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(54) Title: DYE COMPOSITION COMPRISING A DIRECT DYE, A PEROXYGENATED SALT AND A CYCLODEXTRIN, AND PROCESS USING THIS COMPOSITION

(57) Abstract: The present invention relates to a composition for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one peroxygenated salt, at least one direct dye and at least one  $\beta$ -cyclodextrin. The invention also relates to a process for dyeing keratin fibres, in particular human keratin fibres such as the hair, using said dye composition, to the use of said composition for dyeing keratin fibres, and also to a process for simultaneously bleaching and dyeing keratin fibres, comprising the application of said dye composition and of an aqueous oxidizing composition to the keratin fibres. The invention also relates to a multi-compartment device containing said dye composition and an aqueous oxidizing composition.



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**Dye composition comprising a direct dye, a peroxygenated salt and a cyclodextrin, and process using this composition**

5       The present invention relates to a composition for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one peroxygenated salt, at least one direct dye and at least one  $\beta$ -cyclodextrin.

10       The invention also relates to a process for dyeing keratin fibres, in particular human keratin fibres such as the hair, using said dye composition, to the use of said composition for dyeing keratin fibres, and also to a process for simultaneously bleaching and dyeing keratin fibres, comprising the application of said dye composition and of an oxidizing composition to the keratin fibres.

      The invention also relates to a multi-compartment device containing said dye composition and an oxidizing composition.

15       Many people have sought for a long time to modify the colour of their hair and in particular to lighten their hair.

      It is known practice to dye keratin fibres with dye compositions containing direct dyes. These compounds are coloured and colouring molecules that have affinity for the fibres. It is known practice, for example, to use direct dyes of the nitrobenzene type, anthraquinone or nitropyridine dyes, and dyes of the azo, xanthene, acridine, azine or triarylmethane type.

      These dyes are usually applied to fibres optionally in the presence of a chemical oxidizing agent if it is desired to obtain simultaneous lightening of the fibres. Once the leave-on time has elapsed, the fibres are rinsed, optionally washed and dried.

25       It is also known practice to lighten the hair in the presence of a persalt (also known as a peroxygenated salt), in particular persulfate, an alkaline agent and hydrogen peroxide when it is desired to achieve higher levels of lightening. However, these bleaching treatments are generally accompanied by the appearance of unattractive orange-yellow tints.

30       Direct dyes may then be introduced into the bleaching compositions to obtain a more aesthetic colour rendition.

      However, direct dyes show little or no resistance to chemical oxidizing agents. This poor stability of direct dyes with respect to oxidation especially has the consequence of producing hair colourings that have poor colour build-up and a poor level of lightening of the keratin fibres.

There is thus a real need to develop dye compositions and/or lightening compositions comprising at least one dye and at least one chemical oxidizing agent, which show good stability over time and which make it possible to obtain colourings in varied shades, which are strong, chromatic, aesthetic and sparingly selective and/or  
5 which show good resistance to the various attacking factors to which the hair may be subjected, such as shampoo washing, light, perspiration and permanent waving, while at the same time having good lightening performance.

In particular, one of the aims of the present invention is to provide dye compositions which show better colour build-up and a better level of lightening of keratin  
10 fibres.

These aims are achieved by the present invention, one subject of which is especially a composition for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising:

- at least one peroxygenated salt, preferably a persulfate,
- 15 - at least one direct dye, and
- at least one  $\beta$ -cyclodextrin.

It is found that the dye composition according to the invention shows better stability over time when compared with conventional dye compositions based on peroxygenated salts, in particular persulfates, especially good stability during the  
20 leave-on time on the head of hair.

The better stability of these direct dyes is especially reflected by less colour variation of the mixture with the peroxygenated salts, in particular persulfates, which makes it possible to lead to improved dyeing properties. It has especially been found  
25 that the keratin fibre colourings obtained with the compositions according to the invention show better colour build-up and also a good level of lightening of keratin fibres.

A subject of the invention is also a process for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying  
30 to said fibres a dye composition as defined previously.

A subject of the invention is also the use of the dye composition as defined previously for dyeing keratin fibres.

Another subject of the invention relates to a process for simultaneously bleaching/dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres:

- a dye composition as described previously, and
- 5       - an oxidizing composition different from the dye composition, comprising one or more chemical oxidizing agents, preferably other than peroxygenated salts, more preferentially chosen from hydrogen peroxide.

A subject of the invention is also a device comprising at least two compartments, a first compartment containing a dye composition as defined previously; a second compartment containing an aqueous oxidizing composition comprising one or more chemical oxidizing agents.

A subject of the invention is also a device comprising at least three compartments, a first compartment containing a composition C1 containing one or more peroxygenated salts, preferably one or more persulfates; a second compartment comprising a composition C2 comprising one or more direct dyes and one or more cyclodextrins; a third compartment containing an oxidizing composition comprising one or more chemical oxidizing agents other than peroxygenated salts.

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

In the present description, and unless otherwise indicated:

- the expression "at least one" is equivalent to the expression "one or more" and can be replaced therewith;
- the expression "between" is equivalent to the expression "ranging from" and can be replaced therewith, and implies that the limits are included.
- According to the present application, the term "keratin fibres" denotes human keratin fibres and more particularly the hair.

#### The peroxygenated salts

The dye composition according to the invention comprises one or more peroxygenated salts.

Preferably, the peroxygenated salts are chosen from persulfates; perborates; alkali metal, alkaline-earth metal or ammonium percarbonates; magnesium peroxide; and mixtures thereof.

More preferentially, the dye composition according to the present invention comprises at least one persulfate.

Persulfates, also known as peroxyulfates, correspond, for the purposes of the invention, to  $\text{SO}_5^{2-}$  anions (peroxomonosulfate anion) or  $\text{S}_2\text{O}_8^{2-}$  anions (peroxodisulfate anion) or to compounds comprising at least one of these anions.

Preferably, the persulfates according to the invention are chosen from peroxodisulfates.

According to a preferred embodiment of the invention, the dye composition according to the invention comprises at least one peroxygenated salt chosen from persulfates; preferably from alkali metal persulfates, alkaline-earth metal persulfates, ammonium persulfates, and mixtures thereof; more preferentially from (bis)tetrabutylammonium persulfate, barium persulfate, magnesium persulfate, calcium persulfate, sodium persulfate, potassium persulfate, ammonium persulfate, and mixtures thereof; even more preferentially from sodium persulfate, potassium persulfate, ammonium persulfate, and mixtures thereof; better still, the dye composition comprises potassium persulfate.

Preferably, the total content of peroxygenated salt(s) present in the dye composition according to the invention is between 1% and 30% by weight, more preferentially between 3% and 25% by weight, even more preferentially between 4% and 20% by weight and better still between 5% and 18% by weight, relative to the total weight of the dye composition.

Preferably, the total content of persulfate(s) present in the dye composition according to the invention is between 1% and 30% by weight, more preferentially between 3% and 25% by weight, even more preferentially between 4% and 20% by weight and even better still between 5% and 18% by weight, relative to the total weight of the dye composition.

30

#### The direct dyes

The dye composition according to the present invention comprises at least one direct dye.

The direct dye(s) that may be used according to the invention are chosen from natural direct dyes, synthetic direct dyes, and mixtures thereof.

Preferably, the direct dye(s) that may be used according to the invention are chosen from ionic direct dyes and nonionic direct dyes, more particularly from cationic  
5 direct dyes, nonionic direct dyes, anionic direct dyes, and mixtures thereof; more preferentially from cationic direct dyes, anionic direct dyes, and mixtures thereof.

The direct dyes are chosen, for example, from neutral, acidic or cationic nitrobenzene direct dyes, neutral (nonionic), acidic (anionic) or cationic azo direct  
10 dyes, tetraazapentamethine dyes, neutral, acidic or cationic quinone and in particular anthraquinone dyes, azine direct dyes, triarylmethane direct dyes, azomethine direct dyes and natural direct dyes.

The cationic direct dye(s) contain at least one quaternized cationic  
15 chromophore or at least one chromophore bearing a quaternized or quaternizable cationic group.

According to a particular embodiment of the invention, the cationic direct dyes comprise at least one quaternized cationic chromophore.

As cationic direct dyes according to the invention, mention may be made of  
20 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; bisisoindolines; carboxanilides; coumarins; cyanines such as azacarbocyanines,  
25 diazacarbocyanines, diazahemicyanines, hemicyanines, or tetraazacarbocyanines; diazines; diketopyrrolopyrroles; dioxazines; diphenylamines; diphenylmethanes; dithiazines; flavonoids such as flavanthrones and flavones; fluorindines; formazans; indamines; indanthrones; indigoids and pseudo-indigoids; indophenols; indoanilines; isoindolines; isoindolinones; isoviolanthrones; lactones; (poly)methines such as  
30 dimethines of stilbene or styryl type; naphthalimides; naphthanilides; naphtholactams; naphthoquinones; nitro, especially nitro(hetero)aromatics; oxadiazoles; oxazines; perilones; perinones; perylenes; phenazines; phenoxazine; phenothiazines; phthalocyanine; polyenes/carotenoids; porphyrins; pyranthrones; pyrazolanthrones; pyrazolones; pyrimidinoanthrones; pyronines; quinacridones; quinolines;

quinophthalones; squaranes; tetrazoliums; thiazines, thioindigo; thiopyronines; triarylmethanes, or xanthenes.

For the cationic azo dyes, mention may be made particularly of those resulting from the cationic dyes described in Kirk-Othmer's Encyclopedia of Chemical Technology, "Dyes, Azo", J. Wiley & Sons, updated on 19 April 2010.

Among the azo dyes 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.

According to a preferred embodiment of the invention, the direct dye(s) are chosen from cationic dyes known as "basic dyes".

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

- Basic Red 22
- Basic Red 76
- Basic Yellow 57
- Basic Brown 16
- Basic Brown 17.

Among the cationic quinone dyes, those mentioned in the abovementioned Colour Index International are suitable and, among these, mention may be made, inter alia, of the following dyes:

- Basic Blue 22
- Basic Blue 99.

Among the azine dyes that are suitable for use, mention may be made of those listed in the Colour Index International, for example the following dyes:

- Basic Blue 17
- Basic Red 2.

Among the cationic triarylmethane dyes that may be used according to the invention, mention may be made, in addition to those listed in the Colour Index, of the following dyes:

- Basic Green 1
- Basic Violet 3
- Basic Violet 14
- Basic Blue 7
- Basic Blue 26.

Mention may also be made of the cationic dyes described in the 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 Dyes" by K. Venkataraman, 1952, Academic Press, vol. 1 to 7, in the "Kirk-Othmer Encyclopedia of 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.

Preferably, the cationic direct dyes are chosen from those resulting from dyes of azo and hydrazono type.

According to a specific embodiment, the direct dyes are cationic azo dyes, described in EP 850 636, FR 2 788 433, EP 920 856, WO 99/48465, FR 2 757 385, EP 850 637, EP 918 053, 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, 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. (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.

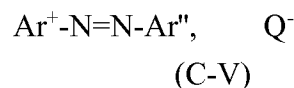
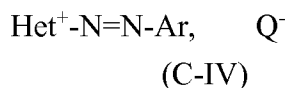
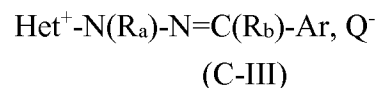
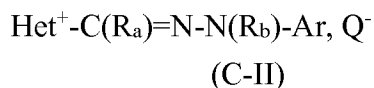
Preferably, the cationic direct dye(s) comprise a quaternary ammonium group; more preferentially, the cationic charge is endocyclic.

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 comprising a cationic heteroaryl group chosen from: acridinium, benzimidazolium, benzobistriazolium, benzopyrazolium, benzopyridazinium, benzoquinolium, benzothiazolium, benzotriazolium, benzoxazolium, bipyridinium, bistetrazolium, dihydrothiazolium, imidazopyridinium, imidazolium, indolium, isoquinolium, naphthoimidazolium, naphthoxazolium, naphthopyrazolium, oxadiazolium, oxazolium, oxazolopyridinium,

oxonium, phenazinium, phenooxazolium, pyrazinium, pyrazolium, pyrazoyltriazolium, pyridinium, pyridinoimidazolium, pyrrolium, pyrylium, quinolium, tetrazolium, thiadiazolium, thiazolium, thiazolopyridinium, thiazoylimidazolium, thiopyrylium, triazolium or xanthylum.

- 5           Mention may be made of the hydrazono cationic dyes of formulae (C-II) and (C-III), the azo dyes of formulae (C-IV) and (C-V) below, and also the optical and geometric isomers thereof and tautomers thereof, the organic or mineral acid or base salts thereof, and also the solvates thereof such as hydrates:



10           in which formulae (C-II) to (C-V):

- Het<sup>+</sup> represents a cationic heteroaryl radical, preferentially bearing an endocyclic cationic charge, such as imidazolium, indolium or pyridinium, which is optionally substituted, preferentially with at least one (C<sub>1</sub>-C<sub>8</sub>) alkyl group such as methyl;
- Ar<sup>+</sup> represents an aryl radical, such as phenyl or naphthyl, bearing an exocyclic cationic charge, preferentially ammonium, particularly tri(C<sub>1</sub>-C<sub>8</sub>)alkylammonium, such as trimethylammonium;
- Ar represents an aryl group, especially phenyl, which is 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'' represents an optionally substituted (hetero)aryl group such as phenyl or pyrazolyl, which are optionally substituted, preferentially with one or more (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 groups;
- R<sub>a</sub> and R<sub>b</sub>, which may be identical or different, representing a hydrogen atom or a (C<sub>1</sub>-C<sub>8</sub>)alkyl group, which is optionally substituted, preferentially with a hydroxyl group;
- or else the R<sub>a</sub> substituent with a substituent of Het<sup>+</sup> and/or R<sub>b</sub> with a substituent of Ar form, together with the atoms that bear them, a (hetero)cycloalkyl; in particular,

$R_a$  and  $R_b$  representing a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group optionally substituted with a hydroxyl group;

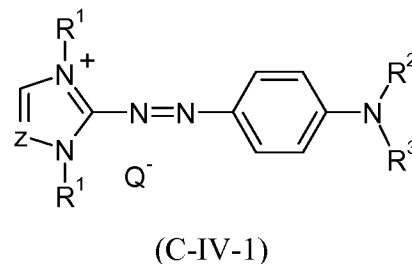
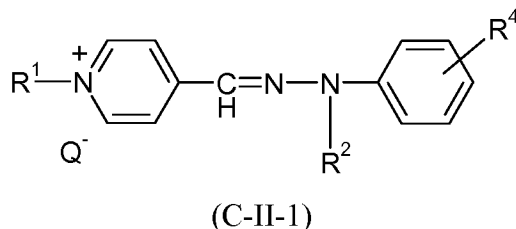
- $Q^-$  represents an organic or mineral anionic counterion, such as a halide or an alkyl sulfate.

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In particular, mention may be made of the azo and hydrazono direct dyes bearing endocyclic cationic charges, of formulae (C-II) to (C-V) as defined previously; more particularly the cationic direct dyes of formulae (C-II) to (C-V) bearing endocyclic cationic charges described in patent applications WO 95/15144, WO 95/01772 and EP-714954.

10

Preferentially, mention may be made of the following direct dyes:

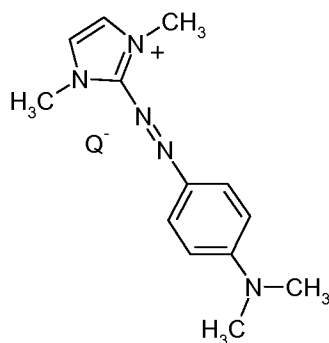


in which formulae (C-II-1) and (C-IV-1):

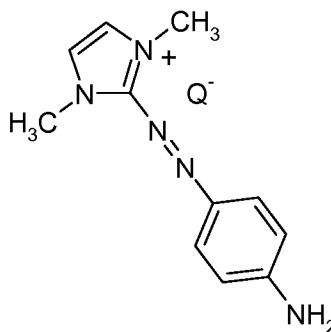
- $R^1$  represents a (C<sub>1</sub>-C<sub>4</sub>)alkyl group such as methyl;
- $R^2$  and  $R^3$ , which may be identical or different, represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group, such as methyl; and
- $R^4$  represents a hydrogen atom or an electron-donating group such as optionally substituted (C<sub>1</sub>-C<sub>8</sub>)alkyl, optionally substituted (C<sub>1</sub>-C<sub>8</sub>)alkoxy, or (di)(C<sub>1</sub>-C<sub>8</sub>)(alkyl)amino optionally substituted on the alkyl group(s) with a hydroxyl group; particularly,  $R^4$  is a hydrogen atom,
- Z represents a CH group or a nitrogen atom, preferentially CH,
- $Q^-$  is an anionic counterion as defined above, in particular a halide, such as chloride, or an alkyl sulfate, such as methyl sulfate or mesityl.

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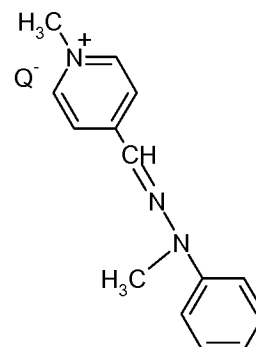
In particular, the dyes of formulae (C-II-1) and (C-IV-1) are chosen from Basic Red 51, Basic Yellow 87 and Basic Orange 31 or derivatives thereof:



Basic Red 51



Basic Orange 31



Basic Yellow 87

with Q' being an anionic counterion as defined above, in particular a halide, such as chloride, or an alkyl sulfate, such as methyl sulfate or mesityl.

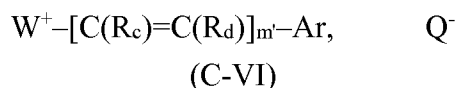
According to a particular embodiment of the invention, the direct dyes are fluorescent, that is to say that they contain at least one fluorescent chromophore as defined previously.

Fluorescent dyes that may be mentioned include the radicals resulting 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}borons (BODIPY<sup>®</sup>), diketopyrrolopyrroles, fluorindines, (poly)methines (in particular cyanines and styryls/hemicyanines), naphthalimides, naphthanilides, naphthylamines (such as dansyls), oxadiazoles, oxazines, perilones, perinones, perylenes, polyenes/carotenoids, squaranes, stilbenes and xanthenes.

Mention may also be made of the fluorescent dyes described in EP 1 133 975, WO 03/029 359, EP 860 636, WO 95/01772, WO 95/15144 and 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 the "Kirk-Othmer Encyclopedia of 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 variant of the invention, the cationic dye(s) are fluorescent and comprise at least one quaternary ammonium radical such as those of formula (C-VI) below, and also the optical and geometric isomers thereof, the tautomers thereof,

the organic or mineral acid or base salts thereof, and also the solvates thereof such as hydrates:

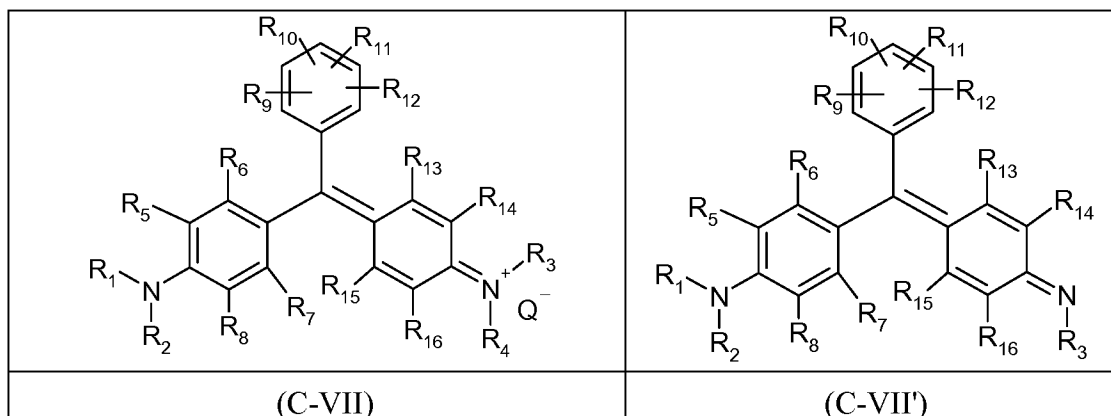


5 in which formula (C-VI):

- $W^+$  represents a cationic heterocyclic or heteroaryl group, particularly comprising a quaternary ammonium optionally substituted with one or more (C<sub>1</sub>-C<sub>8</sub>)alkyl groups, optionally substituted especially with one or more hydroxyl groups;
- 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 as piperazinyl, piperidyl or 5- or 6-membered heteroaryl such as pyrrolidinyl, pyridyl and imidazolyl;
- $m'$  represents an integer between 1 and 4 inclusive, and in particular  $m$  has the value 1 or 2; more preferentially 1;
- $R_c$  and  $R_d$ , which may be identical or different, represent a hydrogen atom or an optionally substituted (C<sub>1</sub>-C<sub>8</sub>)alkyl group, preferentially of C<sub>1</sub>-C<sub>4</sub>, or alternatively  $R_c$  contiguous with  $W^+$  and/or  $R_d$  contiguous with Ar form, with the atoms that bear them, a (hetero)cycloalkyl; particularly,  $R_c$  is contiguous with  $W^+$  and they form a (hetero)cycloalkyl such as cyclohexyl;
- $Q^-$  is an organic or mineral anionic counterion as defined previously.

Among the cationic direct dyes, mention may also be made of triarylmethane cationic dyes.

30 Preferably, the triarylmethane direct dye(s) according to the invention are chosen from the cationic dyes of formulae (C-VII) and (C-VII') below:



and also the organic or mineral acid or base addition salts thereof, the geometrical isomers, optical isomers and tautomers thereof, and the mesomeric forms thereof, and the solvates thereof such as hydrates:

5 in which preceding formulae (C-VII) and (C-VII'):

\* 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 group from among: (C<sub>1</sub>-C<sub>6</sub>)alkyl which is optionally substituted, preferably with a hydroxyl group; aryl such as phenyl, aryl(C<sub>1</sub>-C<sub>4</sub>)alkyl such as benzyl, heteroaryl, heteroaryl(C<sub>1</sub>-C<sub>4</sub>)alkyl, or else two groups R<sub>1</sub> and R<sub>2</sub>, and/or R<sub>3</sub> and R<sub>4</sub>, borne by the same nitrogen atom, form, together with the nitrogen atom which bears them, an optionally substituted heterocycloalkyl group such as morpholino, piperazino or piperidino; preferably, 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 group;

\* R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub>, which may be identical or different, represent a hydrogen or halogen atom or a group chosen from i) hydroxyl, ii) thiol, iii) amino, iv) (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)amino, v) (di)arylamino such as (di)phenylamino, vi) nitro, vii) acylamino (-NR-C(O)R') in which the radical R is a hydrogen atom, 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; viii) carbamoyl ((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; ix) carboxylic acid or ester, (-O-C(O)R') or (-C(O)OR'), in which the radical R' is a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl optionally bearing at least one hydroxyl group and the radical R' is a C<sub>1</sub>-C<sub>2</sub> alkyl radical; x) alkyl optionally substituted especially with a hydroxyl group; xi) alkylsulfonylamino (R'SO<sub>2</sub>-NR-) 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; xii) aminosulfonyl ((R)<sub>2</sub>N-SO<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, xiii) (C<sub>1</sub>-C<sub>4</sub>)alkoxy, and xiv) (C<sub>1</sub>-C<sub>4</sub>)alkylthio;

\* or else two radicals borne by two contiguous carbon atoms R<sub>5</sub> and R<sub>6</sub> and/or R<sub>7</sub> and R<sub>8</sub> and/or R<sub>9</sub> and R<sub>10</sub> and/or R<sub>11</sub> and R<sub>12</sub> and/or R<sub>13</sub> and R<sub>14</sub> and/or R<sub>15</sub> and R<sub>16</sub> form, together with the carbon atoms which bear them, an aryl or heteroaryl, preferably benzo, 6-membered fused ring, said ring possibly also being optionally substituted, preferably an unsubstituted benzo ring;

\* Q<sup>-</sup> represents an anionic counterion for achieving electrical neutrality, preferably chosen from halides such as chloride or bromide, and phosphate.

When the cationic dye comprises one or more anionic substituents such as COOR or SO<sub>3</sub>R with R denoting a hydrogen or a cation, it is understood that there are then more cationic substituents than anionic substituents, such that the overall resulting charge of the triarylmethane structure is cationic.

According to a preferred embodiment, the triarylmethane dye(s) of the invention are chosen from those of formula (C-VII) or (C-VII'), in which, taken together or separately,

- R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group such as methyl or ethyl;

- R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub> represent a hydrogen atom, a halogen atom, such as chlorine, or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group such as methyl or ethyl, an amino group, a (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)amino group and, preferably, at least one of the groups R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub> or R<sub>12</sub> represents a hydrogen atom, a halogen atom (Cl), or an amino group, or a (C<sub>1</sub>-C<sub>4</sub>)(alkyl)amino or (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)amino group, preferably in the para position relative to the phenyl group.

Preferably, the direct dye(s) of triarylmethane structure are chosen from Basic Violet 1, Basic Violet 2, Basic Violet 3, Basic Violet 4, Basic Violet 14, Basic Blue 1, Basic Blue 7, Basic Blue 26, Basic green 1, Basic Blue 77 (also known as HC Blue 15), and mixtures thereof.

Preferably, when the composition according to the invention comprises one or more cationic direct dyes, the total content of cationic direct dye(s) present in the

dye composition according to the invention is between 0.001% and 20% by weight, more preferentially between 0.005% and 10% by weight, even more preferentially between 0.01% and 5% by weight, relative to the total weight of the dye composition according to the invention.

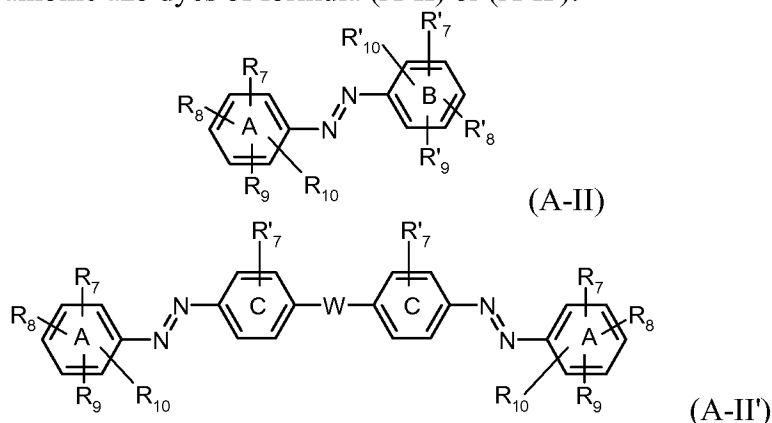
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The composition according to the invention may comprise one or more anionic direct dyes. The anionic direct dyes of the invention are dyes commonly referred to as "acid" direct dyes owing to their affinity for alkaline substances. The term "anionic direct dye" means any direct dye including in its structure at least one  $\text{CO}_2\text{R}$  or  $\text{SO}_3\text{R}$  substituent with R denoting a hydrogen atom or a cation originating from a metal or an amine, or an ammonium ion. The anionic dyes may be chosen from direct nitro acid dyes, azo acid dyes, azine acid dyes, triarylmethane acid dyes, indoamine acid dyes, anthraquinone acid dyes, indigoid dyes and natural acid dyes.

According to the invention, the anionic direct dye(s) may be chosen, alone or as a mixture, from the anionic direct dyes of formulae (A-II), (A-II'), (A-III), (A-III'), (A-IV), (A-IV'), (A-V), (A-V'), (A-VI), (A-VII), (A-VIII) and (A-IX) below:

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a) the diaryl anionic azo dyes of formula (A-II) or (A-II'):



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in which formulae (A-II) and (A-II'):

- $\text{R}_7$ ,  $\text{R}_8$ ,  $\text{R}_9$ ,  $\text{R}_{10}$ ,  $\text{R}'_7$ ,  $\text{R}'_8$ ,  $\text{R}'_9$  and  $\text{R}'_{10}$ , which may be identical or different, represent a hydrogen atom or a group chosen from:
  - alkyl;
  - alkoxy, alkylthio;
  - hydroxyl, mercapto;
  - nitro, nitroso;
  - $\text{R}^\circ\text{-C(X)-X}'\text{-}$ ,  $\text{R}^\circ\text{-X}'\text{-C(X)-}$ ,  $\text{R}^\circ\text{-X}'\text{-C(X)-X}''\text{-}$  with  $\text{R}^\circ$  representing a

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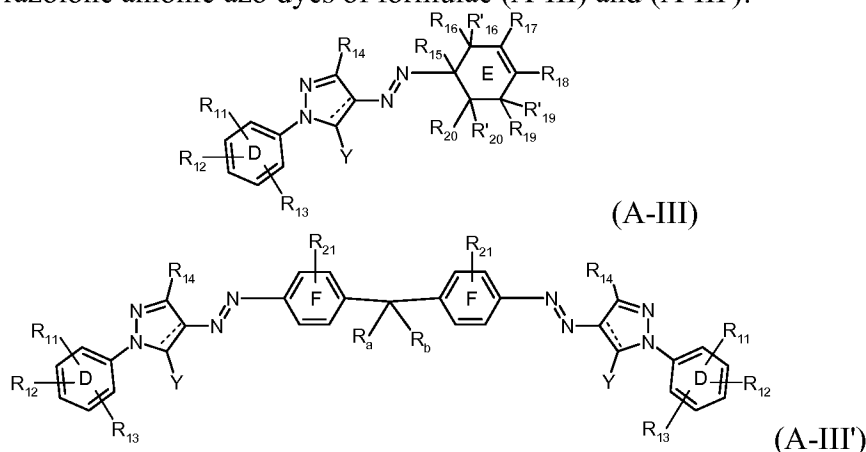
- hydrogen atom or an alkyl or aryl group; X, X' and X'', which may be identical or different, representing an oxygen or sulfur atom, or NR with R representing a hydrogen atom or an alkyl group;
- (O)<sub>2</sub>S(O<sup>-</sup>)-, M<sup>+</sup> with M<sup>+</sup> representing a hydrogen atom or a cationic counterion;
  - (O)CO<sup>-</sup>-, M<sup>+</sup> with M<sup>+</sup> as defined previously;
  - R''-S(O)<sub>2</sub>-, with R'' representing a hydrogen atom or an alkyl, aryl, (di)(alkyl)amino or aryl(alkyl)amino group; preferentially a phenylamino or phenyl group;
  - R'''-S(O)<sub>2</sub>-X'- with R''' representing an alkyl or optionally substituted aryl group, X' as defined previously;
  - (di)(alkyl)amino;
  - aryl(alkyl)amino optionally substituted with one or more groups chosen from i) nitro; ii) nitroso; iii) (O)<sub>2</sub>S(O<sup>-</sup>)-, M<sup>+</sup> and iv) alkoxy with M<sup>+</sup> as defined previously;
  - optionally substituted heteroaryl; preferentially a benzothiazolyl group;
  - cycloalkyl; especially cyclohexyl;
  - Ar-N=N- with Ar representing an optionally substituted aryl group; preferentially a phenyl optionally substituted with one or more alkyl, (O)<sub>2</sub>S(O<sup>-</sup>)-, M<sup>+</sup> or phenylamino groups;
  - or alternatively two contiguous groups R<sub>7</sub> with R<sub>8</sub> or R<sub>8</sub> with R<sub>9</sub> or R<sub>9</sub> with R<sub>10</sub> together form a fused benzo group A'; and R'<sub>7</sub> with R'<sub>8</sub> or R'<sub>8</sub> with R'<sub>9</sub> or R'<sub>9</sub> with R'<sub>10</sub> together form a fused benzo group B'; with A' and B' optionally substituted with one or more groups chosen from i) nitro; ii) nitroso; iii) (O)<sub>2</sub>S(O<sup>-</sup>)-, M<sup>+</sup>; iv) hydroxyl; v) mercapto; vi) (di)(alkyl)amino; vii) R<sup>o</sup>-C(X)-X'-; viii) R<sup>o</sup>-X'-C(X)-; ix) R<sup>o</sup>-X'-C(X)-X''-; x) Ar-N=N- and xi) optionally substituted aryl(alkyl)amino; with M<sup>+</sup>, R<sup>o</sup>, X, X', X'' and Ar as defined previously;
  - W represents a sigma bond σ, an oxygen or sulfur atom, or a divalent radical
    - i) -NR- with R as defined previously, or ii) methylene -C(R<sub>a</sub>)(R<sub>b</sub>)- with R<sub>a</sub> and R<sub>b</sub>, which may be identical or different, representing a hydrogen atom or an aryl group, or alternatively R<sub>a</sub> and R<sub>b</sub> form, together with the carbon atom that bears them, a spiro cycloalkyl; preferentially, W represents a sulfur atom or R<sub>a</sub> and R<sub>b</sub> together form a cyclohexyl;

it being understood that formulae (A-II) and (A-II') comprise at least one sulfonate radical  $(O)_2S(O^-)$ -,  $M^+$  or one carboxylate radical  $(O)CO^-$ -,  $M^+$  on one of the rings A, A', B, B' or C; preferentially sodium sulfonate;

As examples of dyes of formula (A-II), mention may be made of: Acid Red 1, Acid Red 4, Acid Red 13, Acid Red 14, Acid Red 18, Acid Red 27, Acid Red 28, Acid Red 32, Acid Red 33, Acid Red 35, Acid Red 37, Acid Red 40, Acid Red 41, Acid Red 42, Acid Red 44, Pigment Red 57, Acid Red 68, Acid Red 73, Acid Red 135, Acid Red 138, Acid Red 184, Food Red 1, Food Red 13, Acid Orange 6, Acid Orange 7, Acid Orange 10, Acid Orange 19, Acid Orange 20, Acid Orange 24, Yellow 6, Acid Yellow 9, Acid Yellow 36, Acid Yellow 199, Food Yellow 3, Acid Violet 7, Acid Violet 14, Acid Blue 113, Acid Blue 117, Acid Black 1, Acid Brown 4, Acid Brown 20, Acid Black 26, Acid Black 52, Food Black 1, Food Black 2, Food Yellow 3 or sunset yellow;

and, as examples of dyes of formula (A-II'), mention may be made of: Acid Red 111, Acid Red 134, Acid Yellow 38;

b) the pyrazolone anionic azo dyes of formulae (A-III) and (A-III'):



in which formulae (A-III) and (A-III'):

- $R_{11}$ ,  $R_{12}$  and  $R_{13}$ , which may be identical or different, represent a hydrogen or halogen atom, an alkyl group or  $-(O)_2S(O^-)$ ,  $M^+$  with  $M^+$  as defined previously;
- $R_{14}$  represents a hydrogen atom, an alkyl group or a group  $-C(O)O^-$ ,  $M^+$  with  $M^+$  as defined previously;
- $R_{15}$  represents a hydrogen atom;
- $R_{16}$  represents an oxo group, in which case  $R'_{16}$  is absent, or alternatively  $R_{15}$  with  $R_{16}$  together form a double bond;
- $R_{17}$  and  $R_{18}$ , which may be identical or different, represent a hydrogen atom, or a

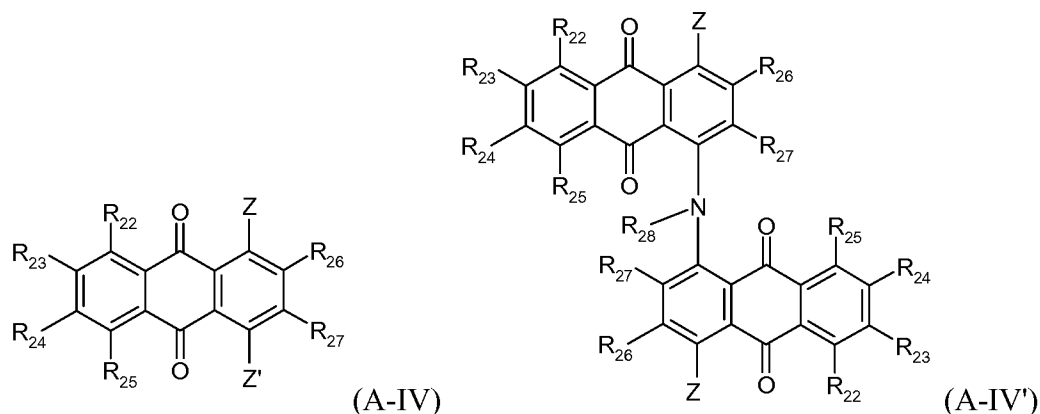
group chosen from:

- $(O)_2S(O^-)-, M^+$  with  $M^+$  as defined previously;
- $Ar-O-S(O)_2-$  with  $Ar$  representing an optionally substituted aryl group; preferentially a phenyl optionally substituted with one or more alkyl groups;
- 5 •  $R_{19}$  and  $R_{20}$  together form either a double bond, or a benzo group  $D'$ , which is optionally substituted;
- $R'_{16}, R'_{19}$  and  $R'_{20}$ , which may be identical or different, represent a hydrogen atom or an alkyl or hydroxyl group;
- $R_{21}$  represents a hydrogen atom or an alkyl or alkoxy group;
- 10 •  $R_a$  and  $R_b$ , which may be identical or different, are as defined previously, preferentially  $R_a$  represents a hydrogen atom and  $R_b$  represents an aryl group;
- $Y$  represents either a hydroxyl group or an oxo group;
- $\text{---}$  represents a single bond when  $Y$  is an oxo group; and represents a double bond when  $Y$  represents a hydroxyl group;

15 it being understood that formulae (A-III) and (A-III') comprise at least one sulfonate radical  $(O)_2S(O^-)-, M^+$  or one carboxylate radical  $-C(O)O^-, M^+$  on one of the rings  $D$  or  $E$ ; preferentially sodium sulfonate;

As examples of dyes of formula (A-III), mention may be made of: Acid Red 195, Acid Yellow 23, Acid Yellow 27, Acid Yellow 76, and, as examples of dyes of formula (A-III'), mention may be made of: Acid Yellow 17;

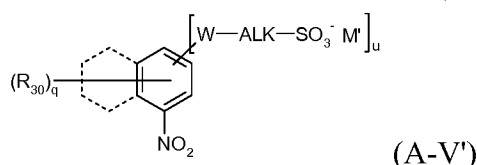
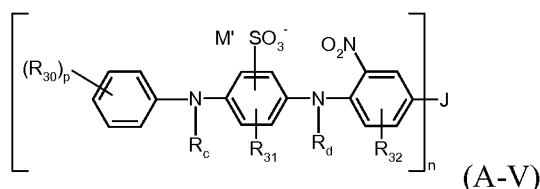
20 c) the anthraquinone dyes of formulae (A-IV) and (A-IV'):



in which formulae (A-IV) and (A-IV'):

- $R_{22}, R_{23}, R_{24}, R_{25}, R_{26}$  and  $R_{27}$ , which may be identical or different, represent a
- 25 hydrogen or halogen atom, or a group chosen from:
- alkyl;

- hydroxyl, mercapto;
  - alkoxy, alkylthio;
  - optionally substituted aryloxy or arylthio, preferentially substituted with one or more groups chosen from alkyl and  $(O)_2S(O^-)$ -,  $M^+$  with  $M^+$  as defined previously;
  - aryl(alkyl)amino optionally substituted with one or more groups chosen from alkyl and  $(O)_2S(O^-)$ -,  $M^+$  with  $M^+$  as defined previously;
  - (di)(alkyl)amino;
  - (di)(hydroxyalkyl)amino;
  - $(O)_2S(O^-)$ -,  $M^+$  with  $M^+$  as defined previously;
  - $Z'$  represents a hydrogen atom or a group  $NR_{28}R_{29}$  with  $R_{28}$  and  $R_{29}$ , which may be identical or different, representing a hydrogen atom or a group chosen from:
    - alkyl;
    - polyhydroxyalkyl such as hydroxyethyl;
    - aryl optionally substituted with one or more groups, particularly i) alkyl such as methyl, n-dodecyl, n-butyl; ii)  $(O)_2S(O^-)$ -,  $M^+$  with  $M^+$  as defined previously; iii)  $R^\circ-C(X)-X'$ -,  $R^\circ-X'-C(X)$ -,  $R^\circ-X'-C(X)-X''$ - with  $R^\circ$ ,  $X$ ,  $X'$  and  $X''$  as defined previously, preferentially  $R^\circ$  represents an alkyl group;
    - cycloalkyl; especially cyclohexyl;
  - $Z$  represents a group chosen from hydroxyl and  $NR'_{28}R'_{29}$  with  $R'_{28}$  and  $R'_{29}$ , which may be identical or different, representing the same atoms or groups as  $R_{28}$  and  $R_{29}$  as defined previously;
- it being understood that formulae (A-IV) and (A-IV') comprise at least one sulfonate radical  $(O)_2S(O^-)$ -,  $M^+$  or one carboxylate radical  $-C(O)O^-$ ,  $M^+$ ; preferentially sodium sulfonate;
- As examples of dyes of formula (A-IV), mention may be made of: Acid Blue 25, Acid Blue 43, Acid Blue 62, Acid Blue 78, Acid Blue 129, Acid Blue 138, Acid Blue 140, Acid Blue 251, Acid Green 25, Acid Green 41, Acid Violet 42, Acid Violet 43, Mordant Red 3; EXT violet No. 2;
- and, as examples of dyes of formula (A-IV'), mention may be made of: Acid Black 48;
- d) the nitro dyes of formulae (A-V) and (A-V'):



in which formulae (A-V) and (A-V'):

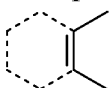
- $R_{30}$ ,  $R_{31}$  and  $R_{32}$ , which may be identical or different, represent a hydrogen or halogen atom, or a group chosen from:
  - alkyl;
  - alkoxy optionally substituted with one or more hydroxyl groups, alkylthio optionally substituted with one or more hydroxyl groups;
  - hydroxyl, mercapto;
  - nitro, nitroso;
  - polyhaloalkyl;
  - $R^\circ\text{-C(X)-X}'\text{-}$ ,  $R^\circ\text{-X}'\text{-C(X)-}$ ,  $R^\circ\text{-X}'\text{-C(X)-X}''\text{-}$  with  $R^\circ$ ,  $X$ ,  $X'$  and  $X''$  as defined previously;
  - $(\text{O})_2\text{S(O}^-\text{)-}$ ,  $\text{M}^+$  with  $\text{M}^+$  as defined previously;
  - $(\text{O})\text{CO-}$ ,  $\text{M}^+$  with  $\text{M}^+$  as defined previously;
  - (di)(alkyl)amino;
  - (di)(hydroxyalkyl)amino;
  - heterocycloalkyl such as piperidino, piperazino or morpholino;

in particular,  $R_{30}$ ,  $R_{31}$  and  $R_{32}$  represent a hydrogen atom;

- $R_c$  and  $R_d$ , which may be identical or different, represent a hydrogen atom or an alkyl group;
- W is as defined previously; W particularly represents a group  $\text{-NH-}$ ;
- ALK represents a linear or branched divalent  $\text{C}_1\text{-C}_6$  alkylene group; in particular, ALK represents a  $\text{-CH}_2\text{-CH}_2\text{-}$  group;
- n is 1 or 2;
- p represents an integer between 1 and 5 inclusive;
- q represents an integer between 1 and 4 inclusive;
- u is 0 or 1;

- when n is 1, J represents a nitro or nitroso group; particularly nitro;
- when n is 2, J represents an oxygen or sulfur atom, or a divalent radical  $-S(O)_m-$  with m representing an integer 1 or 2; preferentially, J represents a radical  $-SO_2-$ ;
- M' represents a hydrogen atom or a cationic counterion;

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- , which may be present or absent, represents a benzo group optionally substituted with one or more groups R<sub>30</sub> as defined previously;

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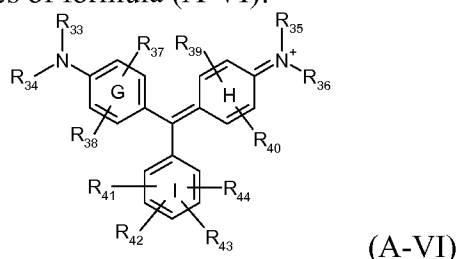
it being understood that formulae (A-V) and (A-V') comprise at least one sulfonate radical  $(O)_2S(O^-)-$ , M<sup>+</sup> or one carboxylate radical  $-C(O)O^-$ , M<sup>+</sup>; preferentially sodium sulfonate;

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As examples of dyes of formula (A-V), mention may be made of: Acid Brown 13 and Acid Orange 3; as examples of dyes of formula (A-V'), mention may be made of: Acid Yellow 1, the sodium salt of 2,4-dinitro-1-naphthol-7-sulfonic acid, 2-piperidino-5-nitrobenzenesulfonic acid, 2-(4'-N,N-(2''-hydroxyethyl)amino-2'-nitro)anilineethanesulfonic acid, 4-β-hydroxyethylamino-3-nitrobenzenesulfonic acid; EXT D&C Yellow 7;

d) the triarylmethane dyes of formula (A-VI):

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in which formula (A-VI):

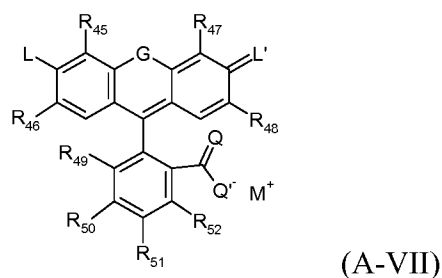
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- R<sub>33</sub>, R<sub>34</sub>, R<sub>35</sub> and R<sub>36</sub>, which may be identical or different, represent a hydrogen atom or a group chosen from alkyl, optionally substituted aryl and optionally substituted arylalkyl; particularly an alkyl and benzyl group optionally substituted with a group  $(O)_mS(O^-)-$ , M<sup>+</sup> with M<sup>+</sup> and m as defined previously;
- R<sub>37</sub>, R<sub>38</sub>, R<sub>39</sub>, R<sub>40</sub>, R<sub>41</sub>, R<sub>42</sub>, R<sub>43</sub> and R<sub>44</sub>, which may be identical or different, represent a hydrogen atom or a group chosen from:
  - alkyl;
  - alkoxy, alkylthio;
  - (di)(alkyl)amino;

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- hydroxyl, mercapto;
  - nitro, nitroso;
  - $R^{\circ}-C(X)-X'-$ ,  $R^{\circ}-X'-C(X)-$ ,  $R^{\circ}-X'-C(X)-X''-$  with  $R^{\circ}$  representing a hydrogen atom or an alkyl or aryl group; X, X' and X'', which may be identical or different, representing an oxygen or sulfur atom, or NR with R representing a hydrogen atom or an alkyl group;
  - $(O)_2S(O^-)-$ ,  $M^+$  with  $M^+$  representing a hydrogen atom or a cationic counterion;
  - $(O)CO^-$ ,  $M^+$  with  $M^+$  as defined previously;
  - or alternatively two contiguous groups  $R_{41}$  with  $R_{42}$  or  $R_{42}$  with  $R_{43}$  or  $R_{43}$  with  $R_{44}$  together form a fused benzo group: I'; with I' optionally substituted with one or more groups chosen from i) nitro; ii) nitroso; iii)  $(O)_2S(O^-)-$ ,  $M^+$ ; iv) hydroxyl; v) mercapto; vi) (di)(alkyl)amino; vii)  $R^{\circ}-C(X)-X'-$ ; viii)  $R^{\circ}-X'-C(X)-$  and ix)  $R^{\circ}-X'-C(X)-X''-$ ; with  $M^+$ ,  $R^{\circ}$ , X, X' and X'' as defined previously;
- particularly,  $R_{37}$  to  $R_{40}$  represent a hydrogen atom, and  $R_{41}$  to  $R_{44}$ , which may be identical or different, represent a hydroxyl group or  $(O)_2S(O^-)-$ ,  $M^+$ ; and when  $R_{43}$  with  $R_{44}$  together form a benzo group, it is preferentially substituted with a group  $(O)_2S(O^-)-$ ;
- it being understood that at least one of the rings G, H, I or I' comprises at least one sulfonate radical  $(O)_2S(O^-)-$  or a carboxylate radical  $-C(O)O^-$ ; preferentially sulfonate;
- As examples of dyes of formula (A-VI), mention may be made of: Acid Blue 1; Acid Blue 3; Acid Blue 7, Acid Blue 9; Acid Violet 49; Acid Green 3; Acid Green 5 and Acid Green 50;

e) the xanthene-based dyes of formula (A-VII):



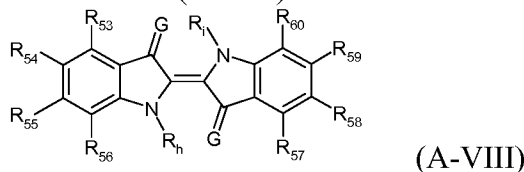
in which formula (A-VII):

- $R_{45}$ ,  $R_{46}$ ,  $R_{47}$  and  $R_{48}$ , which may be identical or different, represent a hydrogen or halogen atom;

- $R_{49}$ ,  $R_{50}$ ,  $R_{51}$  and  $R_{52}$ , which may be identical or different, represent a hydrogen or halogen atom, or a group chosen from:
  - alkyl;
  - alkoxy, alkylthio;
  - 5 - hydroxyl, mercapto;
  - nitro, nitroso;
  - $(O)_2S(O^-)$ -,  $M^+$  with  $M^+$  representing a hydrogen atom or a cationic counterion;
  - $(O)CO^-$ -,  $M^+$  with  $M^+$  as defined previously;
 particularly,  $R_{53}$ ,  $R_{54}$ ,  $R_{55}$  and  $R_{48}$  represent a hydrogen or halogen atom;
- 10 • G represents an oxygen or sulfur atom or a group  $NR_e$  with  $R_e$  as defined previously; particularly G represents an oxygen atom;
- L represents an alkoxide  $O^-$ ,  $M^+$ ; a thioalkoxide  $S^-$ ,  $M^+$  or a group  $NR_f$ , with  $R_f$  representing a hydrogen atom or an alkyl group and  $M^+$  as defined previously;  $M^+$  is particularly sodium or potassium;
- 15 • L' represents an oxygen or sulfur atom or an ammonium group:  $N^+R_fR_g$ , with  $R_f$  and  $R_g$ , which may be identical or different, representing a hydrogen atom, an alkyl or optionally substituted aryl group; L' represents particularly an oxygen atom or a phenylamino group optionally substituted with one or more alkyl or  $(O)_mS(O^-)$ -,  $M^+$  groups with m and  $M^+$  as defined previously;
- 20 • Q and Q', which may be identical or different, represent an oxygen or sulfur atom; particularly, Q and Q' represent an oxygen atom;
- $M^+$  is as defined previously;

As examples of dyes of formula (A-VII), mention may be made of: Acid Yellow 73; Acid Red 51; Acid Red 52; Acid Red 87; Acid Red 92; Acid Red 95; Acid Violet 9;

f) the indole-based dyes of formula (A-VIII):

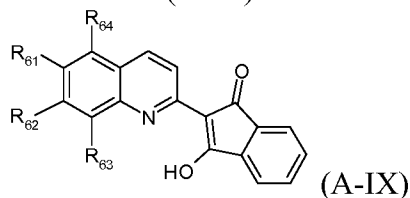


in which formula (A-VIII):

- 30 •  $R_{53}$ ,  $R_{54}$ ,  $R_{55}$ ,  $R_{56}$ ,  $R_{57}$ ,  $R_{58}$ ,  $R_{59}$  and  $R_{60}$ , which may be identical or different, represent a hydrogen atom or a group chosen from:

- alkyl;
- alkoxy, alkylthio;
- hydroxyl, mercapto;
- nitro, nitroso;
- 5 -  $R^{\circ}-C(X)-X'-$ ,  $R^{\circ}-X'-C(X)-$ ,  $R^{\circ}-X'-C(X)-X''-$  with  $R^{\circ}$  representing a hydrogen atom or an alkyl or aryl group; X, X' and X'', which may be identical or different, representing an oxygen or sulfur atom, or NR with R representing a hydrogen atom or an alkyl group;
- $(O)_2S(O^-)-$ ,  $M^+$  with  $M^+$  representing a hydrogen atom or a cationic counterion;
- 10 -  $(O)CO^-$ ,  $M^+$  with  $M^+$  as defined previously;
- G represents an oxygen or sulfur atom or a group  $NR_e$  with  $R_e$  as defined previously; particularly G represents an oxygen atom;
- $R_i$  and  $R_h$ , which may be identical or different, represent a hydrogen atom or an alkyl group;
- 15 it being understood that formula (A-VIII) comprises at least one sulfonate radical  $(O)_2S(O^-)-$ ,  $M^+$  or one carboxylate radical  $-C(O)O^-$ ,  $M^+$ ; preferentially sodium sulfonate;

As an example of dyes of formula (A-VIII), mention may be made of: Acid Blue 74.  
g) the quinoline-based dyes of formula (A-IX):



20

in which formula (A-IX):

- $R_{61}$  represents a hydrogen or halogen atom or an alkyl group;
- $R_{62}$ ,  $R_{63}$ , and  $R_{64}$ , which may be identical or different, represent a hydrogen atom or a group  $(O)_2S(O^-)-$ ,  $M^+$  with  $M^+$  representing a hydrogen atom or a cationic counterion;
- 25 • or alternatively  $R_{61}$  with  $R_{62}$ , or  $R_{61}$  with  $R_{64}$ , together form a benzo group optionally substituted with one or more groups  $(O)_2S(O^-)-$ ,  $M^+$  with  $M^+$  representing a hydrogen atom or a cationic counterion;
- it being understood that formula (A-IX) comprises at least one sulfonate radical  $(O)_2S(O^-)-$ ,  $M^+$ , preferentially sodium sulfonate.
- 30

As examples of dyes of formula (A-IX), mention may be made of: Acid

Yellow 2, Acid Yellow 3 and Acid Yellow 5.

More particularly, the dye composition comprises one or more anionic direct dyes chosen, alone or as a mixture, from the following anionic direct dyes:

|              |                                                                                                                                    |
|--------------|------------------------------------------------------------------------------------------------------------------------------------|
| (C.I. 45380) | Acid Red 87 (A-VII)                                                                                                                |
| (C.I. 10316) | Sodium salt of 2,4-dinitro-1-naphthol-7-sulfonic acid (A-V')                                                                       |
| (C.I. 10383) | Acid Orange 3 (A-V)                                                                                                                |
| (C.I. 13015) | Acid Yellow 9 / Food Yellow 2 (A-II)                                                                                               |
| (C.I. 14780) | / Direct Red 45 / Food Red 13 (A-II)                                                                                               |
| (C.I. 13711) | Acid Black 52 (A-II)                                                                                                               |
| (C.I. 13065) | Acid Yellow 36 (A-II)                                                                                                              |
| (C.I. 14700) | Sodium salt of 1-hydroxy-2-(2',4'-xylyl-5-sulfonatoazo)naphthalene-4-sulfonic acid / Food Red 1 (A-II)                             |
| (C.I. 14720) | Acid Red 14 / Food Red 3 / Mordant Blue 79 (A-II)                                                                                  |
| (C.I. 14805) | Sodium salt of 4-hydroxy-3-[(2-methoxy-5-nitrophenyl)diaza]-6-(phenylamino)naphthalene-2-sulfonic acid / Acid Brown 4 (A-II)       |
| (C.I. 15510) | Acid Orange 7 / Pigment Orange 17 / Solvent Orange 49 (A-II)                                                                       |
| (C.I. 15985) | Food Yellow 3 / Pigment Yellow 104 (A-II)                                                                                          |
| (C.I. 16185) | Acid Red 27 / Food Red 9 (A-II)                                                                                                    |
| (C.I. 16230) | Acid Orange 10 / Food Orange 4 (A-II)                                                                                              |
| (C.I. 16250) | Acid Red 44 (A-II)                                                                                                                 |
| (C.I. 17200) | Acid Red 33 / Food Red 12 (A-II)                                                                                                   |
| (C.I. 15685) | Acid Red 184 (A-II)                                                                                                                |
| (C.I. 19125) | Acid Violet 3 (A-II)                                                                                                               |
| (C.I. 18055) | Sodium salt of 1-hydroxy-2-(4'-acetamidophenylazo)-8-acetamidonaphthalene-3,6-disulfonic acid / Acid Violet 7 / Food Red 11 (A-II) |
| (C.I. 18130) | Acid Red 135 (A-II)                                                                                                                |
| (C.I. 19130) | Acid Yellow 27 (A-III)                                                                                                             |
| (C.I. 19140) | Acid Yellow 23 / Food Yellow 4 (A-III)                                                                                             |
| (C.I. 20170) | 4'-(Sulfonato-2'',4''-dimethyl)bis(2,6-phenylazo)-1,3-dihydroxybenzene / Acid Orange 24 (A-II)                                     |
| (C.I. 20470) | Sodium salt of 1-amino-2-(4'-nitrophenylazo)-7-phenylazo-8-hydroxynaphthalene-3,6-disulfonic acid / Acid Black 1 (A-II)            |

|              |                                                                                                                                                      |
|--------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| (C.I. 23266) | (4-((4-Methylphenyl)sulfonyloxy)phenylazo)-2,2'-dimethyl-4-((2-hydroxy-5,8-disulfonato)naphthylazo)biphenyl / Acid Red 111 (A-II')                   |
| (C.I. 27755) | Food Black 2 (A-II)                                                                                                                                  |
| (C.I. 25440) | 1-(4'-Sulfonatophenylazo)-4-((2"-hydroxy-3"-acetylamino-6",8"-disulfonato)naphthylazo)-6-sulfonatophthalene (tetrasodium salt) / Food Black 1 (A-II) |
| (C.I. 42090) | Acid Blue 9 (A-VI)                                                                                                                                   |
| (C.I. 60730) | Acid Violet 43 (A-IV)                                                                                                                                |
| (C.I. 61570) | Acid Green 25 (A-IV)                                                                                                                                 |
| (C.I. 62045) | Sodium salt of 1-amino-4-cyclohexylamino-9,10-anthraquinone-2-sulfonic acid / Acid Blue 62 (A-IV)                                                    |
| (C.I. 62105) | Acid Blue 78 (A-IV)                                                                                                                                  |
| (C.I. 14710) | Sodium salt of 4-hydroxy-3-((2-methoxyphenyl)azo)-1-naphthalenesulfonic acid / Acid Red 4 (A-II)                                                     |
|              | 2-Piperidino-5-nitrobenzenesulfonic acid (V')                                                                                                        |
|              | 2-(4'-N,N-(2"-Hydroxyethyl)amino-2'-nitro)anilineethanesulfonic acid (A-V')                                                                          |
|              | 4-β-Hydroxyethylamino-3-nitrobenzene sulfonic acid (A-V')                                                                                            |
| (C.I. 42640) | Acid Violet 49 (A-VI)                                                                                                                                |
| (C.I. 42080) | Acid Blue 7 (A-VI)                                                                                                                                   |
| (C.I. 58005) | Sodium salt of 1,2-dihydroxy-3-sulfoanthraquinone / Mordant Red 3 (A-IV)                                                                             |
| (C.I. 62055) | Sodium salt of 1-amino-9,10-dihydro-9,10-dioxo-4-(phenylamino)-2-anthracenesulfonic acid / Acid Blue 25 (A-IV)                                       |
| (C.I. 14710) | Sodium salt of 4-hydroxy-3-((2-methoxyphenyl)azo)-1-naphthalenesulfonic acid / Acid Red 4 (A-II)                                                     |

Most of these dyes are described in particular in the Colour Index published by The Society of Dyers and Colourists, P.O. Box 244, Perkin House, 82 Grattan Road, Bradford, Yorkshire, BD1 2LU England.

5

The anionic dyes that are most particularly preferred are the dyes designated in the Colour Index under the code C.I. 58005 (monosodium salt of 1,2-dihydroxy-

9,10-anthraquinone-3-sulfonic acid), C.I. 60730 (monosodium salt of 2-[(9,10-dihydro-4-hydroxy-9,10-dioxo-1-anthracenyl)amino]-5-methylbenzenesulfonic acid), C.I. 15510 (monosodium salt of 4-[(2-hydroxy-1-naphthalenyl)azo]benzenesulfonic acid), C.I. 15985 (disodium salt of 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid), C.I. 17200 (disodium salt of 5-amino-4-hydroxy-3-(phenylazo)-2,7-naphthalenedisulfonic acid), C.I. 20470 (disodium salt of 1-amino-2-(4'-nitrophenylazo)-7-phenylazo-8-hydroxy-3,6-naphthalenedisulfonic acid), C.I. 42090 (disodium salt of N-ethyl-N-[4-[[4-ethyl(3-sulfophenyl)methyl]amino]phenyl](2-sulfophenyl)methylene]-2,5-cyclohexadien-1-ylidene]-3-sulfobenzenemethanaminium hydroxide, inner salt), C.I. 61570 (disodium salt of 2,2'-[(9,10-dihydro-9,10-dioxo-1,4-anthracenediyl)diimino]bis[5-methyl]benzenesulfonic acid).

Use may also be made of compounds corresponding to the mesomeric or tautomeric forms of structures (A-II) to (A-IX).

Among the natural direct dyes that may be used according to the invention, mention may be made of hennotannic acid, juglone, alizarin, purpurin, carminic acid, kermesic acid, purpurogallin, protocatechaldehyde, indigo, isatin, curcumin, spinulosin, apigenidin and orcein. Extracts or decoctions containing these natural dyes and in particular henna-based poultices or extracts may also be used.

Preferably, when the composition according to the invention comprises one or more anionic direct dyes, the total content of anionic direct dye(s) present in the dye composition according to the invention is between 0.001% and 20% by weight, more preferentially between 0.005% and 10% by weight, even more preferentially between 0.01% and 5% by weight, relative to the total weight of the dye composition according to the invention.

The nonionic direct dyes may be chosen from nitrobenzene dyes, azo dyes and anthraquinone dyes.

Preferably, when the composition according to the invention comprises one or more nonionic direct dyes, the total content of nonionic direct dye(s) present in the dye composition according to the invention is between 0.001% and 20% by weight, more preferentially between 0.005% and 10% by weight, even more preferentially

between 0.01% and 5% by weight, relative to the total weight of the dye composition according to the invention.

According to a preferred embodiment of the invention, the dye composition  
5 comprises at least one direct dye chosen from cationic direct dyes; more preferentially at least one cationic direct dye chosen from triarylmethane cationic direct dyes, in particular those of formula (C-VII) or (C-VII') such as HC Blue 15 and/or Basic Violet 2; azo cationic direct dyes, in particular those of formula C-IV-1, such as Basic Red 51 and/or Basic Orange 31; hydrazono cationic direct dyes, in particular those of  
10 formula C-II-1, such as Basic Yellow 87; and mixtures thereof.

Preferably, the total content of direct dye(s) present in the dye composition according to the invention is between 0.001% and 20% by weight, more preferentially between 0.005% and 10% by weight, even more preferentially between 0.01% and 5%  
15 by weight, relative to the total weight of the dye composition according to the invention.

#### The cyclodextrins

The dye composition according to the present invention comprises at least one  
20  $\beta$ -cyclodextrin (abbreviated as  $\beta$ -CD).

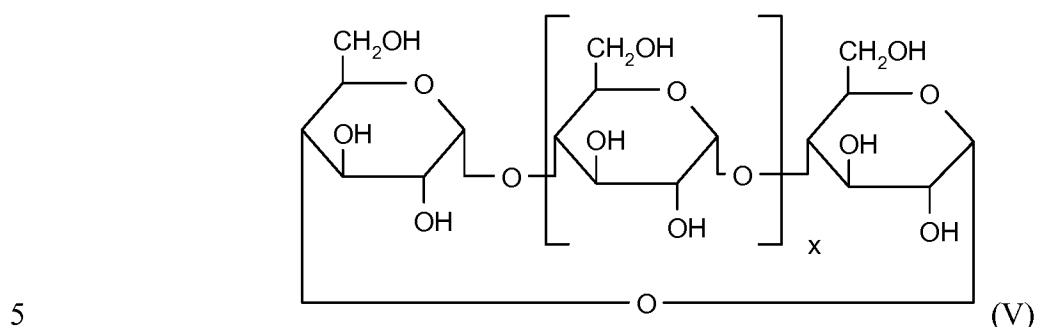
The cyclodextrins according to the invention may or may not be modified.

Cyclodextrins (abbreviated as CDs) are cyclic oligosaccharides constituted of ( $\alpha$ -1,4)  $\alpha$ -D-glucopyranose units with a lipophilic central cavity and a hydrophilic outer surface (Frömming KH, Szejtli J: "Cyclodextrins in pharmacy", Kluwer Academic  
25 Publishers, Dordrecht, 1994). The most common natural CDs are  $\alpha$ -cyclodextrins (abbreviated as  $\alpha$ -CDs),  $\beta$ -cyclodextrins (abbreviated as  $\beta$ -CDs) and  $\gamma$ -cyclodextrins (abbreviated as  $\gamma$ -CDs).

$\alpha$ -CDs (also known under the name Schardinger's  $\alpha$ -dextrin, alpha-cyclodextrin, cyclomaltohexaose, cyclohexaglucan, cyclohexaamylose,  $\alpha$ -CD, ACD, C6A) comprise 6 glucopyranose units.  $\beta$ -CDs (also known under the name  
30 Schardinger's  $\beta$ -dextrin, beta-cyclodextrin, cyclomaltoheptaose, cycloheptaglucan, cycloheptaamylose,  $\beta$ -CD, BCD, C7A) comprise 7 glucopyranose units, and  $\gamma$ -CDs (also known under the name Schardinger's  $\gamma$ -dextrin, gamma-cyclodextrin,

cyclomaltooctaose, cyclooctaglucan, cyclooctaamylose,  $\gamma$ -CD, GCD, C8A) comprise 8 glucopyranose units.

The cyclodextrins are especially oligosaccharides of formula (V):



in which formula (V)  $x$  represents an integer equal to 4 (corresponding to  $\alpha$ -cyclodextrin), equal to 5 (corresponding to  $\beta$ -cyclodextrin) or equal to 6 (corresponding to  $\gamma$ -cyclodextrin).

10 According to the invention, the  $\beta$ -CDs are preferably those of formula (V) above in which  $x$  represents an integer equal to 5.

Use may in particular be made of a  $\beta$ -CD sold by the company Wacker under the name Cavamax W7 and a  $\gamma$ -CD sold by the company Wacker under the name Cavamax W8.

15 CD derivatives may also be used in the present invention. In the CDs, each glucopyranose unit bears three free hydroxyl groups that differ in their function and their reactivity.

20 The term "*CD derivative*" means a CD of which all or some of the hydroxyl groups have been modified by reaction or substitution of the hydroxyl group(s) or of the hydrogen atom(s). Mention may be made especially of derivatives comprising ester, ether, anhydro, deoxy-, acidic or basic groups and which may be prepared by chemical or enzymatic reactions well known to those skilled in the art.

25 For example, in the  $\beta$ -CDs, 21 hydroxyl groups may be modified by substituting the hydrogen atom or the hydroxyl group with a wide variety of groups such as alkyl, hydroxyalkyl, carboxyalkyl, amino-, thio-, tosyl-, glucosyl-, maltosyl-, etc. groups. Among the preferred derivatives, mention may be made of the derivatives of  $\beta$ -CDs and in particular the methylated derivatives of CDs such as methyl- $\beta$ -cyclodextrin sold by the company Wacker under the name Cavasol W7; TRIMEBs

(heptakis(2,3,6-trimethyl)- $\beta$ -cyclodextrin), DIMEBs (heptakis(2,6-dimethyl)- $\beta$ -cyclodextrin) or RAMEBs (Randomly Methylated  $\beta$ -Cyclodextrin); 2-hydroxypropyl- $\beta$ -cyclodextrin (HPCD); 2-hydroxyethyl- $\beta$ -cyclodextrin; 2-hydroxypropyl- $\gamma$ -cyclodextrin and 2-hydroxyethyl- $\gamma$ -cyclodextrin.

5           Mention may also be made of CDs crosslinked with epichlorohydrin (EPC). In particular, mention may be made of HPCD sold especially under the name Kleptose HPB® by the company Roquette and RAMEB sold by the company Wacker.

          Mention may also be made of the MCT reactive CDs from Wacker (chlorotriazine-functionalized cyclodextrin)  $\beta$ -cyclodextrin (Cavasol® W7 MCT).

10           Finally, mention may also be made of CD dimers or bis-CDs. It is possible to obtain these CD dimers or bis-CDs via standard methods known to those skilled in the art, for example by chemical reaction between two CDs and a reagent (linker) comprising two groups that can react with the hydrogen atoms or the hydroxyl groups of each CD (see, for example, *Tetrahedron*, 51, 377 (1995); *Chem. Rev.* 97, 1647-1668 (1997), *J. Org. Chem.*, 64, 7781-7787 (1999)).

15           According to a particular embodiment, the CDs are not dimers, i.e. the CDs are monomers.

          According to a preferred embodiment of the invention, the  $\beta$ -cyclodextrin(s) present in the dye composition according to the invention are chosen from  $\beta$ -cyclodextrin, methyl- $\beta$ -cyclodextrin, heptakis(2,3,6-trimethyl)- $\beta$ -cyclodextrin, heptakis(2,6-dimethyl)- $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin, 2-hydroxyethyl- $\beta$ -cyclodextrin, and mixtures thereof; more preferentially from  $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin, 2-hydroxyethyl- $\beta$ -cyclodextrin, and mixtures thereof; and better still from  $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin, and mixtures thereof. Most particularly preferably, the dye composition comprises at least 2-hydroxypropyl- $\beta$ -cyclodextrin.

30           Preferably, the total content of  $\beta$ -cyclodextrin(s) present in the dye composition according to the invention is between 0.1% and 25% by weight, more preferentially between 0.5% and 20% by weight, even more preferentially between 1% and 15% by weight and even better still between 2% and 10% by weight, relative to the total weight of the dye composition according to the invention.

          More preferentially, the total content of cyclodextrin(s) present in the dye

composition according to the invention is between 0.1% and 25% by weight, more preferentially between 0.5% and 20% by weight, even more preferentially between 1% and 15% by weight and even better still between 2% and 10% by weight, relative to the total weight of the dye composition according to the invention.

5

The alkaline agents

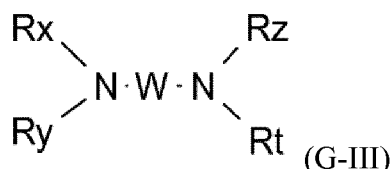
The dye composition according to the invention may optionally comprise at least one alkaline agent.

10 Among the alkaline agents that may be used according to the invention, mention may be made of organic alkaline agents.

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

15

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



20 in which W is a C<sub>1</sub>-C<sub>6</sub> alkane residue optionally substituted with a hydroxyl group or a C<sub>1</sub>-C<sub>6</sub> alkyl radical; Rx, Ry, Rz and Rt, 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.

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

The term “alkanolamine” means an organic amine comprising a primary, secondary or tertiary amine function, and one or more linear or branched C<sub>1</sub>-C<sub>8</sub> alkyl groups bearing one or more hydroxyl radicals. Alkanolamines such as monoalkanolamines, dialkanolamines or trialkanolamines comprising from one to three identical or different C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radicals are in particular suitable for performing the invention.

30

Examples that may be mentioned include monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, N-dimethylaminoethanolamine, 2-amino-2-methyl-1-propanol, triisopropanolamine and tris(hydroxymethylamino)methane.

5

Preferably, the alkaline agent(s) are inorganic alkaline agents.

The alkaline agent(s) may be chosen, for example, from dibasic or tribasic ammonium phosphates, water-soluble silicates such as alkali metal or alkaline-earth metal silicates, for instance sodium disilicate, sodium silicate (also known as the disodium salt of silicic acid or disodium metasilicate), dibasic or tribasic alkali metal or alkaline-earth metal phosphates, or carbonates of alkali metals or alkaline-earth metals, such as lithium, sodium, potassium, magnesium, calcium and barium, and mixtures thereof.

10

15

Preferably, the alkaline agent(s) are chosen from water-soluble silicates such as alkali metal or alkaline-earth metal silicates, dibasic or tribasic alkali metal or alkaline-earth metal phosphates, and alkali metal or alkaline-earth metal carbonates, and mixtures thereof.

20

For the purposes of the invention, the term "water-soluble silicate" means a silicate which has a solubility in water at 25°C of greater than 0.5%, preferably greater than 1% by weight.

These water-soluble silicates differ from aluminium silicates and derivatives thereof, especially clays, such as mixed silicates of natural or synthetic origin that are insoluble in water.

25

30

According to a preferred embodiment of the invention, the dye composition comprises at least one alkaline agent; preferably chosen from inorganic alkaline agents; more preferentially chosen from dibasic or tribasic ammonium phosphates, water-soluble silicates such as alkali metal or alkaline-earth metal silicates, for instance sodium disilicate, sodium silicate, dibasic or tribasic alkali metal or alkaline-earth metal phosphates, or alkali metal or alkaline-earth metal carbonates, and mixtures thereof; even more preferentially from water-soluble silicates such as alkali metal or alkaline-earth metal silicates; better still from sodium disilicate, sodium silicate, and mixtures thereof; even better still from sodium silicate.

Preferably, when it is (they are) present in the dye composition according to the invention, the total content of alkaline agent(s) is between 0.1% and 40% by weight, more preferentially between 0.5% and 30% by weight, even more particularly between 1% and 25% by weight, relative to the total weight of the dye composition.

5

The dye composition according to the invention may be anhydrous or aqueous, preferably aqueous.

The term "aqueous dye composition" according to the present patent application means a dye composition in which the total water content is greater than or equal to 10% by weight relative to the weight of the dye composition.

When the composition according to the invention is aqueous, preferably, the total water content present in the dye composition according to the invention is greater than or equal to 20% by weight, more preferentially greater than or equal to 30% by weight of water, even more preferentially greater than or equal to 40% by weight, better still greater than or equal to 50% by weight and better still between 50% and 98% by weight, relative to the total weight of the dye composition.

Besides water, the composition according to the present invention may optionally comprise one or more organic solvents, or mixtures thereof.

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

The dye composition according to the present invention may also optionally comprise one or more additives, different from the compounds of the invention and among which mention may be made of cationic, anionic, nonionic, amphoteric or zwitterionic surfactants, and mixtures thereof, fatty substances, cationic, anionic, nonionic or amphoteric polymers, or mixtures thereof, antidandruff agents, anti-seborrhoea agents, vitamins and provitamins including panthenol, sunscreens, mineral or organic pigments, sequestrants, plasticizers, solubilizers, acidifying agents, mineral or organic thickeners, especially polymeric thickeners, opacifiers, nacreous agents, antioxidants, hydroxy acids, fragrances, preserving agents and ceramides.

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 composition according to the invention are not, or are not substantially, adversely affected by the envisaged addition(s).

5           The above additives may generally be present in an amount, for each of them, of between 0 and 20% by weight relative to the total weight of the composition.

When the composition is aqueous, the pH of the dye composition according to the present invention is preferably greater than or equal to 7, and more preferentially between 7 and 12; even more preferentially between 7.5 and 10.5.

10

The composition according to the invention is advantageously in cream, lotion or gel form.

15           A subject of the invention is especially a process for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres a keratin fibre dye composition as described previously.

20           According to a preferred embodiment of the dyeing process according to the invention, the dye composition as defined previously is prepared less than one hour, more preferentially less than 30 minutes, even more preferentially less than 15 minutes and better still less than 5 minutes before the application to said keratin fibres.

25           According to a particular embodiment, the dyeing process according to the invention uses at least one chemical oxidizing agent other than the peroxygenated salts described previously. Preferably, the chemical oxidizing agent is hydrogen peroxide. The chemical oxidizing agent other than peroxygenated salts may be present in an oxidizing composition (A) which is mixed with the dye composition as defined previously at the time of use.

30           According to this embodiment, the process according to the invention uses a ready-to-use dye composition obtained by extemporaneous mixing of a dye composition according to the invention and of an oxidizing composition (A) comprising at least one chemical oxidizing agent other than peroxygenated salts, preferably hydrogen peroxide. It is understood in this embodiment that the dye

composition according to the invention then does not contain any chemical oxidizing agents other than the peroxygenated salts.

For the purposes of the present invention, the term “*chemical oxidizing agent*” more particularly means an oxidizing agent other than atmospheric oxygen.

5           The chemical oxidizing agent(s) included in the oxidizing composition (A) may be chosen from hydrogen peroxide, urea peroxide, peracids and oxidase enzymes (with the possible cofactors thereof), among which mention may be made of peroxidases, 2-electron oxidoreductases such as uricases and 4-electron oxygenases such as laccases, and mixtures thereof; preferentially, the chemical oxidizing agent(s)  
10           included in the oxidizing composition (A) comprise hydrogen peroxide.

In particular, the dye composition is applied to wet or dry keratin fibres.

It is usually left in place on the fibres for a time generally of from 1 minute to 1 hour 30 minutes, preferably from 5 minutes to 60 minutes.

15           The temperature during the dyeing process conventionally ranges from room temperature (from 15°C to 25°C) to 80°C, preferably from room temperature to 60°C.

According to another preferred embodiment of the dyeing process according to the invention, a step of rinsing the keratin fibres is performed after the step(s) of applying a dye composition according to the invention to said fibres.

20           A step of drying the keratin fibres may be envisaged in the dyeing process according to the invention, especially using a heating means such as a hair dryer, a straightening iron, a steam iron or a heating hood, the heating means possibly heating to a temperature ranging from 150°C to 230°C, preferably from 200°C to 220°C.

25           A subject of the invention is also the use of the dye composition as defined previously for dyeing keratin fibres.

A subject of the invention is also a process for simultaneously bleaching/dyeing keratin fibres, in particular human keratin fibres such as the hair,  
30           comprising at least one step of applying to said fibres:

- a keratin fibre dye composition as described previously, and
- an oxidizing composition (B) different from the dye composition, comprising one or more chemical oxidizing agents preferably other than

the peroxygenated salts as described previously, more preferentially chosen from hydrogen peroxide.

The oxidizing composition (B) is preferably aqueous.

5 According to the present patent application, the term "aqueous oxidizing composition (B)" means an oxidizing composition (B") in which the total water content is greater than or equal to 10% by weight relative to the weight of the aqueous oxidizing composition.

10 The aqueous oxidizing composition (B) used in the simultaneous keratin fibre bleaching/dyeing process according to the invention comprises one or more chemical oxidizing agents preferably other than peroxygenated salts.

15 Preferably, the chemical oxidizing agent(s) included in the oxidizing composition (B) are chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulfates, in particular sodium persulfate, potassium persulfate and ammonium persulfate, peracids and oxidase enzymes (with the optional cofactors thereof) such as peroxidases, 2-electron oxidoreductases such as uricases and 4-electron oxygenases such as laccases, and mixtures thereof; preferentially, the oxidizing composition (B) comprises hydrogen peroxide.

20 Preferably, the total content of chemical oxidizing agent(s), preferably other than peroxygenated salts, is between 1% and 50% by weight, more preferentially between 3% and 30% by weight, even more preferentially between 5% and 20% by weight, relative to the total weight of the oxidizing composition (B).

25 According to a particular embodiment of the simultaneous keratin fibre bleaching/dyeing process according to the invention, the dye composition and the oxidizing composition are applied to wet or dry keratin fibres, successively and without intermediate rinsing; more particularly, the dye composition is applied and the oxidizing composition is then applied or the oxidizing composition is applied and the dye composition is then applied.

30

According to a preferred embodiment of the simultaneous keratin fibre bleaching/dyeing process according to the invention, the simultaneous bleaching/dyeing process comprises a step of extemporaneous mixing of said dye

composition according to the invention with said oxidizing composition before said step(s) of application to said keratin fibres.

5 According to this preferred embodiment, the extemporaneous mixture of said dye composition with said oxidizing composition is preferentially prepared less than one hour, more preferentially less than 30 minutes, even more preferentially less than 15 minutes and better still less than 5 minutes before the application to said keratin fibres.

10 According to another preferred embodiment of the simultaneous keratin fibre bleaching/dyeing process according to the invention, the dye composition as defined previously is prepared less than one hour, more preferentially less than 30 minutes, even more preferentially less than 15 minutes and better still less than 5 minutes before the application to said keratin fibres.

15 According to this embodiment, the dye composition according to the invention is preferentially obtained by mixing a composition C1 comprising one or more peroxygenated salts as described previously, preferably one or more persulfates, and a composition C2 comprising one or more direct dyes as described previously and one or more cyclodextrins as described previously.

20 In addition, independently of the embodiments used in the simultaneous bleaching/dyeing process, the mixture present on the fibres (resulting either from the extemporaneous mixing of compositions, or from the successive application of these compositions) is left in place for a time, generally, from about 1 minute to 1 hour 30 minutes and preferably from 5 minutes to 60 minutes.

25 The temperature during the simultaneous bleaching/dyeing process is conventionally between room temperature (between 15°C and 25°C) and 80°C and preferably between room temperature and 60°C.

30 After the treatment, the human keratin fibres are optionally rinsed with water, optionally washed with a shampoo and then rinsed with water, before being dried or left to dry naturally.

Preferably, the pH of the oxidizing composition (A) and/or of the oxidizing composition (B), when they are aqueous, is between 3 and 11 and especially between 4 and 10.

The pH of the oxidizing composition (A) and/or of the oxidizing composition (B) may be adjusted to the desired value by means of basifying agents or acidifying agents. Among the basifying agents, mention may be made of aqueous ammonia, monoethanolamine and mineral or organic hydroxides. Among the acidifying agents, examples that may be mentioned include mineral acids, for instance hydrochloric acid or orthophosphoric acid, or else acetic acid, tartaric acid, citric acid and lactic acid, and sulfonic acids.

The oxidizing composition (B) different from the dye composition used in the simultaneous keratin fibre bleaching/dyeing process according to the invention may optionally also comprise one or more additives such as those described previously, in the total contents described previously.

A subject of the invention is also a device comprising at least two compartments, a first compartment containing a composition for dyeing keratin fibres as defined previously; a second compartment containing an oxidizing composition, which is preferably aqueous, comprising one or more chemical oxidizing agents preferably other than the peroxygenated salts as described previously.

A subject of the invention is also a device comprising at least three compartments, a first compartment containing a composition C1 comprising one or more peroxygenated salts, preferably one or more persulfates, as described previously; a second compartment containing a composition C2 comprising one or more direct dyes and one or more cyclodextrins as described previously; a third compartment containing an oxidizing composition comprising one or more chemical oxidizing agents other than the peroxygenated salts as described previously.

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

EXAMPLES:

Compositions A to E below are prepared from the ingredients shown in the table below, the amounts of which are expressed as weight percentages of active material (AM).

| Ingredients                            | Composition A<br>(control) | Composition B<br>(comparative) | Composition C<br>(comparative) | Composition D<br>(invention) | Composition E<br>(invention) |
|----------------------------------------|----------------------------|--------------------------------|--------------------------------|------------------------------|------------------------------|
| Sodium silicate                        | 14                         | 14                             | 14                             | 14                           | 14                           |
| HC Blue 15                             | 0                          | 0.105                          | 0                              | 0.105                        | 0                            |
| Basic Red 51                           | 0                          | 0                              | 0.105                          | 0                            | 0.105                        |
| 2-Hydroxypropyl- $\beta$ -cyclodextrin | 0                          | 0                              | 0                              | 7.86                         | 7.86                         |
| Potassium persulfate                   | 12.7                       | 12.7                           | 12.7                           | 12.7                         | 12.7                         |
| Water                                  | qs 100                     | qs 100                         | qs 100                         | qs 100                       | qs 100                       |

Once compositions A to E have been prepared, mixtures M1 to M5 are then prepared.

Mixture M1 (control) corresponds to a mixture of 10 g of composition A with 10 g of oxidizing composition comprising hydrogen peroxide at 12 g% AM.

Mixture M2 (comparative) corresponds to a mixture of 10 g of composition B with 10 g of oxidizing composition comprising hydrogen peroxide at 12 g% AM.

Mixture M3 (comparative) corresponds to a mixture of 10 g of composition C with 10 g of oxidizing composition comprising hydrogen peroxide at 12 g% AM.

Mixture M4 (invention) corresponds to a mixture of 10 g of composition D with 10 g of oxidizing composition comprising hydrogen peroxide at 12 g% AM.

Mixture M5 (invention) corresponds to a mixture of 10 g of composition E with 10 g of oxidizing composition comprising hydrogen peroxide at 12 g% AM.

Each mixture M1 to M5 is then applied to a lock of natural hair containing 90% white hairs, at a rate of 10 g of mixture per 1 g of hair.

Each treated lock of hair is then left to stand for 50 minutes on a hotplate at a temperature of 33°C.

*Spectrocolorimetric evaluation:*

5 The colour of the locks was then evaluated in the CIE L\* a\* b\* system, using a Minolta CM3600D spectrophotometer colorimeter (illuminant D65, angle 10°). In this L\* a\* b\* system, the three parameters respectively denote the intensity of the colour (L\*), the green/red colour axis (a\*) and the blue/yellow colour axis (b\*).

10 The variation in colouring between the dyed locks of hair and the locks of hair that have only been lightened is defined by ( $\Delta E^*$ ) according to the following equation:

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

In this equation, L\*, a\* and b\* represent the values measured on locks of hair treated with the mixtures M2 to M5 and L<sub>0</sub>\*, a<sub>0</sub>\* and b<sub>0</sub>\* represent the values measured on locks of hair treated with M1.

The higher the value of  $\Delta E^*$ , the greater the colour difference.

The results are collated in Table 1 below.

| LOCKS OF HAIR        | L*    | a*    | b*    | $\Delta E^*$ |
|----------------------|-------|-------|-------|--------------|
| Lock treated with M1 | 80.02 | 2.57  | 19.25 | -            |
| Lock treated with M2 | 76.67 | -4.36 | 14.60 | 8.99         |
| Lock treated with M3 | 73.91 | 11.41 | 16.78 | 11.03        |
| Lock treated with M4 | 74.11 | -7.74 | 11.45 | 14.21        |
| Lock treated with M5 | 71.86 | 16.51 | 14.99 | 16.70        |

20

It is found that the value of  $\Delta E^*$  is greater for the mixture M4 according to the invention relative to the comparative mixture M2. Similarly, the value of  $\Delta E^*$  is greater for the mixture M5 according to the invention relative to the comparative mixture M3.

Moreover, the mixture M4 according to the invention leads to a higher L\* value than the comparative mixture M2 and thus to a more intense colouring.

25 Similarly, the mixture M5 according to the invention leads to a higher L\* value than the comparative mixture M3 and thus to a more intense colouring.

The mixture M4 according to the invention thus makes it possible to obtain better dyeing performance than the comparative mixture M2.

The mixture M5 according to the invention thus makes it possible to obtain better dyeing performance than the comparative mixture M3.

## CLAIMS

1. Composition for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising:

- 5
- at least one peroxygenated salt,
  - at least one direct dye, and
  - at least one  $\beta$ -cyclodextrin.

10

2. Composition according to the preceding claim, characterized in that the peroxygenated salt(s) are chosen from persulfates; preferably from alkali metal persulfates, alkaline-earth metal persulfates, ammonium persulfates, and mixtures thereof; more preferentially from (bis)tetrabutylammonium persulfate, barium persulfate, magnesium persulfate, calcium persulfate, sodium persulfate, potassium persulfate, ammonium persulfate, and mixtures thereof; even more preferentially from sodium persulfate, potassium persulfate, ammonium persulfate, and mixtures thereof;

15

better still, it comprises potassium persulfate.

20

3. Composition according to either of the preceding claims, characterized in that the total content of peroxygenated salt(s) is between 1% and 30% by weight, preferably between 3% and 25% by weight, more preferentially between 4% and 20% by weight and even more preferentially between 5% and 18% by weight, relative to the total weight of the composition.

25

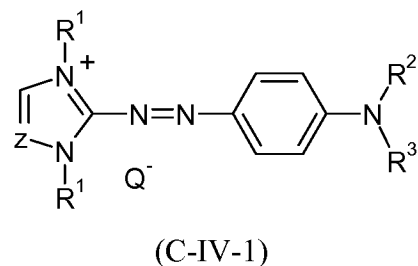
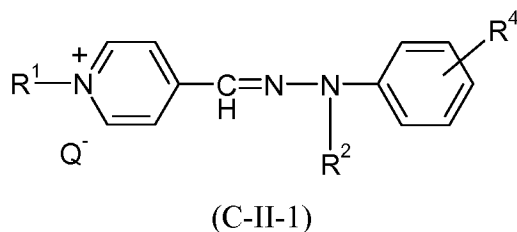
4. Composition according to any one of the preceding claims, characterized in that the direct dye(s) are chosen from cationic direct dyes, nonionic direct dyes, anionic direct dyes, and mixtures thereof.

30

5. Composition according to any one of the preceding claims, characterized in that the direct dye(s) are chosen from cationic direct dyes: preferably chosen from triarylmethane cationic direct dyes, azo cationic direct dyes, hydrazono cationic direct dyes, and mixtures thereof;

more preferentially from:

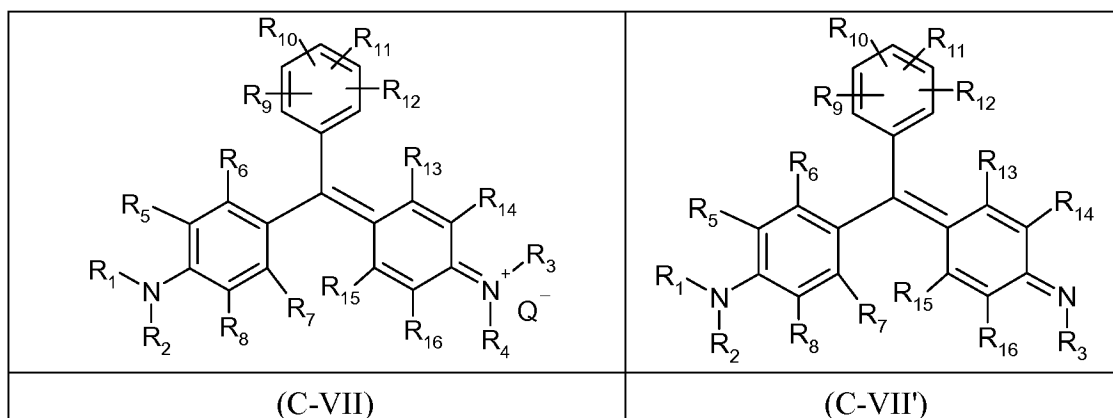
- the dyes of formula C-II-1 or C-IV-1 below:



in which formulae (C-II-1) and (C-IV-1):

- R<sup>1</sup> represents a (C<sub>1</sub>-C<sub>4</sub>)alkyl group such as methyl;
- R<sup>2</sup> and R<sup>3</sup>, which may be identical or different, represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl group, such as methyl; and
- 5       - R<sup>4</sup> represents a hydrogen atom or an electron-donating group such as optionally substituted (C<sub>1</sub>-C<sub>8</sub>)alkyl, optionally substituted (C<sub>1</sub>-C<sub>8</sub>)alkoxy, or (di)(C<sub>1</sub>-C<sub>8</sub>)(alkyl)amino optionally substituted on the alkyl group(s) with a hydroxyl group; particularly, R<sup>4</sup> is a hydrogen atom,
- Z represents a CH group or a nitrogen atom, preferentially CH,
- 10       - Q<sup>-</sup> is an anionic counterion as defined previously, in particular a halide, such as chloride, or an alkyl sulfate, such as methyl sulfate or mesityl;

- the triarylmethane cationic direct dye(s) of formulae (C-VII) and (C-VII') below:



and also the organic or mineral acid or base addition salts thereof, the geometrical isomers, optical isomers and tautomers thereof, and the mesomeric forms thereof, and the solvates thereof such as hydrates:

in which preceding formulae (C-VII) and (C-VII'):

\* 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 group from among: (C<sub>1</sub>-C<sub>6</sub>)alkyl which is optionally substituted, preferably with a hydroxyl group; aryl such as phenyl, aryl(C<sub>1</sub>-C<sub>4</sub>)alkyl such as benzyl, heteroaryl, heteroaryl(C<sub>1</sub>-C<sub>4</sub>)alkyl, or else two groups R<sub>1</sub> and R<sub>2</sub>, and/or R<sub>3</sub> and R<sub>4</sub>, borne by the same nitrogen atom, form, together with the nitrogen atom which bears them, an optionally substituted heterocycloalkyl group such as morpholino, piperazino or piperidino; preferably, 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 group;

\* R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub>, which may be identical or different, represent a hydrogen or halogen atom or a group chosen from i) hydroxyl, ii) thiol, iii) amino, iv) (di)(C<sub>1</sub>-C<sub>4</sub>)(alkyl)amino, v) (di)arylamino such as (di)phenylamino, vi) nitro, vii) acylamino (-NR-C(O)R') in which the radical R is a hydrogen atom, 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; viii) carbamoyl ((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; ix) carboxylic acid or ester, (-O-C(O)R') or (-C(O)OR'), in which the radical R' is a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl optionally bearing at least one hydroxyl group and the radical R' is a C<sub>1</sub>-C<sub>2</sub> alkyl radical; x) alkyl optionally substituted especially with a hydroxyl group; xi) alkylsulfonylamino (R'SO<sub>2</sub>-NR-) 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; xii) aminosulfonyl ((R)<sub>2</sub>N-SO<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, xiii) (C<sub>1</sub>-C<sub>4</sub>)alkoxy, and xiv) (C<sub>1</sub>-C<sub>4</sub>)alkylthio;

\* or else two radicals borne by two contiguous carbon atoms R<sub>5</sub> and R<sub>6</sub> and/or R<sub>7</sub> and R<sub>8</sub> and/or R<sub>9</sub> and R<sub>10</sub> and/or R<sub>11</sub> and R<sub>12</sub> and/or R<sub>13</sub> and R<sub>14</sub> and/or R<sub>15</sub> and R<sub>16</sub> form, together with the carbon atoms which bear them, an aryl or heteroaryl, preferably benzo, 6-membered fused ring, said ring possibly also being optionally substituted, preferably an unsubstituted benzo ring;

\* Q<sup>-</sup> represents an anionic counterion for achieving electrical neutrality, preferably chosen from halides such as chloride or bromide, and phosphate;

it being understood that when the cationic dye comprises one or more anionic substituents such as COOR or SO<sub>3</sub>R with R denoting a hydrogen or a cation, it is

understood that there are then more cationic substituents than anionic substituents, such that the overall resulting charge of the triarylmethane structure is cationic.

5           6. Composition according to any one of the preceding claims, characterized in that the total content of direct dye(s) is between 0.001% and 20% by weight, preferably between 0.005% and 10% by weight, more preferentially between 0.01% and 5% by weight, relative to the total weight of the dye composition.

10           7. Composition according to any one of the preceding claims, characterized in that the  $\beta$ -cyclodextrin(s) are chosen from  $\beta$ -cyclodextrin, methyl- $\beta$ -cyclodextrin, heptakis(2,3,6-trimethyl)- $\beta$ -cyclodextrin, heptakis(2,6-dimethyl)- $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin, 2-hydroxyethyl- $\beta$ -cyclodextrin, and mixtures thereof; preferably from  $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin, 2-hydroxyethyl- $\beta$ -cyclodextrin, and mixtures thereof; and more preferentially from  $\beta$ -cyclodextrin, 2-hydroxypropyl- $\beta$ -cyclodextrin, and mixtures thereof.

20           8. Composition according to any one of the preceding claims, characterized in that the total content of  $\beta$ -cyclodextrin(s) is between 0.1% and 25% by weight, more preferentially between 0.5% and 20% by weight, even more preferentially between 1% and 15% by weight, even better still between 2% and 10% by weight, relative to the total weight of the dye composition.

25           9. Composition according to any one of the preceding claims, characterized in that it comprises at least one alkaline agent; preferably chosen from inorganic alkaline agents, more preferentially chosen from dibasic or tribasic ammonium phosphates, water-soluble silicates such as alkali metal or alkaline-earth metal silicates, for instance sodium disilicate, sodium silicate, dibasic or tribasic alkali metal or alkaline-earth metal phosphates, or alkali metal or alkaline-earth metal carbonates, and mixtures thereof; even more preferentially from water-soluble silicates such as alkali metal or alkaline-earth metal silicates; better still from sodium disilicate, sodium silicate, and mixtures thereof; even better still from sodium silicate.

35           10. Process for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres a dye composition as defined according to any one of Claims 1 to 9.

11. Use of the dye composition as defined according to any one of Claims 1 to 9, for dyeing keratin fibres.

5 12. Process for simultaneously bleaching/dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres:

- a dye composition as defined according to any one of Claims 1 to 9, and
- an oxidizing composition (B) different from the dye composition, comprising one or more chemical oxidizing agents, preferably other than  
10 peroxygenated salts, more preferentially chosen from hydrogen peroxide.

13. Simultaneous bleaching/dyeing process according to the preceding claim, characterized in that it comprises a step of extemporaneous mixing of said dye composition with said oxidizing composition before said step(s) of application to said  
15 keratin fibres.

14. Device comprising at least two compartments, a first compartment containing a dye composition as defined according to any one of Claims 1 to 9; a second compartment containing an oxidizing composition comprising one or more  
20 chemical oxidizing agents, preferably other than peroxygenated salts.

15. Device comprising at least three compartments, a first compartment containing a composition C1 comprising one or more peroxygenated salts, preferably one or more persulfates as defined according to either of Claims 1 and 2; a second  
25 compartment containing a composition C2 comprising one or more direct dyes as defined according to any one of Claims 1, 4 or 5, and one or more cyclodextrins, as defined according to any one of Claims 1 or 7; a third compartment containing an oxidizing composition comprising one or more chemical oxidizing agents other than peroxygenated salts.

30

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2019/066688

## A. CLASSIFICATION OF SUBJECT MATTER

INV. A61Q5/06 A61K8/73 A61K8/22  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61Q A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                               | Relevant to claim No. |
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Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

21 August 2019

Date of mailing of the international search report

03/09/2019

Name and mailing address of the ISA/

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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2019/066688

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                                |                       |
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/066688

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)  | Publication<br>date    |
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| -----                                     |                     |                             |                        |