecule of formula (I).

In particular, mention may be made of the azo and hydrazono chromophores bearing an endocyclic cationic charge of formulae (II) to (IV') as defined previously. More particularly those of formulae (II) to (IV') derived from the dyes described in patent applications WO 95/15144, WO 95/01772 and EP-714954. Preferentially the following chromophores:



(II-1)



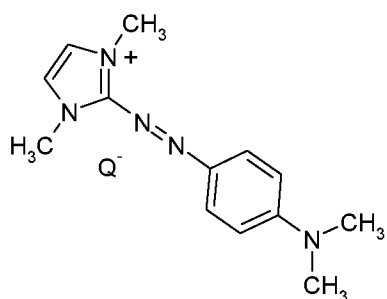
(IV-1)

formulae (III-1) and (IV-1) with:

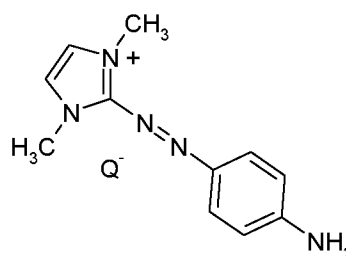
- $R^1$  representing a group ( $C_1$ - $C_4$ )alkyl such as methyl;
- $R^2$  and  $R^3$ , which may be identical or different, representing a hydrogen atom or a group ( $C_1$ - $C_4$ )alkyl such as methyl; and
- 5 -  $R^4$  representing a hydrogen atom or an electron-donating group such as optionally substituted ( $C_1$ - $C_8$ )alkyl, optionally substituted ( $C_1$ - $C_8$ )alkoxy, or (di)( $C_1$ - $C_8$ )(alkyl)amino optionally substituted on the alkyl group(s) with a hydroxyl group; particularly,  $R^4$  is a hydrogen atom,
- $Z$  represents a group CH or a nitrogen atom, preferentially CH,
- 10 -  $Q^-$  is as defined previously;

it being understood that the chromophore (II-1) or (IV-1) is linked to the rest of the molecule of formula (I) by  $R^2$ ,  $R^1$  or  $R^4$  in which case one of the hydrogen atoms of  $R^2$ ,  $R^1$  or  $R^4$  is substituted with  $X$  or  $X'$  if  $p = 1$  or  $p' = 1$  or alternatively with  $C_{sat}$  or  $C_{sat}'$  if  $p = 0$  or  $p' = 0$ .

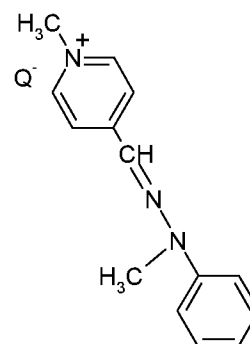
- 15 Particularly, the chromophores (II-1) and (IV-1) are derived from Basic Red 51, Basic Yellow 87 and Basic Orange 31 or derivatives thereof:



Basic Red 51



Basic Orange 31



Basic Yellow 87

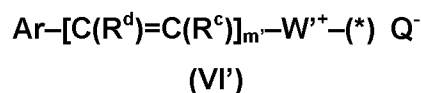
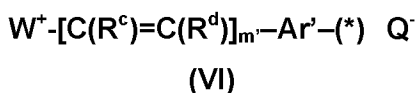
with  $Q^-$  being an anionic counterion as defined previously, particularly a halide such as chloride or an alkyl sulfate such as methyl sulfate or mesityl.

- 20 According to one particular embodiment of the invention, the dyes of formula (I) are fluorescent, i.e. they contain at least one fluorescent chromophore as defined previously.

As fluorescent chromophores **A** and/or **A'** that are useful in the present invention, mention may be made of radicals derived from the following dyes: acridines, acridones, benzanthrones, benzimidazoles, benzimidazolones, benzindoles, benzoxazoles, benzopyrans, benzothiazoles, coumarins, difluoro{2-[(2H-pyrrol-2-ylidene-kN)methyl]-1H-pyrrolato-kN}bores (BODIPY ®), diketopyrrolopyrroles, fluorindines, (poly)methines (especially cyanins and styryls/hemicyanins), naphthalimides, naphthanilides, naphthylamine (such as dansyls), oxadiazoles, oxazines, perilones, perinones, perylenes, polyenes/carotenoids, squaranes, stilbenes and xanthenes.

Mention may also be made of the fluorescent dyes **A** and/or **A'** described in documents EP 1 133 975, WO 03/029 359, EP 860 636, WO 95/01772, WO 95/15144, EP 714 954 and those listed in the encyclopaedia *The chemistry of synthetic dyes* by K. Venkataraman, 1952, Academic Press, vol. 1 to 7, in Kirk Othmer's encyclopaedia *Chemical Technology*, in the chapter "Dyes and dye Intermediates", 1993, Wiley and Sons, and in various chapters of *Ullmann's Encyclopedia of Industrial Chemistry* 7th edition, Wiley and Sons, and in *The Handbook — A Guide to Fluorescent Probes and Labeling Technologies*, 10th Ed Molecular Probes/Invitrogen – Oregon 2005 circulated on the Internet or in the preceding printed editions.

According to one preferred variant of the invention, the fluorescent chromophore **A** and/or **A'** is cationic and comprises at least one quaternary ammonium radical such as those derived from the polymethine dyes of formulae (VI) and (VI') below:



formula (VI) or (VI') with:

- **W<sup>+</sup>** representing a cationic heterocyclic or heteroaryl group, particularly comprising a quaternary ammonium optionally substituted with one or more groups (C<sub>1</sub>-C<sub>8</sub>)alkyl optionally substituted especially with one or more hydroxyl groups;
- **W'<sup>+</sup>** representing a divalent heterocyclic or heteroaryl radical as defined for **W<sup>+</sup>**;
- **Ar** representing an aryl group such as phenyl or naphthyl, optionally substituted preferentially with i) one or more halogen atoms such as chlorine or fluorine; ii) one or more groups (C<sub>1</sub>-C<sub>8</sub>)alkyl, preferably of C<sub>1</sub>-C<sub>4</sub> such as methyl; iii) one or more hydroxyl groups; iv) one or more (C<sub>1</sub>-C<sub>8</sub>)alkoxy groups such as methoxy; v) one or more hydroxy(C<sub>1</sub>-C<sub>8</sub>)alkyl groups such as hydroxyethyl, vi) one or more amino groups or (di)(C<sub>1</sub>-C<sub>8</sub>)alkylamino, preferably with the C<sub>1</sub>-C<sub>4</sub> alkyl part optionally substituted with one or more hydroxyl groups, such as (di)hydroxyethylamino, vii) with one or more acylamino groups; viii) one or more heterocycloalkyl groups such



N(R)-, preferably in the para position on Ar relative to the olefin function -C(R<sup>c</sup>)=C(R<sup>d</sup>)-.

Particularly, in one variant, p=1, z=t'=0, t=1 and T represents -N(R)-, preferably in the para position on Ar relative to the styryl function -C(R<sup>c</sup>)=C(R<sup>d</sup>)- and T' represents a group -N(R)- or -N<sup>+</sup>(R)(R<sup>o</sup>)- or an imidazolium.

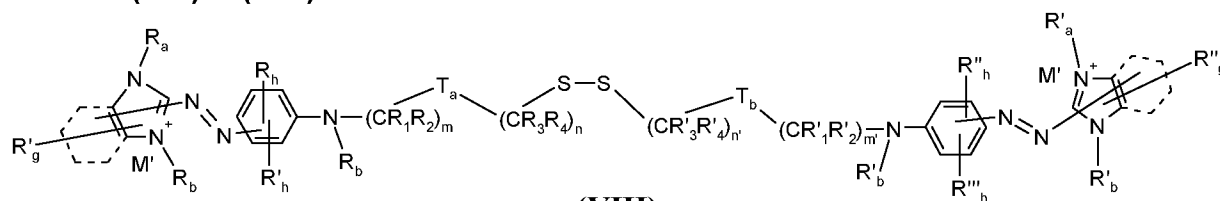
Preferably, W<sup>+</sup> or W'<sup>+</sup> is an imidazolium, pyridinium, benzimidazolium, pyrazolium, benzothiazolium or quinolinium optionally substituted with one or more identical or different C<sub>1</sub>-C<sub>4</sub> alkyl radicals.

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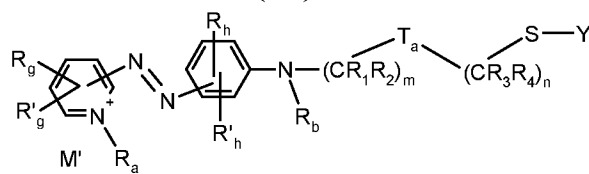
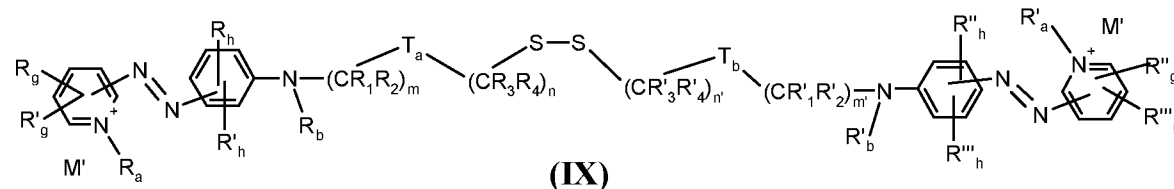
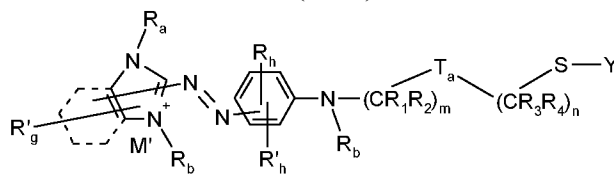
According to one particularly preferred embodiment of the invention, A and/or A' represent the chromophore (VI') as defined previously with m' = 1, Ar representing a phenyl group substituted para to the styryl group -C(R<sup>d</sup>)=C(R<sup>c</sup>)- with a group (di)(hydroxy)(C<sub>1</sub>-C<sub>6</sub>)(alkyl)amino such as dihydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino, and W'<sup>+</sup> representing an imidazolium or pyridinium group, preferentially ortho- or para-pyridinium.

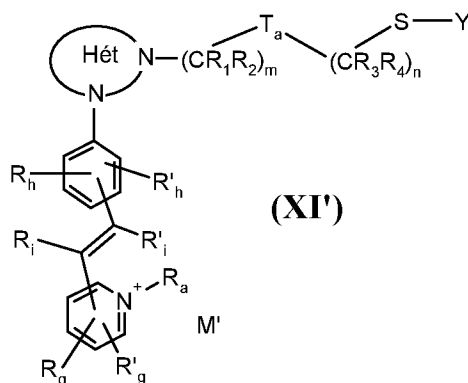
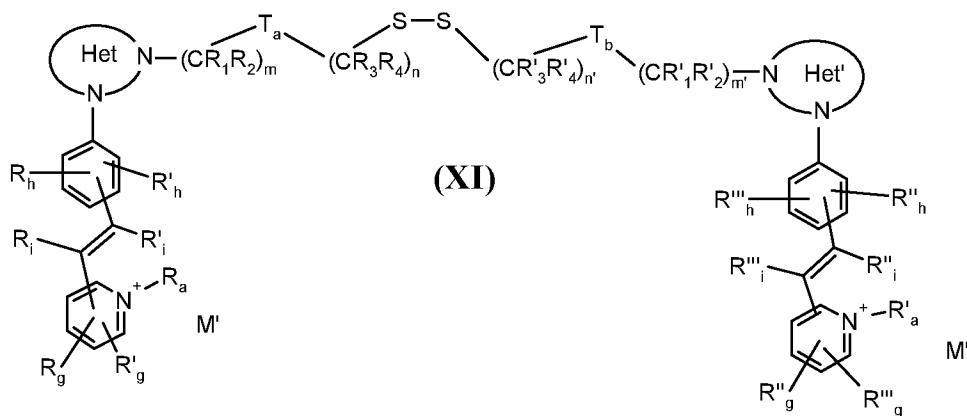
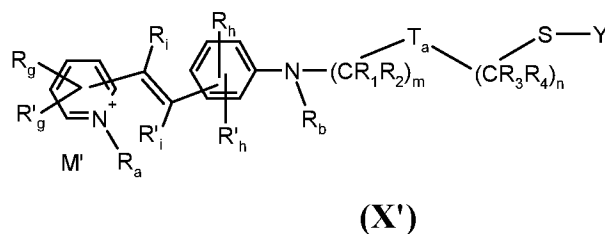
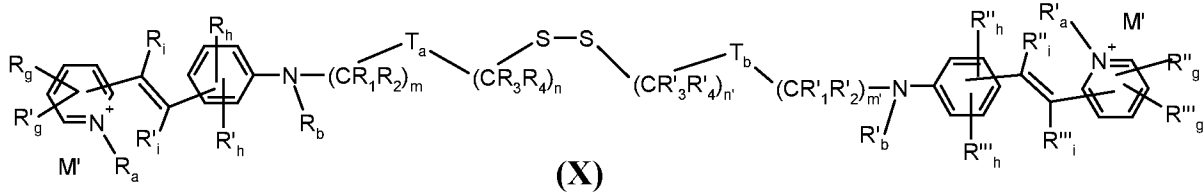
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As examples of dyes of the invention, mention may be made of the disulfide dyes chosen from formulae (VIII) to (XIV) and the thiol or protected-thiol dyes chosen from formulae (VIII') to (XIV') below:

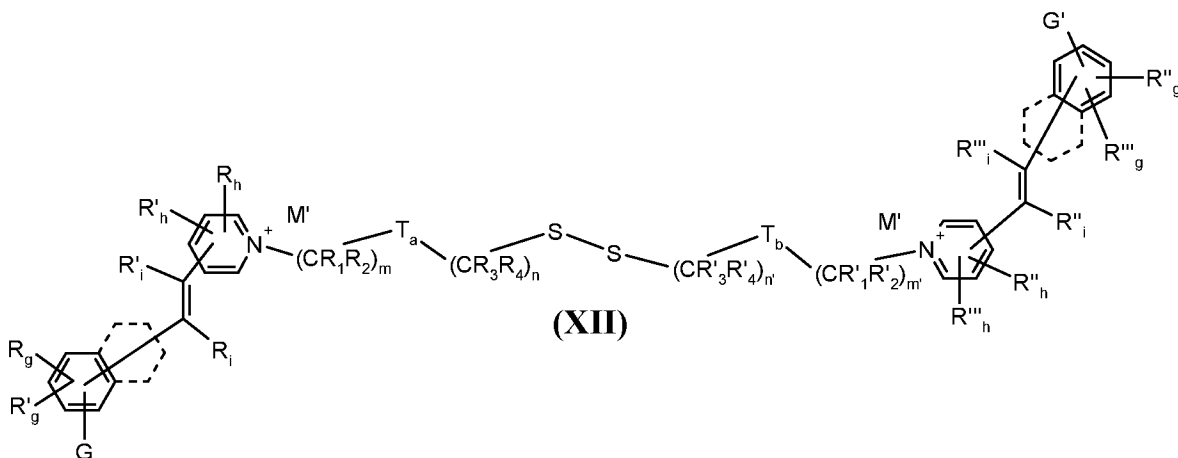


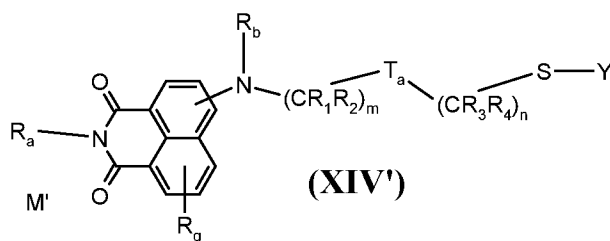
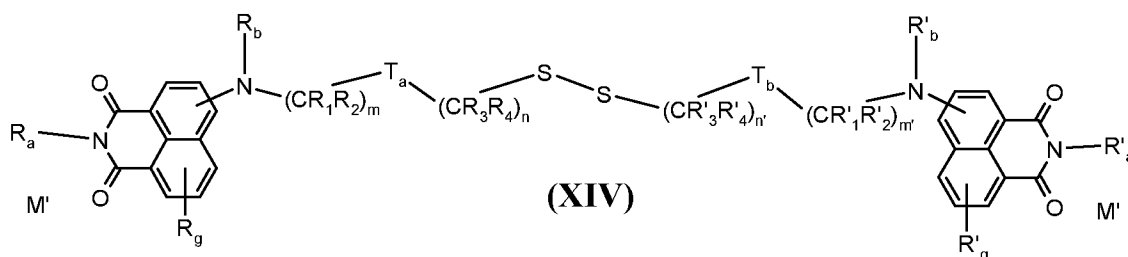
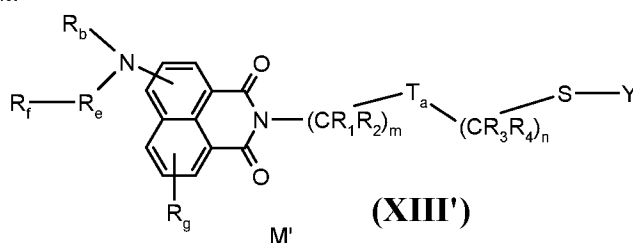
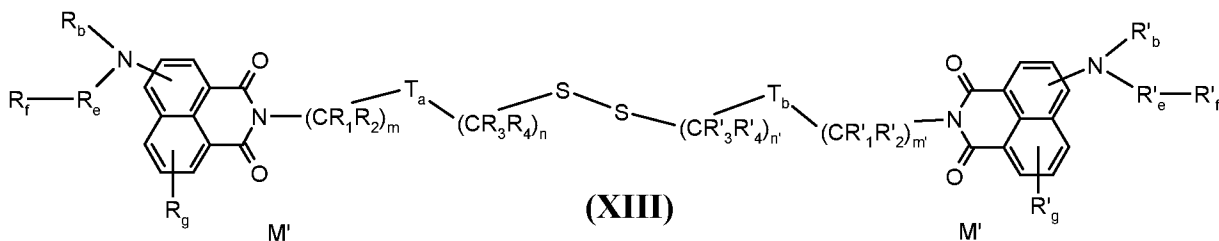
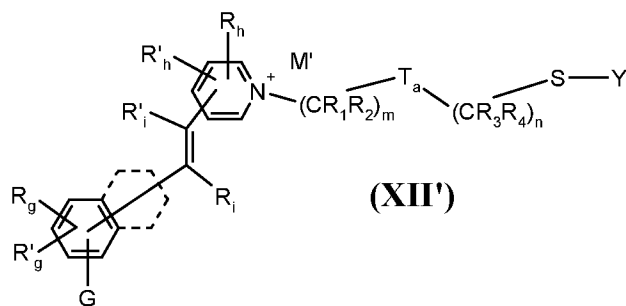
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in which formulae (VIII) to (XIV) and (VIII') to (XIV'):

- G and G', which may be identical or different, represent a group -NR<sub>c</sub>R<sub>d</sub>, -NR'<sub>c</sub>R'<sub>d</sub> or C<sub>1</sub>-C<sub>6</sub> alkoxy which is optionally substituted, preferentially unsubstituted; preferentially, G and G' represent a group -NR<sub>c</sub>R<sub>d</sub> or -NR'<sub>c</sub>R'<sub>d</sub>, respectively;
- R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup>, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>6</sub> alkyl group; preferentially a hydrogen atom;
- R<sub>a</sub> and R'<sub>a</sub>, which may be identical or different, represent an aryl(C<sub>1</sub>-C<sub>4</sub>)alkyl group or a C<sub>1</sub>-C<sub>6</sub> alkyl group optionally substituted with a hydroxyl or amino, C<sub>1</sub>-C<sub>4</sub> alkylamino or C<sub>1</sub>-C<sub>4</sub> dialkyl amino group, the said alkyl radicals possibly forming,

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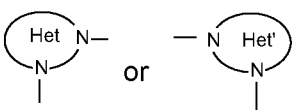
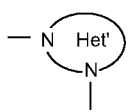
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
with the nitrogen atom that bears them, a 5- to 7-membered heterocycle, optionally comprising another nitrogen or non-nitrogen heteroatom; preferentially,  $R_a$  and  $R'_a$  represent a  $C_1$ - $C_3$  alkyl group optionally substituted with a hydroxyl group, or a benzyl group;

- 5
- $R_b$  and  $R'_b$ , which may be identical or different, represent a hydrogen atom, an aryl( $C_1$ - $C_4$ )alkyl group or a  $C_1$ - $C_6$  alkyl group that is optionally substituted; preferentially,  $R_b$  and  $R'_b$  represent a hydrogen atom or a  $C_1$ - $C_3$  alkyl or benzyl group;
  - $R_c$ ,  $R'_c$ ,  $R_d$  and  $R'_d$ , which may be identical or different, represent a hydrogen atom,  
10 an aryl( $C_1$ - $C_4$ )alkyl or  $C_1$ - $C_6$  alkoxy group or a  $C_1$ - $C_6$  alkyl group that is optionally substituted;  $R_c$ ,  $R'_c$ ,  $R_d$  and  $R'_d$  preferentially represent a hydrogen atom, a hydroxyl,  $C_1$ - $C_3$  alkoxy, amino or  $C_1$ - $C_3$  (di)alkylamino group, or a  $C_1$ - $C_3$  alkyl group that is optionally substituted with i) a hydroxyl group, ii) amino, iii)  $C_1$ - $C_3$  (di)alkylamino, or iv) quaternary ammonium  $(R'')(R''')(R''''N^+$ ;  
15 or alternatively two adjacent radicals  $R_c$  and  $R_d$ ,  $R'_c$  and  $R'_d$  borne by the same nitrogen atom together form a heterocyclic or heteroaryl group; preferentially, the heterocycle or heteroaryl is monocyclic and 5- to 7-membered; more preferentially, the groups are chosen from imidazolyl and pyrrolidinyl;
  - $R_e$  and  $R'_e$ , which may be identical or different, represent a linear or branched  $C_1$ - $C_6$   
20 alkylene or  $C_2$ - $C_6$  alkenylene hydrocarbon-based chain;
  - $R_f$  and  $R'_f$ , which may be identical or different, represent a group di( $C_1$ - $C_4$ )alkylamino,  $(R'')(R''')N-$  or a quaternary ammonium group  $(R'')(R''')(R''''N^+$  in which  $R''$ ,  $R'''$  and  $R''''$ , which may be identical or different, represent a hydrogen atom or a  $C_1$ - $C_4$  alkyl group or alternatively  $(R'')(R''')(R''''N^+$  represents an  
25 optionally substituted cationic heteroaryl group, preferentially an imidazolium group optionally substituted with a  $C_1$ - $C_3$  alkyl group;
  - $R_g$ ,  $R'_g$ ,  $R''_g$ ,  $R'''_g$ ,  $R_h$ ,  $R'_h$ ,  $R''_h$ , and  $R'''_h$ , which may be identical or different, represent a hydrogen atom, a halogen atom, an amino,  $C_1$ - $C_4$  alkylamino,  $C_1$ - $C_4$  dialkylamino, cyano, carboxyl, hydroxyl or trifluoromethyl group, an acylamino,  $C_1$ -  
30  $C_4$  alkoxy, (poly)hydroxy( $C_2$ - $C_4$ )alkoxy, alkylcarbonyloxy, alkoxy carbonyl or alkylcarbonylamino radical, an acylamino, carbamoyl or alkylsulfonylamino radical, an aminosulfonyl radical, or a  $C_1$ - $C_{16}$  alkyl radical optionally substituted with a group chosen from  $C_1$ - $C_{12}$  alkoxy, hydroxyl, cyano, carboxyl, amino,  $C_1$ - $C_4$  alkylamino and  $C_1$ - $C_4$  dialkylamino, or alternatively two alkyl radicals borne by the nitrogen atom of  
35 the amino group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom; preferentially,  $R_g$ ,  $R'_g$ ,  $R''_g$ ,  $R'''_g$ ,  $R_h$ ,  $R'_h$ ,  $R''_h$ , and  $R'''_h$  represent a hydrogen or halogen atom or a  $C_1$ - $C_3$  alkyl group;

- or alternatively two groups  $R_g$  and  $R'_g$ ;  $R''_g$  and  $R'''_g$ ;  $R_h$  and  $R'_h$ ;  $R''_h$  and  $R'''_h$  borne by two adjacent carbon atoms together form a benzo or indeno ring, a fused heterocycloalkyl or fused heteroaryl group; the benzo, indeno, heterocycloalkyl or heteroaryl ring being optionally substituted with a halogen atom, an amino, C<sub>1</sub>-C<sub>4</sub> alkylamino, C<sub>1</sub>-C<sub>4</sub> dialkylamino, nitro, cyano, carboxyl, hydroxyl or trifluoromethyl group, an acylamino, C<sub>1</sub>-C<sub>4</sub> alkoxy, (poly)hydroxy(C<sub>2</sub>-C<sub>4</sub>)alkoxy, alkylcarbonyloxy, alkoxy carbonyl or alkylcarbonylamino radical, an acylamino, carbamoyl or alkylsulfonylamino radical, an aminosulfonyl radical, or a C<sub>1</sub>-C<sub>16</sub> alkyl radical optionally substituted with: a group chosen from C<sub>1</sub>-C<sub>12</sub> alkoxy, hydroxyl, cyano, carboxyl, amino, C<sub>1</sub>-C<sub>4</sub> alkylamino, C<sub>1</sub>-C<sub>4</sub> dialkylamino, or alternatively two alkyl radicals borne by the nitrogen atom of the amino group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom; preferentially,  $R_g$  and  $R'_g$ ;  $R''_g$  and  $R'''_g$  together form a benzo group;
- or alternatively two groups  $R_i$  and  $R_g$ ;  $R''_i$  and  $R'''_i$ ;  $R'_i$  and  $R'_h$ ; and/or  $R''_i$  and  $R''_h$  together form a fused (hetero)cycloalkyl, preferentially cycloalkyl such as cyclohexyl;
- or alternatively when G represents  $-NR_cR_d$  and G' represents  $-NR'_cR'_d$ , two groups  $R_c$  and  $R'_c$ ;  $R'_c$  and  $R''_c$ ;  $R_d$  and  $R_g$ ;  $R'_d$  and  $R'''_g$  together form a saturated heteroaryl or heterocycle, optionally substituted with one or more groups (C<sub>1</sub>-C<sub>6</sub>)alkyl, preferentially a 5- to 7-membered heterocycle containing one or two heteroatoms chosen from nitrogen and oxygen; more preferentially the heterocycle is chosen from morpholinyl, piperazinyl, piperidyl and pyrrolidinyl groups;
- $R_i$ ,  $R'_i$ ,  $R''_i$ , and  $R'''_i$ , which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group;
- $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$ , which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>12</sub> alkoxy, hydroxyl, cyano, carboxyl, amino, C<sub>1</sub>-C<sub>4</sub> alkylamino or C<sub>1</sub>-C<sub>4</sub> dialkylamino group, the said alkyl radicals possibly forming with the nitrogen that bears them a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom; preferentially,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  are hydrogen atoms or an amino group; more preferentially,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R'_1$ ,  $R'_2$ ,  $R'_3$ , and  $R'_4$  represent a hydrogen atom;
- $T_a$ ,  $T_b$ , which may be identical or different, represent i) either a covalent  $\sigma$  bond, ii) or one or more radicals or combinations thereof chosen from  $-SO_2-$ ,  $-O-$ ,  $-S-$ ,  $-N(R)-$ ,  $-N^+(R)(R^\circ)-$ ,  $-CO-$ , with R,  $R^\circ$ , which may be identical or different, representing a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical, or an aryl(C<sub>1</sub>-C<sub>4</sub>)alkyl; preferentially,  $T_a$  is identical to  $T_b$  and they represent a covalent  $\sigma$  bond or a group

chosen from  $-N(R)-$ ,  $-C(O)-N(R)-$ ,  $-N(R)-C(O)-$ ,  $-O-C(O)-$ ,  $-C(O)-O-$  and  $-N^+(R)(R^\circ)-$ , with R,  $R^\circ$ , which may be identical or different, representing a hydrogen atom or a  $C_1-C_4$  alkyl group; more preferentially,  $T_a$  and  $T_b$  represent a  $\sigma$  bond; iii) or a cationic or non-cationic, preferentially monocyclic, preferentially identical heterocycloalkyl or heteroaryl radical, preferentially containing two heteroatoms (more preferentially two nitrogen atoms) and preferentially being 5- to 7-membered, such as imidazolium;

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- 10
-  or , identical or different, represent an optionally substituted heterocycle; preferentially, the heterocycles are identical, monocyclic, saturated and 5- to 8-membered and comprise in total two nitrogen atoms;

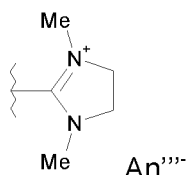
- 15
-  represents an aryl or heteroaryl group fused to the imidazolium or phenyl ring; or alternatively is absent from the imidazolium or phenyl ring; preferentially, when the ring is present, the ring is a benzo;

- 20
- m, m', n and n', which may be identical or different, represent an integer between 0 and 6 inclusive, with m+n and m'+n', which may be identical or different, representing an integer between 1 and 10 inclusive; preferentially, m+n = m'+n' = an integer between 2 and 4 inclusive; more preferentially, m+n = m'+n' = an integer equal to 2;
  - Y is as defined previously; in particular, Y represents a hydrogen atom or a protecting group such as:

- 25
- 30
- 35
- $(C_1-C_4)$ alkylcarbonyl, for instance methylcarbonyl or ethylcarbonyl;
  - arylcarbonyl, for instance phenylcarbonyl;
  - $(C_1-C_4)$ alkoxycarbonyl;
  - aryloxycarbonyl;
  - aryl $(C_1-C_4)$ alkoxycarbonyl;
  - (di) $(C_1-C_4)$ (alkyl)aminocarbonyl, for instance dimethylaminocarbonyl;
  - $(C_1-C_4)$ (alkyl)arylamino carbonyl;
  - optionally substituted aryl such as phenyl;
  - 5- or 6-membered monocyclic heteroaryl such as imidazolyl or pyridyl;
  - cationic 5- or 6-membered monocyclic heteroaryl such as pyrylium, pyridinium, pyrimidinium, pyrazinium, pyridazinium, triazinium, imidazolium; these groups being optionally substituted with one or more identical or different  $(C_1-C_4)$ alkyl groups such as methyl;
  - cationic 8- to 11-membered bicyclic heteroaryl such as benzimidazolium or benzoxazolium; these groups being optionally substituted with one or more

identical or different (C<sub>1</sub>-C<sub>4</sub>)alkyl groups such as methyl;

- cationic heterocycle having the following formula:

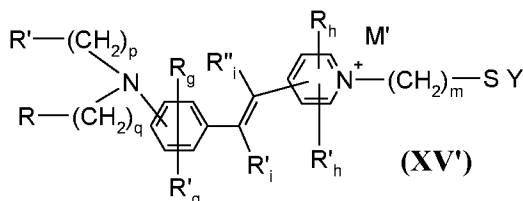
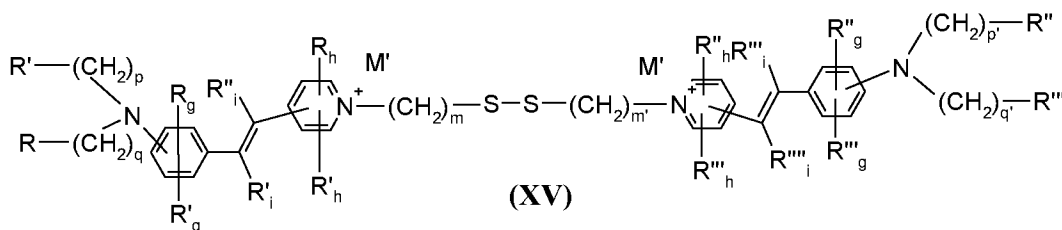


- -C(NH<sub>2</sub>)=N<sup>+</sup>H<sub>2</sub>; An'''<sup>-</sup>; with An'''<sup>-</sup> being an anionic counterion as defined previously;
- -C(NH<sub>2</sub>)=NH;
- SO<sub>3</sub><sup>-</sup>, M<sup>+</sup> with M<sup>+</sup> representing an alkali metal such as sodium or potassium; and

- M' representing an anionic counterion, derived from a salt of an organic or mineral acid, or from an organic or mineral base that ensures the electrical neutrality of the molecule.

In particular, the dyes of formula (I) are chosen from dyes with a naphthalimidyl disulfide, thiol or protected-thiol chromophore, chosen from formulae (XIII), (XIII'), (XIV) and (XIV') as defined previously.

According to one preferred mode of the invention, the dyes of formula (I) are chosen from disulfide, thiol or protected-thiol dyes chosen from formulae (XV) to (XV') below:



the organic or mineral acid salts, optical isomers, geometrical isomers, and solvates such as hydrates thereof;

in which formulae (XV) and (XV'):

- R and R''', which may be identical or different, represent a hydroxyl group, an amino group (NR<sub>a</sub>R<sub>b</sub>) or an ammonium group (N<sup>+</sup>R<sub>a</sub>R<sub>b</sub>R<sub>c</sub>), An<sup>-</sup>; preferentially hydroxyl; with

R<sub>a</sub>, R<sub>b</sub> and R<sub>c</sub>, which may be identical or different, representing a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group;

or alternatively two alkyl groups R<sub>a</sub> and R<sub>b</sub> of the amino or ammonium group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom, such as morpholinyl, piperazinyl, piperidyl, pyrrolyl, morpholinium, piperazinium, piperidinium or pyrrolinium, and An<sup>-</sup> representing an anionic counterion;

➤ R' and R'', which may be identical or different, represent a hydrogen atom or a group as defined for R and R''', respectively;

➤ R<sub>g</sub>, R'<sub>g</sub>, R''<sub>g</sub>, R'''<sub>g</sub>, R<sub>h</sub>, R'<sub>h</sub>, R''<sub>h</sub> and R'''<sub>h</sub>, which may be identical or different, represent a hydrogen or halogen atom, an amino, (di)(C<sub>1</sub>-C<sub>4</sub>)alkylamino, cyano, carboxyl, hydroxyl, trifluoromethyl, acylamino, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>2</sub>-C<sub>4</sub> (poly)hydroxyalkoxy, (C<sub>1</sub>-C<sub>4</sub>)alkylcarbonyloxy, (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl, (C<sub>1</sub>-C<sub>4</sub>)alkylcarbonylamino, acylamino, carbamoyl or (C<sub>1</sub>-C<sub>4</sub>)alkylsulfonylamino group, an aminosulfonyl radical or a radical (C<sub>1</sub>-C<sub>16</sub>)alkyl optionally substituted with a group chosen from (C<sub>1</sub>-C<sub>12</sub>)alkoxy, hydroxyl, cyano, carboxyl, amino and (di)(C<sub>1</sub>-C<sub>4</sub>)alkylamino, or alternatively the two alkyl radicals borne by the nitrogen atom of the amino group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom; in particular, R<sub>g</sub>, R'<sub>g</sub>, R''<sub>g</sub>, R'''<sub>g</sub>, R<sub>h</sub>, R'<sub>h</sub>, R''<sub>h</sub> and R'''<sub>h</sub> represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>) alkyl group;

➤ R'<sub>i</sub>, R''<sub>i</sub>, R'''<sub>i</sub> and R''''<sub>i</sub>, which may be identical or different, represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group; in particular R'<sub>i</sub>, R''<sub>i</sub>, R'''<sub>i</sub>, and R''''<sub>i</sub> represent a hydrogen atom;

➤ m, m', which may be identical or different, represent an integer between 1 and 10 inclusive; in particular an integer between 2 and 4 inclusive; preferentially, m and m' are equal to 2;

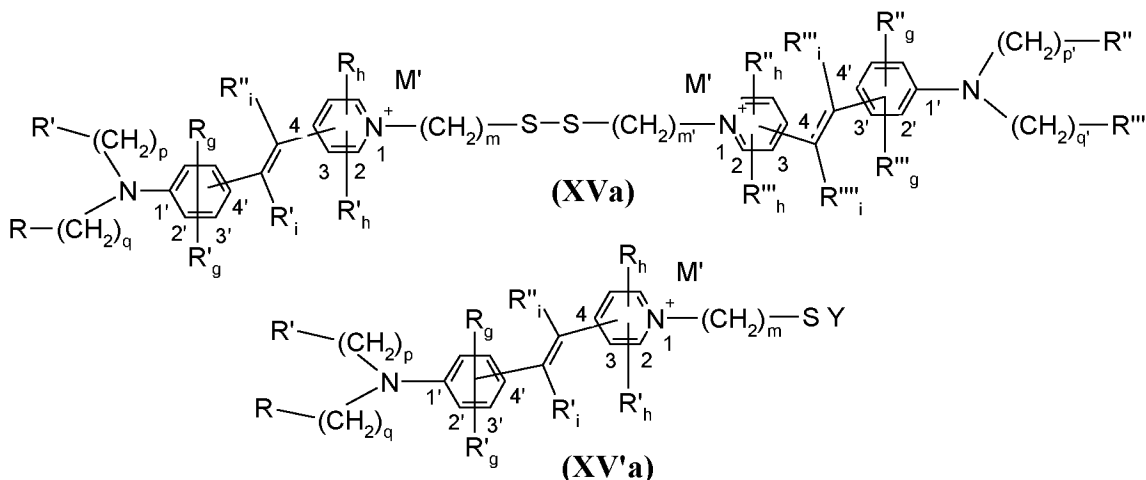
➤ p, p', q and q', which may be identical or different, represent an integer between 1 and 6 inclusive;

➤ M' represents an anionic counterion; and

➤ Y is as defined previously;

it being understood that when the compound of formula **(XV)** or **(XV')** contains other cationic parts, it is combined with one or more anionic counterions that afford formula **(XV)** or **(XV')** electrical neutrality.

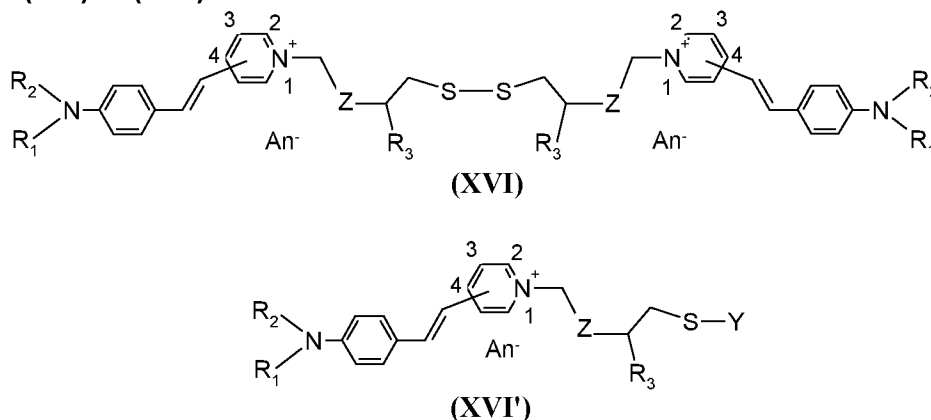
According to one particular mode of the invention, the dyes of the invention belong to formula **(XVa)** or **(XV'a)** which bear an ethylene group connecting the pyridinium part to the phenyl ortho or para to the pyridinium, i.e. 2-4', 4-2', 4-4':



with R, R', R'', R''', R<sub>g</sub>, R'<sub>g</sub>, R''<sub>g</sub>, R'''<sub>g</sub>, R<sub>h</sub>, R'<sub>h</sub>, R''<sub>h</sub>, R'''<sub>h</sub>, R'<sub>i</sub>, R''<sub>i</sub>, R'''<sub>i</sub>, R''''<sub>i</sub>, m, m', p, p', q, q', Y and M' as defined previously in formulae (XV) and (XV'). In particular, R<sub>h</sub> and R''<sub>h</sub> are ortho to the pyridinium group and R'<sub>h</sub> and R'''<sub>h</sub> represent a hydrogen atom. Another aspect of the invention concerns the dyes of formula (XVa) or (XV'a) bearing groups R<sub>g</sub>, R'<sub>g</sub> in position 3' and R'<sub>g</sub>/R''<sub>g</sub> which represent a hydrogen atom.

Advantageously, the dyes of formulae (XVa) and (XV'a) bear their ethylene group para to the phenyl bearing the amino group: R'(CH<sub>2</sub>)<sub>p</sub>-N-(CH<sub>2</sub>)<sub>q</sub>-R and/or R''(CH<sub>2</sub>)<sub>p</sub>-N-(CH<sub>2</sub>)<sub>q</sub>-R''', i.e. in position 4', preferentially bear an ethylene or styryl group linking the pyridinium part to the phenyl ortho to the pyridinium, i.e. 2-4'.

According to another particular mode of the invention, the dyes of the invention belong to formula (XVI) or (XVI'):



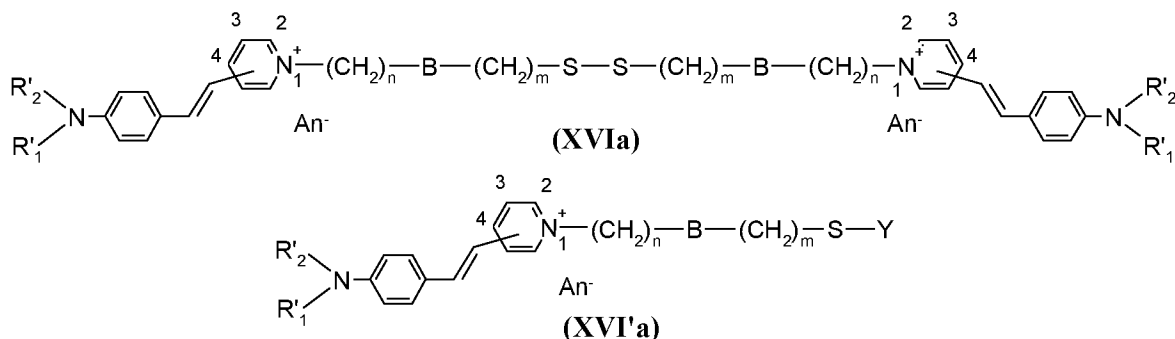
in which formula (XVI) or (XVI'):

- R<sub>1</sub> represents a C<sub>1</sub>-C<sub>6</sub> alkyl group substituted with one or more hydroxyl groups or -C(O)OR' with R' representing a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl group or a group -C(O)-O<sup>-</sup> and, in the latter case, an anionic counterion An<sup>-</sup> is absent; in particular R<sub>1</sub> represents a C<sub>1</sub>-C<sub>6</sub> alkyl group substituted with one or more hydroxyl groups and more specifically with only one hydroxyl group;
- R<sub>2</sub> represents a C<sub>1</sub>-C<sub>6</sub> alkyl group optionally substituted with one or more hydroxyl groups;

- or alternatively the groups  $R_1$  and  $R_2$  form, together with the nitrogen atom that bears them, a saturated heterocyclic radical substituted with at least one hydroxyl, (poly)hydroxy( $C_1$ - $C_4$ )alkyl and/or  $-C(O)OR'$  group with  $R'$  representing a hydrogen atom, a  $C_1$ - $C_4$  alkyl group or a group  $-C(O)-O^-$  and, in the latter case, an anionic counterion  $An^-$  is absent; such as pyrrolidinyl and piperidyl;
- $R_3$  represents a hydrogen atom or a group  $-C(O)OR''$  with  $R''$  representing a hydrogen atom, an alkali metal or a  $C_1$ - $C_6$  alkyl group or alternatively  $R_3$  represents a group  $-C(O)-O^-$  and, in the latter case, an anionic counterion  $An^-$  is absent;
- $Z$  represents a divalent amido group  $-C(O)-N(R)-$ ,  $-N(R)-C(O)-$ , or a divalent  $C_1$ - $C_{10}$  alkylene group interrupted with an amido group  $-C(O)-N(R)-$ ,  $-N(R)-C(O)-$  such as  $-(CH_2)_n-C(O)-N(R)-(CH_2)_p-$ ,  $-(CH_2)_n-N(R)-C(O)-(CH_2)_p-$ , with  $n'$  representing an integer between 0 and 3 inclusive; preferentially,  $n'$  is equal to 0, 2, 3;  $p$  representing an integer between 0 and 4 inclusive,  $n''$  representing an integer between 0 and 3 inclusive and especially  $n'=n''=p=0$  and  $R$  representing a hydrogen atom or a  $C_1$ - $C_6$  alkyl group;
- $An^-$  represents an anionic counterion;
- $Y$  is as defined previously;

it being understood that when the compound of formula (XVI) or (XVI') contains other cationic parts, it is combined with one or more anionic counterions that afford formula (XVI) or (XVI') electrical neutrality.

According to another particular mode of the invention, the dyes of the invention belong to formula (XVIa) or (XVI'a):



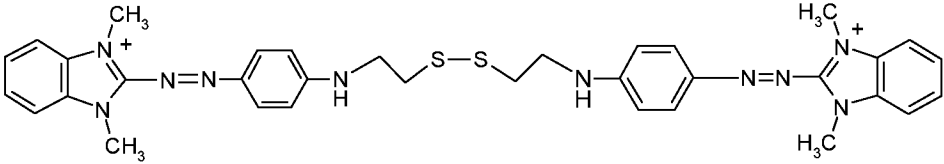
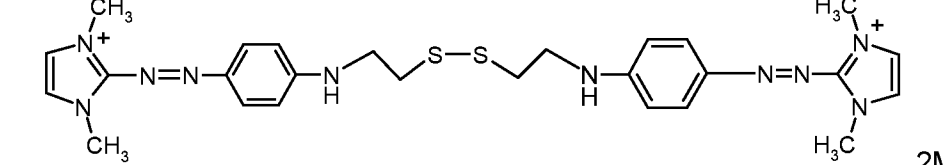
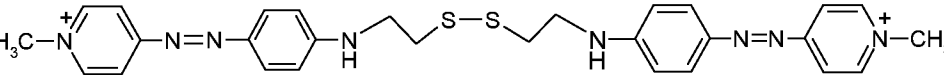
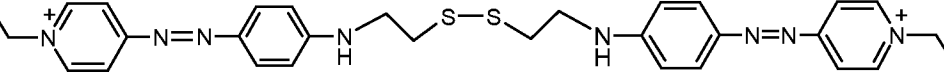
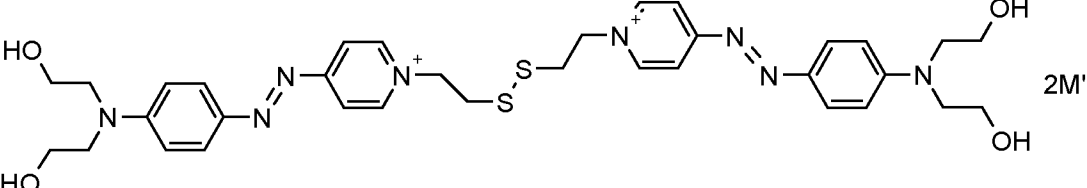
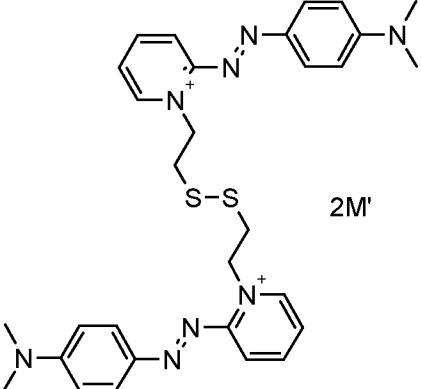
in which formulae (Ia) and (Ib):

- $R'_1$  represents a  $C_1$ - $C_4$  alkyl group substituted with one or more hydroxyl groups, particularly with only one hydroxyl group, or  $-C(O)OR'$  with  $R'$  representing a hydrogen atom, a  $C_1$ - $C_4$  alkyl group or a group  $-C(O)-O^-$  and, in the latter case, an anionic counterion  $An^-$  is absent; preferentially,  $R'_1$  represents a  $C_1$ - $C_4$  alkyl group substituted with a hydroxyl group;
- $R'_2$  represents a  $C_1$ - $C_4$  alkyl group optionally substituted with one or more hydroxyl groups, particularly with only one hydroxyl group; more particularly,  $R'_1$  and  $R'_2$  are identical;
- $An^-$  represents an anionic counterion as defined previously;

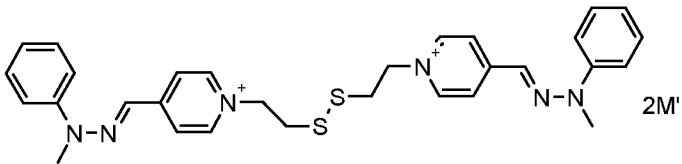
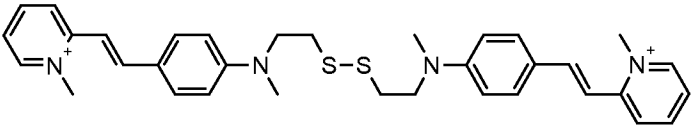
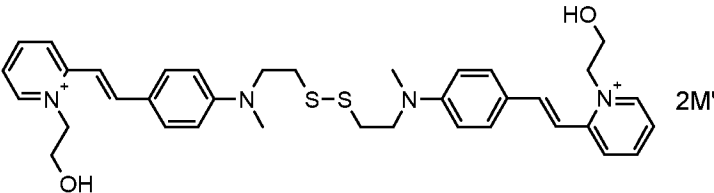
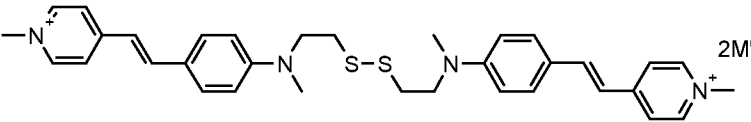
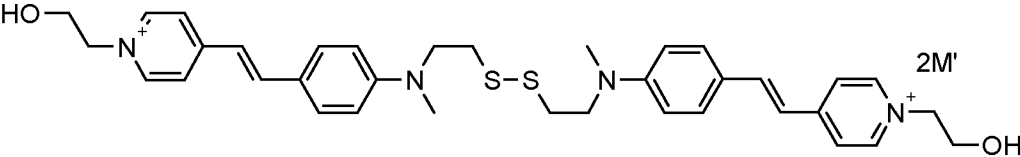
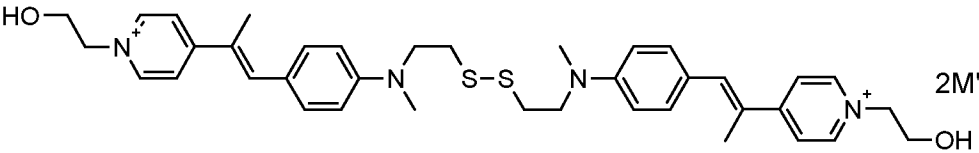
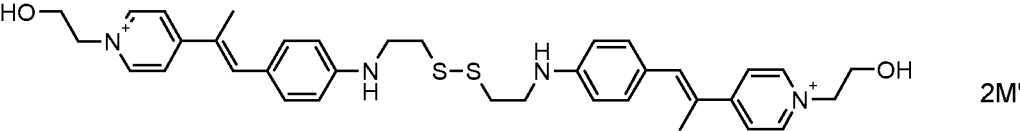
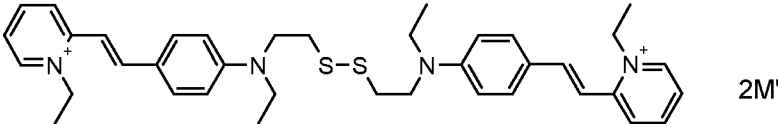
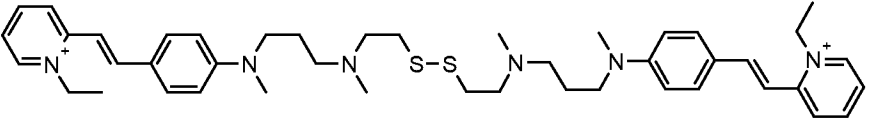
- B represents a divalent amido group -C(O)-N(R)-, -N(R)-C(O)-, with R representing a hydrogen atom or a group (C<sub>1</sub>-C<sub>6</sub>)alkyl; preferentially, R=H;
- n and m, which may be identical or different, represent an integer between 1 and 4 inclusive; preferentially, n is equal to 3 and m is equal to 2;
- Y is as defined previously;

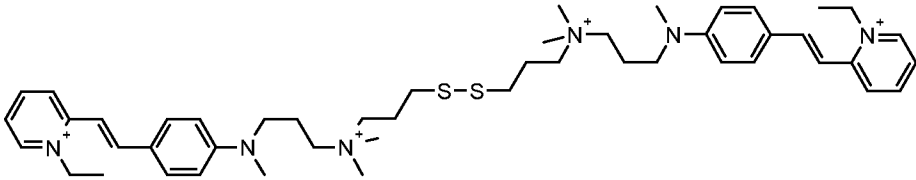
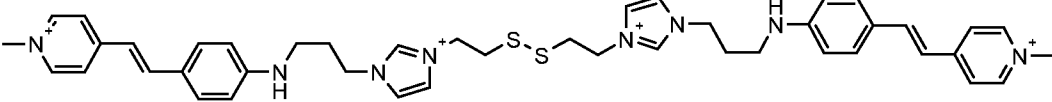
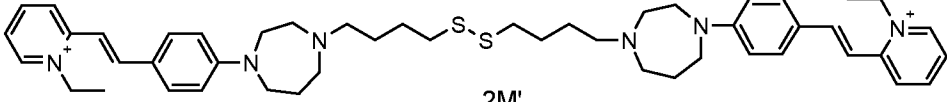
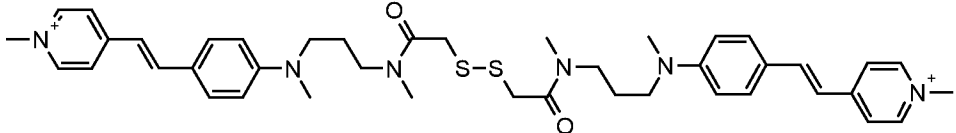
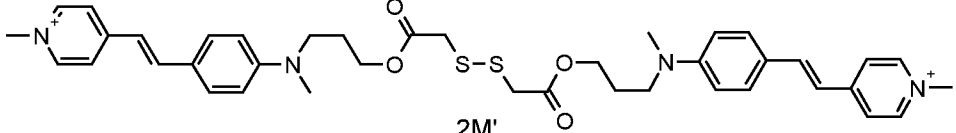
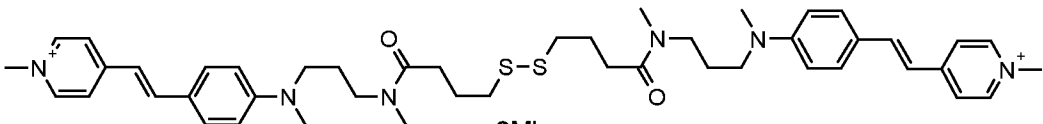
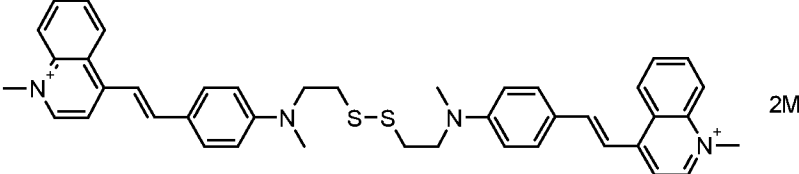
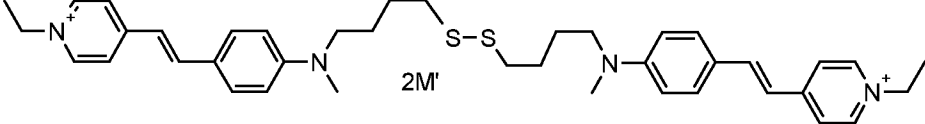
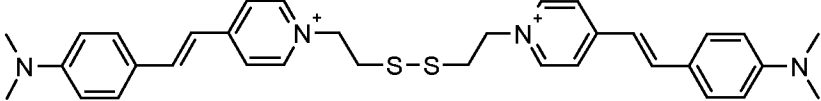
it being understood that the bond between the pyridinium ring and the double bond of the ethylene or styryl group is located in position 2 or 4 of the pyridinium, preferentially at 4.

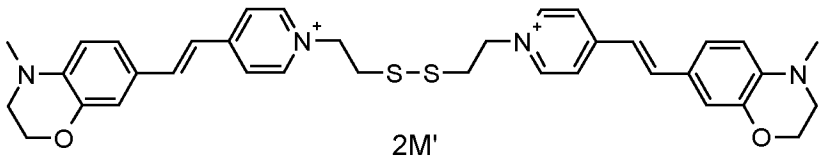
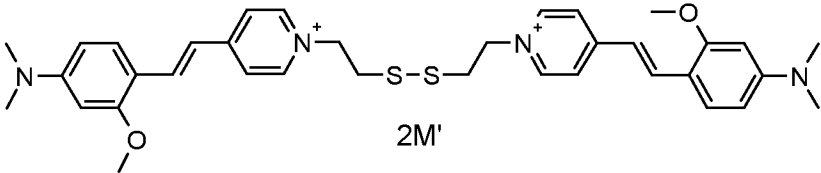
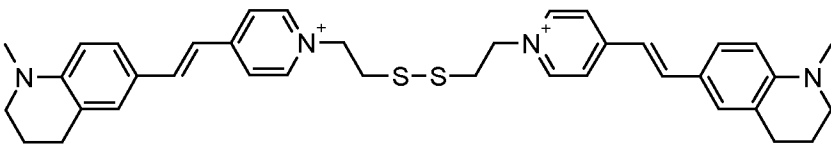
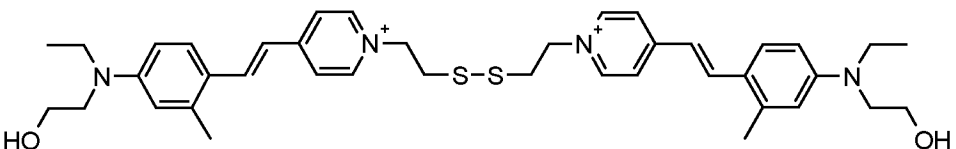
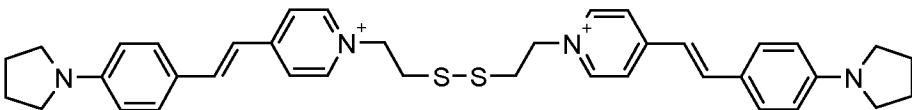
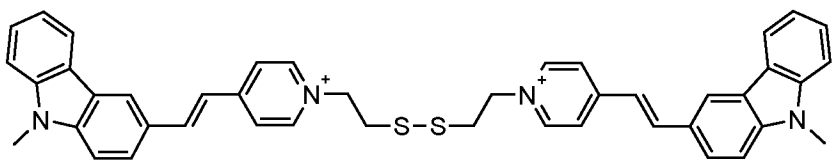
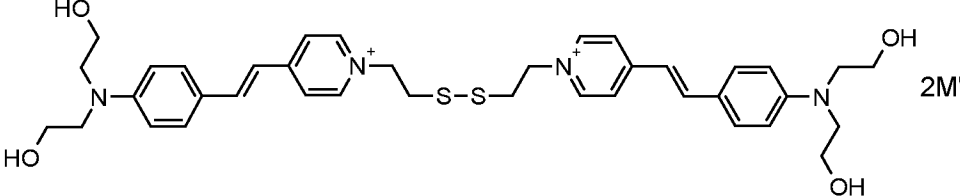
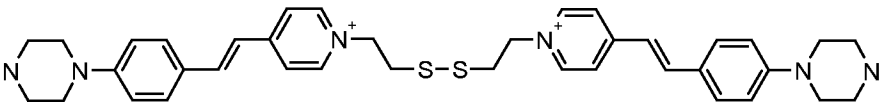
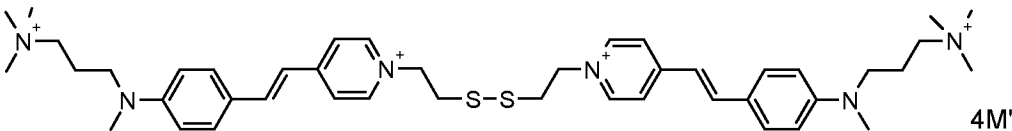
As examples of disulfide, thiol and protected-thiol direct dyes of formula (I) of the invention, mention may be made of those having the following chemical structures:

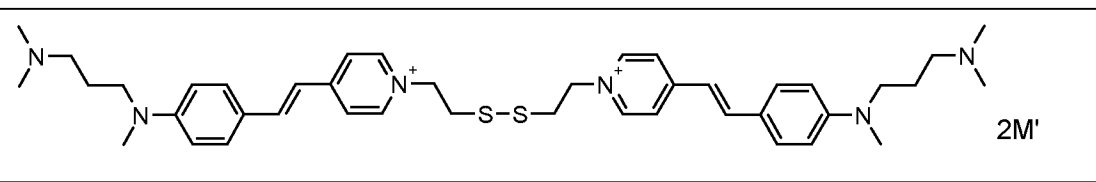
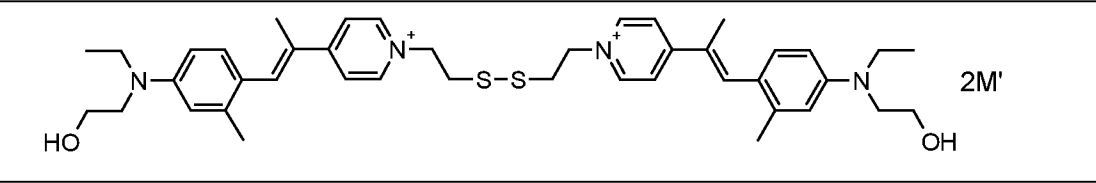
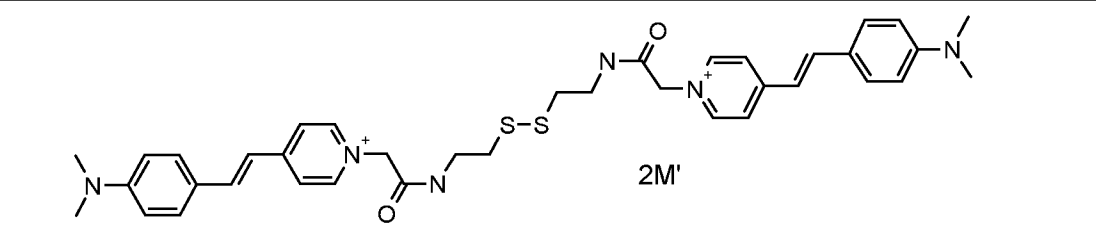
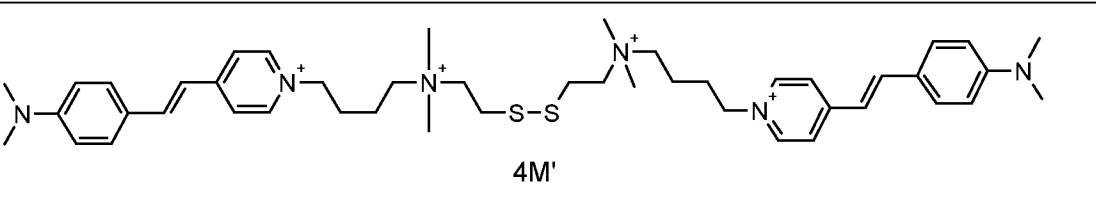
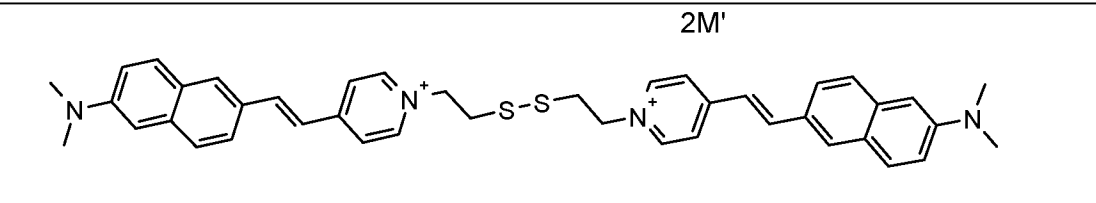
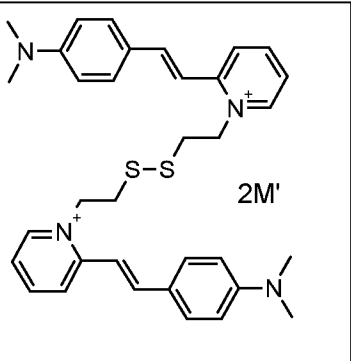
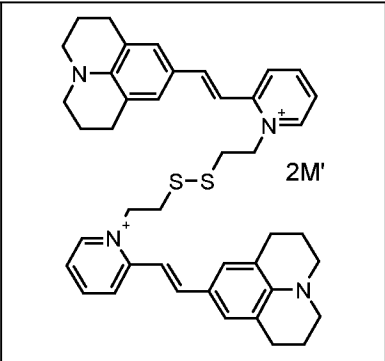
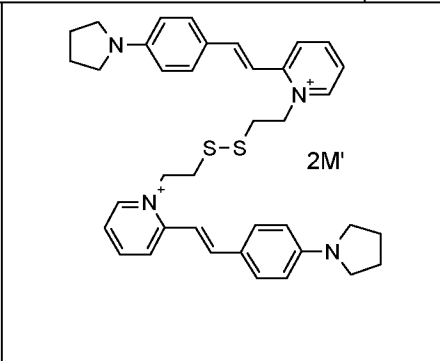
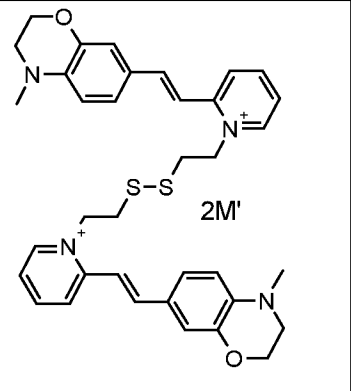
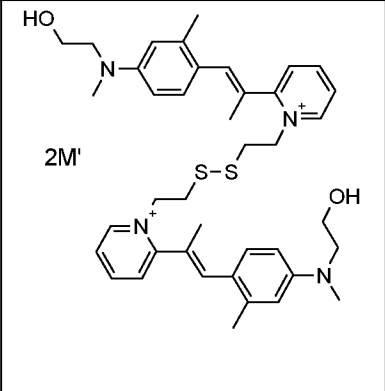
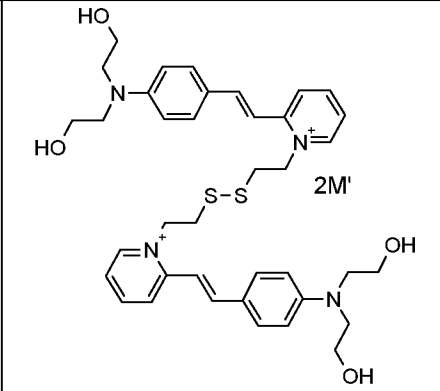
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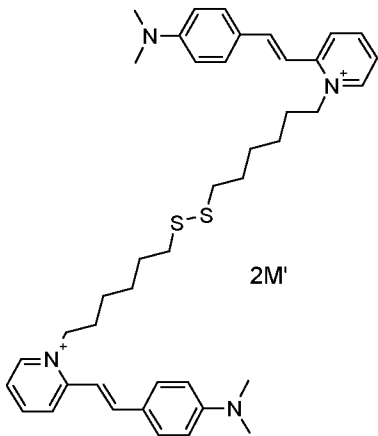
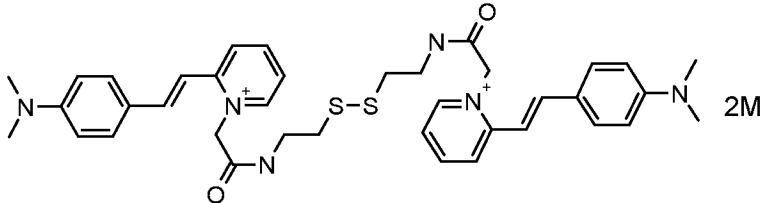
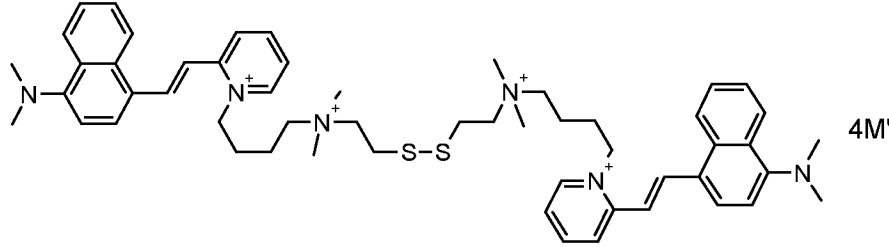
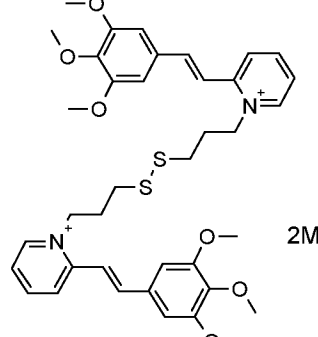
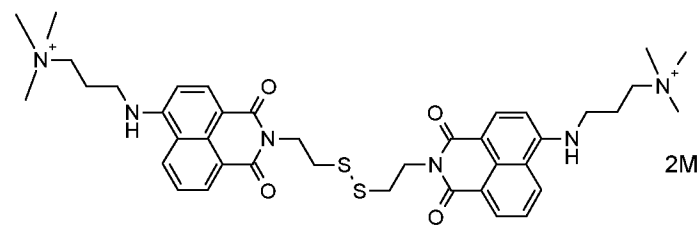
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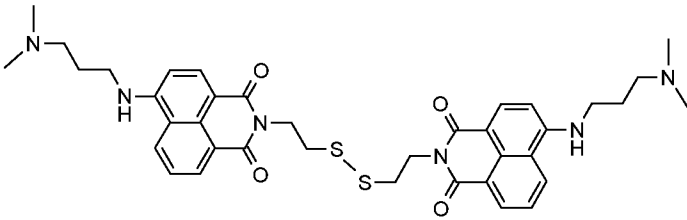
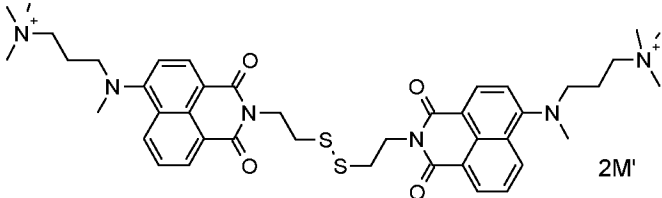
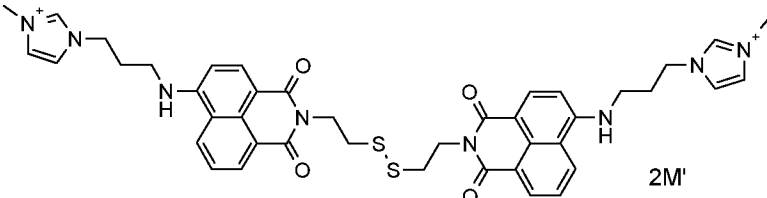
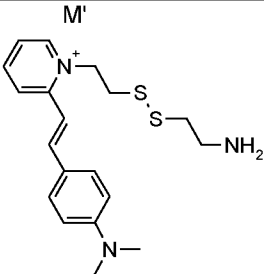
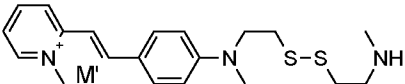
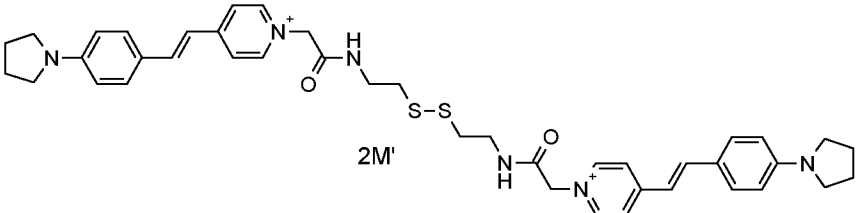
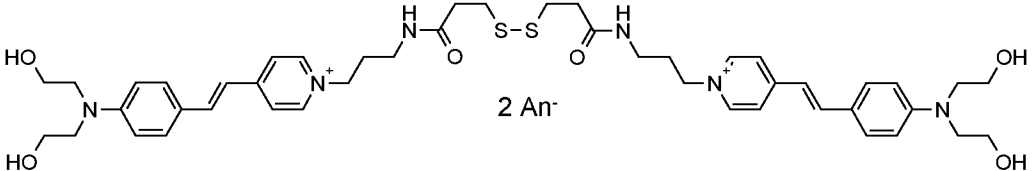
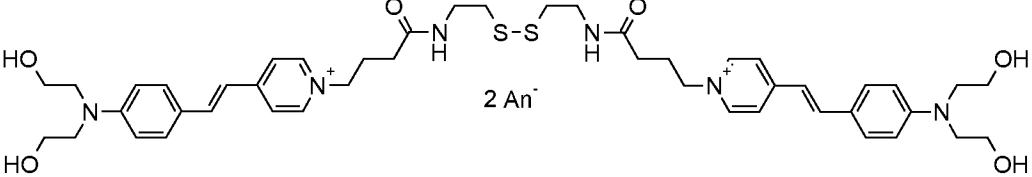
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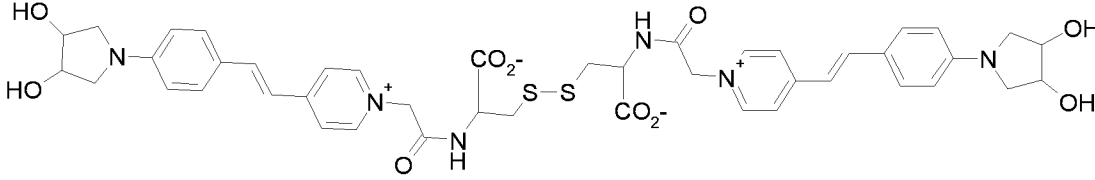
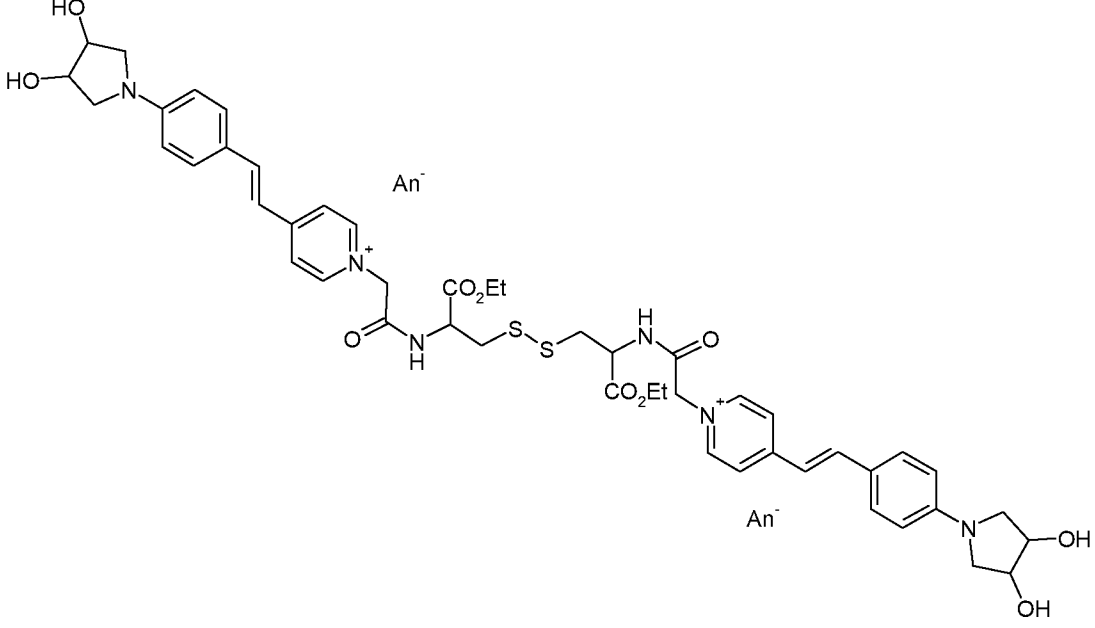
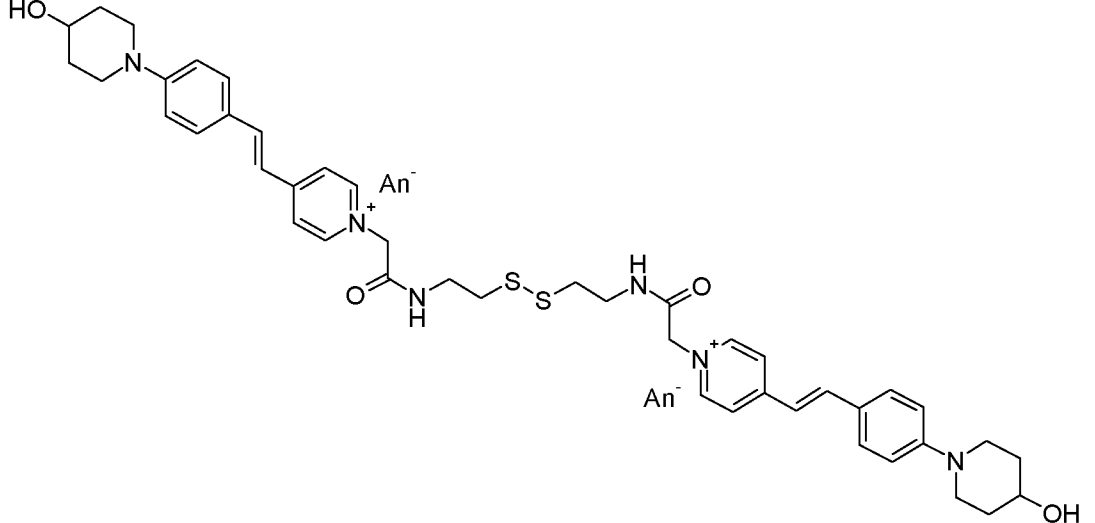
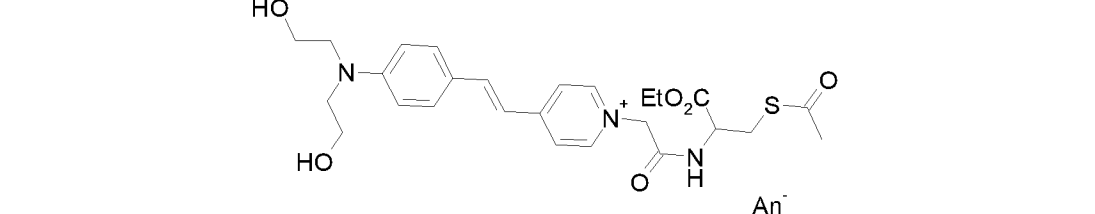
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 <p style="text-align: center;">2M'</p>	<u>32</u>
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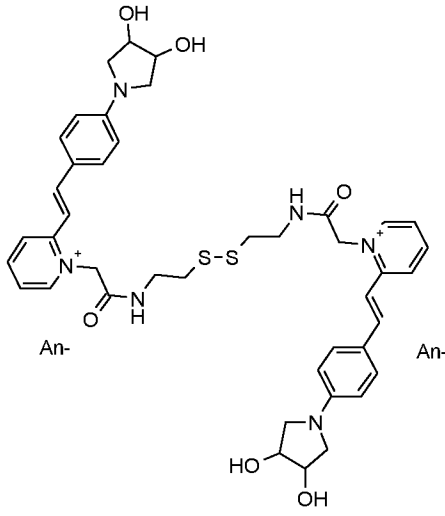
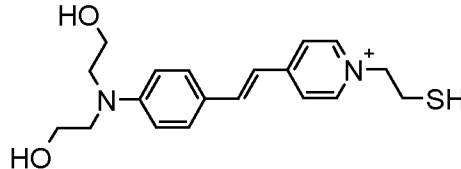
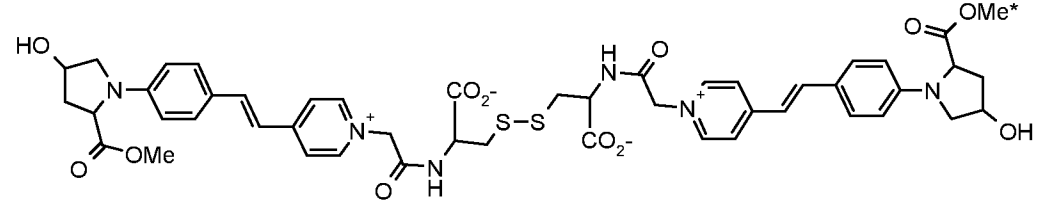
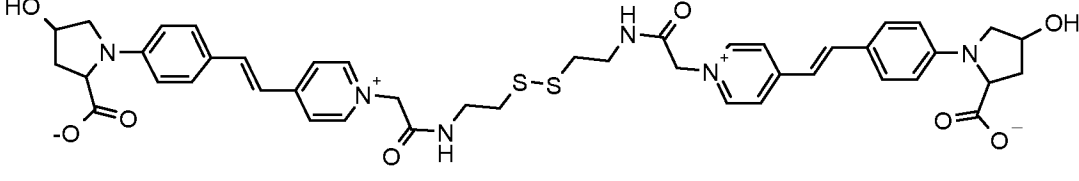
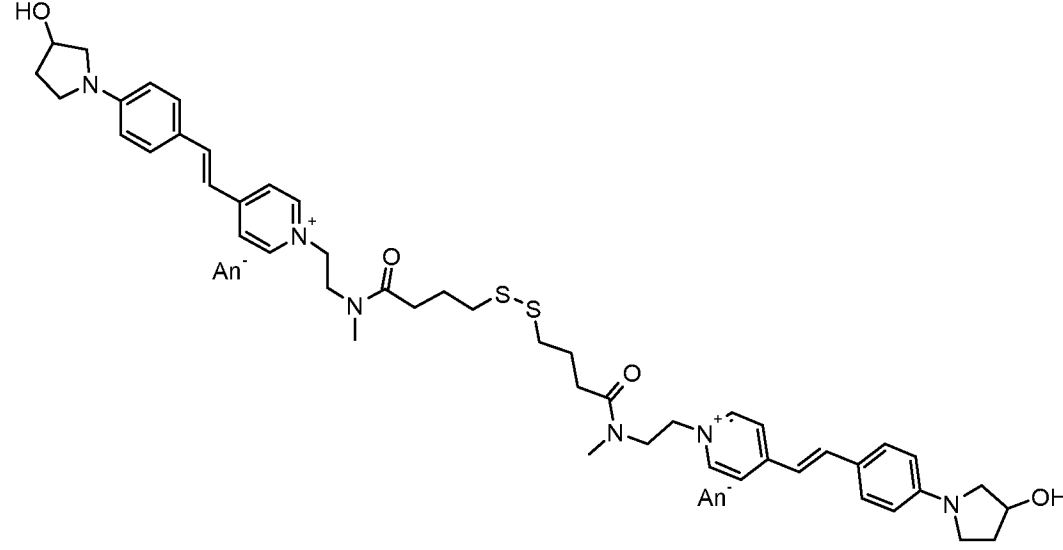
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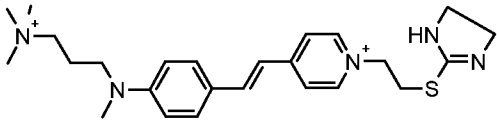
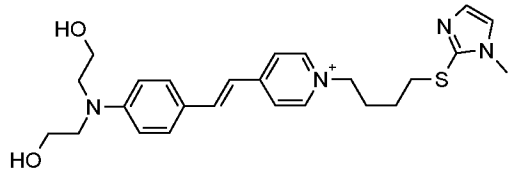
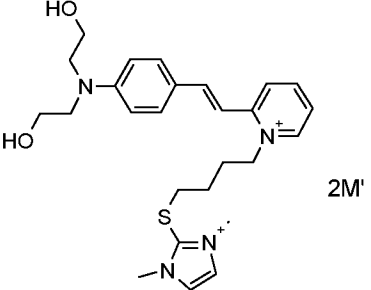
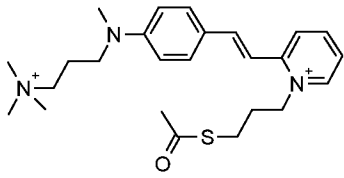
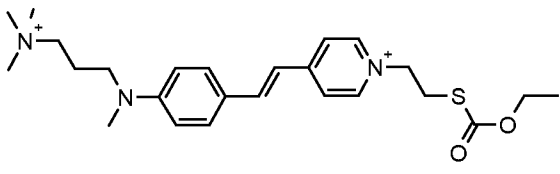
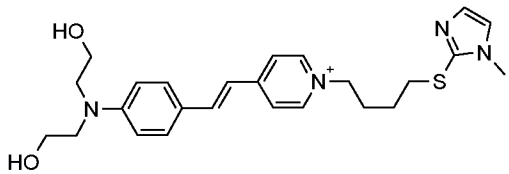
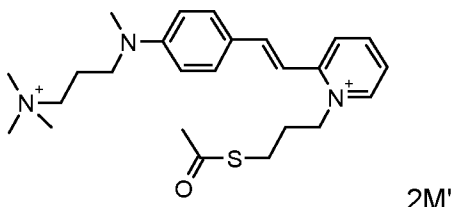
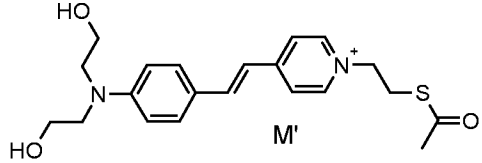
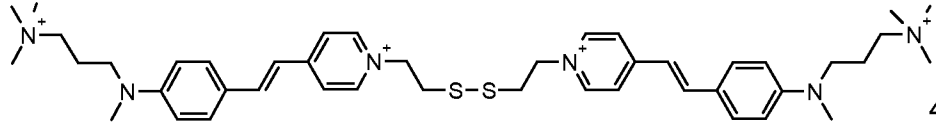
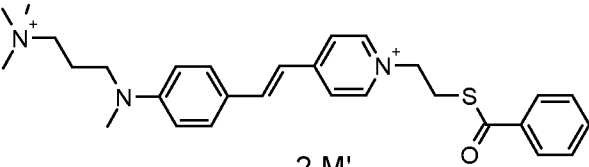
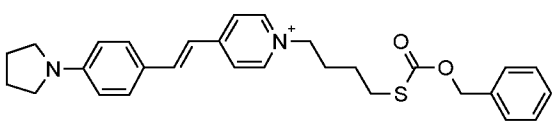
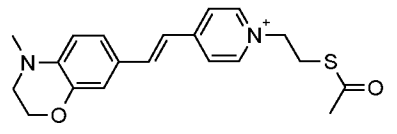
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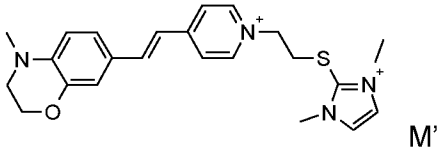
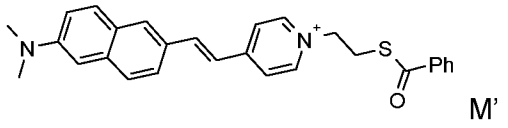
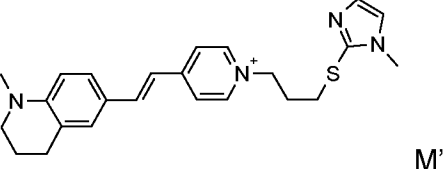
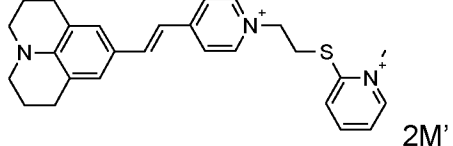
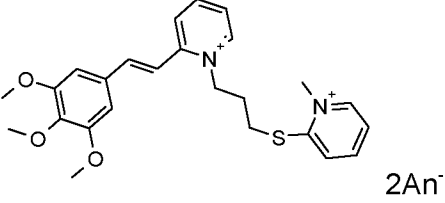
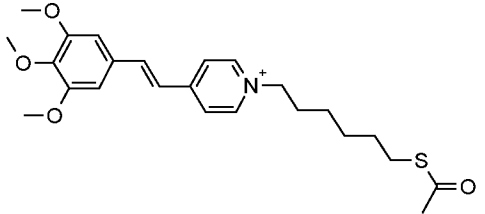
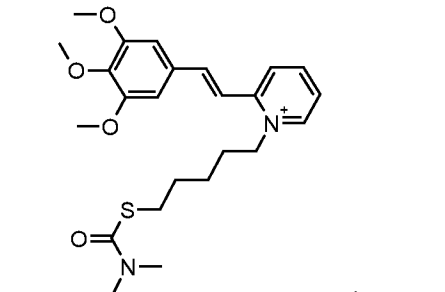
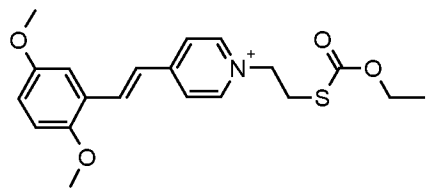
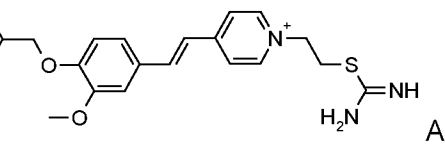
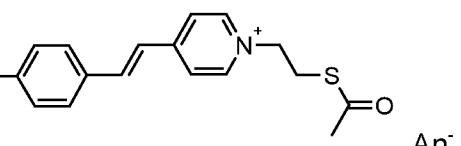
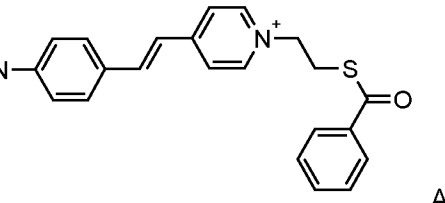
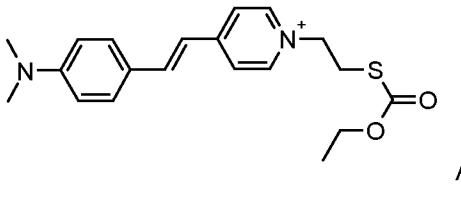
 <p>An-</p>	 <p>An-</p>
<p><b>75</b></p>	<p><b>76</b></p>
 <p>Me<sup>+</sup> represents an alkali metal or ½ an alkaline-earth metal; or a methyl</p>	<p><b>77</b></p>
	<p><b>78</b></p>
 <p>An<sup>-</sup></p> <p>An<sup>-</sup></p>	<p><b>79</b></p>

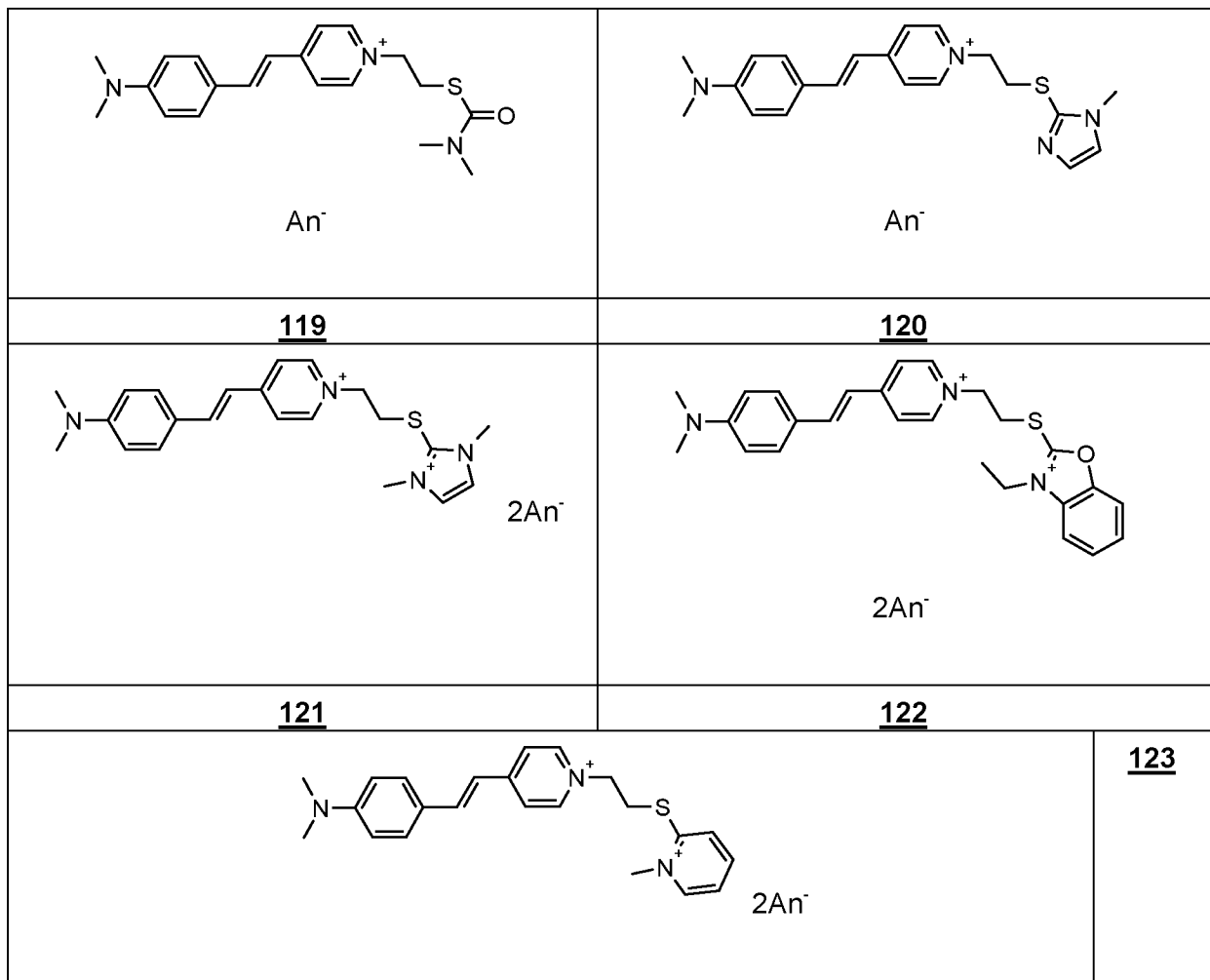
<p>Chemical structure 80: A bis-iminium salt. The left iminium ring is connected to a benzene ring with a bis(2-hydroxyethyl)amino group. The right iminium ring is connected to a benzene ring with a bis(2-hydroxyethyl)amino group. The two iminium rings are linked via a chain: -N<sup>+</sup>(CH<sub>2</sub>)<sub>4</sub>-C(=O)-CH<sub>2</sub>-CH<sub>2</sub>-S-S-CH<sub>2</sub>-CH<sub>2</sub>-C(=O)-N(CH<sub>2</sub>)<sub>4</sub>-.</p>	<b>80</b>
<p>Chemical structure 81: A bis-iminium salt. The left iminium ring is connected to a benzene ring with a bis(2-carboxyethyl)amino group. The right iminium ring is connected to a benzene ring with a bis(2-carboxyethyl)amino group. The two iminium rings are linked via a chain: -N<sup>+</sup>(CH<sub>2</sub>)<sub>4</sub>-C(=O)-NH-CH<sub>2</sub>-CH<sub>2</sub>-S-S-CH<sub>2</sub>-CH<sub>2</sub>-NH-C(=O)-CH<sub>2</sub>-CH<sub>2</sub>-.</p>	<b>81</b>

<p style="text-align: center;">2 An<sup>-</sup></p>	<p><b>82</b></p>
	<p style="text-align: center;">2 An<sup>-</sup></p>
<p><b>83</b></p>	<p><b>84</b></p>
<p style="text-align: center;">2M'</p>	<p><b>85</b></p>

<p style="text-align: right;">2M'</p>	<p><b>86</b></p>
<p style="text-align: right;">2M'</p>	<p><b>87</b></p>
<p style="text-align: right;">4M'</p>	<p style="text-align: right;">2M'</p>
<p><b>88</b></p>	<p><b>89</b></p>
<p style="text-align: right;">2M'</p>	<p style="text-align: right;">2M'</p>
<p><b>90</b></p>	<p><b>91</b></p>
<p style="text-align: right;">4M'</p>	<p style="text-align: right;">2M'</p>
<p><b>92</b></p>	<p><b>93</b></p>
<p style="text-align: right;">2M'</p>	<p style="text-align: right;">2M'</p>
<p><b>94</b></p>	<p><b>95</b></p>

 <p>2M'</p>	 <p>M'</p>
<p><b>96</b></p>	<p><b>97</b></p>
 <p>2M'</p>	 <p>2M'</p>
<p><b>98</b></p>	<p><b>99</b></p>
 <p>2M'</p>	 <p>M'</p>
<p><b>100</b></p>	<p><b>101</b></p>
 <p>2M'</p>	 <p>M'</p>
<p><b>102</b></p>	<p><b>102</b></p>
 <p>4M'</p>	<p><b>103</b></p>
 <p>2 M'</p>	<p><b>104</b></p>
 <p>M'</p>	 <p>M'</p>
<p><b>105</b></p>	<p><b>106</b></p>

 <p style="text-align: right;"><math>M'</math></p>	 <p style="text-align: right;"><math>M'</math></p>
<p><b>107</b></p>	<p><b>108</b></p>
 <p style="text-align: right;"><math>M'</math></p>	 <p style="text-align: right;"><math>2M'</math></p>
<p><b>109</b></p>	<p><b>110</b></p>
 <p style="text-align: right;"><math>2An^-</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>111</b></p>	<p><b>112</b></p>
 <p style="text-align: right;"><math>An^-</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>113</b></p>	<p><b>114</b></p>
 <p style="text-align: right;"><math>An^-</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>115</b></p>	<p><b>116</b></p>
 <p style="text-align: right;"><math>An</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>117</b></p>	<p><b>118</b></p>



with An<sup>-</sup> and M', which may be identical or different, preferentially identical, representing anionic counterions. More particularly, the anionic counterion is chosen from halides such as chloride, alkyl sulfates such as methyl sulfate, mesylate and  $\frac{1}{2} (\text{O}=\text{)}_2\text{SO}^{2-}$  or  $\frac{1}{2} \text{SO}_4^{2-}$ .

- 5 More preferentially, the dyes *j*) as defined previously are chosen from compounds **44**, **49**, **49a** and **55**, especially **44**, **49** and **55**.

10 According to one particularly advantageous embodiment of the invention, the dye *j*) is a dye comprising a "permanent" cationic charge, i.e. containing in its structure at least one quaternized nitrogen atom (ammonium) or quaternized phosphorus atom (phosphonium); preferentially quaternized nitrogen.

15 The composition according to the invention contains, in a cosmetic medium, an amount of dyes bearing a disulfide, thiol or protected-thiol function as defined previously, especially of formula (I) as defined previously, generally inclusively between 0.001% and 30% relative to the total weight of the composition.

Preferably, the amount of dyes bearing a disulfide, thiol or protected-thiol function as defined previously, especially of formula (I), is inclusively between 0.01% and 5% by

weight relative to the total weight of the composition. By way of example, the dye(s) are in an amount of between 0.01% and 2%.

*i).5). The cosmetically acceptable organic or mineral acid salt and counterion of the dyes of the invention.*

They are chosen from the "*organic or mineral acid salt*" and "*anionic counterion*" as defined previously.

Moreover, the addition salts that may be used in the context of the invention may be chosen from addition salts with a cosmetically acceptable base such as basifying agents as defined below, for instance alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, aqueous ammonia, amines or alkanolamines.

*ii) at least one fatty substance;*

The composition of the invention comprises one or more fatty substances. The fatty substances of the invention are not oxyalkylenated.

Preferably, the fatty substances of the invention are chosen from hydrocarbons, fatty alcohols, fatty esters, silicones and fatty ethers, or mixtures thereof.

The fatty substances of the invention may be liquid or non-liquid at room temperature (25°C) and at atmospheric pressure (760 mmHg; i.e.  $1.013 \times 10^5$  Pa).

The liquid fatty substances of the invention preferably have a viscosity of less than or equal to 2 Pa.s, better still less than or equal to 1 Pa.s and even better still less than or equal to 0.1 Pa.s at a temperature of 25°C and at a shear rate of  $1 \text{ s}^{-1}$ .

The term "liquid hydrocarbon" means a hydrocarbon composed solely of carbon and hydrogen atoms, which is liquid at ordinary temperature (25°C) and at atmospheric pressure (760 mmHg; i.e.  $1.013 \times 10^5$  Pa).

More particularly, the liquid hydrocarbons are chosen from:

- linear or branched, optionally cyclic, C<sub>6</sub>-C<sub>16</sub> lower alkanes. Examples that may be mentioned include hexane, undecane, dodecane, tridecane, and isoparaffins, for instance isohexadecane, isododecane and isodecane.

- linear or branched hydrocarbons of mineral, animal or synthetic origin, containing more than 16 carbon atoms, such as liquid paraffins, liquid petroleum jelly, polydecenes and hydrogenated polyisobutenes such as Parleam®, and squalane.

In one preferred variant, the liquid hydrocarbon(s) are chosen from liquid paraffins and liquid petroleum jelly.

The term "liquid fatty alcohol" means a non-glycerolated and non-oxyalkylenated fatty alcohol that is liquid at ordinary temperature (25°C) and at atmospheric pressure (760

mmHg; i.e.  $1.013 \times 10^5$  Pa).

Preferably, the liquid fatty alcohols of the invention comprise from 8 to 30 carbon atoms.

The liquid fatty alcohols of the invention may be saturated or unsaturated.

5 The saturated liquid fatty alcohols are preferably branched. They may optionally comprise in their structure at least one aromatic or non-aromatic ring. They are preferably acyclic.

More particularly, the liquid saturated fatty alcohols of the invention are chosen from octyldodecanol, isostearyl alcohol and 2-hexyldecanol.

10 Octyldodecanol is most particularly preferred.

These unsaturated liquid fatty alcohols exhibit, in their structures, at least one double or triple bond. Preferably, the fatty alcohols of the invention bear in their structure one or more double bonds. When several double bonds are present, there are preferably 2 or 3 of them, and they may be conjugated or unconjugated.

15 These unsaturated fatty alcohols may be linear or branched.

They may optionally comprise in their structure at least one aromatic or non-aromatic ring. They are preferably acyclic.

More particularly, the liquid unsaturated fatty alcohols of the invention are chosen from oleyl alcohol, linoleyl alcohol, linolenyl alcohol and undecylenyl alcohol.

20 Oleyl alcohol is most particularly preferred.

The term "liquid fatty ester" means an ester derived from a fatty acid and/or from a fatty alcohol and that is liquid at ordinary temperature ( $25^\circ\text{C}$ ) and at atmospheric pressure ( $760$  mmHg; i.e.  $1.013 \times 10^5$  Pa).

25 The esters are preferably liquid esters of saturated or unsaturated, linear or branched  $\text{C}_1\text{-C}_{26}$  aliphatic monoacids or polyacids and of saturated or unsaturated, linear or branched  $\text{C}_1\text{-C}_{26}$  aliphatic monoalcohols or polyalcohols, the total number of carbon atoms of the esters being greater than or equal to 10.

Preferably, for the esters of monoalcohols, at least one from among the alcohol and the acid from which the esters of the invention are derived is branched.

30 Among the monoesters of monoacids and of monoalcohols, mention may be made of ethyl palmitate, isopropyl palmitate, alkyl myristates such as isopropyl myristate or ethyl myristate, isocetyl stearate, 2-ethylhexyl isononanoate, isodecyl neopentanoate and isostearyl neopentanoate.

35 Esters of  $\text{C}_4\text{-C}_{22}$  dicarboxylic or tricarboxylic acids and of  $\text{C}_1\text{-C}_{22}$  alcohols and esters of monocarboxylic, dicarboxylic or tricarboxylic acids and of non-sugar  $\text{C}_4\text{-C}_{26}$  dihydroxy, trihydroxy, tetrahydroxy or pentahydroxy alcohols may also be used.

40 Mention may especially be made of: diethyl sebacate; diisopropyl sebacate; bis(2-ethylhexyl) sebacate; diisopropyl adipate; di-n-propyl adipate; dioctyl adipate; bis(2-ethylhexyl) adipate; diisostearyl adipate; bis(2-ethylhexyl) maleate; triisopropyl citrate; triisocetyl citrate; triisostearyl citrate; glyceryl trilactate; glyceryl trioctanoate; trioctyldodecyl citrate; trioleyl citrate; neopentyl glycol diheptanoate; diethylene glycol diisononanoate.

The composition may also comprise, as liquid fatty ester, sugar esters and diesters of C<sub>6</sub>-C<sub>30</sub> and preferably C<sub>12</sub>-C<sub>22</sub> fatty acids. It is recalled that the term "sugar" means oxygen-bearing hydrocarbon-based compounds containing several alcohol functions, with or without aldehyde or ketone functions, and which comprise at least 4 carbon atoms.

5 These sugars may be monosaccharides, oligosaccharides or polysaccharides.

Examples of suitable sugars that may be mentioned include sucrose (or saccharose), glucose, galactose, ribose, fucose, maltose, fructose, mannose, arabinose, xylose and lactose, and derivatives thereof, especially alkyl derivatives, such as methyl derivatives, for instance methylglucose.

10 The sugar esters of fatty acids may be chosen especially from the group comprising the esters or mixtures of esters of sugars described previously and of linear or branched, saturated or unsaturated C<sub>6</sub>-C<sub>30</sub> and preferably C<sub>12</sub>-C<sub>22</sub> fatty acids. If they are unsaturated, these compounds may have one to three conjugated or non-conjugated carbon-carbon double bonds.

15 The esters according to this variant may also be selected from monoesters, diesters, triesters, tetraesters and polyesters, and mixtures thereof.

These esters may be, for example, oleates, laurates, palmitates, myristates, behenates, cocoates, stearates, linoleates, linolenates, caprates and arachidonates, or mixtures thereof such as, especially, oleopalmitate, oleostearate and palmitostearate

20 mixed esters.

More particularly, use is made of monoesters and diesters and especially sucrose, glucose or methylglucose monooleates or dioleates, stearates, behenates, oleopalmitates, linoleates, linolenates and oleostearates.

An example that may be mentioned is the product sold under the name Glucate® DO

25 by the company Amerchol, which is a methylglucose dioleate.

Finally, natural or synthetic esters of mono-, di- or triacids with glycerol may also be used.

Among these, mention may be made of plant oils.

As oils of plant origin or synthetic triglycerides that may be used in the composition of

30 the invention as liquid fatty esters, examples that may be mentioned include:

- triglyceride oils of plant or synthetic origin, such as liquid fatty acid triglycerides comprising from 6 to 30 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, sunflower oil, castor

35 oil, avocado oil, caprylic/capric acid triglycerides, for instance those sold by the company Stéarineries Dubois or those sold under the names Miglyol® 810, 812 and 818 by the company Dynamit Nobel, jojoba oil and shea butter oil.

Liquid fatty esters derived from monoalcohols will preferably be used as esters according to the invention.

40 Isopropyl myristate and isopropyl palmitate are particularly preferred.

The term "liquid silicone" means an organopolysiloxane that is liquid at ordinary

temperature (25°C) and at atmospheric pressure (760 mmHg; i.e.  $1.013 \times 10^5$  Pa).

Preferably, the silicone is chosen from liquid polydialkylsiloxanes, especially liquid polydimethylsiloxanes (PDMS) and liquid polyorganosiloxanes comprising at least one aryl group.

5 These silicones may also be organomodified. 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.

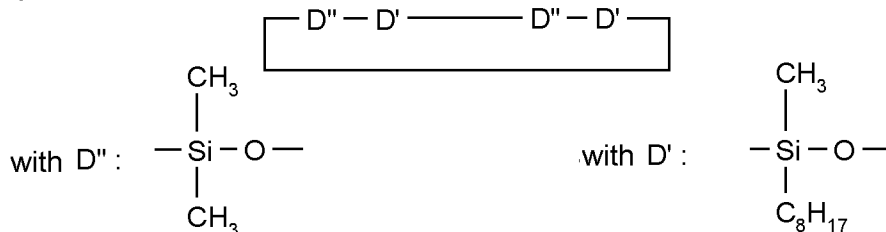
10 Organopolysiloxanes are defined in greater detail in Walter Noll's *Chemistry and Technology of Silicones* (1968), Academic Press. They may be volatile or non-volatile.

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:

(i) cyclic polydialkylsiloxanes comprising from 3 to 7 and preferably 4 to 5 silicon atoms.

15 These are, for example, octamethylcyclotetrasiloxane sold in particular under the name Volatile Silicone® 7207 by Union Carbide or Silbione® 70045 V2 by Rhodia, decamethylcyclopentasiloxane sold under the name Volatile Silicone® 7158 by Union Carbide, Silbione® 70045 V5 by Rhodia, and dodecamethylcyclopentasiloxane sold under the name Silsoft 1217 by Momentive Performance Materials, and mixtures thereof.

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



25 Mention may also be made of mixtures of cyclic polydialkylsiloxanes 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;

30 (ii) linear volatile polydialkylsiloxanes containing 2 to 9 silicon atoms and having a viscosity of less than or equal to  $5 \times 10^{-6}$  m<sup>2</sup>/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*, Vol. 91, Jan. 76, pp. 27-32, Todd & Byers, *Volatile Silicone Fluids for Cosmetics*. The viscosity of the silicones is measured at 25°C according to ASTM standard 445 Appendix C.

35 Non-volatile polydialkylsiloxanes may also be used.

These non-volatile silicones are more particularly chosen from polydialkylsiloxanes,

among which mention may be made mainly of polydimethylsiloxanes containing trimethylsilyl end groups.

Among these polydialkylsiloxanes, 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 mm<sup>2</sup>/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 polydimethylsiloxanes containing dimethylsilanol end groups known under the name dimethiconol (CTFA), such as the oils of the 48 series from the company Rhodia.

- 15 Among the silicones containing aryl groups are polydiarylsiloxanes, especially polydiphenylsiloxanes and polyalkylarylsiloxanes. Examples that may be mentioned include the products sold under the following names:

- the Silbione® oils of the 70 641 series from Rhodia;
- the oils of the Rhodorsil® 70 633 and 763 series from Rhodia;
- 20 - the oil Dow Corning 556 Cosmetic Grade Fluid from Dow Corning;
- the silicones of the PK series from Bayer, such as the product PK20;
- certain oils of the SF series from General Electric, such as SF 1023, SF 1154, SF 1250 and SF 1265.

- 25 The organomodified liquid silicones may especially contain polyethyleneoxy and/or polypropyleneoxy groups. Mention may thus be made of the silicone KF-6017 proposed by Shin-Etsu, and the oils Silwet® L722 and L77 from the company Union Carbide.

The liquid fatty acids are preferably unsaturated and/or branched fatty acids. Mention may be made in particular of oleic acid.

The liquid fatty ethers are chosen from liquid dialkyl ethers such as dicaprylyl ether.

- 30 The fatty substances may be non-liquid at room temperature and at atmospheric pressure.

The term "non-liquid" preferably means a solid compound or a compound that has a viscosity of greater than 2 Pa.s at a temperature of 25°C and at a shear rate of 1 s<sup>-1</sup>.

- 35 More particularly, the non-liquid fatty substances are chosen from fatty alcohols, fatty acid and/or fatty alcohol esters, nonsilicone waxes, silicones or fatty ethers which are non-liquid and preferably solid.

- The non-liquid fatty alcohols that are suitable for use in the invention are more particularly chosen from saturated or unsaturated, linear or branched alcohols comprising from 8 to 30 carbon atoms. Mention may be made, for example, of cetyl alcohol, stearyl alcohol and a mixture thereof (cetylstearyl alcohol).
- 40

As regards the non-liquid esters of fatty acids and/or of fatty alcohols, mention may

be made especially of solid esters derived from C<sub>9</sub>-C<sub>26</sub> fatty acids and from C<sub>9</sub>-C<sub>26</sub> fatty alcohols.

Among these esters, mention may be made of octyldodecyl behenate; isocetyl behenate; cetyl lactate; stearyl octanoate; octyl octanoate; cetyl octanoate; decyl oleate; myristyl stearate; octyl palmitate; octyl pelargonate; octyl stearate; alkyl myristates such as cetyl, myristyl or stearyl myristate; hexyl stearate.

Still within the context of this variant, esters of C<sub>4</sub>-C<sub>22</sub> dicarboxylic or tricarboxylic acids and of C<sub>1</sub>-C<sub>22</sub> alcohols and esters of monocarboxylic, dicarboxylic or tricarboxylic acids and of C<sub>2</sub>-C<sub>26</sub> dihydroxy, trihydroxy, tetrahydroxy or pentahydroxy alcohols may also be used.

Mention may be made especially of: diethyl sebacate; diisopropyl sebacate; diisopropyl adipate; di-n-propyl adipate; dioctyl adipate; dioctyl maleate.

Among all the additional esters mentioned above, it is preferred to use myristyl, cetyl or stearyl palmitates, alkyl myristates such as cetyl myristate, and stearyl myristyl myristate.

The (non-silicone) 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 starting materials that may be used according to the invention are especially marine waxes such as the product sold by the company Sophim under the reference M82, and polyethylene waxes or polyolefin waxes in general.

The non-liquid silicones in accordance with the invention may be present in the form of waxes, resins or gums.

Preferably, the non-liquid silicone is chosen from polydialkylsiloxanes, especially polydimethylsiloxanes (PDMS), and organomodified polysiloxanes comprising at least one functional group chosen from poly(oxyalkylene) groups, amino groups and alkoxy groups.

The silicone gums that can be used in accordance with the invention are especially polydialkylsiloxanes and preferably polydimethylsiloxanes with 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.

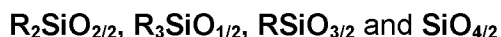
Products that can be used more particularly in accordance with the invention are mixtures such as:

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

- 5 - 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 m<sup>2</sup>/s and of an oil SF 96 with a viscosity of 5×10<sup>-6</sup> m<sup>2</sup>/s. This product preferably comprises 15% of gum SE 30 and 85% of an oil SF 96.

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



in which formulae:

15 **R** represents an alkyl containing 1 to 16 carbon atoms. Among these products, the ones that are particularly preferred are those in which **R** denotes a C<sub>1</sub>-C<sub>4</sub> lower alkyl group, more particularly methyl.

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.

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

The additional organomodified silicones include the polyorganosiloxanes containing:

- 25 - substituted or unsubstituted amine groups, for instance the products sold under the names Q2 8220 and Dow Corning 929 or 939 by the company Dow Corning. The substituted amine groups are, in particular, C<sub>1</sub>-C<sub>4</sub> aminoalkyl groups;
- alkoxy groups, such as the product sold under the name Abil Wax® 2428, 2434 and 2440 by the company Goldschmidt.

30 The non-liquid fatty ethers are chosen from dialkyl ethers and especially dicetyl ether and distearyl ether, alone or as a mixture.

Preferably, the compositions of the invention contain one or more fatty substances that are liquid at ordinary temperature (25°C) and at atmospheric pressure (760 mmHg; i.e. 1.013×10<sup>5</sup> Pa), optionally combined with one or more fatty substances that are non-liquid under the same conditions.

35 Preferably, the fatty substance is chosen from liquid petroleum jelly, polydecenes and liquid esters, or mixtures thereof.

40 The fatty substance(s) used in the composition according to the present invention may be present in the composition in an amount ranging from 25% to 90%, preferably in an amount ranging from 30% to 80% and even more preferentially in an amount ranging from

35% to 70% by weight relative to the total weight of the composition.

iii) at least one alkaline agent:

5 The composition according to the invention comprises one or more alkaline agents. This agent may be chosen from mineral or organic or hybrid alkaline agents, or mixtures thereof.

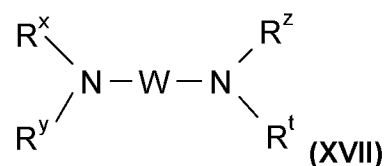
The mineral alkaline agent(s) are preferably chosen from aqueous ammonia, alkali carbonates or bicarbonates such as sodium or potassium carbonates and sodium or potassium bicarbonates, sodium hydroxide or potassium hydroxide, or mixtures thereof.

10 According to one advantageous embodiment of the invention, the alkaline agent(s) are organic amines, i.e. they contain at least one substituted or unsubstituted amino group.

The organic alkaline agent(s) are preferentially chosen from organic amines with a  $pK_b$  at 25°C of less than 12, preferably less than 10 and even more advantageously less than 6. It should be noted that it is the  $pK_b$  corresponding to the function of highest basicity.

Hybrid compounds that may be mentioned include the salts of the amines mentioned previously with acids such as carbonic acid or hydrochloric acid.

The organic alkaline agent(s) are chosen, for example, from alkanolamines, oxyethylenated and/or oxypropylenated ethylenediamines, amino acids and the compounds of formula (XVII) below:



in which formula (XVII):

- **W** is a divalent  $C_1$ - $C_6$  alkylene radical optionally substituted with a hydroxyl group or a  $C_1$ - $C_6$  alkyl radical, and/or optionally interrupted with one or more heteroatoms such as oxygen or  $NR^u$ ;
- **R<sup>x</sup>**, **R<sup>y</sup>**, **R<sup>z</sup>**, **R<sup>t</sup>** and **R<sup>u</sup>**, which may be identical or different, represent a hydrogen atom or a  $C_1$ - $C_6$  alkyl,  $C_1$ - $C_6$  hydroxyalkyl or  $C_1$ - $C_6$  aminoalkyl radical.

Examples of such amines that may be mentioned include 1,3-diaminopropane, 1,3-diamino-2-propanol, spermine and spermidine.

30 The term "alkanolamine" means an organic amine comprising a primary, secondary or tertiary amine function, and one or more linear or branched  $C_1$ - $C_8$  alkyl groups bearing one or more hydroxyl radicals.

Alkanolamines such as monoalkanolamines, dialkanolamines or trialkanolamines comprising from one to three identical or different  $C_1$ - $C_4$  hydroxyalkyl radicals are in particular suitable for performing the invention.

35 Among compounds of this type, mention may be made of monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, N-dimethylaminoethanolamine, 2-amino-2-methyl-1-propanol, triisopropanolamine, 2-amino-

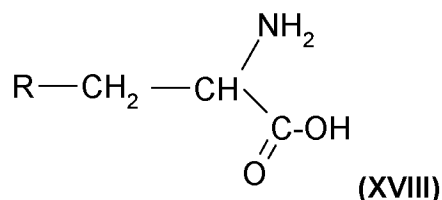
2-methyl-1,3-propanediol, 3-amino-1,2-propanediol, 3-dimethylamino-1,2-propanediol and tris(hydroxymethylamino)methane.

More particularly, the amino acids that may be used are of natural or synthetic origin, in their L, D or racemic form, and comprise at least one acid function chosen more particularly from carboxylic acid, sulfonic acid, phosphonic acid or phosphoric acid functions. The amino acids may be in neutral or ionic form.

As amino acids that may be used in the present invention, mention may be made especially of aspartic acid, glutamic acid, alanine, arginine, ornithine, citrulline, asparagine, carnitine, cysteine, glutamine, glycine, histidine, lysine, isoleucine, leucine, methionine, N-phenylalanine, proline, serine, taurine, threonine, tryptophan, tyrosine and valine.

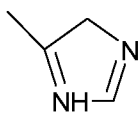
Advantageously, the amino acids are basic amino acids comprising an additional amine function optionally included in a ring or in a ureido function.

Such basic amino acids are preferably chosen from those corresponding to formula (XVIII) below:

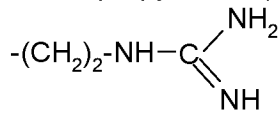


in which formula (XVIII):

- R denotes a group chosen from:



, aminopropyl:  $-(\text{CH}_2)_3-\text{NH}_2$ , aminoethyl  $-(\text{CH}_2)_2-\text{NH}_2$ ,



$-(\text{CH}_2)_2-\text{NH}-\text{C}(\text{O})-\text{NH}_2$  and

The compounds corresponding to formula (XVIII) are histidine, lysine, arginine, ornithine and citrulline.

The organic amine may also be chosen from organic amines of heterocyclic type. Besides histidine that has already been mentioned in the amino acids, mention may be made in particular of pyridine, piperidine, imidazole, triazole, tetrazole and benzimidazole.

The organic amine may also be chosen from amino acid dipeptides. As amino acid dipeptides that may be used in the present invention, mention may be made especially of carnosine, anserine and baleine.

The organic amine is chosen from compounds comprising a guanidine function. As amines of this type that may be used in the present invention, besides arginine, which has already been mentioned as an amino acid, mention may be made especially of creatine, creatinine, 1,1-dimethylguanidine, 1,1-diethylguanidine, glycoamine, metformin, agmatine, N-amidinoalanine, 3-guanidinopropionic acid, 4-guanidinobutyric acid and 2-([amino(imino)methyl]amino)ethane-1-sulfonic acid.

Mention may be made in particular of the use of guanidine carbonate or

monoethanolamine hydrochloride as hybrid compounds.

The composition of the invention preferably contains one or more alkanolamines and/or one or more basic amino acids, more advantageously one or more alkanolamines. More preferentially still, the organic amine is monoethanolamine.

5 According to one particular embodiment, the composition of the invention comprises, as alkaline agent, one or more alkanolamines.

Preferably, the alkanolamine is ethanolamine (or monoethanolamine).

10 In one variant of the invention, the composition comprises, as alkaline agent, one or more alkanolamines (preferably ethanolamine) and aqueous ammonia. In this variant, the alkanolamine(s) are present in a predominant amount relative to the aqueous ammonia.

Advantageously, the composition according to the invention has a content of alkaline agent(s) ranging from 0.01% to 30% by weight, preferably from 0.1% to 20% by weight and better still from 1% to 10% by weight relative to the weight of the said composition.

15 iv) at least one reducing agent.

The composition of the invention comprises one or more reducing agents.

20 Preferably, the reducing agent(s) are chosen from thiols such as thioglycolic acid, thiolactic acid, 3-mercaptopropionic acid, thiomalic acid, 2,3-dimercaptosuccinic acid, cysteine, N-glycyl-L-cysteine, L-cysteinylglycine and also esters and salts thereof, thioglycerol, cysteamine and C<sub>1</sub>-C<sub>4</sub> acyl derivatives thereof, N-mesylycysteamine, N-acetylcysteine, N-mercaptoalkylamides of sugars such as N-(mercapto-2-ethyl) gluconamide, pantetheine, N-(mercaptoalkyl)- $\omega$ -hydroxyalkylamides, for example those described in patent application EP-A-354 835, N-mono- or N,N-dialkylmercapto-4-  
25 butyramides, for example those described in patent application EP-A-368 763, aminomercaptoalkyl amides, for example those described in patent application EP-A-432 000, N-(mercaptoalkyl)succinamic acids and N-(mercaptoalkyl)succinimides, for example those described in patent application EP-A-465 342, alkylamino mercaptoalkyl amides, for example those described in patent application EP-A-514 282, the azeotropic mixture of 2-  
30 hydroxypropyl thioglycolate and of (2-hydroxy-1-methyl)ethyl thioglycolate as described in patent application FR-A-2 679 448, mercaptoalkylamino amides, for example those described in patent application FR-A-2 692 481, and N-mercaptoalkylalkanediamides, for example those described in patent application EP-A-653 202.

35 The reducing agent may alternatively be chosen from hydrides such as sodium or potassium borohydride or alkali metal or alkaline-earth metal sulfites or bisulfites; or alternatively from phosphorus derivatives such as phosphines or phosphites.

The reducing agent(s) are preferably chosen from thiols.

The preferred reducing agents are thioglycolic acid and cysteine, or salts thereof. The reducing agent is preferably used as an aqueous solution.

40 In general, the concentration of reducing agent(s) is inclusively between 0.01% and 30% by weight, preferably between 0.1% and 25% by weight and more particularly

between 0.5% and 10% by weight relative to the total weight of the composition applied to the keratin fibres.

v) optionally at least one oxidizing agent

5

The composition according to the invention may also comprise one or more chemical oxidizing agent(s). The term "*chemical oxidizing agent*" means an oxidizing agent other than atmospheric oxygen.

10 The chemical oxidizing agents are for example chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts, for instance persulfates, perborates, peracids and precursors thereof and percarbonates of alkali metals or alkaline-earth metals. Advantageously, the oxidizing agent is hydrogen peroxide.

15 The content of oxidizing agent(s) more particularly represents from 0.1% to 20% by weight and preferably from 0.5% to 10% by weight relative to the weight of the composition containing them.

vi) optionally at least one thickening organic polymer;

20 The composition according to the invention may also contain *vi)* one or more thickening organic polymers.

25 The term "*thickening polymer*" means a polymer which, when introduced at 1% by weight in an aqueous solution or an aqueous-alcoholic solution containing 30% ethanol, and at pH 7, or in an oil chosen from liquid petroleum jelly, isopropyl myristate or cyclopentadimethylsiloxane, makes it possible to achieve a viscosity of at least 100 cps and preferably of at least 500 cps, at 25°C and at a shear rate of 1 s<sup>-1</sup>. This viscosity may be measured using a cone/plate viscometer (Haake R600 rheometer or the like). The thickening polymers may thicken the aqueous phase and/or the fatty phase, preferentially the aqueous phase.

30 The term "*organic thickening polymer*" means a thickening polymer as defined previously, which is formed from carbon and hydrogen, and possibly nitrogen, oxygen, sulfur, halogens such as fluorine, chlorine or bromine, and also phosphorus, alkali metals such as sodium or potassium, or alkaline-earth metals such as magnesium or calcium. The organic polymers according to the invention do not comprise silicon.

35 The organic thickening polymers according to the invention may be of natural or synthetic origin.

The thickening polymers may be anionic, cationic, amphoteric or nonionic associative or non-associative polymers.

They may be thickeners for the aqueous or oily phases.

40 Aqueous-phase-thickening polymers that may be mentioned include non-associative thickening polymers bearing sugar units.

For the purposes of the present invention, the term "sugar unit" means a unit derived

from a carbohydrate of formula  $C_n(H_2O)_{n-1}$  or  $(CH_2O)_n$ , which may be optionally modified by substitution and/or by oxidation and/or by dehydration.

The sugar units that may be included in the composition of the thickening polymers of the invention are preferably derived from the following sugars:

- 5       ▪ glucose;
- galactose;
- arabinose;
- rhamnose;
- mannose;
- 10      ▪ xylose;
- fucose;
- anhydrogalactose;
- galacturonic acid;
- glucuronic acid;
- 15      ▪ mannuronic acid;
- galactose sulfate;
- anhydrogalactose sulfate and
- fructose.

20       Thickening polymers of the invention that may especially be mentioned include native gums such as:

- a) tree or shrub exudates, including:
  - 25       ▪ gum arabic (branched polymer of galactose, arabinose, rhamnose and glucuronic acid);
  - ghatti gum (polymer derived from arabinose, galactose, mannose, xylose and glucuronic acid);
  - karaya gum (polymer derived from galacturonic acid, galactose, rhamnose and glucuronic acid);
  - 30       ▪ gum tragacanth (or tragacanth) (polymer of galacturonic acid, galactose, fucose, xylose and arabinose);
- b) gums derived from algae, including:
  - 35       ▪ agar (polymer derived from galactose and anhydrogalactose);
  - alginates (polymers of mannuronic acid and of glucuronic acid);
  - carrageenans and furcellerans (polymers of galactose sulfate and of anhydrogalactose sulfate);
- c) gums derived from seeds or tubers, including:
  - 40       ▪ guar gum (polymer of mannose and galactose);
  - locust bean gum (polymer of mannose and galactose);
  - fenugreek gum (polymer of mannose and galactose);
  - tamarind gum (polymer of galactose, xylose and glucose);
  - konjac gum (polymer of glucose and mannose);

d) microbial gums, including:

- xanthan gum (polymer of glucose, mannose acetate, mannose/pyruvic acid and glucuronic acid);
- gellan gum (polymer of partially acylated glucose, rhamnose and glucuronic acid);
- 5 ▪ scleroglucan gum (glucose polymer);

e) plant extracts, including:

- cellulose (glucose polymer);
- starch (glucose polymer).
- inulin.

10

These polymers may be physically or chemically modified. A physical treatment that may especially be mentioned is the temperature.

Chemical treatments that may be mentioned include esterification, etherification, amidation and oxidation reactions. These treatments can lead to polymers that may especially be nonionic, anionic or amphoteric.

15

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

The nonionic guar gums that may be used according to the invention may be modified with C<sub>1</sub>-C<sub>6</sub> (poly)hydroxyalkyl groups.

20

Among the C<sub>1</sub>-C<sub>6</sub> (poly)hydroxyalkyl groups that may be mentioned, for example, are hydroxymethyl, hydroxyethyl, hydroxypropyl and hydroxybutyl groups.

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

25

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

Such nonionic guar gums optionally modified with hydroxyalkyl groups are sold, for example, under the trade names Jaguar HP8, Jaguar HP60 and Jaguar HP120 by the company Rhodia Chimie.

30

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

35

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

Distarch phosphates or compounds rich in distarch phosphate will preferentially be used, for instance the products sold under the references Prejel VA-70-T AGGL (gelatinized hydroxypropyl cassava distarch phosphate), Prejel TK1 (gelatinized cassava distarch phosphate) and Prejel 200 (gelatinized acetyl cassava distarch phosphate) by the

40

company Avebe, or Structure Zea from National Starch (gelatinized corn distarch phosphate).

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

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

The non-associative thickening polymers of the invention may be cellulose-based polymers not comprising any C<sub>10</sub>-C<sub>30</sub> fatty chains in their structure.

According to the invention, the term "*cellulose-based polymer*" means any polysaccharide compound bearing in its structure sequences of glucose residues connected via  $\beta$ -1,4 bonds; besides unsubstituted celluloses, the cellulose derivatives may be anionic, cationic, amphoteric or nonionic.

Thus, the cellulose-based polymers of the invention may be chosen from unsubstituted celluloses, including those in a monocrystalline form, and cellulose ethers.

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

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

Among the nonionic cellulose ethers not containing a C<sub>10</sub>-C<sub>30</sub> fatty chain, i.e. "non-associative", mention may be made of (C<sub>1</sub>-C<sub>4</sub>)alkylcelluloses such as methylcelluloses and ethylcelluloses (for example Ethocel Standard 100 Premium from Dow Chemical); (poly)hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylcelluloses such as hydroxymethylcelluloses, hydroxyethylcelluloses (for example Natrosol 250 HHR sold by Aqualon) and hydroxypropylcelluloses (for example Klucel EF from Aqualon); mixed celluloses (poly)-hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl(C<sub>1</sub>-C<sub>4</sub>)alkylcelluloses such as hydroxypropyl methylcelluloses (for example Methocel E4M from Dow Chemical), hydroxyethyl methylcelluloses, hydroxyethyl ethylcelluloses (for example Bermocoll E 481 FQ from Akzo Nobel) and hydroxybutyl methylcelluloses.

Among the anionic cellulose ethers not containing a fatty chain, mention may be

made of (poly)carboxy(C<sub>1</sub>-C<sub>4</sub>)alkylcelluloses, and salts thereof. Examples that may be mentioned include carboxymethylcelluloses, carboxymethylmethylcelluloses (for example Blanose 7M from the company Aqualon) and carboxymethylhydroxyethylcelluloses, and the sodium salts thereof.

5 Among the cationic cellulose ethers not containing a fatty chain, mention may be made of cationic cellulose derivatives grafted with a water-soluble quaternary ammonium monomer, and disclosed in particular in US 4 131 576, such as (poly)hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl celluloses, for instance hydroxymethyl, hydroxyethyl or hydroxypropyl celluloses grafted in particular with a methacryloylethyltrimethylammonium, 10 methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt. The commercial products corresponding to this definition are more particularly the products sold under the names Celquat® L 200 and Celquat® H 100 by the company National Starch.

Among the nonassociative thickening polymers not bearing sugar units that may be used, mention may be made of crosslinked acrylic or methacrylic acid homopolymers or 15 copolymers, crosslinked 2-acrylamido-2-methylpropanesulfonic acid homopolymers and crosslinked acrylamide copolymers thereof, ammonium acrylate homopolymers, or copolymers of ammonium acrylate and of acrylamide, alone or mixtures thereof.

A first family of nonassociative thickening polymers that is suitable for use is 20 represented by crosslinked acrylic acid homopolymers.

Among the homopolymers of this type, mention may be made of those crosslinked with an allyl alcohol ether of the sugar series, such as, for example, the products sold under the names Carbopol 980, 981, 954, 2984 and 5984 by the company Noveon or the products sold under the names Synthalen M and Synthalen K by the company 3 VSA.

25 The nonassociative thickening polymers may also be crosslinked (meth)acrylic acid copolymers, such as the polymer sold under the name Aqua SF1 by the company Noveon.

The nonassociative thickening polymers may be chosen from crosslinked 2-acrylamido-2-methylpropanesulfonic acid homopolymers and the crosslinked acrylamide copolymers thereof.

30 Among the partially or totally neutralized crosslinked copolymers of 2-acrylamido-2-methylpropanesulfonic acid and of acrylamide, mention may be made in particular of the product described in Example 1 of document EP 503 853, and reference may be made to said document as regards these polymers.

The composition may similarly comprise, as nonassociative thickening polymers, 35 ammonium acrylate homopolymers or copolymers of ammonium acrylate and of acrylamide.

Among the ammonium acrylate homopolymers that may be mentioned is the product sold under the name Microsap PAS 5193 by the company Hoechst. Among the copolymers of ammonium acrylate and of acrylamide that may be mentioned is the product sold under 40 the name Bozopol C Nouveau or the product PAS 5193 sold by the company Hoechst. Reference may be made especially to documents FR 2 416 723, US 2 798 053 and US 2

923 692 as regards the description and preparation of such compounds.

Among the aqueous-phase thickening polymers, mention may also be made of the non-cellulose-based associative polymers that are well known to those skilled in the art and especially of nonionic, anionic, cationic or amphoteric nature.

It is recalled that "*associative polymers*" are polymers that are capable, in an aqueous medium, of reversibly associating with each other or with other molecules.

Their chemical structure more particularly comprises at least one hydrophilic region and at least one hydrophobic region.

The term "*hydrophobic group*" means a radical or polymer with a saturated or unsaturated, linear or branched hydrocarbon-based chain, comprising at least 10 carbon atoms, preferably from 10 to 30 carbon atoms, in particular from 12 to 30 carbon atoms and more preferentially from 18 to 30 carbon atoms.

Preferentially, the hydrocarbon-based group is derived from a monofunctional compound. By way of example, the hydrophobic group may be derived from a fatty alcohol such as stearyl alcohol, dodecyl alcohol or decyl alcohol. It may also denote a hydrocarbon-based polymer, for instance polybutadiene.

Among the associative polymers of anionic type that may be mentioned are:

- **(a)** those comprising at least one hydrophilic unit and at least one fatty-chain allyl ether unit, more particularly those whose hydrophilic unit is formed by an ethylenic unsaturated anionic monomer, more particularly a vinylcarboxylic acid and most particularly an acrylic acid or a methacrylic acid or mixtures thereof.

Among these anionic associative polymers, those that are particularly preferred according to the invention are polymers formed from 20% to 60% by weight of acrylic acid and/or of methacrylic acid, from 5% to 60% by weight of lower alkyl (meth)acrylates, from 2% to 50% by weight of fatty-chain allyl ether, and from 0 to 1% by weight of a crosslinking agent which is a well-known copolymerizable unsaturated polyethylenic monomer, for instance diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate or methylenebisacrylamide.

Among the latter polymers, those most particularly preferred are crosslinked terpolymers of methacrylic acid, of ethyl acrylate and of polyethylene glycol (10 EO) stearyl alcohol ether (Steareth-10), in particular those sold by the company Ciba under the names Salcare SC 80® and Salcare SC 90®, which are aqueous 30% emulsions of a crosslinked terpolymer of methacrylic acid, of ethyl acrylate and of steareth-10 allyl ether (40/50/10).

-**(b)** polymers comprising i) at least one hydrophilic unit of unsaturated olefinic carboxylic acid type, and ii) at least one hydrophobic unit of the type such as a (C<sub>10</sub>-C<sub>30</sub>) alkyl ester of an unsaturated carboxylic acid.

(C<sub>10</sub>-C<sub>30</sub>)alkyl esters of unsaturated carboxylic acids that are useful in the invention

comprise, for example, lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate and dodecyl acrylate, and the corresponding methacrylates, lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate.

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

Among the anionic associative polymers of this type, use will be made more particularly of those formed from 95% to 60% by weight of acrylic acid (hydrophilic unit), 4% to 40% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit) and 0 to 6% by weight of crosslinking polymerizable monomer, or alternatively those formed from 98% to 96% by  
10 weight of acrylic acid (hydrophilic unit), 1% to 4% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit) and 0.1% to 0.6% by weight of crosslinking polymerizable monomer such as those described previously.

Among the said above polymers, those most particularly preferred according to the present invention are the products sold by the company Goodrich under the trade names  
15 Pemulen TR1®, Pemulen TR2® and Carbopol 1382®, and even more preferentially Pemulen TR1®, and the product sold by the company SEPPIC under the name Coatex SX®.

Mention may also be made of the acrylic acid/lauryl methacrylate/vinylpyrrolidone terpolymer sold under the name Acrylidone LM by the company ISP.

20 **-(c)** maleic anhydride/C<sub>30</sub>-C<sub>38</sub>  $\alpha$ -olefin/alkyl maleate terpolymers, such as the product (maleic anhydride/C<sub>30</sub>-C<sub>38</sub>  $\alpha$ -olefin/isopropyl maleate) sold under the name Performa V 1608® by the company Newphase Technologies.

**-(d)** acrylic terpolymers comprising:

- 25 i) about 20% to 70% by weight of an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid [A],
- ii) about 20% to 80% by weight of an  $\alpha,\beta$ -monoethylenically unsaturated non-surfactant monomer other than [A],
- iii) about 0.5% to 60% by weight of a nonionic monourethane which is the product of  
30 reaction of a monohydric surfactant with a monoisocyanate containing monoethylenic unsaturation,

such as those described in patent application EP-A-0 173 109 and more particularly the terpolymer described in Example 3, namely a methacrylic acid/methyl acrylate/behenyl alcohol dimethyl-meta-isopropenylbenzylisocyanate ethoxylated (40 EO) terpolymer, as  
35 an aqueous 25% dispersion.

**-(e)** copolymers comprising among their monomers an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid and an ester of an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid and of an oxyalkylenated fatty alcohol.

40 Preferentially, these compounds also comprise as monomer an ester of an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid and of a C<sub>1</sub>-C<sub>4</sub> alcohol.

An example of a compound of this type that may be mentioned is Aculyn 22® sold by the company Röhm & Haas, which is a methacrylic acid/ethyl acrylate/oxyalkylenated stearyl methacrylate terpolymer.

- 5 - (f) amphiphilic polymers comprising at least one ethylenically unsaturated monomer bearing a sulfonic group, in free or partially or totally neutralized form and comprising at least one hydrophobic part. These polymers may be crosslinked or noncrosslinked. They are preferably crosslinked.

10 The ethylenically unsaturated monomers bearing a sulfonic group are especially chosen from vinylsulfonic acid, styrenesulfonic acid, (meth)acrylamido(C<sub>1</sub>-C<sub>22</sub>)alkylsulfonic acids, N-(C<sub>1</sub>-C<sub>22</sub>)alkyl(meth)acrylamido(C<sub>1</sub>-C<sub>22</sub>)alkylsulfonic acids such as undecylacrylamidomethanesulfonic acid, and also partially or totally neutralized forms thereof.

15 Use will more preferably be made of (meth)acrylamido(C<sub>1</sub>-C<sub>22</sub>)alkylsulfonic acids, such as, for example, acrylamidomethanesulfonic acid, acrylamidoethanesulfonic acid, acrylamidopropanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, methacrylamido-2-methylpropanesulfonic acid, 2-acrylamido-n-butanesulfonic acid, 2-acrylamido-2,4,4-trimethylpentanesulfonic acid, 2-methacrylamidododecylsulfonic acid, 2-acrylamido-2,6-dimethyl-3-heptanesulfonic acid, and also partially or totally neutralized forms thereof.

20 2-Acrylamido-2-methylpropanesulfonic acid (AMPS), and also partially or totally neutralized forms thereof, will more particularly be used.

25 The amphiphilic polymers in accordance with the invention may be chosen especially from random amphiphilic AMPS polymers modified by reaction with a C<sub>6</sub>-C<sub>22</sub> n-monoalkylamine or di-n-alkylamine, and such as those described in Patent Application WO 00/31154. These polymers may also contain other ethylenically unsaturated hydrophilic monomers selected, for example, from (meth)acrylic acids, β-substituted alkyl derivatives thereof or esters thereof obtained with monoalcohols or mono- or polyalkylene glycols, (meth)acrylamides, vinylpyrrolidone, maleic anhydride, itaconic acid or maleic acid, or mixtures of these compounds.

30 The preferred polymers of this family are chosen from amphiphilic copolymers of AMPS and of at least one ethylenically unsaturated hydrophobic monomer.

35 These same copolymers may also contain one or more ethylenically unsaturated monomers not comprising a fatty chain, such as (meth)acrylic acids, β-substituted alkyl derivatives thereof or esters thereof obtained with monoalcohols or mono- or polyalkylene glycols, (meth)acrylamides, vinylpyrrolidone, maleic anhydride, itaconic acid or maleic acid, or mixtures of these compounds.

These copolymers are described especially in patent application EP-A-750 899, patent US 5 089 578 and in the following Yotaro Morishima publications:

- 40
- *Self-assembling amphiphilic polyelectrolytes and their nanostructures* - Chinese Journal of Polymer Science Vol. 18, No. 40 (2000), 323-336;

- *Micelle formation of random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate and a nonionic surfactant macromonomer in water as studied by fluorescence and dynamic light scattering* - *Macromolecules*, 2000, Vol. 33, No. 10 - 3694-3704;
- 5 ○ *Solution properties of micelle networks formed by nonionic moieties covalently bound to a polyelectrolyte: salt effects on rheological behavior* - *Langmuir*, Vol. 16, No. 12, (2000) 5324-5332;
- *Stimuli responsive amphiphilic copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate and associative macromonomers* - *Polym. Preprint, Div. Polym. Chem.*, 40(2), (1999), 220-221.

Among these polymers, mention may be made of:

- 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 15 85% by weight of (C<sub>8</sub>-C<sub>16</sub>)alkyl(meth)acrylamide units or of (C<sub>8</sub>-C<sub>16</sub>)alkyl(meth)acrylate units, with respect to the polymer, such as those described in Application EP-A-750 899;
- terpolymers comprising from 10 mol% to 90 mol% of acrylamide units, from 0.1 mol% to 10 mol% of AMPS units and from 5 mol% to 80 mol% of n-(C<sub>6</sub>- 20 C<sub>18</sub>)alkylacrylamide units, such as those described in Patent US-5 089 578.

Mention may also be made of copolymers of totally neutralized AMPS and of dodecyl methacrylate, and also crosslinked and non-crosslinked copolymers of AMPS and of n-dodecylmethacrylamide, such as those described in the Morishima articles mentioned above.

25

Among the cationic associative polymers that may be mentioned are:

- (I) cationic associative polyurethanes;
- 30 - (II) the compound sold by the company Noveon under the name Aqua CC and which corresponds to the INCI name Polyacrylate-1 Crosspolymer. Polyacrylate-1 Crosspolymer is the product of polymerization of a monomer mixture comprising:
  - a di(C<sub>1</sub>-C<sub>4</sub> alkyl)amino(C<sub>1</sub>-C<sub>6</sub> alkyl) methacrylate,
  - 35 ○ one or more C<sub>1</sub>-C<sub>30</sub> alkyl esters of (meth)acrylic acid,
  - a polyethoxylated C<sub>10</sub>-C<sub>30</sub> alkyl methacrylate (20-25 mol of ethylene oxide units),
  - a 30/5 polyethylene glycol/polypropylene glycol allyl ether,
  - a hydroxy(C<sub>2</sub>-C<sub>6</sub> alkyl) methacrylate, and
  - an ethylene glycol dimethacrylate.
- 40 - (III) quaternized (poly)hydroxyethylcelluloses modified with groups comprising at least

one fatty chain, such as alkyl, arylalkyl or alkylaryl groups comprising at least 8 carbon atoms, or mixtures thereof. The alkyl radicals borne by the above quaternized celluloses or hydroxyethylcelluloses preferably comprise from 8 to 30 carbon atoms. The aryl radicals preferably denote phenyl, benzyl, naphthyl or anthryl groups. Examples of quaternized alkyhydroxyethylcelluloses containing C<sub>8</sub>-C<sub>30</sub> fatty chains that may be mentioned include the products Quatrisoft LM 200®, Quatrisoft LM-X 529-18-A®, Quatrisoft LM-X 529-18B® (C<sub>12</sub> alkyl) and Quatrisoft LM-X 529-8® (C<sub>18</sub> alkyl) sold by the company Aqualon, and the products Crodacel QM®, Crodacel QL® (C<sub>12</sub> alkyl) and Crodacel QS® (C<sub>18</sub> alkyl) sold by the company Croda, and the product Softcat SL 100® sold by the company Aqualon.

- (IV) cationic polyvinylactam polymers.

Such polymers are described, for example, in patent application WO-00/68282.

As cationic poly(vinylactam) polymers according to the invention, vinylpyrrolidone/dimethylaminopropylmethacrylamide/dodecyldimethylmethacrylamido-propylammonium tosylate terpolymers, vinylpyrrolidone/dimethylaminopropylmethacrylamide/cocoyldimethylmethacrylamido-propylammonium tosylate terpolymers, vinylpyrrolidone/dimethylaminopropylmethacrylamide/lauryldimethylmethacrylamido-propylammonium tosylate or chloride terpolymers are used in particular.

The amphoteric associative polymers are preferably chosen from those comprising at least one non-cyclic cationic unit. Even more particularly, the ones that are preferred are those prepared from or comprising 1 mol% to 20 mol%, preferably 1.5 mol% to 15 mol% and even more particularly 1.5 mol% to 6 mol% of fatty-chain monomer relative to the total number of moles of monomers.

Amphoteric associative polymers according to the invention are described and prepared, for example, in patent application WO 98/44012.

Among the amphoteric associative polymers according to the invention, the ones that are preferred are acrylic acid/(meth)acrylamidopropyltrimethylammonium chloride/stearyl methacrylate terpolymers.

The associative polymers of nonionic type that may be used according to the invention are preferably chosen from:

- (a) copolymers of vinylpyrrolidone and of fatty-chain hydrophobic monomers, of which examples that may be mentioned include:

- the products Antaron V216® and Ganex V216® (vinylpyrrolidone/hexadecene copolymer) sold by the company ISP.

- the products Antaron V220® and Ganex V220® (vinylpyrrolidone/eicosene copolymer) sold by the company ISP.

- (b) copolymers of C<sub>1</sub>-C<sub>6</sub> alkyl methacrylates or acrylates and of amphiphilic

monomers comprising at least one fatty chain, such as, for example, the oxyethylenated methyl acrylate/stearyl acrylate copolymer sold by the company Goldschmidt under the name Antil 208®.

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

- (d) polyurethane polyethers comprising in their chain both hydrophilic blocks usually of polyoxyethylenated nature and hydrophobic blocks, which may be aliphatic sequences alone and/or cycloaliphatic and/or aromatic sequences.

10 - (e) polymers with an aminoplast ether backbone containing at least one fatty chain, such as the Pure Thix® compounds sold by the company Sud-Chemie.

- (f) celluloses or derivatives thereof, modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups or mixtures thereof in which the alkyl groups are of C<sub>8</sub>, and in particular:

15 \* nonionic alkylhydroxyethylcelluloses such as the products Natrosol Plus Grade 330 CS and Polysurf 67 (C<sub>16</sub> alkyl) sold by the company Aqualon;

\* nonionic nonoxynylhydroxyethylcelluloses such as the product Amercell HM-1500 sold by the company Amerchol;

20 \* nonionic alkylcelluloses such as the product Bermocoll EHM 100 sold by the company Berol Nobel;

- (g) associative guar derivatives, for instance hydroxypropyl guar modified with a fatty chain, such as the product Esaflor HM 22 (modified with a C<sub>22</sub> alkyl chain) sold by the company Lamberti; the product Miracare XC 95-3 (modified with a C<sub>14</sub> alkyl chain) and the product RE 205-146 (modified with a C<sub>20</sub> alkyl chain) sold by Rhodia Chimie.

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

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

40 The nonionic fatty-chain polyurethane polyethers may be triblock copolymers in which the hydrophilic block is a polyoxyethylenated chain comprising from 50 to 1000 oxyethylene groups. The nonionic polyurethane polyethers comprise a urethane bond between the hydrophilic blocks, whence arises the name.

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

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

Mention may also be made of the product Elfacos T210® containing a C<sub>12-14</sub> alkyl chain, and the product Elfacos T212® containing a C<sub>18</sub> alkyl chain, from Akzo.

The product DW 1206B® from Röhm & Haas containing a C<sub>20</sub> alkyl chain and a urethane bond, sold at a solids content of 20% in water, may also be used.

It is also possible to use solutions or dispersions of these polymers, especially in water or in aqueous-alcoholic medium. Examples of such polymers that may be mentioned are Rheolate® 255, Rheolate® 278 and Rheolate® 244 sold by the company Rheox. The products DW 1206F and DW 1206J sold by the company Röhm & Haas may also be used.

The polyurethane polyethers that may be used according to the invention are in particular those described in the article by G. Fonnum, J. Bakke and Fk. Hansen - *Colloid Polym. Sci.* 271, 380.389 (1993).

It is even more particularly preferred to use a polyurethane polyether that may be obtained by polycondensation of at least three compounds comprising (i) at least one polyethylene glycol comprising from 150 to 180 mol of ethylene oxide, (ii) stearyl alcohol or decyl alcohol, and (iii) at least one diisocyanate.

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

Use may also be made of fatty-phase-thickening polymers.

Preferably, the polymers for structuring the oily phase via physical interactions are chosen from polyamides, silicone polyamides, saccharide or polysaccharide mono- or polyalkyl esters, N-acylamino acid amide derivatives, and copolymers comprising an alkylene or styrene block, these copolymers possibly being diblock, triblock, multiblock or radial-block polymers, also known as star copolymers, or alternatively comb polymers.

#### 1) Polymers bearing at least one crystallizable block in the backbone

These are also polymers that are soluble or dispersible in the oil or fatty phase by heating above their melting point m.p. These polymers are especially block copolymers

consisting of at least two blocks of different chemical nature, one of which is crystallizable.

As polymers bearing in the backbone at least one crystallizable block that are suitable for use in the invention, mention may be made of:

i). the polymers defined in document US-A-5 156 911;

5 ii). block copolymers of olefin or of cycloolefin containing a crystallizable chain, for instance those derived from the block polymerization of:

- cyclobutene, cyclohexene, cyclooctene, norbornene (i.e. bicyclo(2,2,1)-2-heptene), 5-methylnorbornene, 5-ethylnorbornene, 5,6-dimethylnorbornene, 5,5,6-trimethylnorbornene, 5-ethylidenenorbornene, 5-phenylnorbornene, 5-benzylnorbornene, 10 5-vinylnorbornene, 1,4,5,8-dimethano-1,2,3,4,4a,5,8a-octahydro-naphthalene, dicyclopentadiene, and mixtures thereof;

- with ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene or 1-eicosene, or mixtures thereof. These block copolymers may be in particular (ethylene/norbornene) block copolymers and 15 (ethylene/propylene/ethylidenenorbornene) block terpolymers.

Those resulting from the block copolymerization of at least two  $C_2$ - $C_{16}$ , and better still  $C_2$ - $C_{12}$ ,  $\alpha$ -olefins such as those mentioned above and in particular block bipolymers of ethylene and of 1-octene may also be used.

Copolymers containing at least one crystallizable block, the rest of the copolymer 20 being amorphous (at room temperature). These copolymers may also contain two crystallizable blocks of different chemical nature. The preferred copolymers are those that simultaneously contain at room temperature a crystallizable block and an amorphous block that are both hydrophobic and lipophilic, sequentially distributed; mention may be made, for example, of polymers containing one of the crystallizable blocks and one of the amorphous 25 blocks below:

- Block that is crystallizable by nature: a) of polyester type, for instance poly(alkylene terephthalate), b) of polyolefin type, for instance polyethylenes or polypropylenes.

- Amorphous and lipophilic block, for instance: amorphous polyolefins or copoly(olefin)s such as poly(isobutylene), hydrogenated polybutadiene or hydrogenated 30 poly(isoprene).

As examples of such copolymers containing a crystallizable block and an amorphous block, mention may be made of:

a) poly( $\delta$ -caprolactone)-b-poly(butadiene) block copolymers, preferably used hydrogenated, such as those described in the article *Melting behaviour of poly( $\delta$ -caprolactone)-block-polybutadiene copolymers* from S. Nojima, *Macromolecules*, 32, 3727-3734 (1999). 35

b) the hydrogenated block or multiblock poly(butylene terephthalate)-b-poly(isoprene) block copolymers cited in the article *Study of morphological and mechanical properties of PP/PBT* by B. Boutevin et al., *Polymer Bulletin*, 34, 117-123 (1995).

40 c) the poly(ethylene)-b-copoly(ethylene/propylene) block copolymers cited in the articles *Morphology of semi-crystalline block copolymers of ethylene-(ethylene-alt-*

*propylene*) by P. Rangarajan et al., *Macromolecules*, 26, 4640-4645 (1993) and *Polymer aggregates with crystalline cores: the system poly(ethylene)poly(ethylene-propylene)* P. Richter et al., *Macromolecules*, 30, 1053-1068 25 (1997).

5 d) the poly(ethylene)-b-poly(ethylene) block copolymers mentioned in the general article *Crystallization in block copolymers* by I.W. Hamley, *Advances in Polymer Science*, vol. 148, 113-137 (1999).

The semi-crystalline polymers that may be used in the context of the invention may be non-crosslinked or partially crosslinked, provided that the degree of crosslinking does not impede their dissolution or dispersion in the liquid oily phase by heating above their  
10 melting point. It may then be a case of chemical crosslinking, by reaction with a multifunctional monomer during the polymerization. It may also be a case of physical crosslinking, which may then be due either to the establishment of bonds of hydrogen or dipolar type between groups borne by the polymer, for instance dipolar interactions between carboxylate ionomers, these interactions being in small amount and borne by the  
15 polymer backbone; or due to a phase separation between the crystallizable blocks and the amorphous blocks borne by the polymer.

Preferably, the semi-crystalline polymers that are suitable for the invention are non-crosslinked.

As particular examples of semi-crystalline polymers that may be used in the  
20 composition according to the invention, mention may be made of the Intelimer® products from the company Landec described in the brochure "Intelimer® polymers". These polymers are in solid form at room temperature (25°C). They bear crystallizable side chains and contain the monomer. Mention may be made especially of Landec IP22®, with a melting point m.p. of 56°C, which is a viscous, impermeable, non-tacky product at room  
25 temperature.

It is also possible to use the semi-crystalline polymers described in Examples 3, 4, 5, 7 and 9 of patent US-A-5 156 911, resulting from the copolymerization of acrylic acid and of C<sub>5</sub> to C<sub>16</sub> alkyl (meth)acrylate, such as those resulting from the copolymerization:

- 30 - of acrylic acid, of hexadecyl acrylate and of isodecyl acrylate in a 1/16/3 ratio,
- of acrylic acid and of pentadecyl acrylate in a 1/19 ratio,
- of acrylic acid, of hexadecyl acrylate and of ethyl acrylate in a 2.5/76.5/20 ratio,
- of acrylic acid, of hexadecyl acrylate and of methyl acrylate in a 5/85/10 ratio,
- of acrylic acid and of octadecyl (meth)acrylate in a 2.5/97.5 ratio.

It is also possible to use the polymer Structure O sold by the company National  
35 Starch, such as the product described in document US-A-5 736 125, of m.p. 44°C, and also semi-crystalline polymers containing crystallizable side chains comprising fluoro groups as described in Examples 1, 4, 6, 7 and 8 of document WO-A-01/19333.

It is also possible to use the semi-crystalline polymers obtained by copolymerization  
40 of stearyl acrylate and of acrylic acid or of NVP, or by copolymerization of behenyl acrylate and of acrylic acid or NVP, as described in document US-A-5 519 063 or EP-A-0 550 745.

According to one particular embodiment variant, the semi-crystalline polymers that

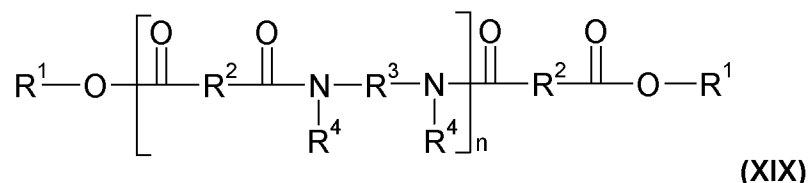
are suitable for use in the present invention are especially alkyl acrylates, among which mention may be made of the Landec copolymers:

- Doresco IPA 13-1®: polystearyl acrylate, m.p. of 49°C and MW of 145 000;
- Doresco IPA 13-3®: polyacrylate/methacrylic acid, m.p. of 65°C and MW of 114 000;
- Doresco IPA 13-4®: polyacrylate/vinylpyrrolidone, m.p. of 44°C and MW of 387 000;
- Doresco IPA13-5®: polyacrylate/hydroxyethyl methacrylate, m.p. of 47°C and MW of 397 600;
- Doresco IPA 13-6®: polybehenyl acrylate, m.p. of 66°C.

## 2) Non-silicone polyamides

The particular polyamides used in the composition according to the invention are preferably those described in document US-A-5 783 657 from the company Union Camp.

Each of these polyamides especially satisfies formula (XIX) below:



in which formula (XIX):

- $n$  denotes a whole number of amide units such that the number of ester groups represents from 10% to 50% of the total number of ester and amide groups;
- $R^1$  is independently in each case an alkyl or alkenyl group containing at least 4 carbon atoms and especially from 4 to 24 carbon atoms;
- $R^2$  represents independently in each case a  $C_4$  to  $C_{55}$  hydrocarbon-based group, on condition that 50% of the groups  $R_2$  represent a  $C_{30}$  to  $C_{55}$  hydrocarbon-based group;
- $R^3$  represents independently in each case an organic group bearing at least two carbon atoms, hydrogen atoms and optionally one or more oxygen or nitrogen atoms; and
- $R^4$  represents independently in each case a hydrogen atom, a  $C_1$  to  $C_{10}$  alkyl group or a direct bond to  $R_3$  or to another  $R_4$  such that the nitrogen atom to which are attached both  $R_3$  and  $R_4$  forms part of a heterocyclic structure defined by  $R_4-N-R_3$ , with at least 50% of the groups  $R_4$  representing a hydrogen atom.

In particular, the ester groups of this polyamide represent from 15% to 40% and at best from 20% to 35% of the total number of ester and amide groups. Furthermore,  $n$  advantageously represents an integer ranging from 1 to 10 and better still from 1 to 5, limits inclusive.

Preferably,  $R^1$  is a  $C_{12}$  to  $C_{22}$  and preferably  $C_{16}$  to  $C_{22}$  alkyl group. Advantageously,  $R^2$  may be a  $C_{10}$  to  $C_{42}$  hydrocarbon-based (alkylene) group. Preferably, at least 50% and

better still at least 75% of the groups  $R^2$  are groups containing from 30 to 42 carbon atoms. The other groups  $R^2$  are  $C_4$  to  $C_{19}$  and better still  $C_4$  to  $C_{12}$  hydrogen-containing groups. Preferably,  $R^3$  represents a  $C_2$  to  $C_{36}$  hydrocarbon-based group or a polyoxyalkylene group and  $R^4$  represents a hydrogen atom. Preferably,  $R^3$  represents a  $C_2$  to  $C_{12}$  hydrocarbon-based group. The hydrocarbon-based groups may be linear, cyclic or branched, and saturated or unsaturated groups. Moreover, the alkyl and alkylene groups may be linear or branched, and saturated or unsaturated groups.

The thickening of the oily phase may be obtained by means of one or more polyamides defined above. In general, these polyamides are in the form of mixtures, these mixtures also possibly containing a synthetic product corresponding to a polyamide as defined above with  $n$  being 0, i.e. a diester.

As structuring polyamides that may be used in the invention, mention may also be made of polyamide resins resulting from the condensation of an aliphatic dicarboxylic acid and a diamine (including compounds containing, respectively, more than two carboxyl groups and more than two amine groups), the carboxyl and amine groups of adjacent individual units being condensed in the form of an amide bond. These polyamide resins are especially the products sold under the brand name Versamid® by the companies General Mills, Inc. and Henkel Corp., under the brand name Onamid®, especially Onamid S or C. These resins have a weight-average molecular mass ranging from 6000 to 9000. For further information regarding these polyamides, reference may be made to US-A-3 645 705 and US-A-3 148 125. Use is made more especially of Versamid® 30 or 744.

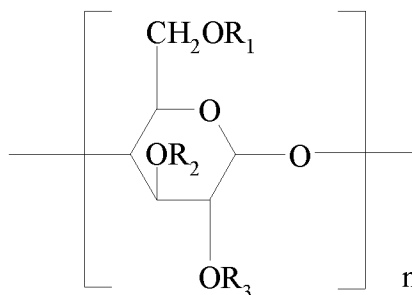
It is also possible to use the polyamides sold or manufactured by the company Arizona under the references Uni-Rez (2658, 2931, 2970, 2621, 2613, 2624, 2665, 1554, 2623, 2662) and the product sold under the reference Macromelt 6212 by the company Henkel. For further information regarding these polyamides, reference may be made to document US-A-5 500 209.

As examples of structuring polyamides that may be used in the composition according to the invention, mention may also be made of the commercial products sold or manufactured by the company Arizona Chemical under the names Uniclear 80 and Uniclear 100. They are sold, respectively, in the form of an 80% (active material) gel and a 100% (active material) gel in a mineral oil. They have a softening point of from 88 to 105°C. These commercial products are a mixture of copolymers of a  $C_{36}$  diacid coupled with ethylenediamine, having an average molecular mass of about 6000. The terminal ester groups result from the esterification of the remaining acid end groups with cetyl alcohol, stearyl alcohol or mixtures thereof (also known as cetylstearyl alcohol).

## 2) Saccharide or polysaccharide mono- or polyalkyl esters

Among the saccharide or polysaccharide monoalkyl or polyalkyl esters that are suitable for use in the invention, mention may be made of dextrin or inulin alkyl or polyalkyl esters.

It may especially be a dextrin mono- or polyester of at least one fatty acid corresponding especially to formula (XX) below:



(XX)

5 in which formula (XX):

- $n$  is an integer ranging from 3 to 200, especially ranging from 20 to 150 and in particular ranging from 25 to 50,
- $R_1$ ,  $R_2$  and  $R_3$ , which may be identical or different, are chosen from hydrogen and an acyl group (R-C(O)-) in which the radical R is a linear or branched, saturated or  
10 unsaturated hydrocarbon-based group containing from 7 to 29, in particular from 7 to 21, especially from 11 to 19, more particularly from 13 to 17, or even 15, carbon atoms, with the proviso that at least one of the said radicals  $R_1$ ,  $R_2$  or  $R_3$  is other than hydrogen.

15 In particular,  $R_1$ ,  $R_2$  and  $R_3$  may represent hydrogen or an acyl group (R-C(O)-) in which R is a hydrocarbon-based radical as defined above, with the proviso that at least two of the said radicals  $R_1$ ,  $R_2$  and  $R_3$  are identical and other than hydrogen.

The radicals  $R_1$ ,  $R_2$  and  $R_3$  may all contain an acyl group (R-C(O)), which is identical or different and especially identical.

20 In particular,  $n$  mentioned above advantageously ranges from 25 to 50 and is especially equal to 38 in the general formula of the saccharide ester that may be used in the present invention.

25 When the radicals  $R_1$ ,  $R_2$  and/or  $R_3$ , which may be identical or different, contain an acyl group (R-C(O)), these radicals may be chosen especially from caprylic, capric, lauric, myristic, palmitic, stearic, arachic, behenic, isobutyric, isovaleric, 2-ethylbutyric, ethylmethylacetic, isoheptanoic, 2-ethylhexanoic, isononanoic, isodecanoic, isotridecanoic, isomyristic, isopalmitic, isostearic, isoarachic, isohexanoic, decenoic, dodecenoic, tetradecenoic, myristoleic, hexadecenoic, palmitoleic, oleic, elaidic, asclepinic, gondoleic, eicosenoic, sorbic, linoleic, linolenic, punicic, stearidonic, arachidonic and stearolic radicals, and mixtures thereof.

30 Preferably, at least one dextrin palmitate is used as fatty acid ester of dextrin. This ester may be used alone or as a mixture with other esters.

Advantageously, the fatty acid ester of dextrin has a degree of substitution of less than or equal to 2.5, especially ranging from 1.5 to 2.5 and preferably from 2 to 2.5 on the basis of one glucose unit. The weight-average molecular weight of the dextrin ester may in

particular be from 10 000 to 150 000, especially from 12 000 to 100 000 and even from 15 000 to 80 000.

Dextrin esters, in particular dextrin palmitates, are commercially available under the name Rheopearl TL or Rheopearl KL by the company Chiba Flour.

5

### 3) N-acylamino acid amide derivatives

The N-acylamino acid amides that may be used are, for example, diamides from the combination of an N-acylamino acid with amines comprising from 1 to 22 carbon atoms, such as those described in document FR 2 281 162. They are, for example, alkylglutamic acid amide derivatives such as the laurylglutamic acid dibutylamide sold by the company Ajinomoto under the name Gelling Agent GP-1, or alternatively the 2-ethylhexylglutamic acid dibutylamide sold by the company Ajinomoto under the name Gelling Agent GA-01.

### 4) Copolymers comprising an alkylene or styrene block

The copolymers may have a comb or the block structure of diblock, triblock, multiblock and/or radial or star type and may comprise at least two thermodynamically incompatible segments.

The structuring agent may comprise, for example, a styrene segment as described in patent applications EP 0 497 144, WO 98/42298, US 6 225 690, US 6 174 968 and US 6 225 390, an ethylene/butylene segment or an ethylene/propylene segment as described in patent applications US 6 225 690, US 6 174 968 and US 6 225 390, a butadiene segment, an isoprene segment, a polyvinyl segment, for instance polyalkyl (meth)acrylate or polyvinyl alcohol or polyvinyl acetate, a silicone segment as described in patent applications US 5 468 477 and US 5 725 882, or a combination of these segments.

A diblock copolymer is usually defined as being of A-B type in which a hard segment (A) is followed by a soft segment (B).

A triblock copolymer is usually defined as being of A-B-A type or as a ratio of a hard segment, a soft segment and a hard segment.

A multiblock, radial or star copolymer may comprise any type of combination of hard segments and soft segments, with the proviso that the characteristics of the hard segments and of the soft segments are conserved.

An example of hard segments of block copolymers that may be mentioned is styrene, and examples of soft segments of block copolymers that may be mentioned include ethylene, propylene and butylene, and a combination thereof.

The triblock copolymers, and especially those of polystyrene/polyisoprene or polystyrene/polybutadiene type, which are suitable for use in the invention may be those sold under the reference Luvitol HSB by the company BASF. Mention may also be made of triblock copolymers of polystyrene/copoly(ethylene-propylene) or polystyrene/copoly(ethylene-butylene) type, such as those sold under the reference Kraton

by the company Shell Chemical Co., or under the reference Gelled Permethyl 99 A by the company Penreco. Such triblock copolymers are particularly preferred according to the invention.

As a further example of block copolymers that may be suitable for use in the present invention, mention may also be made of the block copolymers sold under the reference Versagel by the company Penreco, those sold under the reference Kraton by the company Shell and those sold under the reference Gel Base by the company Brooks Industries.

Among the fatty-phase thickening polymers, polymers bearing in the backbone at least one crystallizable block are preferred.

The aqueous-phase or fatty-phase thickening polymers may be used alone or as mixtures in all proportions.

Preferably, the thickeners are aqueous-phase thickeners.

Preferably, the polymers in the cosmetic compositions in accordance with the present invention advantageously have in solution or in dispersion, at 1% active material in water, a viscosity, measured using a Rheomat RM 180 rheometer at 25°C, of greater than 0.1 ps and even more advantageously greater than 0.2 cp, at a shear rate of 200 s<sup>-1</sup>.

According to one particular embodiment of the invention, the organic thickening polymer(s) are chosen from cellulose-based polymers.

The organic thickening polymer(s) are present in the composition according to the invention in a content ranging from 0.01% to 10% by weight and preferably from 0.1% to 5% by weight relative to the total weight of the composition.

vii) optionally at least one surfactant:

According to one particular embodiment, the composition of the invention contains at least one surfactant.

The surfactant(s) may be nonionic, anionic, cationic, amphoteric or zwitterionic.

Preferably, the composition of the invention contains at least one nonionic surfactant.

Among the nonionic surfactants according to the invention, mention may be made, alone or as mixtures, of fatty alcohols,  $\alpha$ -diols and alkylphenols, these three types of compound being polyethoxylated, polypropoxylated and/or polyglycerolated and containing a fatty chain comprising, for example, 8 to 40 carbon atoms, the number of ethylene oxide or propylene oxide groups possibly ranging especially from 2 to 50 and the number of glycerol groups possibly ranging especially from 2 to 30. Mention may also be made of ethylene oxide and propylene oxide copolymers, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides preferably having from 2 to 30 ethylene oxide units, 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 ethylene oxide units; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, N-alkylglucamine derivatives, amine oxides such

as (C<sub>10</sub>-C<sub>14</sub>)alkylamine oxides or N-acylaminopropylmorpholine oxides.

Preferably the nonionic surfactant is chosen from:

- (poly)ethoxylated fatty alcohols;
- 5 • glycerolated fatty alcohols;
- alkylpolyglycosides.

The term "fatty chain" means a linear or branched, saturated or unsaturated hydrocarbon-based chain comprising from 6 to 30 carbon atoms and preferably from 8 to  
10 30 carbon atoms.

As regards the alkylpolyglycosides, they are well known and may be represented more particularly by the following general formula:



15 in which formula (XXI):

- R<sub>1</sub> represents a linear or branched alkyl and/or alkenyl radical comprising from about 8 to 24 carbon atoms, or an alkylphenyl radical whose linear or branched alkyl radical comprises from 8 to 24 carbon atoms;
- R<sub>2</sub> represents an alkylene radical comprising from about 2 to 4 carbon atoms;
- 20 • G represents a sugar unit comprising from 5 to 6 carbon atoms;
- t is an integer between 0 and 10, preferably between 0 and 4 and in particular between 0 and 4; and
- v denotes an integer between 1 and 15 inclusive.

25 Preferred alkylpolyglycosides according to the present invention are compounds of formula (V) in which R<sub>1</sub> more particularly denotes a linear or branched, saturated or unsaturated alkyl radical comprising from 8 to 18 carbon atoms, t denotes a value ranging from 0 to 3 and more particularly equal to 0, and G may denote glucose, fructose or galactose, preferably glucose. The degree of polymerization, i.e. the value of v in formula  
30 (XXI), may range from 1 to 15 and preferably from 1 to 4. The average degree of polymerization is more particularly between 1 and 2 and even more preferentially from 1.1 to 1.5.

The glycoside bonds between the sugar units are of 1-6 or 1-4 type and preferably of 1-4 type.

35 Compounds of formula (XXI) are especially represented by the products sold by the company Cognis under the names Plantaren<sup>®</sup> (600 CS/U, 1200 and 2000) or Plantacare<sup>®</sup> (818, 1200 and 2000). It is also possible to use the products sold by the company SEPPIC under the names Triton CG 110 (or Oramix CG 110) and Triton CG 312 (or Oramix<sup>®</sup> NS 10), the products sold by the company BASF under the name Lutensol GD 70 or those  
40 sold by the company Chem Y under the name AG10 LK.

It is also possible to use, for example, (C<sub>8</sub>-C<sub>16</sub>)alkyl-1,4-polyglucoside as an aqueous

53% solution, sold by the company Cognis under the reference Plantacare® 818 UP.

As regards the mono- or polyglycerolated surfactants, they preferably comprise on average from 1 to 30 glycerol groups, more particularly from 1 to 10 and in particular from 1.5 to 5 glycerol groups.

5

The monoglycerolated or polyglycerolated surfactants are preferably chosen from the compounds of the following formulae:



in which formulae:

- 10
- **R** represents a saturated or unsaturated, linear or branched hydrocarbon-based radical comprising from 8 to 40 carbon atoms and preferably from 10 to 30 carbon atoms; **m** is an integer between 1 and 30, preferably between 1 and 10 and more particularly from 1.5 to 6; **R** may optionally comprise heteroatoms, for instance oxygen and nitrogen. In particular, **R** may optionally comprise one or more hydroxyl and/or ether and/or amide groups. **R** preferably denotes optionally mono- or polyhydroxylated C<sub>10</sub>-C<sub>20</sub> alkyl and/or alkenyl radicals.
- 15

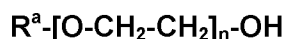
Use may be made, for example, of the polyglycerolated (3.5 mol) hydroxylauryl ether sold under the name Chimexane® NF from Chimex.

20

The (poly)ethoxylated fatty alcohols that are suitable for performing the invention are chosen more particularly from alcohols containing from 8 to 30 carbon atoms, and preferably from 12 to 22 carbon atoms.

25 The (poly)ethoxylated fatty alcohols more particularly contain one or more linear or branched, saturated or unsaturated hydrocarbon-based groups, comprising 8 to 30 carbon atoms, which are optionally substituted, in particular with one or more (in particular 1 to 4) hydroxyl groups. If they are unsaturated, these compounds may have one to three conjugated or non-conjugated carbon-carbon double bonds.

30 The (poly)ethoxylated fatty alcohol(s) preferably have the following formula:



with

- **R**<sup>a</sup> representing a linear or branched C<sub>8</sub>-C<sub>40</sub> alkyl or linear or branched C<sub>8</sub>-C<sub>30</sub> alkenyl (preferentially C<sub>8</sub>-C<sub>30</sub> alkyl) group and
- 35 - **n** is an integer between 1 and 200 inclusive, preferentially between 2 and 50 and more particularly between 2 and 30, such as 20.

The (poly)ethoxylated fatty alcohols are more particularly fatty alcohols comprising from 8 to 22 carbon atoms, oxyethylenated with 1 to 30 mol of ethylene oxide (1 to 30 EO).  
40 Among these, mention may be made more particularly of lauryl alcohol 2 EO, lauryl alcohol 3 EO, decyl alcohol 3 EO, decyl alcohol 5 EO and oleyl alcohol 20 EO.

Mixtures of these (poly)oxyethylenated fatty alcohols may also be used.

Among the nonionic surfactants, use is preferably made of C<sub>6</sub>-C<sub>24</sub> alkyl polyglucosides and (poly)ethoxylated fatty alcohols, and C<sub>8</sub>-C<sub>16</sub> alkyl polyglucosides are more particularly used.

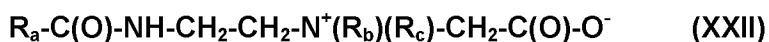
The amount of nonionic surfactant preferably ranges from 0.5% to 25% by weight, in particular from 1% to 20% by weight and more particularly from 2% to 10% by weight relative to the total weight of the composition of the invention.

As indicated previously, the composition according to the invention may contain one or more amphoteric surfactants.

The amphoteric or zwitterionic surfactant(s) that may be used in the present invention may especially be optionally quaternized secondary or tertiary aliphatic amine derivatives containing at least one anionic group, for instance a carboxylate, sulfonate, sulfate, phosphate or phosphonate group, and in which the aliphatic group or at least one of the aliphatic groups is a linear or branched chain comprising from 8 to 22 carbon atoms.

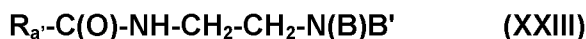
Mention may be made in particular of (C<sub>8</sub>-C<sub>20</sub>)alkylbetaines, sulfobetaines, (C<sub>8</sub>-C<sub>20</sub> alkyl)amido(C<sub>2-8</sub> alkyl)betaines and (C<sub>8</sub>-C<sub>20</sub> alkyl)amido(C<sub>2-8</sub> alkyl)sulfobetaines.

Among the optionally quaternized secondary or tertiary aliphatic amine derivatives that may be used, as defined above, mention may also be made of the compounds of respective structures (XXII) and (XXIII) below:



in which formula (XXII):

- R<sub>a</sub> represents a C<sub>10</sub>-C<sub>30</sub> alkyl or alkenyl group derived from an acid R<sub>a</sub>-C(O)-OH preferably present in hydrolysed coconut oil, or a heptyl, nonyl or undecyl group;
- R<sub>b</sub> represents a β-hydroxyethyl group; and
- R<sub>c</sub> represents a carboxymethyl group; and



in which formula (XXIII):

- B represents -CH<sub>2</sub>CH<sub>2</sub>OX';
- B' represents -(CH<sub>2</sub>)<sub>z</sub>-Y', with z = 1 or 2;
- X' represents the group -CH<sub>2</sub>-C(O)-OH, -CH<sub>2</sub>-C(O)-OZ', -CH<sub>2</sub>CH<sub>2</sub>-C(O)-OH, -CH<sub>2</sub>-CH<sub>2</sub>-C(O)-OZ', or a hydrogen atom;
- Y' represents -C(O)-OH, -C(O)-OZ' or the group -CH<sub>2</sub>-CH(OH)-SO<sub>3</sub>H or -CH<sub>2</sub>-CH(OH)-SO<sub>3</sub>Z';
- Z' represents an ion derived from an alkali or alkaline-earth metal, such as sodium, potassium or magnesium; an ammonium ion; or an ion derived from an organic amine and in particular from an aminoalcohol, such as mono-, di- and triethanolamine, mono-, di- or triisopropanolamine, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol and tris(hydroxymethyl)aminomethane;

- $R_a$  represents a  $C_{10}$ - $C_{30}$  alkyl or alkenyl group of an acid  $R_aC(O)-OH$  preferably present in coconut oil or in hydrolysed linseed oil, an alkyl group, especially of  $C_{17}$  and its iso form, or an unsaturated  $C_{17}$  group.

The compounds corresponding to formula **(XXIII)** are preferred. These compounds are also classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroampho-diacetate, disodium caprylamphodiacetate, disodium caprylampho-diacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylampho-dipropionate, disodium caprylamphodipropionate, lauroamphodipropionic acid, cocoampho-dipropionic acid.

By way of example, mention may be made of the N-cocoamidocarboxymethyl glycinate of an alkali metal such as sodium, or cocoamphodiacetate sold by the company Rhodia under the trade name Miranol<sup>®</sup> C2M Concentrate.

Among all the amphoteric or zwitterionic surfactants mentioned above, use is preferably made of cocoylamidopropylbetaine, cocoylbetaine and the N-cocoamidocarboxymethyl glycinate of an alkali metal such as sodium.

The composition according to the invention preferably comprises from 0.01% to 20% by weight, in particular from 0.5% to 10% by weight and better still from 1% to 5% by weight of amphoteric or zwitterionic surfactant(s), relative to the total weight of the composition.

Preferably, the composition of the invention contains at least one nonionic surfactant. Among the surfactants according to the invention, use is made more particularly of  $C_6$ - $C_{24}$  alkyl polyglucosides and more particularly  $C_8$ - $C_{16}$  alkyl polyglucosides.

According to the present invention, the surfactant(s) are preferably present in the composition in an amount ranging from 0.01% to 40% by weight, preferably from 0.05% to 30% by weight, better still from 0.1% to 20% and even better still from 0.2% to 10% by weight, relative to the total weight of the composition.

#### ix) Adjuvants:

The composition comprising the ingredients *i)* to *iv)* as defined previously and optionally the ingredients *v)* to *viii)* may also contain various adjuvants conventionally used in hair dye compositions, such as anionic, cationic, nonionic, amphoteric or zwitterionic polymers, or mixtures thereof, mineral thickeners, penetrants, sequestrants, fragrances, buffers, dispersants, film-forming agents, preserving agents and opacifiers.

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

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

x) Additional dyes:

5 The composition comprising the dye(s) bearing a disulfide, thiol or protected-thiol function especially of formula (I) as defined previously of the process of the invention may also contain one or more additional direct dyes other than the disulfide, thiol or protected-thiol direct dyes of formula (I) according to the invention. These direct dyes are chosen, for example, from those conventionally used in direct dyeing, and among which mention may be made of any commonly used aromatic and/or non-aromatic dye such as neutral, acidic or cationic nitrobenzene direct dyes, neutral, acidic or cationic azo direct dyes, natural direct dyes, neutral, acidic or cationic quinone and in particular anthraquinone direct dyes, azine, triarylmethane, indoamine, methine, styryl, porphyrin, metalloporphyrin, phthalocyanine, cyanine and methine direct dyes, and fluorescent dyes, other than the dyes of formula (I).

15

The composition comprising the dye(s) bearing a disulfide, thiol or protected-thiol function especially of formula (I) as defined previously of the process of the invention may also contain one or more oxidation bases and/or one or more couplers conventionally used for the dyeing of keratin fibres.

20

Among the oxidation bases, mention may be made of para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, bis-para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.

25

Among these couplers, mention may be made especially of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers, and the addition salts thereof.

30

The coupler(s) are each generally present in an amount inclusively between 0.001% and 10% by weight and preferably between 0.005% and 6% by weight relative to the total weight of the dye composition.

35

The oxidation base(s) present in the dye composition are each generally present in an amount inclusively between 0.001% and 10% by weight and preferably between 0.005% and 6% by weight relative to the total weight of the dye composition.

40

In general, the addition salts of the oxidation bases and couplers used in the context of the invention are especially chosen from the salts of addition with an acid, such as the hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates, and the salts of addition with a base, such as alkali metal hydroxides, for instance sodium hydroxide, potassium hydroxide, ammonia, amines or alkanolamines.

45

According to one particular embodiment, the composition of the process of the invention contains at least one oxidation base and optionally at least one coupler as defined above.

50

This embodiment may be implemented in the presence of one or more chemical

oxidizing agents. The term "chemical oxidizing agent" means chemical oxidizing agents other than atmospheric oxygen, such as those described previously.

The use of hydrogen peroxide is particularly preferred.

5 The content of oxidizing agent(s) is generally inclusively between 1% and 40% by weight relative to the weight of the composition and preferably between 1% and 20% by weight relative to the weight of the composition containing them.

*The pH:*

10 The pH of the composition according to the invention is generally inclusively between 2 and 12 approximately and preferably between 3 and 11 approximately. It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres, or alternatively using standard buffer systems.

15 The pH of the composition is preferentially inclusively between 6 and 9, particularly between 7 and 9, and more particularly between 7.5 and 9.

Among the acidifying agents that may be mentioned, for example, are mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid or sulfuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid and lactic acid, and sulfonic acids.

20 Among the alkaline agents that may be mentioned, for example, are aqueous ammonia, alkali metal carbonates, alkanolamines such as monoethanolamine, diethanolamine and triethanolamine, and other alkaline agents iv) as defined previously.

*Forms of the composition:*

25

The dye composition comprising *i)* the dye(s) bearing a disulfide, thiol or protected-thiol function especially of formula (I) as defined previously and the ingredients *ii)*, *iii)*, *iv)* and optionally the ingredients *v)* to *ix)* as defined previously may be in various galenical forms, such as in the form of liquids, lotions, creams or gels, or in any other form that is suitable for dyeing keratin fibres. They may also be conditioned under pressure in an aerosol can in the presence of a propellant or in a non-aerosol can, and form a mousse.

30

## 2). Dyeing processes of the invention

35 The process for dyeing keratin fibres, especially dark keratin fibres, according to the invention comprises the step of applying to the keratin fibres:

*i)* at least one cationic direct dye bearing a disulfide function, a thiol function or a protected-thiol function as defined previously;

*ii)* at least 25% of one or more fatty substances as defined previously;

40

*iii)* at least one alkaline agent as defined previously;

- iv)* at least one reducing agent as defined previously;
- vi)* optionally at least one thickening organic polymer as defined previously; and
- vii)* optionally at least one surfactant as defined previously;

the ingredients *i)* to *iv)*, *vi)* and *vii)* possibly being applied either together onto the said  
5 fibres or separately.

When it is desired to lighten dark keratin fibres without the use of a chemical oxidizing agent, an ingredient *i)* that is fluorescent is used in the dye composition or the dyeing process. Preferentially, the fluorescent dyes of formula (I) are chosen from the dyes of  
10 formulae (XIII), (XIII'), (XIV), (XIV'), (XVa), (XV'a), (XV) to (XV'), (XVI), (XVI'), (XVIa) and (XVI'a) as defined previously. More particularly, the fluorescent dyes *i)* as defined previously used for lightening keratin fibres are chosen from compounds 44, 49, 49a and 55.

15 The dyeing process according to the invention may be performed in one step by applying to the keratin fibres the composition according to the invention comprising the ingredients *i)* to *v)* and *vi)* to *vii)* as defined previously, in one or more steps.

According to one particular embodiment of the process of the invention, the reducing agent *iv)* as defined previously may be applied as a pretreatment before the application of  
20 the dye composition containing the ingredients *i)* to *iii)* and *vi)* to *vii)* as defined previously.

According to another interesting variant of the invention, the reducing composition comprising the reducing agent *iv)* and the ingredients *iii)* and optionally *vii)* as defined previously is applied to the keratin fibres as a pretreatment before the application of the dye composition comprising the ingredients *i)* and *ii)* as defined previously and optionally  
25 the ingredients *v)* and *vii)* as defined previously.

According to another interesting variant of the invention, the reducing composition comprising the reducing agent *iv)* and the ingredients *iii)* and *vii)* as defined previously is applied to the keratin fibres as a pretreatment before the application of the dye composition comprising the ingredients *i)* and *ii)* as defined previously and the ingredients *v)* and *vii)* as  
30 defined previously.

According to yet another variant of the invention, the reducing composition comprising the reducing agent *iv)* and the ingredient *iii)* as defined previously is applied to the keratin fibres as a pretreatment before the application of the dye composition comprising the ingredients *i)*, *ii)* and *vi)* as defined previously.

35 According to another variant of the invention, the reducing composition comprising the reducing agent *iv)* and the ingredient *iii)* as defined previously is applied to the keratin

fibres as a pretreatment before the application of the dye composition comprising the ingredients *i)*, *ii)* and *vii)* as defined previously.

According to one particular embodiment of the invention, the process of the invention comprises a first step of reducing pretreatment with a reducing composition that is applied to the keratin fibres, comprising the ingredients *iv)* and *iii)* as defined previously, followed, in a second step, by the application of a dye composition comprising the ingredients *i)* and *ii)* as defined previously.

According to another particular embodiment of the invention, the process of the invention comprises a first step of reducing pretreatment with a reducing composition that is applied to the keratin fibres, comprising the ingredients *iv)* and optionally *vii)* as defined previously, followed, in a second step, by the application of a dye composition comprising the ingredients *i)*, *ii)* and *iii)* as defined previously, and possibly the ingredients *v)* and *vii)* as defined previously.

The reducing pretreatment may be of short duration, especially from 1 second to 30 minutes and preferably from 1 minute to 15 minutes, with one or more reducing agents as mentioned previously.

Between the reducing pretreatment step and the dyeing step using the composition comprising the ingredient *i)* as defined previously, the keratin fibres are preferentially rinsed with water.

The leave-on time of the dye composition, i.e. comprising the ingredient *i)* as defined previously, is inclusively between 5 minutes and 1 hour and preferably between 10 minutes and 40 minutes.

The dye composition, i.e. the composition comprising the ingredient *i)*, is generally applied at room temperature. However, it may be applied at temperatures ranging from 20 to 180°C.

According to another variant, instead of using the reducing agent as a pretreatment, it is used as a post-treatment, after the application of the dye composition.

According to another particular dyeing process of the invention, the dyeing process does not comprise any reducing pretreatment or post-treatment step. In this case, the dyeing process comprises the step of applying the composition according to the invention, which comprises the ingredients *i)* to *iv)* and optionally *vi)* to *vii)* as defined previously.

When the ingredient *i)* is a protected-thiol dye, i.e. the thiol dye of formula (I) as defined previously in which  $U = Y$  with  $Y$  being a protecting group, the process of the invention may

be preceded by a deprotection step for restoring the SH function *in situ*.

By way of example, it is possible to deprotect the function S-Y of the dyes of the invention with Y being a protecting group, by adjusting the pH as follows:

Y: protecting group	deprotection
alkylcarbonyl,	pH>9
arylcarbonyl,	pH>9
alkoxycarbonyl,	pH>9
aryloxy carbonyl,	pH>9
arylalkoxycarbonyl,	pH>9
(di)(alkyl)aminocarbonyl,	pH>9
(alkyl)arylaminocarbonyl,	pH>9
optionally substituted aryl such as phenyl,	pH>9
5-, 6- or 7-membered monocyclic heteroaryl such as oxazolium,	pH>9
8- to 11-membered bicyclic heteroaryl such as benzimidazolium or benzoxazolium	pH>9

5

The deprotection step may also be performed during a step of pretreatment of the hair, for instance the hair reducing pretreatment.

10 A treatment with one or more chemical oxidizing agents may optionally be performed after the application of ingredients *i)* to *iii)* and optionally *vi)* to *vii)* as defined previously to the keratin fibres.

To do this, a fixing composition comprising at least one cosmetic chemical oxidizing agent such as the ingredient *v)* as defined previously and optionally the ingredient *vi)* as defined previously may be used. Thus, it may be chosen especially from hydrogen  
 15 peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulfates, and also enzymes, among which mention may be made of peroxidases, 2-electron oxidoreductases such as uricases, and 4-electron oxygenases such as laccases. The use of hydrogen peroxide is particularly preferred.

20 The leave-on time of the oxidizing (fixing) composition is inclusively between 1 second and 40 minutes and preferably between 15 seconds and 15 minutes.

Preferentially, the application of the oxidizing composition takes place after the application of the dye composition, i.e. the composition comprising the ingredient *i)* as defined previously and optionally the ingredient *vi)* as defined previously.

Between the dyeing step using the composition comprising the ingredient *j*) as defined previously and optionally the ingredient *vi*) as defined previously, and the fixing step, the keratin fibres are preferentially rinsed with water.

5 When the ingredients *i*) and *iv*) and optionally *vi*) to *vii*) as defined previously are not in the same composition, the pH of the composition that contains *i*) is preferentially inclusively between 4 and 10 and particularly between 5 and 7; and the pH of the composition that contains *iv*) is preferentially inclusively between 4 and 10 and particularly between 7 and 10.

10 The dyeing and/or lightening process according to the invention may be followed by shampooing with a standard shampoo and/or drying of the keratin fibres.

According to particularly advantageous embodiments, the process is performed in three different ways using compositions A, B and C in which:

15 ➤ the dye composition A contains:

*i*) at least one fluorescent disulfide dye in a concentration inclusively between 0.01 g% and 5 g% and preferably between 0.05 g% and 2 g%;

20 *ii*) at least 25% of a fatty substance preferably chosen from mineral oils such as liquid petroleum jelly, in a concentration preferably inclusively between 30 g% and 80 g%; and optionally

*vii*) optionally at least one surfactant;

the pH of composition A preferably being inclusively between 4 and 10, and more particularly between 5 and 7;

25 ➤ the reducing composition B comprises:

*iv*) at least one thiol reducing agent in a concentration preferably inclusively between 0.5 g% and 50 g% and more particularly inclusively between 10 g% and 30 g%;

30 *iii*) at least one alkaline agent preferably comprising an amine group, in a concentration preferably inclusively between 0.1 g% and 30 g% and more particularly between 0.5 g% and 5 g%;

and optionally at least one fragrance in a concentration preferably inclusively between 0.01 g% and 10 g% and more particularly inclusively between 0.2 g% and 2 g%;

the pH of composition B preferably being inclusively between 5 and 12, and more particularly inclusively between 7 and 10;

35

➤ the fixing composition C comprises: *v*) at least one oxidizing agent in a concentration preferably inclusively between 0.01 g% and 30 g% and more particularly between 0.5

g% and 5 g%, the pH of composition C preferably being inclusively between 1.5 and 7 and more particularly between 2 and 5;

the fixing composition may also comprise a thickening organic polymer *vi)* as defined previously; just like compositions A and/or B.

5

Variant 1:

The dye composition A is mixed with the reducing composition B in the following proportions: Mixing of 9 volumes of composition A with 1 volume of composition B in a bowl. The mixture is applied to the hair with a leave-on time preferably inclusively between 10 minutes and 1 hour and preferably between 10 minutes and 40 minutes. The hair is rinsed and is then optionally shampooed, shampooing preferably being performed, and the hair is then dried.

Variant 2:

15 The dyeing formula A is mixed with the reducing composition B in the following proportions: Mixing of 9 volumes of composition A with 1 volume of composition B in a bowl. The mixture is applied to the hair with a leave-on time preferably inclusively between 5 minutes and 1 hour and more particularly inclusively between 10 minutes and 40 minutes.

20 The hair is optionally rinsed, preferably rinsed. The fixing composition C is then applied to the hair with a leave-on time preferably inclusively between 1 minute and 30 minutes and more particularly inclusively between 3 minutes and 10 minutes.

The hair is rinsed and is then optionally shampooed, shampooing preferably being performed, and the hair is then dried.

25

Variant 3:

The reducing formula is applied to the hair with a leave-on time preferably inclusively between 5 minutes and 1 hour and more particularly inclusively between 10 minutes and 40 minutes. The hair is optionally rinsed, preferably rinsed. The dye formula is applied to the hair with a leave-on time preferably inclusively between 5 minutes and 1 hour and more particularly inclusively between 10 minutes and 40 minutes. The hair is optionally rinsed, preferably rinsed. The fixing composition C is then applied to the hair with a leave-on time preferably inclusively between 1 minute and 30 minutes and more particularly between 3 minutes and 10 minutes. The hair is rinsed and is then optionally shampooed, shampooing preferably being performed, and the hair is then dried.

35

### 3). Dyeing kit of the invention

5 A subject of the invention is also a multi-compartment dyeing device or "kit" comprising a first compartment containing a dye composition comprising the composition containing the ingredient *i)*; a second compartment which contains a reducing agent *iv)* as defined previously; the ingredients *ii)* to *iii)* and optionally the ingredients *v)* to *vii)* as defined previously being divided among the first two compartments, and optionally a third compartment comprising at least one oxidizing agent as defined previously.

10 According to one variant, the device comprises a first compartment which contains a dye composition comprising the composition containing the ingredients *i)*, *ii)* and optionally the ingredients *vi)* to *vii)* as defined previously; a second compartment which contains at least one reducing agent *iv)* as defined previously and *iii)*, and optionally the ingredients *vi)* as defined previously, and optionally a third compartment comprising at least one oxidizing agent *v)* as defined previously.

15 Alternatively, the dyeing device contains a first compartment containing a dye composition that comprises at least *i)* a protected-thiol dye, and the ingredients *ii)* and optionally the ingredients *vii)* as defined previously, a second compartment containing an agent capable of deprotecting the protected thiol to liberate the thiol, a third compartment that contains at least one reducing agent *iv)* as defined previously, and optionally the ingredients *vii)* as defined previously, and optionally a fourth compartment comprising an oxidizing agent *v)* as defined previously.

According to other variants:

- 25 - the first compartment contains *i)* and *ii)* as defined previously and optionally the ingredients *vii)* and *vii)* as defined previously, and the second compartment comprises the ingredients *iv)* and *iii)* as defined previously;
- or alternatively the first compartment contains ingredients *i)* and *ii)* as defined previously and the second compartment comprises the ingredients *iv)* and *iii)* and optionally the ingredients *vii)* as defined previously.

30 For these variants, a third compartment may be present, which contains an oxidizing agent *v)* as defined previously, and optionally a fourth compartment containing an agent that is capable of deprotecting the protected thiol to liberate the thiol if the ingredient *i)* of the first compartment is a protected thiol.

35 Each of the devices mentioned above may be equipped with a means for applying the desired mixture to the hair, for instance the devices described in patent FR 2 586 913.

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

5 The direct thiol, protected thiol or disulfide dyes of formula (I) that are useful in the present invention are known compounds and may be prepared according to methods known to those skilled in the art, especially from the methods described in patent applications EP 1 647 580, EP 2 004 759, WO 2007/110 541, WO 2007/110 540, WO 2007/110 539, WO 2007/110 538, WO 2007/110 537, WO 2007/110 536, WO 2007/110 535, WO 2007/110 534, WO 2007/110 533, WO 2007/110 532, WO 2007/110 531, EP 2  
10 070 988 and WO 2009/040 354.

## EXAMPLES OF DYEING

Concentration of the starting materials in unmodified form

## Composition A:

5

Ingredient	Commercial name	Supplier	Amount
Disulfide dye of formula <b>44</b> having as counterion the disulfate ion $S(O)_2O_2^-$ (ingredient <i>i</i> )			0.5 g%
Liquid petroleum jelly (ingredient <i>ii</i> )	Blandol	Sonneborn	60 g%
Oxyethylenated stearyl alcohol (20 EO) (ingredient <i>vii</i> )	Tego alkanol S20P	Croda	3.88 g%
Oxyethylenated stearyl alcohol (2 EO) (ingredient <i>vii</i> )	Brij S2-SO-(SG)	Croda	4.5 g%
(50/50 C <sub>8</sub> /C <sub>10</sub> ) Alkyl polyglucoside (2) as an aqueous 60% solution (ingredient <i>vii</i> )	Oramix CG 110	SEPPIC	8 g%
Cationic cellulose ether (ingredient <i>vi</i> )	Sofcat Polymer SL-100	Amerchol	0.2 g%
Water			qs 100%

## Composition B

Ingredient	Commercial name	Supplier	Amount
Ammonium thioglycolate as a 71% aqueous solution (pH 6) (ingredient <i>iv</i> )	71% Ammonium thioglycolate	Bruno bock	20 g%
Diethylenetriaminepentaacetic acid, pentasodium salt as a 40% aqueous solution	Versenex 80	Univar	0.4 g%
Fresh mint fragrance	Fresh mint	Mane	0.8 g%
Monoethanolamine (ingredient <i>iii</i> )	Monoethanolamine Care	Univar	1.21 g%
Oxyethylenated oleyl alcohol (20 EO) (ingredient <i>vii</i> )	Brij O20-SO-(MV)	Croda	6 g%
Water			qs 100%

10

**Composition C**

Ingredient	Commercial name	Supplier	Amount
Hydrogen peroxide as a 50% aqueous solution (200 vol. aqueous hydrogen peroxide solution) (Ingredient v))	H <sub>2</sub> O <sub>2</sub> Interox ST-50	Brenntag	0.48 g%
Etidronic acid, tetrasodium salt, as a 30% aqueous solution	Turpinal 4 NL	Brenntag	0.02 g%
Sodium salicylate	Sodium salicylate	Merck	0.0035 g%
Tetrasodium pyrophosphate decahydrate	Tetrasodium pyrophosphate decahydrate PRS	Penreac	0.004 g%
Polydimethyldiallylammonium chloride at 40% in water	Merquat 100	Nalco	0.125 g%
Phosphoric acid	Prayphos P5 85	Prayon	0.012 g%
Crosslinked ethyltrimethylammonium methacrylate chloride homopolymer as a 50% inverse emulsion in mineral oil (ingredient vi))	Salcare SC 95	Ciba	1.3 g%
Water			qs 100%

9 volumes of composition A are mixed with 1 volume of composition B in a bowl.

- 5 The mixture is applied to brown hair (dark hair having a tone height of 4 (TH4)), with a leave-on time of 20 minutes.

The hair is rinsed.

The fixing formula C is applied to the hair, with a leave-on time of 5 minutes.

The hair is rinsed and is then shampooed, and the hair is then dried.

10

**Colorimetric evaluation Results in the L\*a\*b\* system for evaluating the coloring of the locks:**

- 15 The color of the locks was evaluated in the L\*a\*b\* system by means of a MINOLTA® CM 3600D spectrophotometer (Illuminant D65).

- 20 In this L\*a\*b\* system, L\* represents the lightness, a\* indicates the green/red color axis and b\* the blue/yellow color axis. The higher the value of L, the lighter or weaker the color. Conversely, the lower the value of L, the darker or much stronger the color. The higher the value of a\*, the redder the shade, and the higher the value of b\*, the more yellow the

shade.

The variation in coloring between the TH4 dyed and treated locks of hair is measured by ( $\Delta E$ ) according to the following equation:

5

$$\Delta E = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$$

In this equation,  $L^*$ ,  $a^*$  and  $b^*$  represent the values after treatment, and  $L_0^*$ ,  $a_0^*$  and  $b_0^*$  represent the values measured before treatment.

10

The greater the value of  $\Delta E$ , the greater the difference in color between the TH4 locks and the uncolored locks.

	$L^*$	$a^*$	$b^*$	$\Delta E^*$
TH4 reference	24.27	3.96	4.72	-----
After treatment A+B+C	25.33	8.98	9.73	7.18

15

It is noted that the  $\Delta E$  value is significantly high after treatment with compositions A+B+C. A mahogany colouration is obtained which is intense and persistent (even after several washing operations).

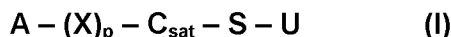
On the other hand the colour changed very little after the shampooing operations, given the number of successive shampooing operations (even after more than 10 shampooing operations). It is also observed that the coloration is particularly resistant vs. perspiration.

20

## CLAIMS

1. Cosmetic composition comprising:

*i)* at least one direct dye bearing a disulfide function, a thiol function or a protected-thiol function, of formula (I):



salts thereof with an organic or mineral acid, optical or geometric isomers thereof, tautomers thereof, and solvates thereof such as the hydrates,

in which formula (I):

• **U** represents a radical chosen from:

a)  $S - C'_{\text{sat}} - (X')_{p'} - A'$ ; and

b)  $Y$ ;

• **A** and **A'**, which may be identical or different, represent a radical containing at least one quaternized cationic chromophore or at least one chromophore bearing a quaternized or quaternizable cationic group;

• **Y** represents i) a hydrogen atom; or ii) a thiol-function protecting group;

• **X** and **X'**, which may be identical or different, represent a linear or branched, saturated or unsaturated divalent  $C_1$ - $C_{30}$  hydrocarbon-based chain, optionally interrupted and/or optionally terminated at one or both of its ends with one or more divalent groups or combinations thereof chosen from:

➤  $-N(R)-$ ,  $-N^+(R)(R)-$ ,  $-O-$ ,  $-S-$ ,  $-CO-$ ,  $-SO_2-$  with **R**, which may be identical or different, chosen from a hydrogen and a  $C_1$ - $C_4$  alkyl, hydroxyalkyl or aminoalkyl radical;

➤ an aromatic or non-aromatic, saturated or unsaturated, fused or non-fused (hetero)cyclic radical optionally comprising one or more identical or different, optionally substituted heteroatoms;

• **p** and **p'**, which may be identical or different, are equal to 0 or 1;

• **C<sub>sat</sub>** and **C'<sub>sat</sub>**, which may be identical or different, represent an optionally cyclic, optionally substituted linear or branched  $C_1$ - $C_{18}$  alkylene chain;

*ii)* at least 25% of one or more fatty substances;

*iii)* at least one alkaline agent; and

*iv)* at least one reducing agent.

2. Composition according to the preceding claim, in which the radicals **A**

and/or **A'** of the dye of formula (I), which may be identical or different, represent a radical containing at least one quaternized cationic chromophore.

3. Composition according to Claim 1 or 2, in which the dye(s) of formula (I)

are disulfide dyes with **U** representing a radical a)  $S - C'_{\text{sat}} - (X')_{p'} - A'$ ; in particular, the dyes of formula (I) according to the invention are symmetrical disulfides, i.e. formula (I) has the following formula:



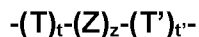
4. Composition according to Claim 1, in which the dye(s) of formula (I) are dyes bearing a thiol or protected-thiol function, i.e. **U** representing the radical *b*) **Y** chosen especially from a hydrogen atom and the following radicals:

- 5           ▪ (C<sub>1</sub>-C<sub>4</sub>)alkylcarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkylthiocarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkoxythiocarbonyl;
- 10          ▪ (C<sub>1</sub>-C<sub>4</sub>)alkylthio-thiocarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminocarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminothiocarbonyl;
- arylcarbonyl, for instance phenylcarbonyl;
- aryloxycarbonyl;
- 15          ▪ aryl(C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminocarbonyl, for instance dimethylaminocarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)(alkyl)arylaminocarbonyl;
- carboxyl;
- SO<sub>3</sub><sup>-</sup>; M<sup>+</sup> with M<sup>+</sup> representing an alkali metal such as sodium or potassium, or
- 20          alternatively a counterion of the cationic chromophore **A** and M<sup>+</sup> are absent;
- optionally substituted aryl;
  - optionally substituted heteroaryl;
  - optionally cationic, optionally substituted heterocycloalkyl;
  - -C(NR<sup>c</sup>R<sup>d</sup>)=N<sup>+</sup>R<sup>e</sup>R<sup>f</sup>; An<sup>m</sup>- with R<sup>c</sup>, R<sup>d</sup>, R<sup>e</sup> and R<sup>f</sup>, which may be identical or
  - 25          different, representing a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group and An<sup>m</sup>-
  - representing a counterion;
  - -C(NR<sup>c</sup>R<sup>d</sup>)=NR<sup>e</sup>; with R<sup>c</sup>, R<sup>d</sup> and R<sup>e</sup> as defined previously;
  - optionally substituted (di)aryl(C<sub>1</sub>-C<sub>4</sub>)alkyl;
  - optionally substituted (di)heteroaryl(C<sub>1</sub>-C<sub>4</sub>)alkyl;
  - 30          ➤ -CR<sup>1</sup>R<sup>2</sup>R<sup>3</sup> with R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>, which may be identical or different, representing a
  - halogen atom or a group chosen from:
    - (C<sub>1</sub>-C<sub>4</sub>)alkyl;
    - (C<sub>1</sub>-C<sub>4</sub>)alkoxy;
    - optionally substituted aryl;
    - 35          - optionally substituted heteroaryl;
    - P(Z<sup>1</sup>)R<sup>1</sup>R<sup>2</sup>R<sup>3</sup> with R<sup>1</sup> and R<sup>2</sup>, which may be identical or different,
    - representing a hydroxyl, (C<sub>1</sub>-C<sub>4</sub>)alkoxy or alkyl group, R<sup>3</sup> representing a
    - hydroxyl or (C<sub>1</sub>-C<sub>4</sub>)alkoxy group, and Z<sup>1</sup> representing an oxygen or sulfur
    - atom;
    - 40          ▪ a sterically hindered ring; and
    - optionally substituted alkoxyalkyl.

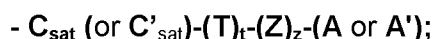
5. Dyeing composition according to any one of the preceding claims, in which the dye(s) of formula (I) are dyes with  $C_{\text{sat}}$  and  $C'_{\text{sat}}$ , which may be identical or different, representing a chain  $-(\text{CH}_2)_k-$  with  $k$  being an integer between 1 and 8 inclusive.

5

6. Composition according to any one of the preceding claims, in which the dye(s) of formula (I) are dyes in which, when  $p$  and  $p'$  is equal to 1,  $X$  and  $X'$ , which may be identical or different, represent the following sequence:



10 the said sequence being linked in formula (I) symmetrically as follows:



in which:

- $T$  and  $T'$ , which may be identical or different, represent one or more radicals or combinations thereof chosen from:  $-\text{O}-$ ;  $-\text{S}-$ ;  $-\text{N}(\text{R})-$ ;  $-\text{N}^+(\text{R})(\text{R}^\circ)-$ ;  $-\text{S}(\text{O})-$ ;  $-\text{S}(\text{O})_2-$ ;  $-\text{C}(\text{O})-$ ; with  $\text{R}$ ,  $\text{R}^\circ$ , which may be identical or different, representing a hydrogen atom, a  $\text{C}_1$ - $\text{C}_4$  alkyl radical,  $\text{C}_1$ - $\text{C}_4$  hydroxyalkyl radical or an aryl( $\text{C}_1$ - $\text{C}_4$ )alkyl radical; and a cationic or non-cationic, preferentially monocyclic heterocycloalkyl or heteroaryl radical, preferentially containing two heteroatoms (more preferentially two nitrogen atoms) and preferentially being 5- to 7-membered, more preferentially imidazolium;
- the indices  $t$  and  $t'$ , which may be identical or different, are equal to 0 or 1;
- $Z$  represents:
  - $-(\text{CH}_2)_m-$  with  $m$  being an integer inclusively between 1 and 8;
  - $-(\text{CH}_2\text{CH}_2\text{O})_q-$  or  $-(\text{OCH}_2\text{CH}_2)_q-$  in which  $q$  is an integer inclusively between 1 and 5;
  - an aryl, alkylaryl or arylalkyl radical in which the alkyl radical is  $\text{C}_1$ - $\text{C}_4$  and the aryl radical is preferably  $\text{C}_6$ , being optionally substituted with at least one group  $\text{SO}_3\text{M}$  with  $\text{M}$  representing a hydrogen atom, an alkali metal or an ammonium group substituted with one or more identical or different, linear or branched  $\text{C}_1$ - $\text{C}_{18}$  alkyl radicals optionally bearing at least one hydroxyl;
- $z$  is 0 or 1.

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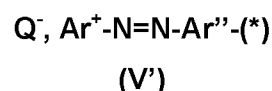
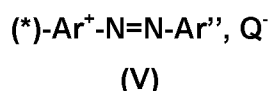
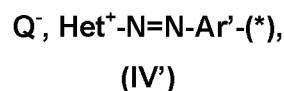
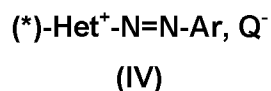
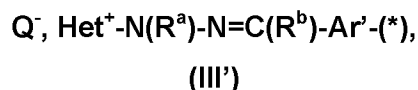
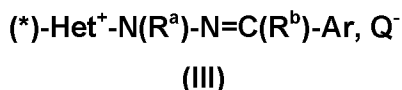
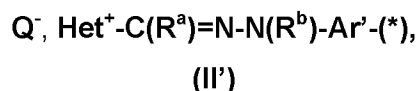
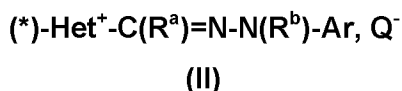
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7. Composition according to any one of the preceding claims, in which the dye(s) of formula (I) comprise a chromophore  $A$  and optionally a chromophore  $A'$ ,  $A$  and  $A'$  being identical or different and being chosen from the hydrazono cationic chromophores of formulae (II) and (III'), the azo chromophores (IV) and (IV') and the diazo chromophores (V) below:

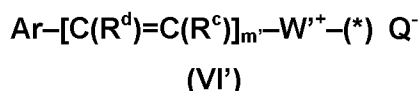
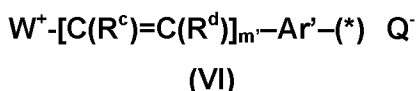


formulae (II) to (V') with:

- **Het**<sup>+</sup> representing a cationic heteroaryl radical;
- **Ar**<sup>+</sup> representing an aryl radical bearing an exocyclic cationic charge;
- **Ar** representing an optionally substituted aryl group;
- 5 - **Ar'** being an optionally substituted divalent (hetero)arylene group;
- **Ar''** being an optionally substituted (hetero)aryl group;
- **R**<sup>a</sup> and **R**<sup>b</sup>, which may be identical or different, representing a hydrogen atom or an optionally substituted group (C<sub>1</sub>-C<sub>8</sub>)alkyl;
- 10 or alternatively the substituent **R**<sup>a</sup> with a substituent of **Het**<sup>+</sup> and/or **R**<sup>b</sup> with a substituent of **Ar** form, together with the atoms that bear them, a (hetero)cycloalkyl;
- **Q**<sup>-</sup> representing an organic or mineral anionic counterion;
- (\*) representing the part of the chromophore linked to the rest of the molecule of formula (I).

15           8.       Composition according to any one of Claims 1 to 6, in which the dye(s) of formula (I) comprise a chromophore **A** and optionally a chromophore **A'**, **A** and **A'** being identical or different and being chosen from:

a) the polymethine radicals of formulae (VI) and (VI') below:



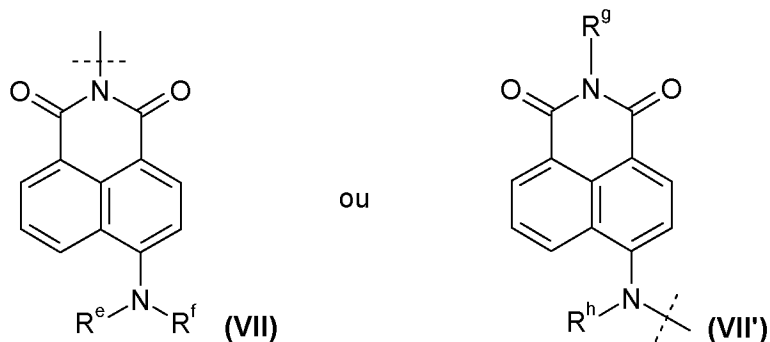
in which formulae (VI) and (VI'):

- 20
- **W**<sup>+</sup> represents a cationic heterocyclic or heteroaryl group;
  - **W'**<sup>+</sup> represents a divalent heterocyclic or heteroaryl radical as defined for **W**<sup>+</sup>;
  - **Ar** represents an optionally substituted aryl group;
  - **Ar'** is a divalent aryl radical as defined for **Ar**;

- $m'$  represents an integer between 1 and 4 inclusive;
- $R^c$  and  $R^d$ , which may be identical or different, represent a hydrogen atom or an optionally substituted ( $C_1$ - $C_8$ )alkyl group, or alternatively  $R^c$  contiguous with  $W^+$  or  $W^{*+}$  and/or  $R^d$  contiguous with  $Ar$  or  $Ar'$  form, with the atoms that bear them, a (hetero)cycloalkyl;
- $Q^-$  is an anionic counterion;
- $(*)$  represents the part of the chromophore linked to the rest of formula (I); and

5

b) the naphthalimidyl radicals of formula (VII) or (VII') below:



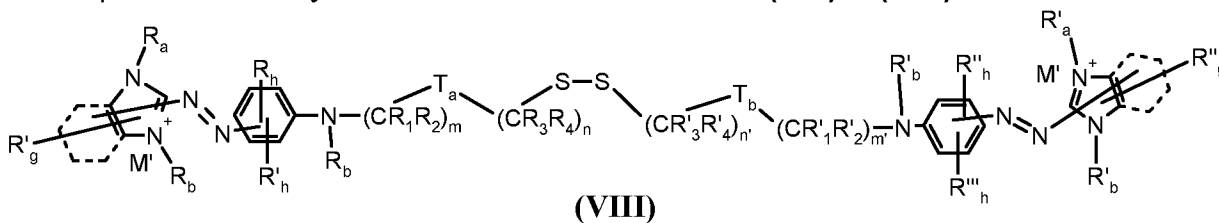
with  $--|$  representing the bond with the groupe X or X',  $C_{sat}$  or  $C'_{sat}$

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

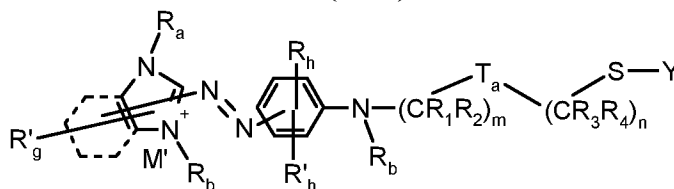
$R^e$ ,  $R^f$ ,  $R^g$  and  $R^h$ , which may be identical or different, represent a hydrogen atom or a ( $C_1$ - $C_6$ ) alkyl group which is optionally substituted, preferentially with a di( $C_1$ - $C_6$ )alkylamino or tri( $C_1$ - $C_6$ )alkyl ammonium group.

15

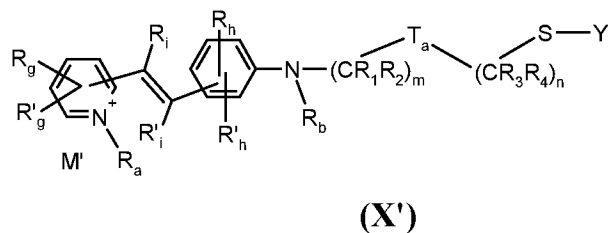
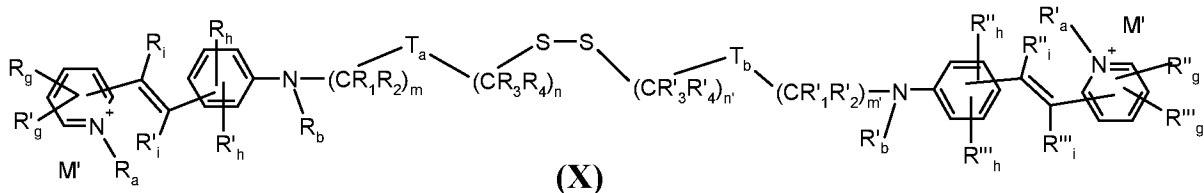
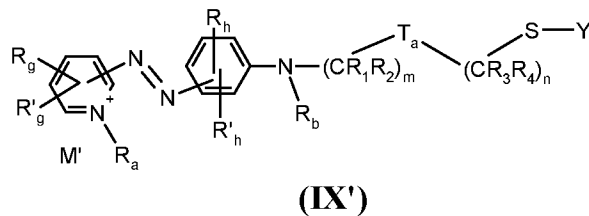
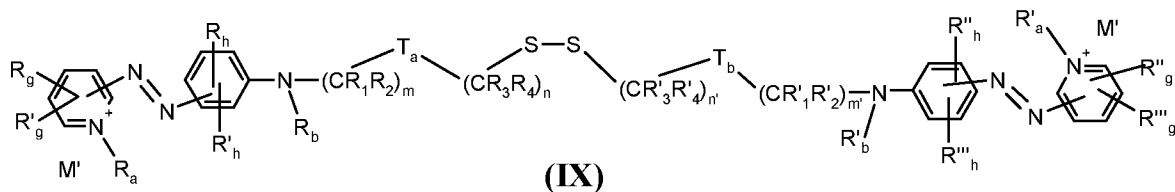
9. Composition according to any one of the preceding claims, in which the dye(s) of formula (I) are disulfide dyes chosen from those of formulae (VIII) to (XIV) and thiol or protected-thiol dyes chosen from those of formulae (VIII') to (XIV') below:



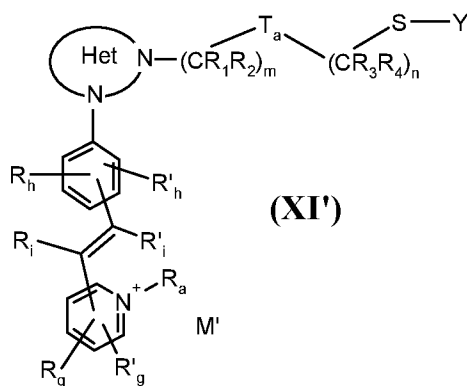
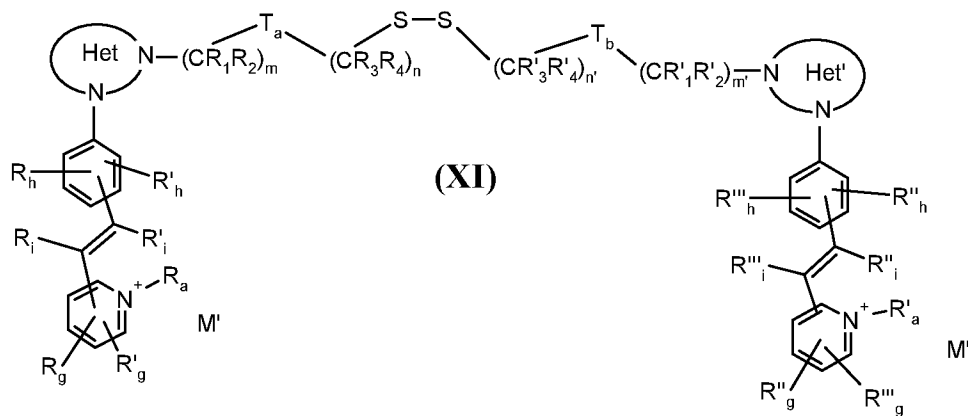
(VIII)



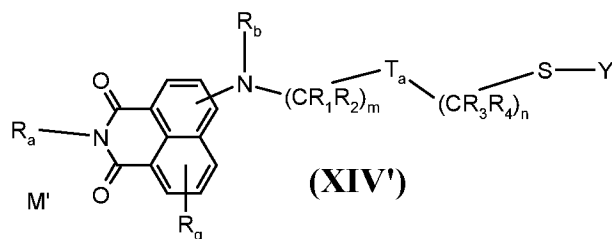
(VIII')



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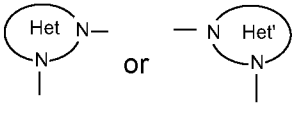



in which formulae (VIII) to (XIV) and (VIII') to (XIV'):

- 5 • **G** and **G'**, which may be identical or different, represent a group  $-NR_cR_d$ ,  $-NR'_cR'_d$  or  $C_1$ - $C_6$  alkoxy which is optionally substituted; in particular, **G** and **G'** represent a group  $-NR_cR_d$  or  $-NR'_cR'_d$ , respectively;
- 10 • **R<sub>a</sub>** and **R'<sub>a</sub>**, which may be identical or different, represent an aryl( $C_1$ - $C_4$ )alkyl group or a  $C_1$ - $C_6$  alkyl group optionally substituted with a hydroxyl or amino,  $C_1$ - $C_4$  alkylamino or  $C_1$ - $C_4$  dialkyl amino group, the said alkyl radicals possibly forming, with the nitrogen atom that bears them, a 5- to 7-membered heterocycle, optionally comprising another nitrogen or non-nitrogen heteroatom; preferentially, **R<sub>a</sub>** and **R'<sub>a</sub>** represent a  $C_1$ - $C_3$  alkyl group optionally substituted with a hydroxyl group, or a benzyl group;
- 15 • **R<sub>b</sub>** and **R'<sub>b</sub>**, which may be identical or different, represent a hydrogen atom, an aryl( $C_1$ - $C_4$ )alkyl group or a  $C_1$ - $C_6$  alkyl group that is optionally substituted; preferentially, **R<sub>b</sub>** and **R'<sub>b</sub>** represent a hydrogen atom or a  $C_1$ - $C_3$  alkyl or benzyl group;
- 20 • **R<sub>c</sub>**, **R'<sub>c</sub>**, **R<sub>d</sub>** and **R'<sub>d</sub>**, which may be identical or different, represent a hydrogen atom, a group aryl( $C_1$ - $C_4$ )alkyl or  $C_1$ - $C_6$  alkoxy or a group  $C_1$ - $C_6$  alkyl which is optionally substituted; or alternatively two adjacent radicals **R<sub>c</sub>** and **R<sub>d</sub>**, **R'<sub>c</sub>** and **R'<sub>d</sub>**, borne by the same nitrogen atom, together form a heterocyclic or heteroaryl group;
- 25 • **R<sub>e</sub>** and **R'<sub>e</sub>**, which may be identical or different, represent a linear or branched  $C_1$ - $C_6$  alkylene or  $C_2$ - $C_6$  alkenylene hydrocarbon-based chain;
- 30 • **R<sub>f</sub>** and **R'<sub>f</sub>**, which may be identical or different, represent a group di( $C_1$ - $C_4$ )alkylamino,  $(R'')(R''')N$ - or a quaternary ammonium group  $(R'')(R''')(R'''' )N^+$  in which **R''**, **R'''** and **R''''**, which may be identical or different, represent a  $C_1$ - $C_4$  alkyl group or alternatively  $(R'')(R''')(R'''' )N^+$  represents an optionally substituted cationic heteroaryl group;
- 35 • **R<sub>g</sub>**, **R'<sub>g</sub>**, **R''<sub>g</sub>**, **R'''<sub>g</sub>**, **R<sub>h</sub>**, **R'<sub>h</sub>**, **R''<sub>h</sub>** and **R'''<sub>h</sub>**, which may be identical or different, represent a hydrogen atom, a halogen atom, an amino,  $C_1$ - $C_4$  alkylamino,  $C_1$ - $C_4$  dialkylamino, cyano, carboxyl, hydroxyl or trifluoromethyl group, an acylamino,  $C_1$ - $C_4$  alkoxy, (poly)hydroxy( $C_2$ - $C_4$ )alkoxy, alkylcarbonyloxy, alkoxy carbonyl or alkylcarbonylamino radical, an acylamino, carbamoyl or alkylsulfonylamino radical, an aminosulfonyl radical, or a  $C_1$ - $C_{16}$  alkyl radical optionally substituted with a group chosen from  $C_1$ - $C_{12}$  alkoxy, hydroxyl, cyano, carboxyl, amino,  $C_1$ - $C_4$  alkylamino and

C<sub>1</sub>-C<sub>4</sub> dialkylamino, or alternatively two alkyl radicals borne by the nitrogen atom of the amino group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom;

- or alternatively two groups R<sub>g</sub> and R'<sub>g</sub>; R''<sub>g</sub> and R'''<sub>g</sub>; R<sub>h</sub> and R'<sub>h</sub>; R''<sub>h</sub> and R'''<sub>h</sub> borne by two adjacent carbon atoms together form a benzo or indeno ring, a fused heterocycloalkyl or fused heteroaryl group; the benzo, indeno, heterocycloalkyl or heteroaryl ring being optionally substituted with a halogen atom, an amino, C<sub>1</sub>-C<sub>4</sub> alkylamino, C<sub>1</sub>-C<sub>4</sub> dialkylamino, nitro, cyano, carboxyl, hydroxyl or trifluoromethyl group, an acylamino, C<sub>1</sub>-C<sub>4</sub> alkoxy, (poly)hydroxy(C<sub>2</sub>-C<sub>4</sub>)alkoxy, alkylcarbonyloxy, alkoxy carbonyl or alkylcarbonylamino radical, an acylamino, carbamoyl or alkylsulfonylamino radical, an aminosulfonyl radical, or a C<sub>1</sub>-C<sub>16</sub> alkyl radical optionally substituted with: a group chosen from C<sub>1</sub>-C<sub>12</sub> alkoxy, hydroxyl, cyano, carboxyl, amino, C<sub>1</sub>-C<sub>4</sub> alkylamino, C<sub>1</sub>-C<sub>4</sub> dialkylamino, or alternatively two alkyl radicals borne by the nitrogen atom of the amino group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom;
- or alternatively two groups R<sub>i</sub> and R<sub>g</sub>; R''<sub>i</sub> and R'''<sub>i</sub>; R'<sub>i</sub> and R'<sub>h</sub>; and/or R''<sub>i</sub> and R''<sub>h</sub> together form a fused (hetero)cycloalkyl;
- or alternatively when G represents -NR<sub>c</sub>R<sub>d</sub> and G' represents -NR'<sub>c</sub>R'<sub>d</sub>, two groups R<sub>c</sub> and R'<sub>g</sub>; R'<sub>c</sub> and R''<sub>g</sub>; R<sub>d</sub> and R<sub>g</sub>; R'<sub>d</sub> and R'''<sub>g</sub> together form a saturated heteroaryl or heterocycle, optionally substituted with one or more groups (C<sub>1</sub>-C<sub>6</sub>)alkyl, preferentially a 5- to 7-membered heterocycle containing one or two heteroatoms chosen from nitrogen and oxygen;
- R<sub>i</sub>, R'<sub>i</sub>, R''<sub>i</sub>, and R'''<sub>i</sub>, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group;
- R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R'<sub>1</sub>, R'<sub>2</sub>, R'<sub>3</sub> and R'<sub>4</sub>, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>12</sub> alkoxy, hydroxyl, cyano, carboxyl, amino, C<sub>1</sub>-C<sub>4</sub> alkylamino or C<sub>1</sub>-C<sub>4</sub> dialkyl amino group, the said alkyl radicals possibly forming, with the nitrogen atom that bears them, a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom;
- T<sub>a</sub> and T<sub>b</sub>, which may be identical or different, represent i) either a covalent σ bond, ii) or one or more radicals or combinations thereof chosen from -SO<sub>2</sub><sup>-</sup>, -O-, -S-, -N(R)-, -N<sup>+</sup>(R)(R<sup>o</sup>)-, -CO-, with R, R<sup>o</sup>, which may be identical or different, representing a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical; or an aryl(C<sub>1</sub>-C<sub>4</sub>)alkyl, iii) or a cationic or non-cationic, heterocycloalkyl or heteroaryl radical;

-  which may be identical or different, represent an optionally group;

-  represents an aryl or heteroaryl group fused to the imidazolium or phenyl ring; or alternatively is absent from the imidazolium or phenyl ring;
- m, m', n and n', which may be identical or different, represent an integer between 0 and 6 inclusive with m+n and m'+n', which may be identical or different, representing an integer between 1 and 10 inclusive;
- Y is as defined in Claim 1 or 3; in particular, Y represents a hydrogen atom or a protecting group chosen from:

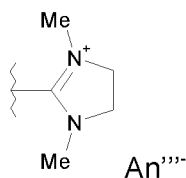
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- (C<sub>1</sub>-C<sub>4</sub>)alkylcarbonyl;
- arylcarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- aryloxycarbonyl;
- aryl(C<sub>1</sub>-C<sub>4</sub>)alkoxycarbonyl;
- (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)aminocarbonyl;
- (C<sub>1</sub>-C<sub>4</sub>)(alkyl)arylamino carbonyl;
- optionally substituted aryl;
- a 5- or 6-membered monocyclic heteroaryl;
- a 5- or 6-membered cationic monocyclic heteroaryl;
- an 8- to 11-membered cationic bicyclic heteroaryl;
- a cationic heterocycle having the following formula:



- -C(NH<sub>2</sub>)=N<sup>+</sup>H<sub>2</sub>; An<sup>'''-</sup>; with An<sup>'''-</sup> being an anionic counterion;
- -C(NH<sub>2</sub>)=NH;
- SO<sub>3</sub><sup>-</sup>, M<sup>+</sup> with M<sup>+</sup> representing a metal; and

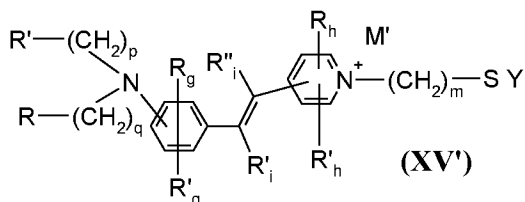
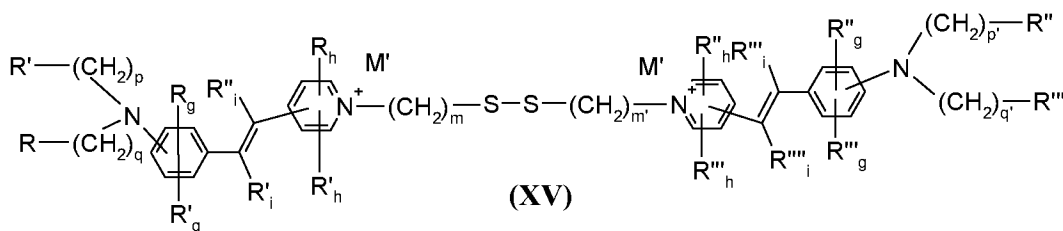
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- M' represents an anionic counterion.

10. Composition according to any one of Claims 1 to 6, 8 and 9, in which the dye(s) of formula (I) are dyes chosen from:

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- the dyes of formulae (XIII), (XIII'), (XIV) and (XIV') as defined in the preceding claim;
- the dyes of formulae (XV) to (XV') below:



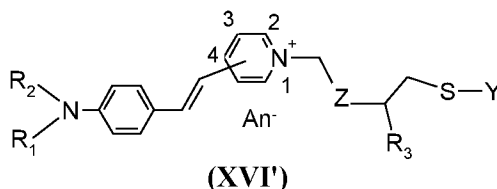
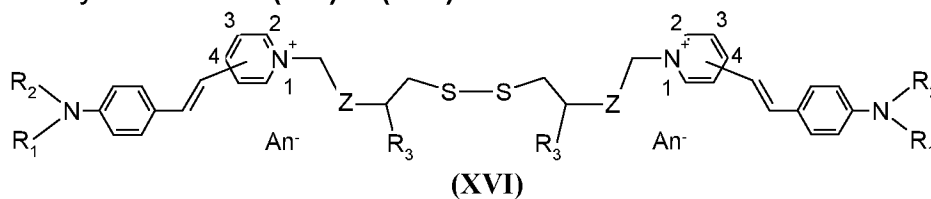
in which formulae **(XV)** and **(XV')**:

- **R** and **R'''**, which may be identical or different, represent a hydroxyl group, an amino group ( $\text{NR}_a\text{R}_b$ ) or an ammonium group ( $\text{N}^+\text{R}_a\text{R}_b\text{R}_c$ ),  $\text{An}^-$ ; with  $\text{R}_a$ ,  $\text{R}_b$  and  $\text{R}_c$ , which may be identical or different, representing a hydrogen atom or a ( $\text{C}_1\text{-C}_4$ )alkyl group;
 

5 or alternatively two alkyl groups  $\text{R}_a$  and  $\text{R}_b$  of the amino or ammonium group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom;
  - **R'** and **R''**, which may be identical or different, represent a hydrogen atom or a group as defined for **R** and **R'''**, respectively;
  - **R<sub>g</sub>**, **R'<sub>g</sub>**, **R''<sub>g</sub>**, **R'''<sub>g</sub>**, **R<sub>h</sub>**, **R'<sub>h</sub>**, **R''<sub>h</sub>** and **R'''<sub>h</sub>**, which may be identical or different, represent a hydrogen or halogen atom, an amino, (di)( $\text{C}_1\text{-C}_4$ )alkylamino, cyano, carboxyl, hydroxyl, trifluoromethyl, acylamino,  $\text{C}_1\text{-C}_4$  alkoxy, (poly)hydroxy( $\text{C}_2\text{-C}_4$ )alkoxy, ( $\text{C}_1\text{-C}_4$ )alkylcarbonyloxy, ( $\text{C}_1\text{-C}_4$ )alkoxycarbonyl, ( $\text{C}_1\text{-C}_4$ )alkylcarbonylamino, acylamino, carbamoyl or ( $\text{C}_1\text{-C}_4$ )alkylsulfonylamino group, a aminosulfonyl radical or a radical ( $\text{C}_1\text{-C}_{16}$ )alkyl optionally substituted with a group chosen from ( $\text{C}_1\text{-C}_{12}$ )alkoxy, hydroxyl, cyano, carboxyl, amino and (di)( $\text{C}_1\text{-C}_4$ )alkylamino, or alternatively the two alkyl radicals borne by the nitrogen atom of the amino group form a 5- to 7-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom;
  - **R'<sub>i</sub>**, **R''<sub>i</sub>**, **R'''<sub>i</sub>** and **R''''<sub>i</sub>**, which may be identical or different, represent a hydrogen atom or a ( $\text{C}_1\text{-C}_4$ )alkyl group;
  - **m** and **m'**, which may be identical or different, represent an integer between 1 and 10 inclusive;
  - **p**, **p'**, **q** and **q'**, which may be identical or different, represent an integer between 1 and 6 inclusive;
  - **M'** represents an anionic counterion; and
  - **Y** is as defined in the preceding claim;
- 30 it being understood that when the compound of formula **(XV)** or **(XV')** contains other

cationic parts, it is combined with one or more anionic counterions that afford formula (XV) or (XV') electrical neutrality;

- and the dyes of formula (XVI) or (XVI') below:



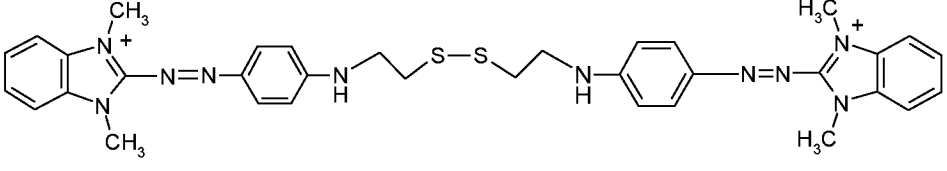
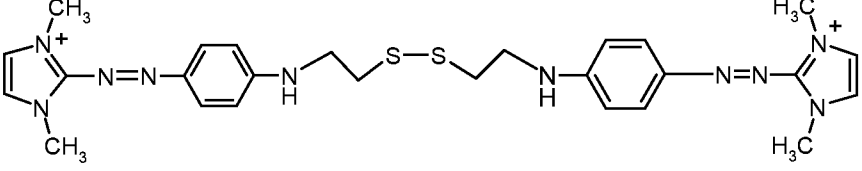
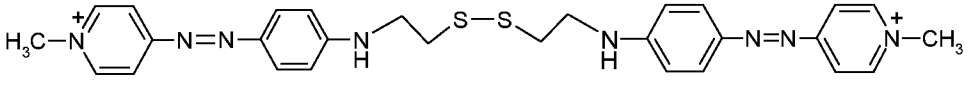
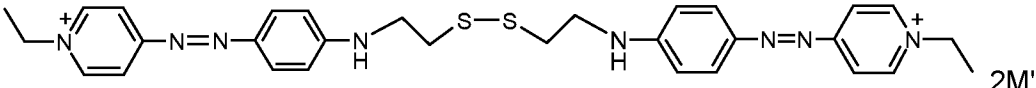
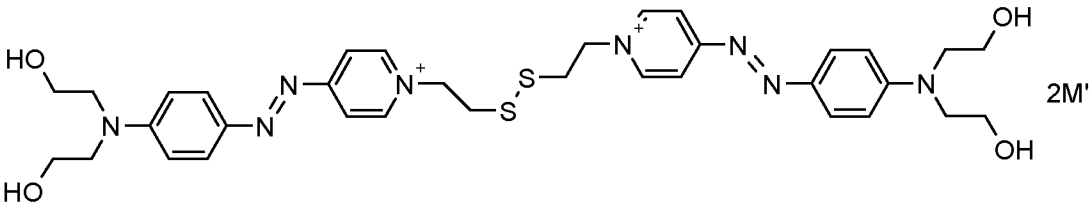
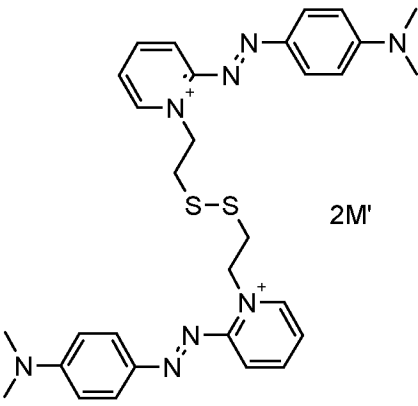
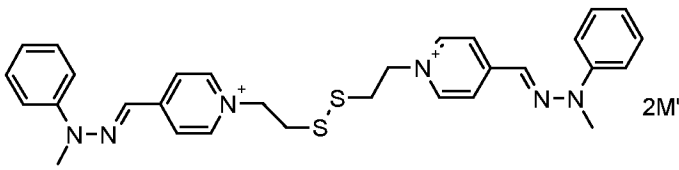
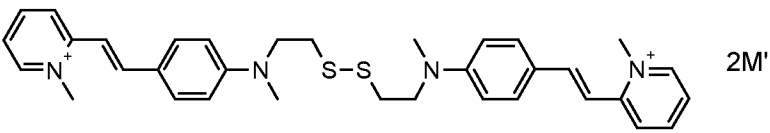
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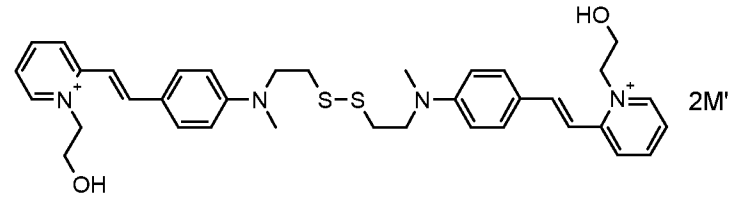
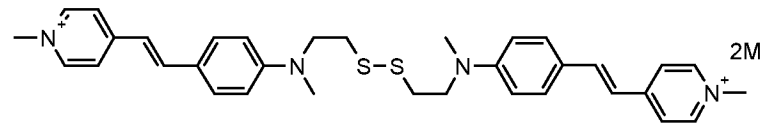
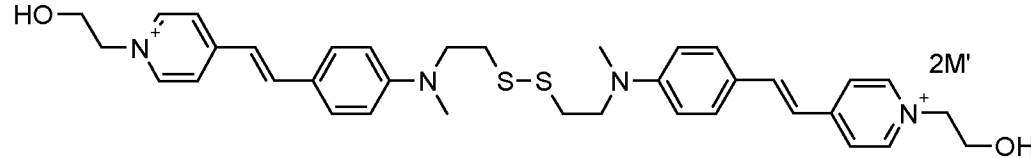
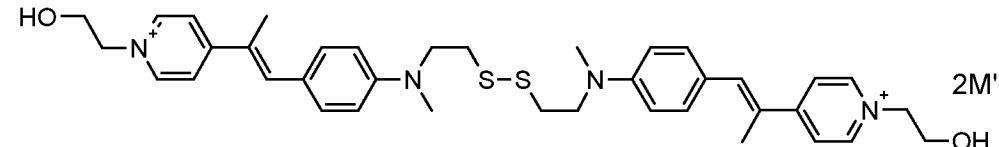
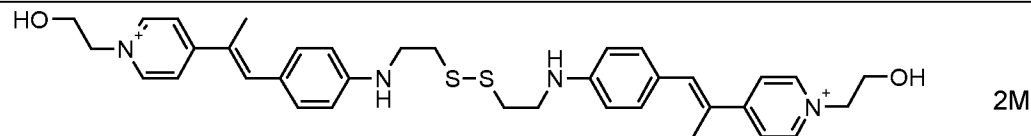
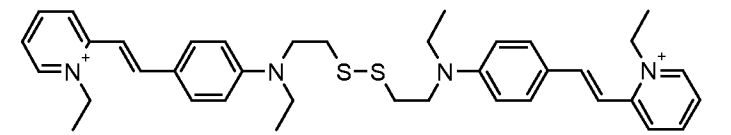
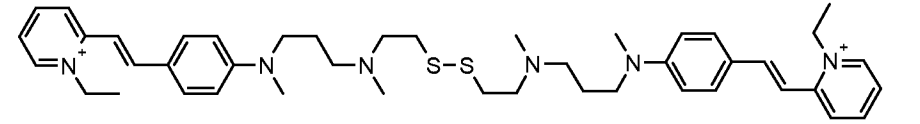
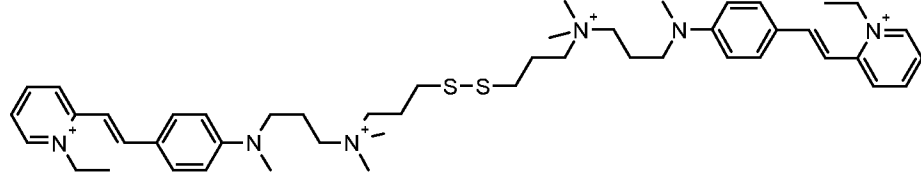
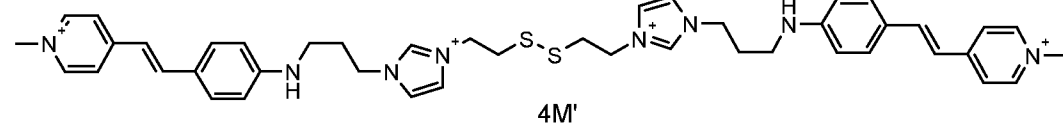
in which formula (XVI) or (XVI'):

- $R_1$  represents a  $C_1$ - $C_6$  alkyl group substituted with one or more hydroxyl groups or -C(O)OR' with R' representing a hydrogen atom, a  $C_1$ - $C_4$  alkyl group or a group -C(O)-O<sup>-</sup> and, in the latter case, an anionic counterion An<sup>-</sup> is absent;
- 10 •  $R_2$  represents a  $C_1$ - $C_6$  alkyl group optionally substituted with one or more hydroxyl groups;
- or alternatively the groups  $R_1$  and  $R_2$  form, together with the nitrogen atom that bears them, a saturated heterocyclic radical substituted with at least one hydroxyl, (poly)hydroxy( $C_1$ - $C_4$ )alkyl and/or -C(O)-OR' group with R' representing a hydrogen atom, a  $C_1$ - $C_4$  alkyl group or a group -C(O)-O<sup>-</sup> and, in the latter case, an anionic counterion An<sup>-</sup> is absent;
- 15 •  $R_3$  represents a hydrogen atom or a group -C(O)OR'' with R'' representing a hydrogen atom, an alkali metal or a  $C_1$ - $C_6$  alkyl group or alternatively  $R_3$  represents a group -C(O)-O<sup>-</sup> and, in the latter case, an anionic counterion An<sup>-</sup> is absent;
- 20 • Z represents a divalent amido group -C(O)-N(R)-, -N(R)-C(O)-, or a divalent  $C_1$ - $C_{10}$  alkylene group interrupted with an amido group -C(O)-N(R)-, -N(R)-C(O)- such as - $(CH_2)_n$ -C(O)-N(R)-(CH<sub>2</sub>)<sub>p</sub>-,  $-(CH_2)_{n''}$ -N(R)-C(O)-(CH<sub>2</sub>)<sub>p</sub>-, with n' representing an integer between 0 and 3 inclusive; preferentially, n' is equal to 0, 2, 3; p representing an integer between 0 and 4 inclusive, n'' representing an integer between 0 and 3 inclusive and especially n'=n''=p=0 and R representing a
- 25 • hydrogen atom or a  $C_1$ - $C_6$  alkyl group;
- An<sup>-</sup> represents an anionic counterion;
- Y is as defined in the preceding claim;

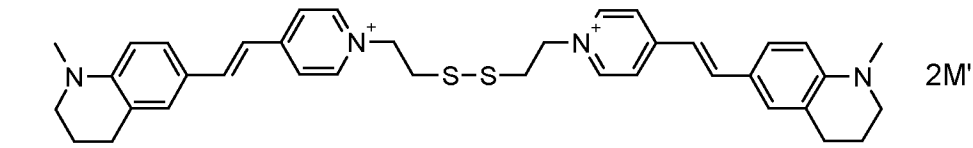
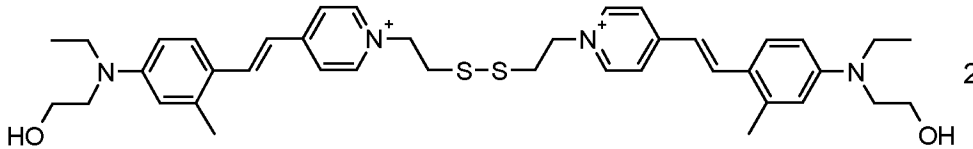
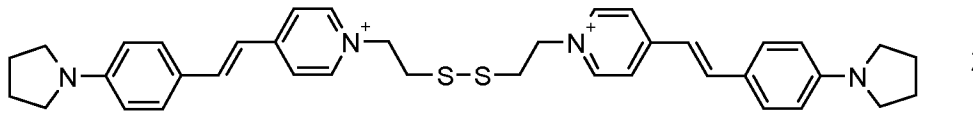
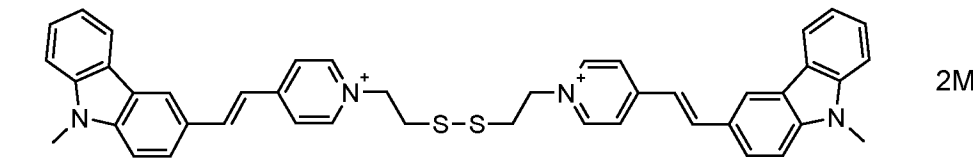
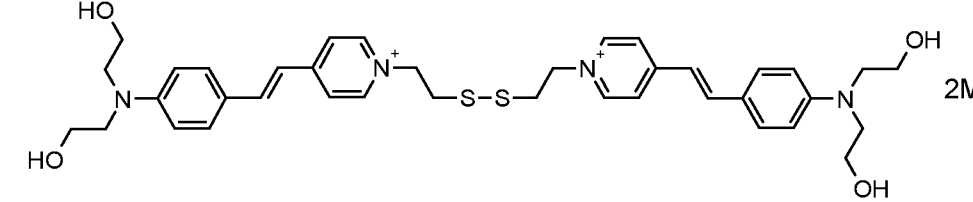
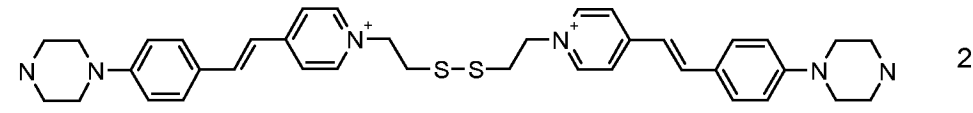
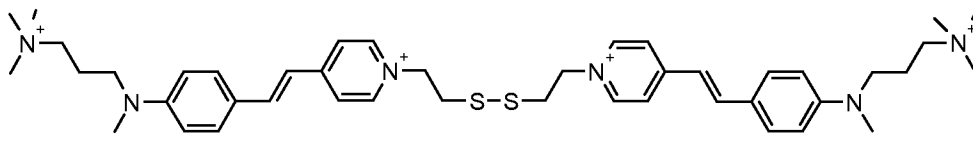
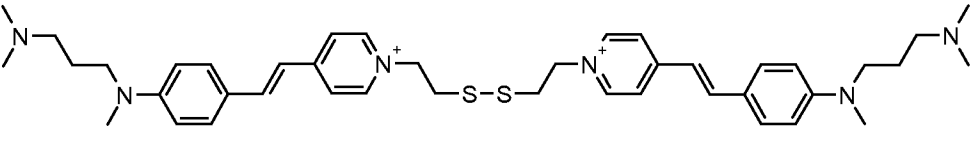
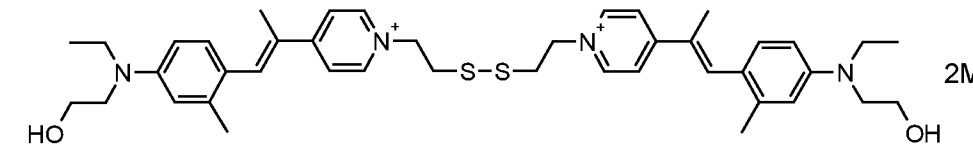
30 it being understood that when the compound of formula (XVI) or (XVI') contains other cationic parts, it is combined with one or more anionic counterions that afford formula (XVI) or (XVI') electrical neutrality.

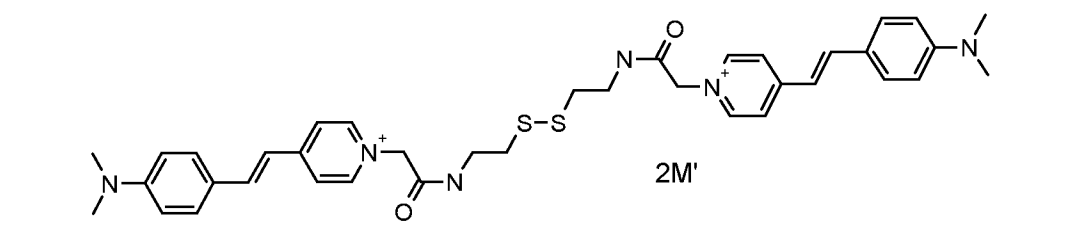
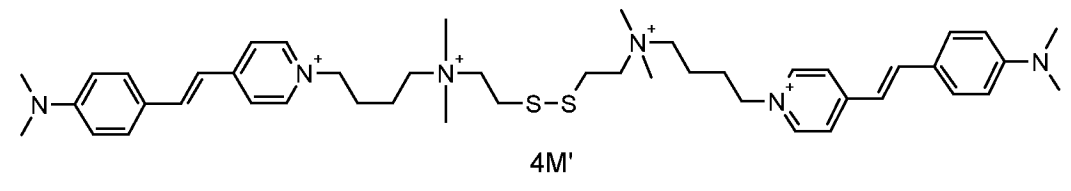
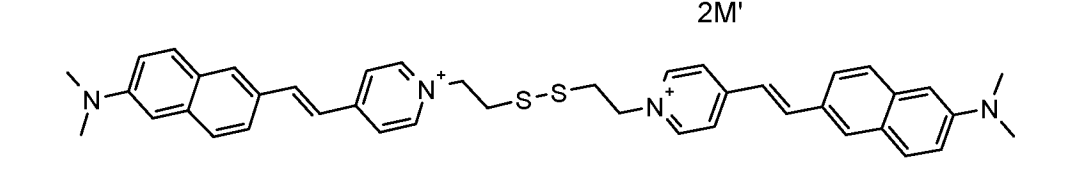
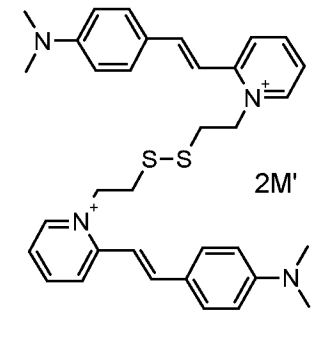
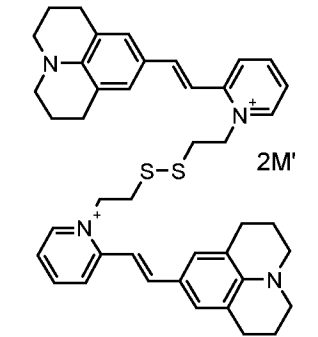
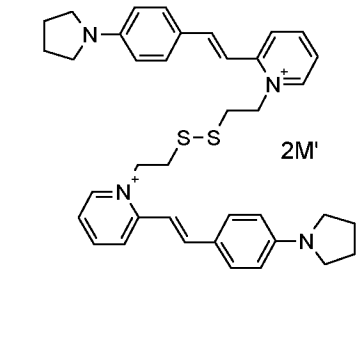
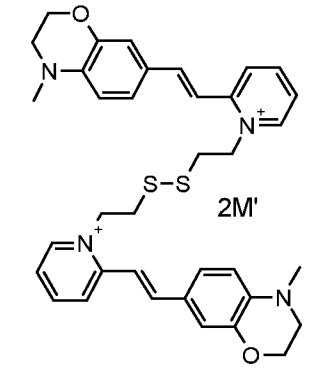
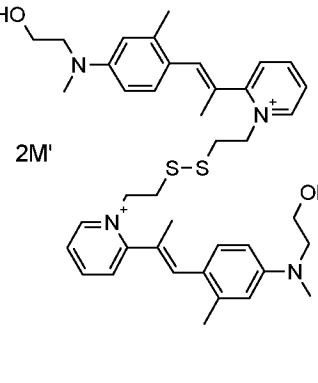
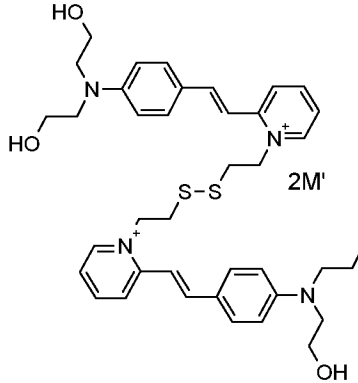
11. Composition according to any one of the preceding claims, in which the dye(s) of formula (I) are those having the following chemical structures:

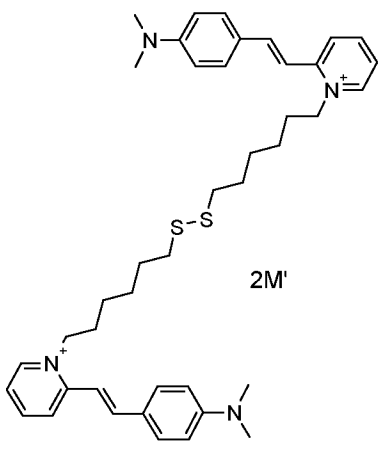
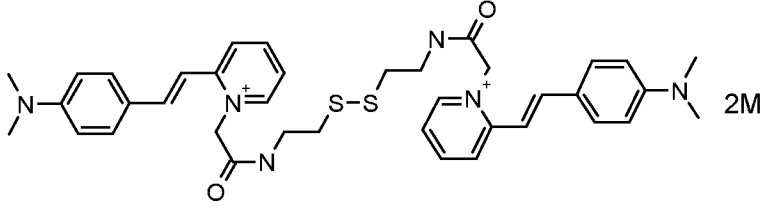
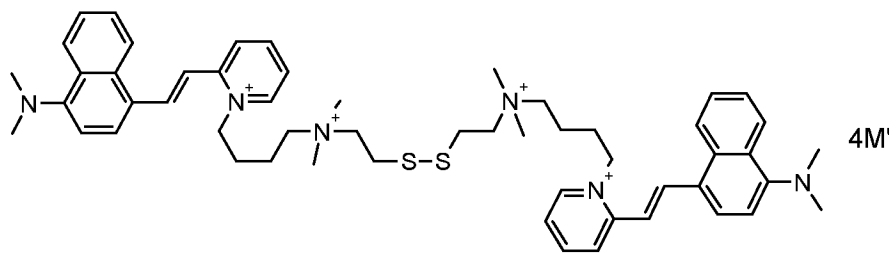
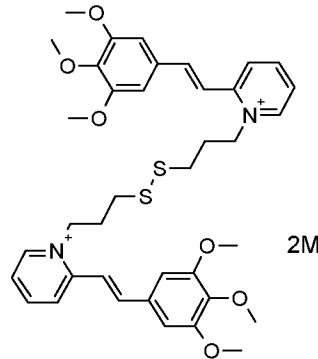
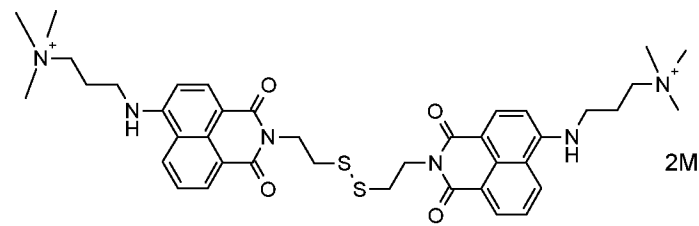
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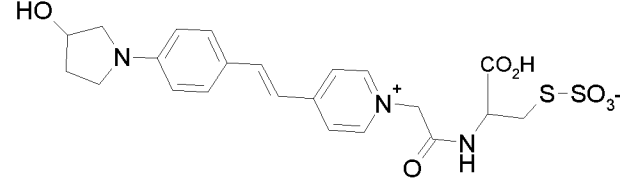
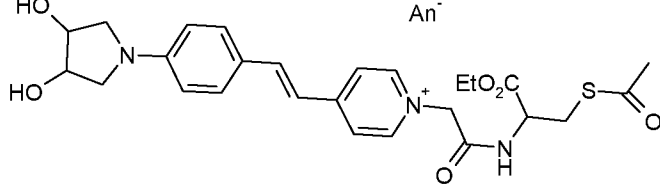
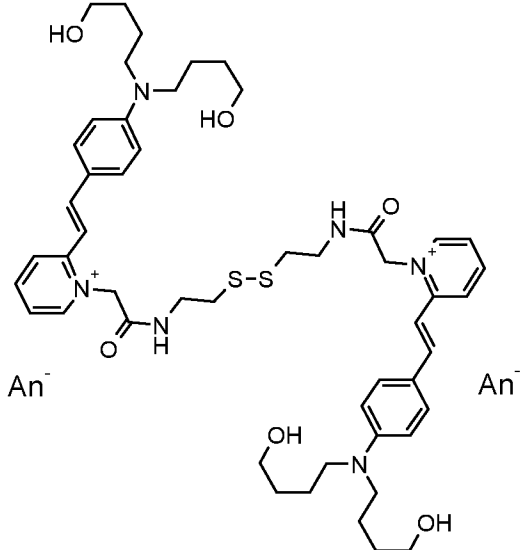
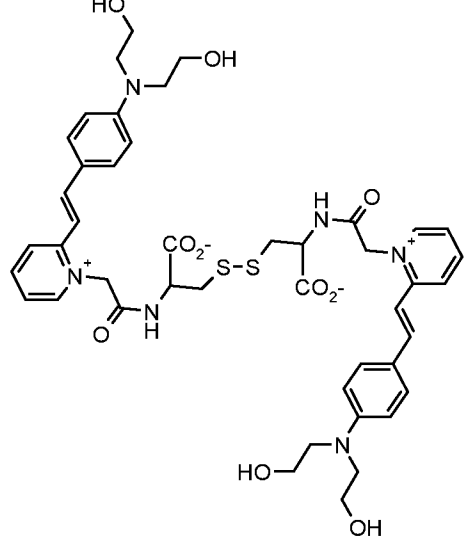
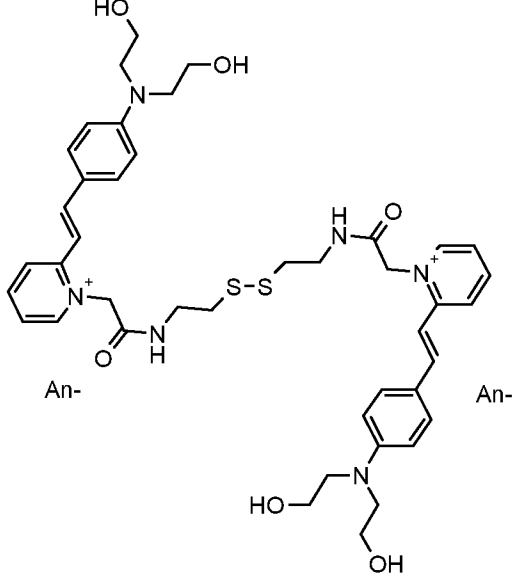
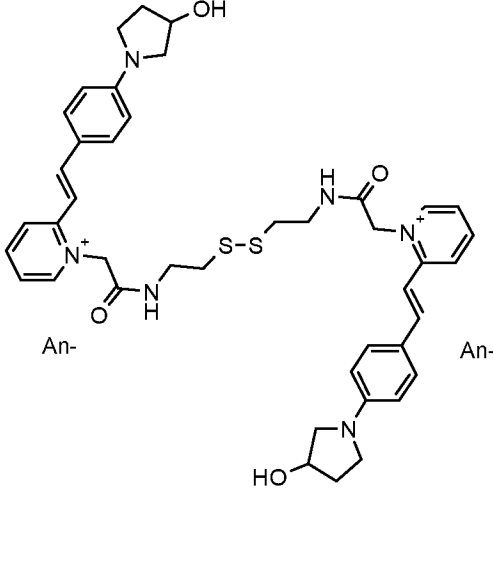
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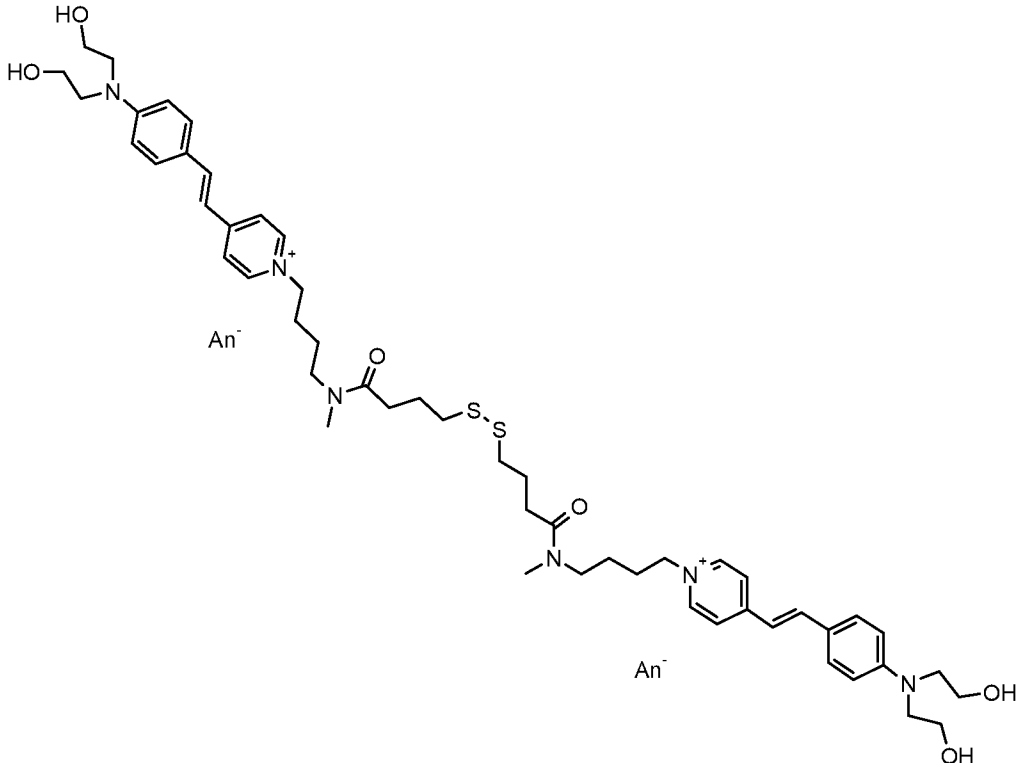
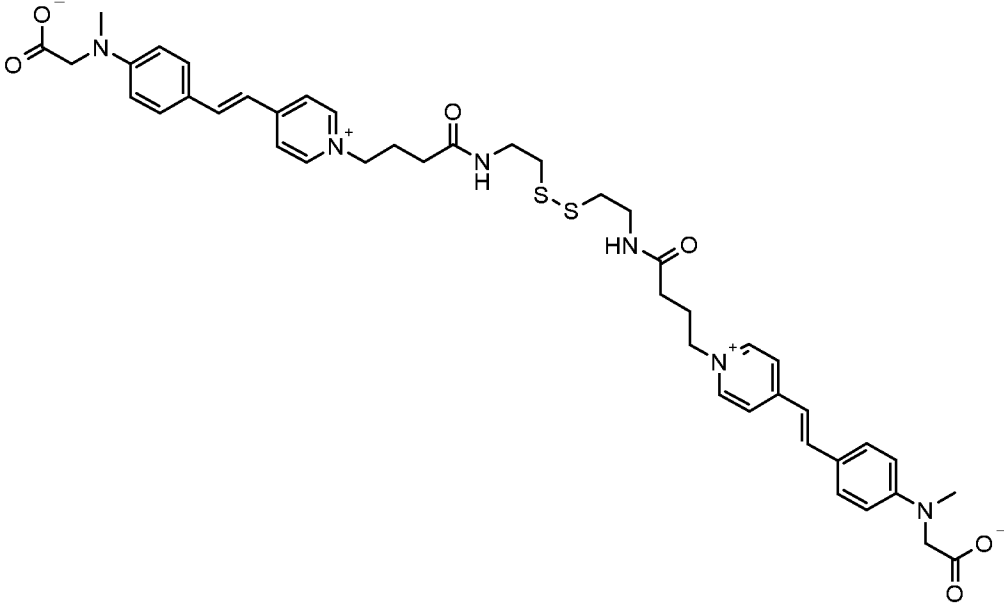
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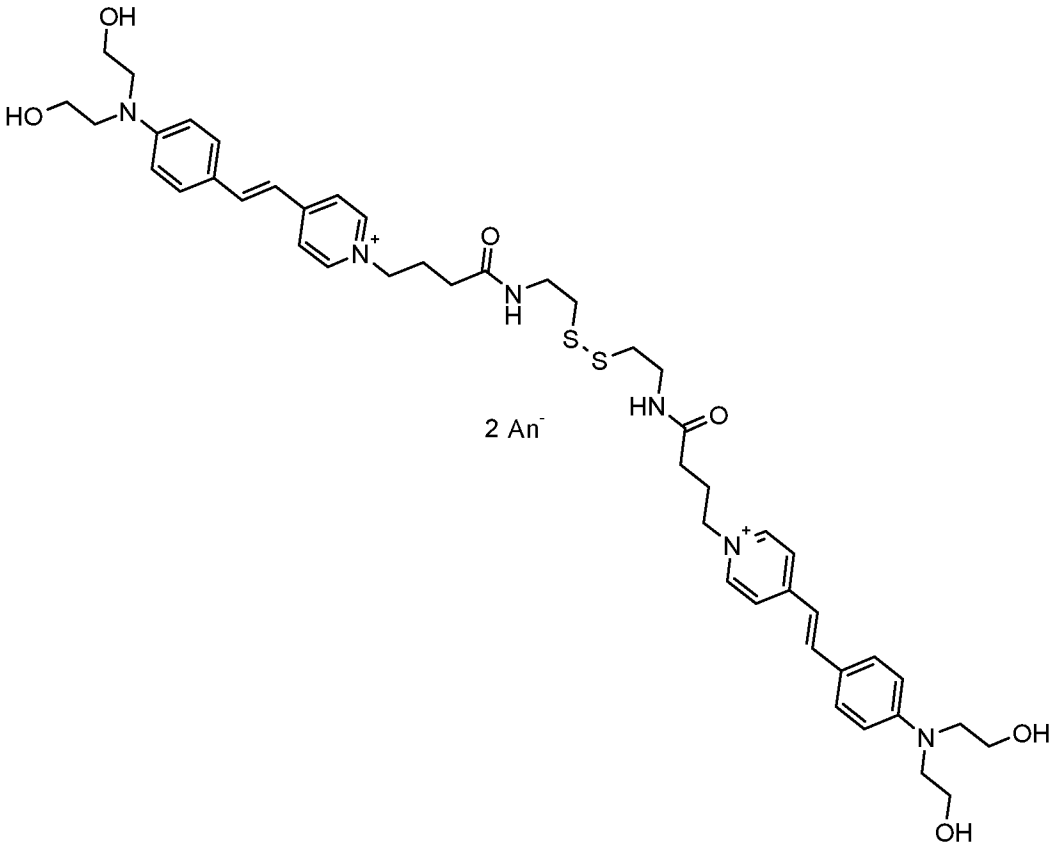
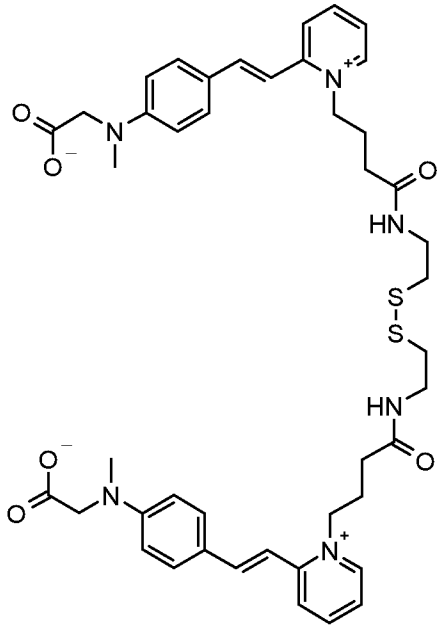
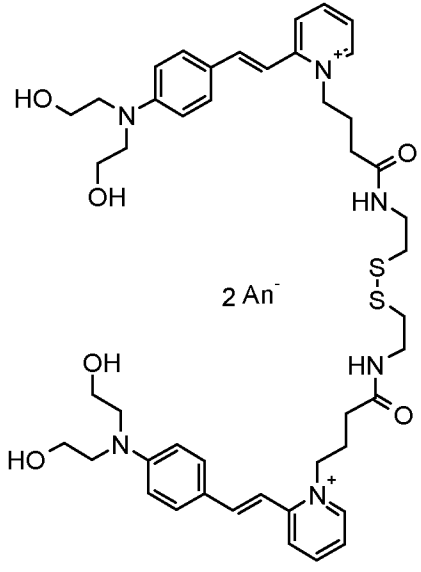
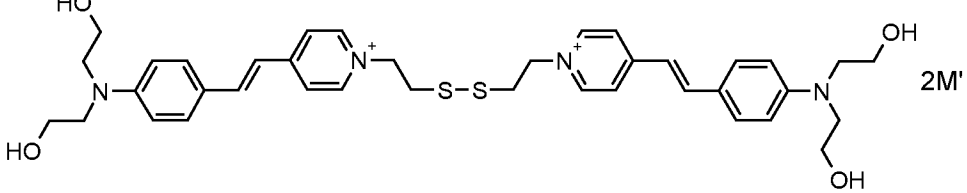
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	<p><b><u>62</u></b></p>
	<p><b><u>63</u></b></p>
	<p><b><u>64</u></b></p>

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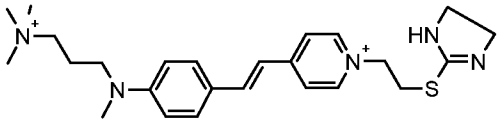
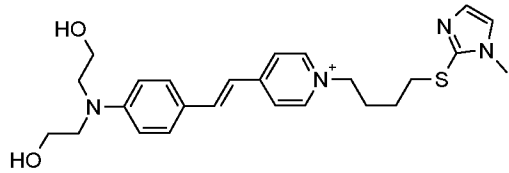
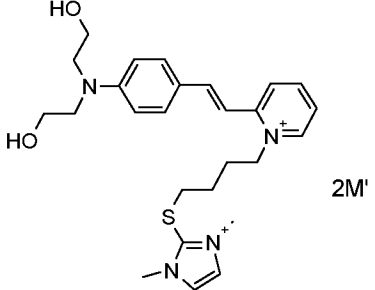
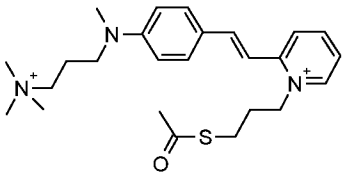
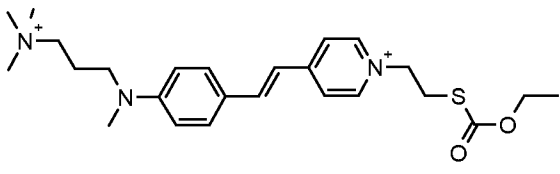
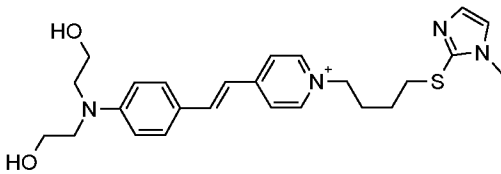
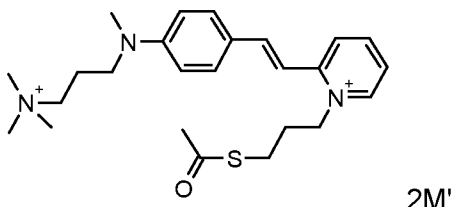
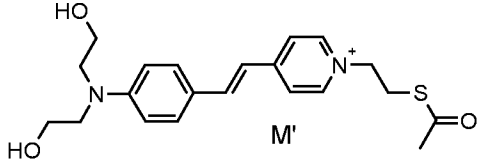
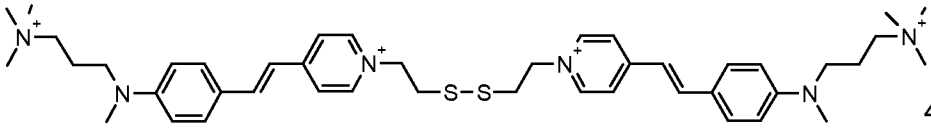
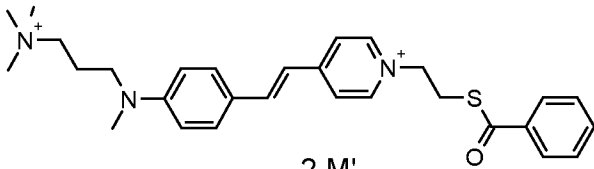
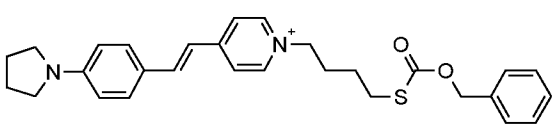
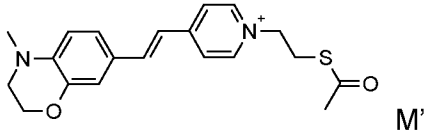
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<p><b>71</b></p>	<p><b>72</b></p>
	
<p><b>73</b></p>	<p><b>74</b></p>

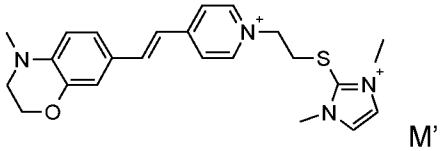
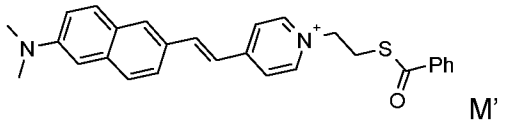
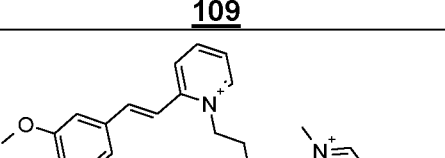
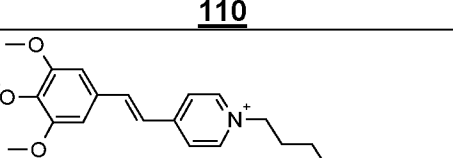
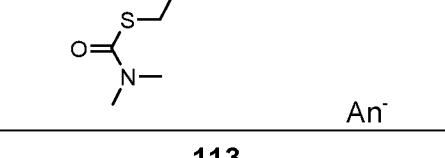
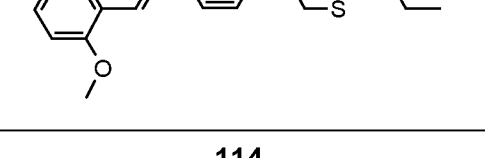
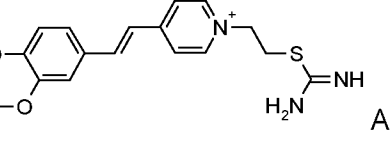
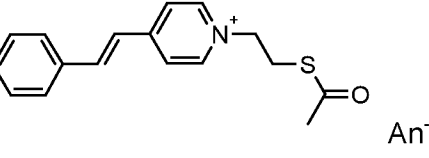
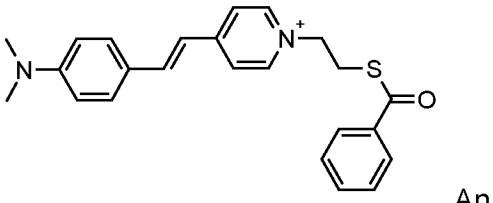
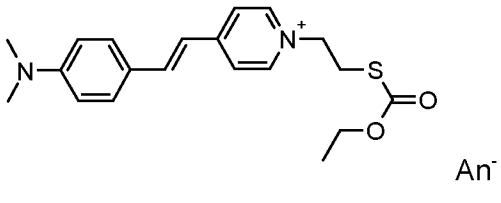


<p>An-</p>	<p>An-</p>
<p><b>75</b></p>	<p><b>76</b></p>
<p>Me<sup>+</sup> represents an alkali metal or ½ an alkaline-earth metal; or a methyl</p>	<p><b>77</b></p>
	<p><b>78</b></p>
<p>An<sup>+</sup></p> <p>An<sup>+</sup></p>	<p><b>79</b></p>

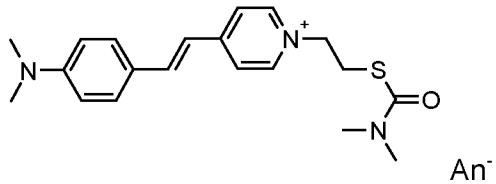
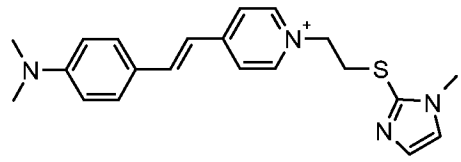
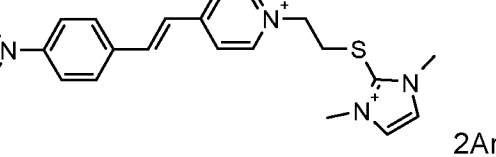
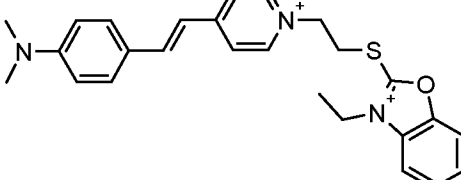
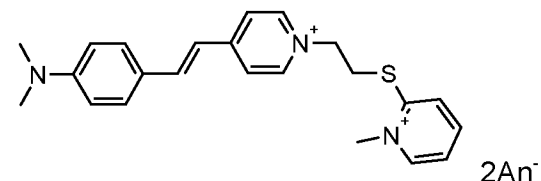
 <p>Chemical structure 80: A bis-iminium salt. The left iminium ring is connected to a piperazine ring with two hydroxymethyl groups. The right iminium ring is connected to a piperazine ring with two hydroxymethyl groups. The two iminium rings are linked via a disulfide bridge (-S-S-) through their respective N-alkyl chains. Anions (An<sup>-</sup>) are shown near each iminium nitrogen.</p>	<b>80</b>
 <p>Chemical structure 81: A bis-iminium salt. The left iminium ring is connected to a piperazine ring with a carboxylate group. The right iminium ring is connected to a piperazine ring with a carboxylate group. The two iminium rings are linked via a disulfide bridge (-S-S-) through their respective N-alkyl chains. Anions (O<sup>-</sup>) are shown near each iminium nitrogen.</p>	<b>81</b>

 <p style="text-align: center;">2 An<sup>-</sup></p>	<p><b>82</b></p>
 <p style="text-align: center;">2 An<sup>-</sup></p>	 <p style="text-align: center;">2 An<sup>-</sup></p>
<p><b>83</b></p>	<p><b>84</b></p>
 <p style="text-align: center;">2M<sup>-</sup></p>	<p><b>85</b></p>

<p style="text-align: right;">2M'</p>	<p><b>86</b></p>
<p style="text-align: right;">2M'</p>	<p><b>87</b></p>
<p style="text-align: right;">4M'</p>	<p style="text-align: right;">2M'</p>
<p><b>88</b></p>	<p><b>89</b></p>
<p style="text-align: right;">2M'</p>	<p style="text-align: right;">2M'</p>
<p><b>90</b></p>	<p><b>91</b></p>
<p style="text-align: right;">4M'</p>	<p style="text-align: right;">2M'</p>
<p><b>92</b></p>	<p><b>93</b></p>
<p style="text-align: right;">2M'</p>	<p style="text-align: right;">2M'</p>
<p><b>94</b></p>	<p><b>95</b></p>

 <p>2M'</p>	 <p>M'</p>
<p><b>96</b></p>	<p><b>97</b></p>
 <p>2M'</p>	 <p>2M'</p>
<p><b>98</b></p>	<p><b>99</b></p>
 <p>2M'</p>	 <p>M'</p>
<p><b>100</b></p>	<p><b>101</b></p>
 <p>2M'</p>	 <p>M'</p>
<p><b>102</b></p>	<p><b>102</b></p>
 <p>4M'</p>	<p><b>103</b></p>
 <p>2 M'</p>	<p><b>104</b></p>
 <p>M'</p>	 <p>M'</p>
<p><b>105</b></p>	<p><b>106</b></p>

 <p style="text-align: right;"><math>M'</math></p>	 <p style="text-align: right;"><math>M'</math></p>
<p><b>107</b></p>	<p><b>108</b></p>
 <p style="text-align: right;"><math>M'</math></p>	 <p style="text-align: right;"><math>2M'</math></p>
<p><b>109</b></p>	<p><b>110</b></p>
 <p style="text-align: right;"><math>2An^-</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>111</b></p>	<p><b>112</b></p>
 <p style="text-align: right;"><math>An^-</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>113</b></p>	<p><b>114</b></p>
 <p style="text-align: right;"><math>An</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>115</b></p>	<p><b>116</b></p>
 <p style="text-align: right;"><math>An</math></p>	 <p style="text-align: right;"><math>An^-</math></p>
<p><b>117</b></p>	<p><b>118</b></p>

 <p style="text-align: right;">An<sup>-</sup></p>	 <p style="text-align: right;">An<sup>-</sup></p>	
<p style="text-align: center;"><b><u>119</u></b></p>  <p style="text-align: right;">2An<sup>-</sup></p>	<p style="text-align: center;"><b><u>120</u></b></p>  <p style="text-align: right;">2An<sup>-</sup></p>	
<p style="text-align: center;"><b><u>121</u></b></p>	<p style="text-align: center;"><b><u>122</u></b></p>	
 <p style="text-align: right;">2An<sup>-</sup></p>		<p style="text-align: center;"><b><u>123</u></b></p>

with An<sup>-</sup> and M', which may be identical or different, preferentially identical, representing anionic counterions; in particular, the anionic counterion is chosen from halide ions such as chloride, alkyl sulfates such as methyl sulfate, mesylate and  $\frac{1}{2}$  SO<sub>4</sub><sup>2-</sup>; preferentially the dyes **44**, **49**, **49a** and **55**.

5

**12.** Composition according to any one of the preceding claims, in which *ij*) the fatty substances are chosen from hydrocarbons, fatty alcohols, fatty esters, silicones and fatty ethers, or mixtures thereof.

10

**13.** Composition according to any one of the preceding claims, in which *ij*) the fatty substance(s) are chosen from fatty substances that are liquid at room temperature (25°C) and at atmospheric pressure (760 mmHg; i.e.  $1.013 \times 10^5$  Pa).

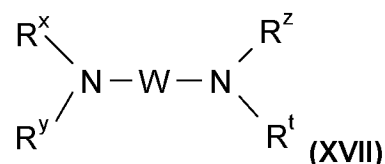
15

**14.** Composition according to any one of the preceding claims, in which *ij*) the fatty substance(s) are chosen from linear or branched C<sub>6</sub>-C<sub>16</sub> lower alkanes, linear or branched hydrocarbons, of mineral, animal or synthetic origin, of more than 16 carbon atoms, such as liquid paraffin, liquid petroleum jelly, polydecenes, hydrogenated

polyisobutylene, squalane, liquid fatty alcohols and liquid fatty esters, and more preferentially from liquid paraffin and liquid petroleum jelly.

5 **15.** Cosmetic composition according to any one of the preceding claims, characterized in that *ii)* the fatty substance(s) are present in an amount ranging from 25% to 90% by weight, preferably in an amount ranging from 30% to 80% by weight and even more preferentially in an amount ranging from 35% to 70% by weight relative to the total weight of the composition.

10 **16.** Composition according to any one of the preceding claims, in which *iii)* the alkaline agents are chosen from aqueous ammonia, alkali metal carbonates or bicarbonates such as sodium or potassium carbonates and sodium or potassium bicarbonates, sodium or potassium hydroxides, or mixtures thereof, alkanolamines, oxyethylenated and/or oxypropylenated ethylenediamines, amino acids and the  
15 compounds of formula (XVII) below:



in which formula (XVII):

- **W** is a divalent C<sub>1</sub>-C<sub>6</sub> alkylene radical optionally substituted with a hydroxyl group or a C<sub>1</sub>-C<sub>6</sub> alkyl radical, and/or optionally interrupted with one or more heteroatoms such as oxygen or NR<sup>u</sup>;
  - **R<sup>x</sup>**, **R<sup>y</sup>**, **R<sup>z</sup>**, **R<sup>t</sup>** and **R<sup>u</sup>**, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl or C<sub>1</sub>-C<sub>6</sub> aminoalkyl radical;
- preferably, the alkaline agent(s) are chosen from alkanolamines such as monoethanolamine.

25

**17.** Composition according to any one of the preceding claims, in which *iv)* the reducing agents are chosen from thiols such as thioglycolic acid, thiolactic acid, 3-mercaptopropionic acid, thiomalic acid, 2,3-dimercaptosuccinic acid, cysteine, N-glycyl-L-cysteine, L-cysteinyglycine and also esters and salts thereof, thioglycerol, cysteamine and C<sub>1</sub>-C<sub>4</sub> acyl derivatives thereof, N-mesylcysteamine, N-acetylcysteine, N-mercaptoalkylamides of sugars such as N-(mercapto-2-ethyl) gluconamide, pantetheine, N-(mercaptoalkyl)- $\omega$ -hydroxyalkylamides, N-mono- or N,N-dialkylmercapto-4-butiramides, aminomercaptoalkyl amides, N-(mercaptoalkyl)succinamic acids and N-(mercaptoalkyl)succinimides, alkylamino mercaptoalkyl amides, the azeotropic mixture of  
30 2-hydroxypropyl thioglycolate and of (2-hydroxy-1-methyl)ethyl thioglycolate, mercaptoalkylamino amides, and N-mercaptoalkylalkanediamides, and preferably from thioglycolic acid and cysteine, or salts thereof.

18. Process for dyeing keratin fibres, especially dark keratin fibres, comprising the step of applying to the keratin fibres:

*i)* at least one direct dye bearing a disulfide, thiol or protected-thiol function as defined in any one of Claims 1 to 11;

5 *ii)* at least 25% of one or more fatty substances as defined in Claims 1 and 12 to 15;

*iii)* at least one alkaline agent as defined in Claim 1 or 16; and

*iv)* at least one reducing agent as defined in Claim 1 or 17;

*v)* optionally at least one chemical oxidizing agent; and

10 the ingredients *i)* to *iv)* and *v)* possibly being applied either together onto the said fibres or separately.

19. Process according to the preceding claim, by applying to the said fibres a composition according to any one of Claims 1 to 17.

15 20. Process according to Claim 18, by applying to the keratin fibres a reducing composition comprising the ingredients *iii)* and *iv)* as defined in Claims 1, 16 and 17, followed by the application of a dye composition comprising the ingredients *i)* and *ii)* as defined in any one of Claims 1 to 15.

20 21. Process for the lightening dyeing of dark keratin fibres, in particular with a tone depth of less than or equal to 6 and preferentially less than or equal to 4, according to any one of Claims 18 to 20, comprising the step of applying to the keratin fibres, in which the ingredient(s) *i)* are of formulae (XIII), (XIII'), (XIV), (XIV'), (XVa), (XV'a), (XV) to (XV'), (XVI), (XVI'), (XVIa) and (XVI'a) as defined in Claims 9 and 10, and in particular the  
25 fluorescent dyes *i)* are chosen from the compounds 44, 49, 49a and 55 as defined in Claim 11.

22. Multi-compartment dyeing device or "kit" in which:

30 - the first compartment contains a dye composition comprising the composition containing the ingredient *i)* as defined in any one of Claims 1 to 11;

- the second compartment contains a reducing agent *iv)* as defined in Claim 1 or 17; and optionally the device comprises a third compartment;

- the third compartment comprising *v)* at least one chemical oxidizing agent;

35 it being understood that the ingredients *ii)* and *iii)* as defined in any one of Claims 1 and 12 to 16 are divided among the first two compartments.