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(71) Applicant: **L'OREAL** [FR/FR]; 14, Rue Royale, F-75008 Paris (FR).

(72) Inventors: **GABIN, Gerard**; 8, rue Pierre Haret, F-75009 Paris (FR). **CHARRIER, Delphine**; 63 rue Nationale, F-92100 Boulogne (FR).

(74) Agent: **CASALONGA**; Casalonga & Associates, 8 Avenue Percier, F-75008 Paris (FR).

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(54) Title: EXPANDED DYEING COMPOSITION COMPRISING AN INERT GAS, AN OXIDATION DYE AND AN OXYALKYLENATED NONIONIC SURFACTANT

(57) Abstract: The invention relates to an expanded dyeing composition comprising: - from 30 to 70 % by weight relative to the total weight of the expanded dyeing composition, of one or more inert gases, -one or more oxidation dyes and -one or more oxyalkylenated nonionic surfactants. It also relates to a method for dyeing keratinic fibres, employing this expanded dyeing composition (A) and an oxidizing composition (B).

## **Expanded dyeing composition comprising an inert gas, an oxidation dye and an oxyalkylenated nonionic surfactant**

5           The present invention relates to an expanded dyeing composition comprising at least one inert gas, at least one oxidation dye and at least one oxyalkylenated nonionic surfactant, and also to a method for dyeing that employs it with an oxidizing composition.

10           The present invention also relates to a ready-to-use composition for the oxidation dyeing of keratin fibres, and more particularly of human keratin fibres such as the hair, of the type comprising the mixing of said expanded dyeing composition with an oxidizing composition (B).

15           Lastly, the present invention relates to a kit for the oxidation dyeing of keratin fibres, comprising the expanded dyeing composition according to the invention and an oxidizing composition (B).

          Many people have for a long time sought to modify the colour of their hair, and especially to dye it in order, for example, to mask their grey hair.

20           In order to dye human keratin fibres durably, dyeing methods have been developed which are referred to as permanent, and are also called oxidation dyeing. These methods employ dyeing compositions containing oxidation dye precursors, also known generally as oxidation bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are  
25           colourless or weakly coloured compounds which, in combination with oxidizing products, are able to give rise to coloured compounds by a process of oxidative condensation.

30           It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or coloration modifiers, the latter being chosen especially from aromatic meta-diaminobenzenes, from meta-aminophenols, from meta-diphenols and from certain heterocyclic compounds such as indole compounds.

The dyeing compositions generally take the form of solutions, gels or more or less fluid creams. Users of cosmetic products are now increasingly looking for products that are pleasant to use and that have a novel texture.

5           The Applicant has now discovered that an expanded dyeing composition comprising from 30 to 70 % by weight relative to the total weight of the expanded dyeing composition, of at least one inert gas, at least one oxidation dye and at least one oxyalkylenated nonionic surfactant, employed during a dyeing method, allows a new texture to  
10 be obtained, with good use qualities, particularly in terms of ease of application, whether used alone, sequentially or as a mixture with an optionally expanded oxidizing composition.

          An expanded composition in the sense of the present patent application refers to a composition into which a gas is introduced in  
15 order to give the composition the appearance of a foam and to reduce its density, more particularly for the purpose of forming gaseous cells within the composition that are separated by thin sheets of base composition and hence to endow the composition with a foam texture.

          One subject of the present invention is thus an expanded dyeing  
20 composition (A) comprising:

- from 30 to 70 % by weight relative to the total weight of the expanded dyeing composition, of one or more inert gases,
- one or more oxidation dyes and
- one or more oxyalkylenated nonionic surfactants.

25           Another subject of the present invention is a method for dyeing keratin fibres, employing said expanded dyeing composition (A) and an oxidizing composition (B) comprising one or more oxidizing agents.

          The expanded dyeing composition, and also the mixture thereof  
30 with an oxidizing composition (B) in the method according to the invention, exhibit very good service qualities, and in particular an especially pleasant and lightened texture.

In particular, the mixing of the compositions (A) and (B) is very easy to accomplish and very easy to apply and to spread over locks of hair, and more particularly to the roots.

5 In addition, it does not run and remains well located at the points of application and spreads easily from the roots to the ends.

Lastly, the use of the expanded dyeing composition (A) according to the invention results in a coloration having very good qualities, especially in terms of establishment, intensity, uniformity and selectivity of the coloration obtained.

10 The invention also relates to a ready-to-use composition for the oxidation dyeing of keratin fibres and more particularly of human keratin fibres such as the hair, comprising the extemporaneous mixing of an expanded dyeing composition (A) according to the invention with an oxidizing composition (B).

15 Another subject of the invention is a colouring kit comprising first an expanded dyeing composition (A) according to the invention, and secondly an oxidizing composition (B).

20 Other characteristics and advantages of the invention will emerge more clearly on reading the description and the examples that follow.

In that which follows and unless otherwise indicated, the limits of a range of values are included within this range, in particular in the expressions "of between" and "ranging from ... to ...".

25 Moreover, the expression "at least one" used in the present description is equivalent to the expression "one or more".

According to the invention, the expanded dyeing composition comprises:

- 30 - from 30 to 70 % by weight relative to the total weight of the expanded dyeing composition, of one or more inert gases,
- one or more oxidation dyes and
- one or more oxyalkylenated nonionic surfactants.

An inert gas in the sense of the present invention is a gas lacking chemical reactivity in the environment in which it is located.

More particularly, the gas according to the invention is inert towards the oxidation of dyes.

5 Examples of inert gas used in the expanded compositions of the invention are nitrogen, carbon dioxide, nitrogen oxides or a noble gas, or a mixture thereof. The inert gas or gases is or are preferably chosen from nitrogen, argon, helium, carbon dioxide and mixtures thereof, better still from nitrogen, argon and mixtures thereof.

10 The expanded compositions used in the method of the invention are formed stably in the form of a foam with the aid of a base composition and one or more inert gases.

The inert gas or gases may represent in particular from 10% to 500% of the volume of the unexpanded composition, preferably from 30% to 200%, more preferably from 35% to 150% and better still from 40% to 140%.

15 This volume may be calculated by comparing the density of the base composition and that of the expanded composition.

This volume corresponds to the degree of expansion of the composition (or level of gas introduced into the composition), and may in particular be calculated by the following formula:

20

$$\text{Degree of expansion} = \frac{d_{\text{before expansion}} - d_{\text{foam}}}{d_{\text{foam}}} \times 100$$

25 Without limitation, this degree of expansion may in particular be measured on a composition which has already been expanded, using the following protocol:

- the expanded composition is introduced into a 100 ml beaker so as to occupy the total beaker volume, while avoiding formation of air bubbles during the filling of the jar;
- it is left to stand for 10 minutes and then the volume VI, 30 corresponding to the volume of the expanded composition, is recorded;
- a turbine is introduced, and the beaker and the turbine are placed under a vacuum bell jar;

- the vacuum is actuated and the blade of the turbine is rotated at a slow speed (500 rpm) for 10 minutes;
- the vacuum is disconnected and the volume  $V_2$ , corresponding to the volume of the unexpanded base composition, is recorded.

5           The degree of expansion is then calculated by the following formula:

$$\text{Degree of expansion} = \frac{V_1 - V_2}{V_2} \times 100$$

10           The quantity of inert gas introduced into the base composition contributes to the adjustment in density of the expanded composition to the desired value.

          The expanded composition of the invention may have a density of less than  $0.95 \text{ g/cm}^3$ . The expanded composition of the invention advantageously possesses a density ranging from  $0.2$  to  $0.9 \text{ g/cm}^3$  and preferably from  $0.3$  to  $0.8 \text{ g/cm}^3$ , this density being measured at a temperature of approximately  $20^\circ\text{C}$  and at atmospheric pressure in the following protocol.

15           The test is carried out on a composition volume of 25 ml, introduced into a 25 ml ( $V_i$ ) smooth plexiglas® jar which defines a cylindrical filling space with a height of 15 mm and a base with a diameter of 46 mm. The jar has a bottom wall 10 mm thick and a side wall 12 mm thick.

          Prior to measurement, the composition to be characterized and the jar are maintained at a temperature of the order of  $20^\circ\text{C}$ . The jar is tared and the weight value is noted ( $M_i$ ). The expanded composition is subsequently introduced into the jar so as to occupy its total volume, while avoiding the formation of air bubbles during the filling of the jar. The combination is left to stand at ambient temperature for 24 hours. The top of the jar is subsequently levelled before it is weighed ( $M_2$ ). The density is evaluated according to the convention  $p = (M_2 - M_i)/25$ .

The expanded composition according to the invention preferably exhibits a satisfactory stability, which may be evaluated by measuring a volume of foam ( $V_2$ ) remaining in the jar after one month at 45°C, according to the protocol described above for the measurement of density.

The ratio  $V_2/V_1$  corresponds to the ratio between the volume of the expanded composition after one month at 45°C and the volume of the expanded composition after 24 hours.

The expression "satisfactory stability" is applied in particular to expanded compositions having a ratio  $V_2/V_1$  of more than 0.85, in particular more than 0.90, for example more than 0.95.

The inert gas content by weight varies from 30% to 70%, preferably between 30% and 60% and more preferably from 30% to 50% of the expanded composition.

As indicated previously, the expanded dyeing composition (A) according to the invention comprises one or more oxidation dyes.

The oxidation dyes that may be used in the present invention are generally chosen from oxidation bases, optionally combined with one or more couplers.

The oxidation bases may be chosen especially from para-phenylene diamines, bis (phenyl) alky lene diamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.

Among the para-phenylenediamines, examples that may be mentioned include para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylene diamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino -N,N- diethyl- 3-methylaniline, N,N-bis ( $\beta$ -hydroxyethyl)-para-phenylenediamine, 4-N,N-bis ( $\beta$ -hydroxyethyl) amino -2-methylaniline, 4-N,N-bis ( $\beta$ -hydroxy ethyl) amino -2-chloro aniline, 2- $\beta$ -hydroxy ethyl-para-phenylenediamine, 2-fluoro-

para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-( $\beta$ -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl  $\beta$ -hydroxy ethyl)-para-phenylenediamine, N-( $\beta,\gamma$ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2-P-acetylaminoethyloxy-para-phenylenediamine, N-(P-methoxy ethyl)-para-phenylenediamine, 4-aminophenylpyrrolidine, 2-thienyl-para-phenylenediamine, 2- $\beta$ -hydroxyethylamino-5-aminotoluene and 3-hydroxy-1-(4'-aminophenyl)pyrrolidine, and the addition salts thereof with an acid.

Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2-P-hydroxyethyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylene diamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis( $\beta$ -hydroxy ethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2-P-acetylaminoethyloxy-para-phenylenediamine, and the addition salts thereof with an acid, are particularly preferred.

Among the bis(phenyl)alkylenediamines, examples that may be mentioned include N,N'-bis(P-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis( $\beta$ -hydroxy ethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)-tetramethylenediamine, N,N'-bis( $\beta$ -hydroxy ethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)-tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine, 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane and the addition salts thereof.

Among the para-aminophenols, examples that may be mentioned include para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-chlorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-

amino methylphenol, 4-amino-2-(P-hydroxyethyl-aminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

5 Among the ortho-aminophenols, examples that may be mentioned include 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof.

10 Among the heterocyclic bases, examples that may be mentioned include pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

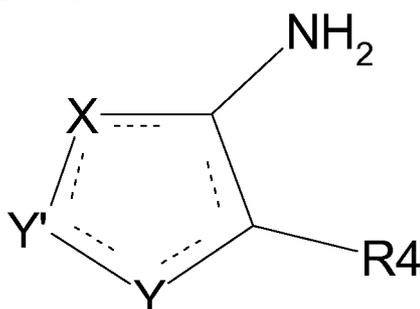
Among the pyridine derivatives, mention may be made of the compounds described, for example, in patents GB 1 026 978 and GB 1 153 196, for instance 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine and 3,4-diaminopyridine, and the addition salts thereof.

15 Other pyridine oxidation bases that are useful in the present invention are the 3-aminopyrazolo[1,5-a]pyridine oxidation bases or the addition salts thereof described, for example, in patent application FR 2 801 308. Examples that may be mentioned include  
20 pyrazolo[1,5-a]pyrid-3-ylamine, 2-acetylamino-pyrazolo[1,5-a]pyrid-3-ylamine, 2-(morpholin-4-yl)pyrazolo[1,5-a]pyrid-3-ylamine, 3-aminopyrazolo[1,5-a]pyridine-2-carboxylic acid, 2-methoxypyrazolo[1,5-a]pyrid-3-ylamine, (3-aminopyrazolo[1,5-a]pyrid-7-yl)methanol, 2-(3-aminopyrazolo[1,5-a]pyrid-5-yl)ethanol, 2-(3-aminopyrazolo[1,5-a]pyrid-7-yl)ethanol, (3-aminopyrazolo[1,5-a]pyrid-2-yl)methanol, 3,6-diaminopyrazolo[1,5-a]pyridine, 3,4-diaminopyrazolo[1,5-a]pyridine, pyrazolo[1,5-a]pyridine-3,7-diamine, 7-(morpholin-4-yl)pyrazolo[1,5-a]pyrid-3-ylamine, pyrazolo[1,5-a]pyridine-3,5-diamine, 5-(morpholin-4-yl)pyrazolo[1,5-a]pyrid-3-ylamine, 2-[(3-aminopyrazolo[1,5-a]pyrid-5-yl)(2-hydroxyethyl)amino]ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrid-7-yl)(2-hydroxyethyl)amino]ethanol, 3-aminopyrazolo[1,5-a]pyridin-5-ol, 3-aminopyrazolo[1,5-a]pyridin-4-ol, 3-aminopyrazolo[1,5-a]pyridin-6-ol, 3-aminopyrazolo[1,5-a]pyridin-7-ol, 2-(2-hydroxyethoxy)-3-aminopyrazolo[1,5-a]pyridine,

and 2-(4-methylpiperazinium-1-yl)-3-aminopyrazolo[1,5-a]pyridine chloride, and the addition salts thereof.

Among the pyrimidine derivatives, mention may be made of the compounds described, for example, in the patents DE 2359399; JP 88-16957 1; JP 05-63 124; EP 0770375 or patent application WO 96/1 5765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the heterocyclic bases, mention may particularly be made of the compounds of the formula (P1), their addition salts and their solvates:



(P1)

15

in which formula (P1):

X denotes a group -CO- or -CR<sub>3</sub>-,

Y denotes a nitrogen atom or a group -NR<sub>1</sub>,

Y' denotes a nitrogen atom or a group -NR<sub>2</sub>,

20 where R<sub>3</sub> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group which is optionally substituted by one or more hydroxyl or amino groups,

R<sub>1</sub> represents a C<sub>1</sub>-C<sub>4</sub> alkyl group which is substituted by one or more hydroxyl or amino groups,

25 R<sub>2</sub> represents a C<sub>1</sub>-C<sub>4</sub> alkyl group which is optionally substituted by one or more hydroxyl or amino groups,

it being possible for R<sub>1</sub> and R<sub>2</sub> and for R<sub>2</sub> and R<sub>3</sub> respectively to form, with the atoms which carry them, a saturated or unsaturated, 5- to 7-membered heterocycle which is optionally substituted by one or

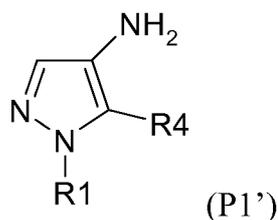
more halogen atoms, or one or more hydroxyl, amino and/or C1-C4 alkyl groups,

R4 represents an amino group, a C1-C4 alkyl group which is optionally substituted by one or more hydroxyl or amino groups, or a C1-C4 alkoxy group which is optionally substituted by one or more hydroxyl or amino groups,

and the ring system containing X, Y and Y' comprises at least one double bond.

The heterocyclic bases of formula (PI) or their addition salts according to the invention may be present in the form of solvates, for example hydrates or solvates of a linear or branched alcohol such as ethanol or isopropanol.

In one preferred variant of the invention, this or these heterocyclic bases is or are chosen from the compounds of formula (P1'), their addition salts and their solvates:



where R1 and R4 have the same definitions as before.

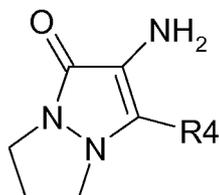
Preferably, R1 represents a C1-C4 alkyl group which is substituted by at least one hydroxyl group, more particularly a hydroxyethyl group, and R4 represents an amino group.

In this variant, preference will be given to using 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol or an addition salt thereof.

In a second variant, R1 and R2, or R2 and R3, respectively, form, with the atoms which carry them, a saturated or unsaturated, 5- to 7-membered heterocycle which is optionally substituted by one or more halogen atoms, or one or more hydroxyl, amino and/or C1-C4 alkyl groups.

In this second variant, the heterocyclic base or bases is or are chosen preferably from:

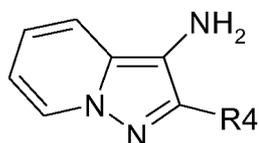
a) the compounds of formula (PI"), their addition salts, and their solvates:



(P1'')

where R4 has the same meaning as before, and preferably R4 represents an amino group;

b) the compounds of formula (P1'''), their addition salts and their solvates:



(P1''')

where R4 has the same meaning as above, R4 preferably representing a C<sub>1</sub>-C<sub>4</sub> alkoxy group which is optionally substituted by one or more hydroxyl groups, more particularly a hydroxyethoxy group; and

c) mixtures thereof.

Among these compounds of formula (PI"), preference will be given to using 2,3-diamino-6,7-dihydro- 1H,5H-pyrazolo[ 1,2-a]pyrazol-1-one or an addition salt thereof.

Among these compounds of formula (P1'''), preference will be given to using 2- {[3-aminopyrazolo[ 1,5-a]pyrid-2-yl]oxy} ethanol or an addition salt thereof.

In one preferred embodiment of the invention, the heterocyclic base or bases is or are chosen from the compounds of formula (PI"), their addition salts and their solvates.

In another preferred embodiment of the invention, the heterocyclic base or bases is or are chosen from the compounds of formula (P1'''), their addition salts and their solvates.

Heterocyclic bases which will be used with preference are 2-(4,5-diamino- 1H-pyrazol- 1-yl)ethanol, and/or 2- {[3-amino-pyrazolo[ 1,5-a]pyrid-2-yl]oxy} ethanol, and/or 2,3-diamino-6,7-

dihydro- 1H,5H-pyrazolo[ 1,2-a]pyrazol- 1-one, and/or 2-(2-hydroxy-ethoxy)-3-amino-pyrazolo[ 1,5-a]pyridine and/or one of their salts.

In one particular embodiment of the invention, the oxidation base or bases is or are chosen from the compounds of formula (PI),  
 5 their addition salts and their solvates, optionally in combination with one or more para-phenylenediamines and/or one or more para-aminophenols.

The couplers that may be used in the present invention may be chosen from those conventionally used for the dyeing of keratin  
 10 fibres.

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

Examples that may be mentioned include 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro- 1,3-dihydroxybenzene, 1-hydroxy- 3-amino benzene, 1-met hy 1-2-hydroxy- 4-β-hydroxyethylamino benzene, 4-amino-2-hydroxytoluene, 5-amino -6-chloro-2 methylphenol, 2,4-diamino- 1-(P-hydroxyethyloxy)benzene, 2-  
 20 amino-4 -(P-hydroxyethylamino)- 1-methoxybenzene, 1,3-diamino-benzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido- 1-dimethylamino benzene, sesamol, 1-P-hydroxyethylamino-3,4-methylenedioxybenzene, a-naphthol, 2-methyl- 1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-  
 25 3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-(β-hydro xyethyl)amino- 3,4 -methylene-dioxybenzene, 2,6-bis (P-hydroxyethylamino)toluene, 6-hydroxy-indoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one, 2,6-dimethylpyrazolo[ 1,5-b]-  
 30 1,2,4-triazole, 2,6-dimethyl[3,2-c]- 1,2,4-triazole and 6-methylpyrazolo[ 1,5-a]benzimidazole, the addition salts thereof with an acid, and mixtures thereof.

In general, the addition salts of the oxidation bases and of the couplers that may be used in the context of the invention are

especially chosen from addition salts with an acid such as hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

5 The oxidation dye or dyes may represent from 0.000 1% to 20% by weight, preferably from 0.0 1% to 15% by weight, better still from 0.1%, to 10%, by weight, relative to the total weight of the expanded dyeing composition (A).

10 The expanded colouring composition according to the invention may also contain one or more direct dyes.

The direct dye(s) may be chosen from synthetic direct dyes and natural direct dyes.

A direct dye is any dye which does not require the presence of a chemical oxidizing agent other than air for colouring.

15 A synthetic direct dye is any direct dye that does not exist in the natural state, including dyes obtained semi-synthetically.

20 Examples of suitable synthetic direct dyes that may be mentioned include azo, methine, carbonyl, azine, xanthene, (hetero)aryl nitro, tri(hetero)arylmethane, (metallo)porphyrin and phthalocyanine direct dyes, alone or as mixtures.

25 More particularly, the synthetic azo direct dyes include a -N=N- function in which the two nitrogen atoms are not simultaneously part of a ring system. However, it is not excluded for one of the two nitrogen atoms of the sequence -N=N- to be part of a ring system.

Examples of azo direct dyes that may be mentioned include the following dyes, described in Colour Index International, 3rd edition:

- Disperse Red 17
- Basic Red 22
- 30 - Basic Red 76
- Basic Yellow 57
- Basic Brown 16
- Basic Brown 17
- Disperse Black 9.

The direct dyes of the methine family are more particularly compounds comprising at least one sequence chosen from  $>C=C<$  and  $-N=C<$  in which the two atoms are not simultaneously part of a ring system. However, it is pointed out that one of the nitrogen or carbon atoms of the sequences may be part of a ring system.

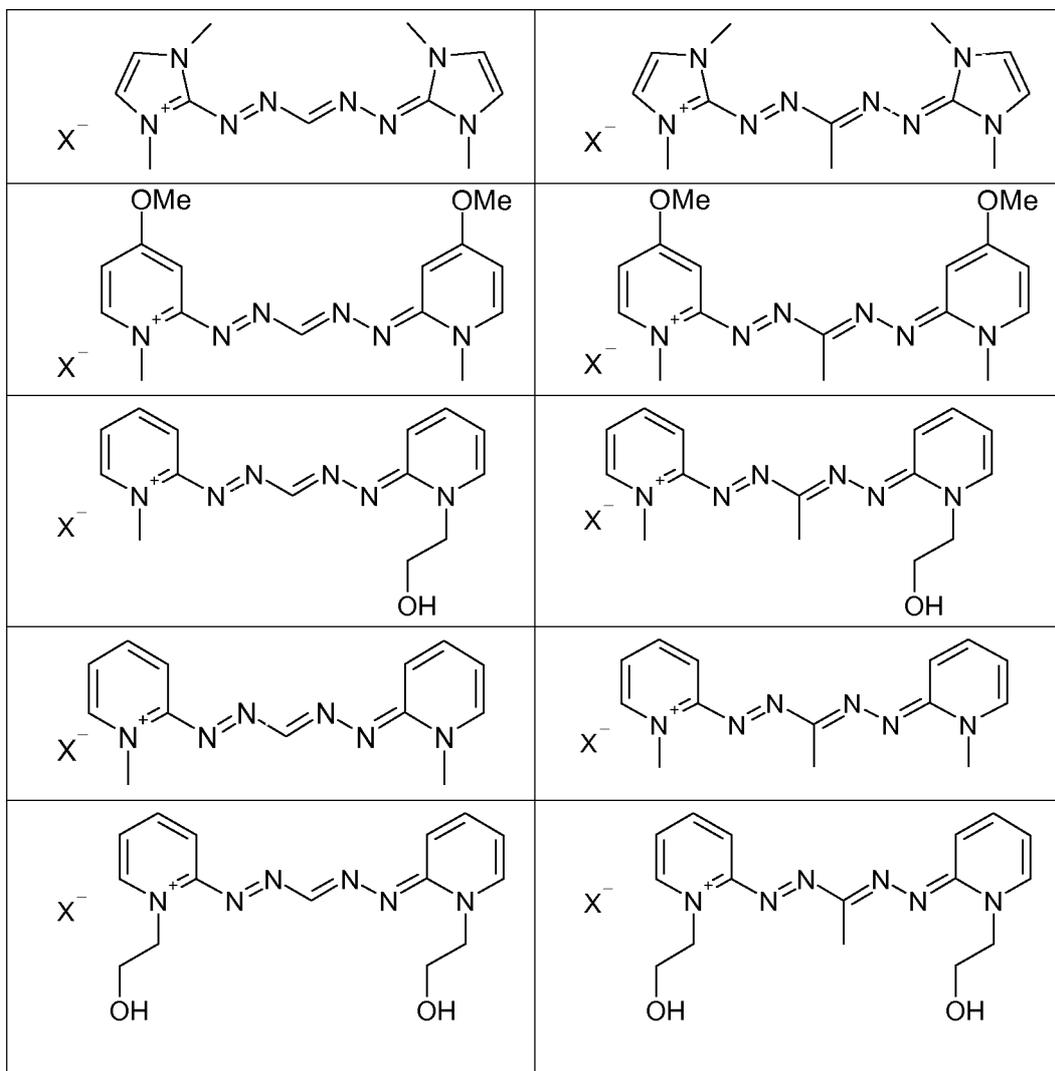
More particularly, the methine dyes are derived from methine, azomethine, hydrazono, mono- and diarylmethane, indoamine (or diphenylamine), indophenol, indoaniline and (hemi)cyanine compounds, such as styryl, streptocyanine, carbocyanine, azacarbocyanine, diazacarbocyanine and tetraazacarbocyanine, such as tetraazapentamethine, dyes, and optical and geometric isomers thereof.

Among the azo, azomethine, methine or tetraazapentamethine direct dyes that may be used according to the invention, mention may be made of the cationic dyes described in patent applications WO 95/1 5 144, WO 95/0 1772 and EP 7 14954; FR 2 189006, FR 2 28585 1, FR 2 140205, EP 1378544, EP 1674073 .

Among the indoamine dyes that can be used according to the invention, mention may be made of the following compounds:

- 2-P-hydroxyethylamino-5-[bis(P-4'-hydroxyethyl)amino]-anilino- 1,4-benzoquinone,
- 2-P-hydroxyethylamino-5-(2'-methoxy-4'-amino) anilino- 1,4-benzoquinone,
- 3-N-(2'-chloro-4'-hydroxy)phenylacetylamino-6-methoxy-1,4-benzoquinone imine,
- 3-N-(3'-chloro-4'-methylamino)phenylureido-6-methyl-1,4-benzoquinone imine,
- 3-[4'-N-(ethyl,carbamylmethyl)amino]phenylureido-6-methyl-1,4-benzoquinone imine.

Among the tetraazapentamethine dyes that may be used according to the invention, mention may be made of the following compounds appearing in the table below:



X<sup>-</sup> representing an anion preferably chosen from chloride, iodide, methyl sulfate, ethyl sulfate, acetate and perchlorate.

As regards the synthetic direct dyes of the carbonyl family, examples that may be mentioned include dyes chosen from quinone, acridone, benzoquinone, anthraquinone, naphthoquinone, 5 benzanthrone, anthranthrone, pyranthrone, pyrazolanthrone, pyrimidinoanthrone, flavanthrone, idanthrone, flavone, (iso)violanthrone, isoindolinone, benzimidazolone, isoquinolinone, anthrapyridone, pyrazoloquinazolone, perinone, quinacridone, 10 quinophthalone, indigoid, thioindigo, naphthalimide, anthrapyrimidine, diketopyrrolopyrrole and coumarin dyes.

Among the quinone direct dyes, mention may be made of the following dyes:

- Disperse Red 15
- Solvent Violet 13
- 5 - Disperse Violet 1
- Disperse Violet 4
- Disperse Blue 1
- Disperse Violet 8
- Disperse Blue 3
- 10 - Disperse Red 11
- Disperse Blue 7
- Basic Blue 22
- Disperse Violet 15
- Basic Blue 99

15 and also the following compounds:

- 1-N-methylmorpholiniumpropylamino-4-hydroxyanthraquinone;
- 1-aminopropylamino-4-methylaminoanthraquinone;
- 1-aminopropylaminoanthraquinone;
- 20 - 5- $\beta$ -hydroxyethyl-1,4-diaminoanthraquinone;
- 2-aminoethylaminoanthraquinone; and
- 1,4-bis (P,y-dihydroxypropylamino)anthraquinone.

As regards the synthetic direct dyes of the azine family, mention may be made especially of azine, fluorindine, acridine, (di)oxazine and (di)thiazine dyes.

25 Examples of azine dyes that may be mentioned include the following compounds:

- Basic Blue 17
- Basic Red 2.

30 As regards the synthetic direct dyes of the xanthene family, mention may be made especially of xanthene, thioxanthene and pyronine dyes.

The nitro(hetero)aryl synthetic direct dyes are more particularly nitrobenzene or nitropyridine direct dyes.

Among the nitrobenzene direct dyes that may be used according to the invention, mention may be made in a nonlimiting manner of the following compounds:

- 1,4-diamino-2-nitrobenzene
- 5 - 1-amino-2-nitro-4-β-hydroxyethylaminobenzene
- 1-amino-2-nitro-4-bis(β-hydroxyethyl)aminobenzene
- 1,4-bis(P-hydroxyethylamino)-2-nitrobenzene
- 1-P-hydroxyethylamino-2-nitro-4-bis(P-hydroxyethylamino)-  
benzene
- 10 - 1-P-hydroxyethylamino-2-nitro-4-aminobenzene
- 1-P-hydroxyethylamino-2-nitro-4-(ethyl)(P-hydroxyethyl)-  
aminobenzene
- 1-amino-3-methyl-4-β-hydroxyethylamino-6-nitrobenzene
- 1-amino-2-nitro-4-β-hydroxyethylamino-5-chlorobenzene
- 15 - 1,2-diamino-4-nitrobenzene
- 1-amino-2-β-hydroxyethylamino-5-nitrobenzene
- 1,2-bis-(P-hydroxyethylamino)-4-nitrobenzene
- 1-amino-2-tris(hydroxymethyl)methylamino-5-nitrobenzene
- 1-hydroxy-2-amino-5-nitrobenzene
- 20 - 1-hydroxy-2-amino-4-nitrobenzene
- 1-hydroxy-3-nitro-4-amino benzene
- 1-hydroxy-2-amino-4,6-dinitrobenzene
- 1-β-hydroxyethylamino-2-β-hydroxyethylamino-5-nitrobenzene
- 1-methoxy-2-β-hydroxyethylamino-5-nitrobenzene
- 25 - 1-hydroxyethoxy-3-methylamino-4-nitrobenzene
- 1-β,γ-dihydroxypropoxy-3-methylamino-4-nitrobenzene
- 1-β-hydroxyethylamino-4-β,γ-dihydroxypropoxy-2-  
nitrobenzene
- 1,γ-dihydroxypropylamino-4-trifluoromethyl-2-  
nitrobenzene
- 30 - 1-hydroxyethylamino-4-trifluoromethyl-2-nitrobenzene
- 1-β-hydroxyethylamino-3-methyl-2-nitrobenzene
- 1-β-aminoethylamino-5-methoxy-2-nitrobenzene
- 1-hydroxy-2-chloro-6-ethylamino-4-nitrobenzene

- 1-hydroxy-2-chloro-6-amino-4-nitrobenzene
- 1-hydroxy-6-bis (P-hydroxyethyl)amino-3-nitrobenzene
- 1-P-hydroxyethylamino-2-nitrobenzene
- 1-hydroxy-4-P-hydroxyethylamino-3-nitrobenzene.

5 Among the triarylmethane dyes that may be used according to the invention, mention may be made of the following compounds:

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

As regards the (metallo)porphyrin or phthalocyanine synthetic direct dyes, use may be made of cationic or non-cationic compounds, optionally comprising one or more metals or metal ions, such as, for  
15 example, alkali metals and alkaline-earth metals, zinc and silicon.

Examples of particularly suitable synthetic direct dyes that may be mentioned include nitrobenzene dyes; azo, methine, azomethine, hydrazono or styryl direct dyes; azacarboyanines such as tetraazacarboyanines (tetraazapentamethines); quinone direct dyes,  
20 and in particular anthraquinone, naphthoquinone or benzoquinone dyes; azine direct dyes; xanthene direct dyes; triarylmethane direct dyes; indoamine direct dyes, indigoid direct dyes, phthalocyanine direct dyes and porphyrin direct dyes, alone or as mixtures.

These dyes may be monochromophoric dyes (meaning that they  
25 comprise only one dye) or polychromophoric dyes, preferably di- or trichromophoric dyes; the chromophores may be identical or different, from the same chemical family or a different family. It should be noted that a polychromophoric dye comprises a plurality of groups each derived from a molecule that absorbs in the visible region  
30 between 400 and 800 nm. Furthermore, this absorbance of the dye does not require any prior oxidation thereof, or combination with any other chemical species.

In the case of polychromophoric dyes, the chromophores are connected together by means of at least one linker L, which may be cationic or non-cationic.

The linker L is preferably a linear, branched or cyclic C<sub>1</sub>-C<sub>20</sub> alkyl chain which is optionally interrupted and/or terminated by at least i) a heteroatom (such as nitrogen N(R), N<sup>+</sup>R, R', Q<sup>-</sup>, oxygen or sulfur), ii) a group C(O), C(S), S(O), or S(O)<sub>2</sub> or iii) a combination thereof, optionally interrupted by at least one heterocycle which is or is not fused with a phenyl nucleus, and which comprises at least one quaternized nitrogen atom forming part of said ring system, and optionally at least one other heteroatom (such as oxygen, nitrogen or sulfur), optionally interrupted by at least one substituted or unsubstituted phenyl or naphthyl, optionally at least one quaternary ammonium group substituted by two C<sub>1</sub>-C<sub>15</sub> alkyl groups which are optionally substituted; the linker does not contain a nitro, nitroso or peroxy group, and R and R', which are identical or different, represent a hydrogen atom or a C<sub>i</sub>-C<sub>6</sub> alkyl group which is optionally substituted, preferably by at least one hydroxyl group, and Q<sup>-</sup> represents an organic or inorganic anionic counterion such as a halide or an alkylsulfate.

If the heterocycles or aromatic nuclei are substituted, they are substituted, for example, with one or more C<sub>i</sub>-C<sub>s</sub> alkyl groups optionally substituted with a hydroxyl, C<sub>1</sub>-C<sub>2</sub> alkoxy, C<sub>2</sub>-C<sub>4</sub> hydroxyalkoxy, acetylamino or amino group substituted with one or two C<sub>1</sub>-C<sub>4</sub> alkyl groups, optionally bearing at least one hydroxyl group, or the two groups possibly forming, with the nitrogen atom to which they are attached, a 5- or 6-membered heterocycle, optionally comprising another nitrogen or non-nitrogen heteroatom; a halogen atom; a hydroxyl group; a C<sub>1</sub>-C<sub>2</sub> alkoxy group; a C<sub>2</sub>-C<sub>4</sub> hydroxyalkoxy group; an amino group; an amino group substituted with one or two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl groups, optionally bearing at least one hydroxyl group.

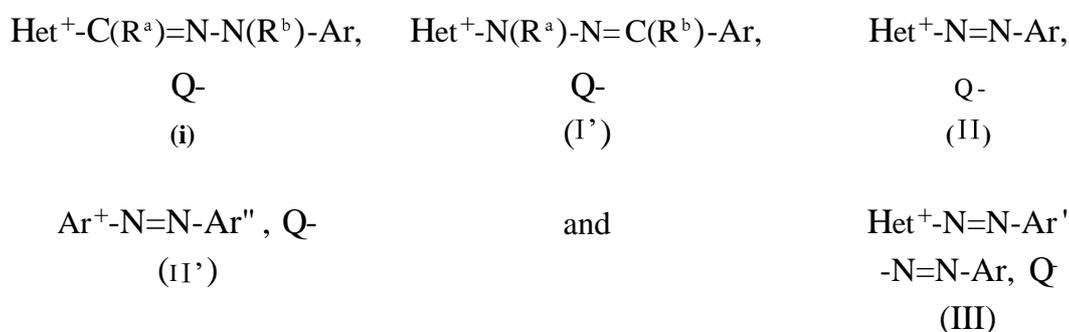
According to one particularly advantageous embodiment of the invention, the direct dye or dyes is or are chosen from (poly)azo dyes

such as (di)azo dyes; hydrazono dyes; (poly)methine dyes such as styryl dyes; anthraquinone dyes or naphthalimide dyes. Preferably, these dyes are (poly)cationic.

According to an even more preferred embodiment of the invention, the direct dyes are chosen from cationic dyes known as "basic dyes".

Mention may be made of the cationic hydrazono dyes of formulae (I) and (I'), the azo dyes (II) and (II') and the diazo dyes (III) below:

10



in which formulae (I), (I'), (II), (II') and (III):

-Het<sup>+</sup> represents a cationic heteroaryl group, preferentially bearing an endocyclic cationic charge, such as imidazolium, indolium or pyridinium, which is optionally substituted, preferentially by one or more Ci-C<sub>8</sub> alkyl groups such as methyl;

- Ar<sup>+</sup> represents an aryl group, such as phenyl or naphthyl, bearing an exocyclic cationic charge, preferentially ammonium, particularly tri(Ci-C<sub>8</sub> alkyl) ammonium 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 (Ci-C<sub>8</sub>)alkyl, ii) optionally substituted (Ci-C<sub>8</sub>)alkoxy, iii) (di)(Ci-C<sub>8</sub> alkyl) amino optionally substituted on the alkyl group(s) with a hydroxyl group, iv) aryl(Ci-C<sub>8</sub> alkyl) amino, v) optionally substituted N-(Ci-C<sub>8</sub> alkyl)-N-aryl(Ci-C<sub>8</sub> alkyl) amino or alternatively Ar represents a julolidine group;

- Ar' is an optionally substituted divalent (hetero)arylene group such as phenylene, particularly para-phenylene, or naphthalene, which are optionally substituted, preferentially with one or more C<sub>1</sub>-C<sub>8</sub> alkyl, hydroxyl or C<sub>i</sub>-C<sub>s</sub> alkoxy groups;

5 - Ar'' is an optionally substituted (hetero)aryl group such as phenyl or pyrazolyl, which are optionally substituted, preferentially with one or more C<sub>i</sub>-C<sub>s</sub> alkyl, hydroxyl, (di)(C<sub>i</sub>-C<sub>s</sub> alkyl)amino, C<sub>i</sub>-C<sub>s</sub> alkoxy or phenyl groups;

10 - R<sup>a</sup> and R<sup>b</sup>, which are identical or different, represent a hydrogen atom or a C<sub>i</sub>-C<sub>s</sub> alkyl group, which is optionally substituted, preferentially with a hydroxyl group;

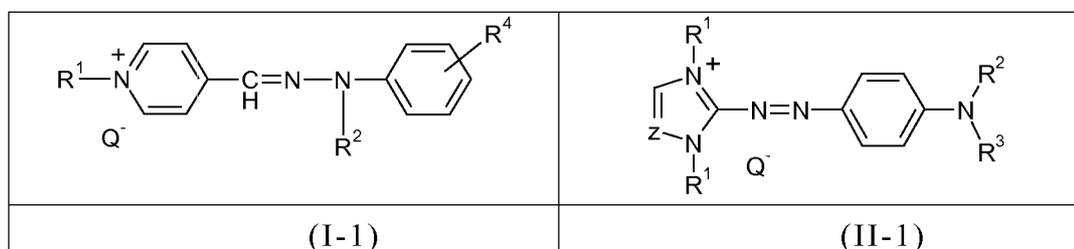
or alternatively the substituent R<sup>a</sup> with a substituent of Het<sup>+</sup> and/or R<sup>b</sup> with a substituent of Ar form, together with the atoms that bear them, a (hetero)cycloalkyl;

15 particularly, R<sup>a</sup> and R<sup>b</sup> represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group, which is optionally substituted with a hydroxyl group;

- Q<sup>-</sup> represents an organic or inorganic anionic counterion, such as a halide or an alkylsulfate.

20 In particular, the dyes of the invention are cationically charged, endocyclic, azo and hydrazono dyes of formulae (I), (Γ) and (II) as defined above. The dyes of formulae (I), (Γ) and (II) described in patent applications WO 95/1 5144, WO 95/0 1772 and EP 714954 are more particularly preferred.

25 Dyes of the invention are preferably chosen from the following compounds:



in which formulae (I-1) and (II-1):

- R<sup>1</sup> represents a C<sub>1</sub>-C<sub>4</sub> alkyl group such as methyl;

-  $R^2$  and  $R^3$  which are identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group such as methyl; and

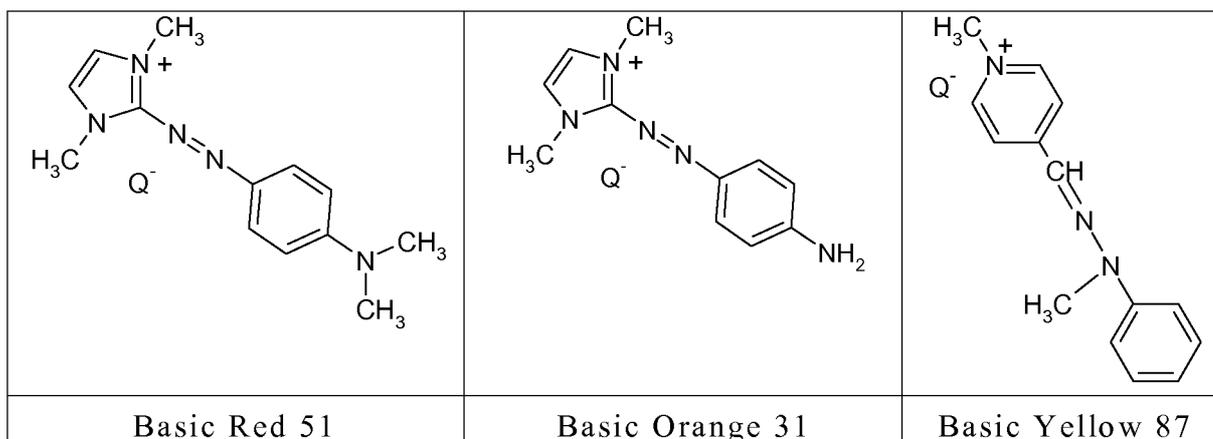
-  $R^4$  represents a hydrogen atom or an electron-donating group such as optionally substituted C<sub>i</sub>-C<sub>8</sub> alkyl, optionally substituted C<sub>i</sub>-C<sub>8</sub> alkoxy, or (di)(C<sub>i</sub>-C<sub>8</sub> alkyl)amino optionally substituted on the alkyl group(s) with a hydroxyl group; particularly,  $R^4$  is a hydrogen atom;

- Z represents a CH group or a nitrogen atom, preferentially CH;

-  $Q^-$  is as defined previously.

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

15



where  $Q^-$  is as defined previously, and represents in particular a halide such as a chloride, or an alkyl sulfate such as methyl sulfate or mesityl.

20 Mention may also be made of 1-(4'-aminodiphenylazo)-2-methyl-4-bis(P-hydroxyethyl)amino benzene.

Among the polychromophoric dyes, mention may be made more particularly of the symmetrical or non-symmetrical di- or trichromophoric azo and/or azomethine (hydrazone) dyes, comprising on the one hand at least one 5- or 6-membered aromatic heterocycle,

25

optionally fused, which comprises at least one quaternized nitrogen atom forming part of the said heterocycle, and optionally at least one other heteroatom (such as nitrogen, sulfur or oxygen), and, on the other hand, at least one optionally substituted phenyl or naphthyl group optionally bearing at least one group OR in which R represents a hydrogen atom, an optionally substituted  $C_i-C_6$  alkyl group, an optionally substituted phenyl nucleus, or at least one group  $N(R')_2$  with R', which may be identical or different, representing a hydrogen atom, an optionally substituted  $C_i-C_6$  alkyl group or an optionally substituted phenyl nucleus; the groups R' possibly forming, with the nitrogen atom to which they are attached, a saturated, 5- or 6-membered heterocycle, or else one and/or both of the groups R' may each form a saturated, 5- or 6-membered heterocycle with the carbon atom of the aromatic ring that is ortho to the nitrogen atom.

Aromatic cationic heterocycles that may preferably be mentioned include 5- or 6-membered rings containing 1 to 3 nitrogen atoms and preferably 1 or 2 nitrogen atoms, one being quaternized; said heterocycle moreover being optionally fused to a benzene nucleus. It should similarly be noted that the heterocycle may optionally comprise another heteroatom other than nitrogen, for instance sulfur or oxygen.

If the heterocycles or phenyl or naphthyl groups are substituted, they are substituted, for example, with one or more  $C_i-C_s$  alkyl groups optionally substituted with a hydroxyl,  $C_i-C_2$  alkoxy,  $C_2-C_4$  hydroxyalkoxy, acetylamino or amino group substituted with one or two  $C_i-C_4$  alkyl groups, optionally bearing at least one hydroxyl group, or the two groups possibly forming, with the nitrogen atom to which they are attached, a 5- or 6-membered heterocycle, optionally comprising another nitrogen or non-nitrogen heteroatom; a halogen atom; a hydroxyl group; a  $C_i-C_2$  alkoxy group; a  $C_2-C_4$  hydroxyalkoxy group; an amino group; an amino group substituted with one or two identical or different  $C_i-C_4$  alkyl groups, optionally bearing at least one hydroxyl group.

These polychromophores are connected together via at least one linker L as defined previously.

5 The bonding between the linker and each chromophore generally takes place via a heteroatom substituent on the phenyl or naphthyl nucleus or via the quaternized nitrogen atom of the cationic heterocycle.

The dye may comprise identical or different chromophores.

10 As examples of such dyes, reference may be made especially to patent applications EP 1 637 566, EP 1 619 221, EP 1 634 926, EP 1 619 220, EP 1 672 033, EP 1 671 954, EP 1 671 955, EP 1 679 312, EP 1 671 951, EP 1 671 952, EP 1 671 971, WO 06/063 866, WO 06/063 867, WO 06/063 868, WO 06/063 869, EP 1 408 919, EP 1 377 264, EP 1 377 262, EP 1 377 261, EP 1 377 263, EP 1 399 425, EP 1 399 117, EP 1 416 909, EP 1 399 116 and EP 15 1 671 560.

It is equally also possible to use cationic synthetic direct dyes which are mentioned in the following patent applications: EP 1 006 153, which describes dyes comprising two chromophores of anthraquinone type connected via a cationic linker; EP 1 433 472, EP 1 433 474, EP 1 433 471 and EP 1 433 473, which describe identical or 20 different dichromophoric dyes, connected via a cationic or non-cationic linker, and also EP 6 291 333, which especially describes dyes comprising three chromophores, one of them being an anthraquinone chromophore, to which are attached two chromophores of azo or diazocarbocyanine type or an isomer thereof. 25

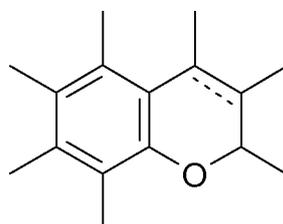
The term "natural dyes" means any dye or dye precursor that is naturally occurring and that is produced either by extraction (and possible purification) from a plant or animal matrix, optionally in the presence of natural compounds such as ash or ammonia, or via 30 chemical synthesis.

Natural dyes that may be mentioned include lawsone, henna, curcumin, chlorophyllin, alizarin, kermesic acid, purpurin, purpurogallin, indigo, Tyrian purple, sorghum, carminic acid, catechin, epicatechin, juglone, bixin, betanin, quercetin, chromene

dyes and chroman dyes, including haematein and brazilein and laccaic acids.

Preferably, the natural dyes used in the invention are chosen from curcumin, chlorophyllin, chromene dyes, chroman dyes and  
5 laccaic acids.

According to the invention, the terms "chromene dye" and "chroman dye" mean dyes which comprise in their structure at least one bicycle of formula (IV) below:

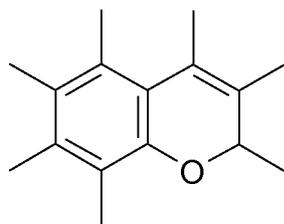


IV

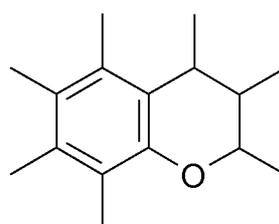
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the endocyclic bond  $\text{---}$  representing a carbon-carbon single bond or a carbon-carbon double bond, as illustrated by formula IV-1 denoting the chromene family and formula IV-2 denoting the chroman family below:



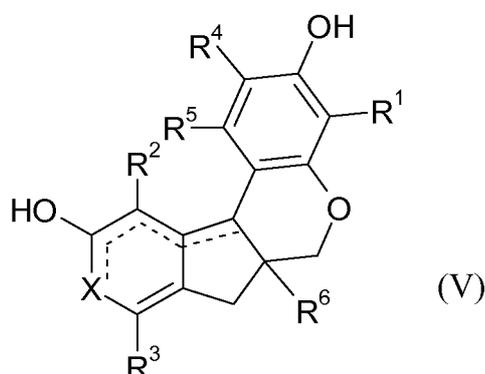
IV-1



IV-2

More particularly, the dyes having in their structure a bicycle of formula (IV) are chosen from the dyes having the following formulae:  
20

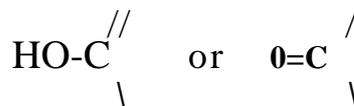
- formula (V), comprising in its structure the bicycle of formula IV-2,



in which:

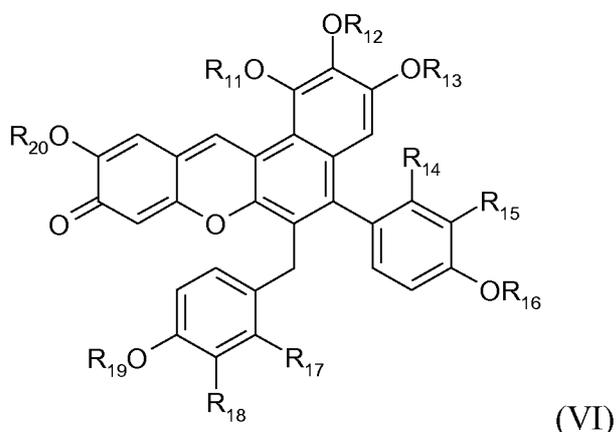
i)  $\text{---}$  represents a carbon-carbon single bond or a carbon-carbon double bond, the sequence of these bonds  $\text{---}$  denotes two carbon-carbon single bonds and two carbon-carbon double bonds, the said bonds being conjugated,

ii) X represents a group:



iii)  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$ , which may be identical or different, represent, independently of each other, a hydrogen atom, a hydroxyl group, an optionally substituted alkyl group, an optionally substituted alkoxy group or an optionally substituted acyloxy group, and also the tautomeric and/or mesomeric forms thereof, the stereoisomers thereof, the addition salts thereof with a cosmetically acceptable acid or base, and the hydrates thereof, and

- formula (VI), comprising in its structure the bicycle of formula IV-1,

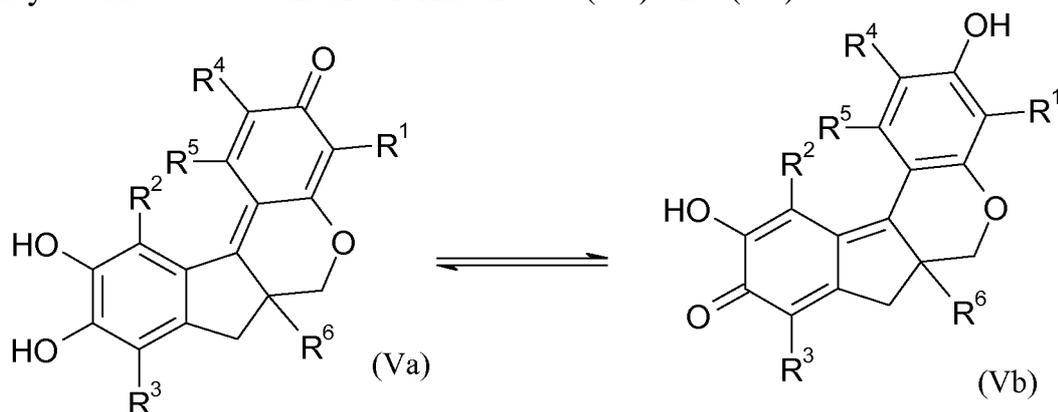


in which:

- R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>16</sub>, R<sub>19</sub> and R<sub>20</sub>, which may be identical or different, represent, independently of each other, a hydrogen atom or a C1-C4 alkyl group,

- R<sub>14</sub>, R<sub>15</sub>, R<sub>17</sub> and R<sub>18</sub>, which may be identical or different, represent, independently of each other, a hydrogen atom, a hydroxyl group or a C1-C4 alkoxy group, and also the tautomeric and/or mesomeric forms thereof, the stereoisomers thereof, the addition salts thereof with a cosmetically acceptable acid or base, and the hydrates thereof.

As regards the dyes of formula (V) as defined previously, they may be in two tautomeric forms noted (Va) and (Vb):



The alkyl groups mentioned in the preceding definitions of the substituents are linear or branched, saturated hydrocarbon groups, generally C1-C20, particularly C1-C10 and preferably C<sub>i</sub>-C<sub>6</sub>, such as methyl, ethyl, propyl, butyl, pentyl and hexyl.

The alkoxy groups are alkyl-oxy groups with alkyl groups as defined previously and preferably the alkoxy groups are Ci-Cio, such as methoxy, ethoxy, propoxy and butoxy.

5 The alkyl or alkoxy groups, when they are substituted, may be substituted with at least one substituent borne by at least one carbon atom, chosen from:

- a halogen atom;
- a hydroxyl group;
- a C1-C2 alkoxy group;
- 10 - a C1-C10 alkoxycarbonyl group;
- a C2-C4 (poly)hydroxyalkoxy group;
- an amino group;
- a 5- or 6-membered heterocycloalkyl group;
- an optionally cationic 5- or 6-membered heteroaryl group,
- 15 preferentially imidazolium, optionally substituted with a (Ci-C4)alkyl group, preferentially methyl;
- an amino group substituted with one or two identical or different Ci-C<sub>6</sub> alkyl groups, optionally bearing at least:
  - \* one hydroxyl group,
  - 20 \* an amino group optionally substituted with one or two optionally substituted C1-C3 alkyl groups, it being possible for the said alkyl groups to form, with the nitrogen atom to which they are attached, a saturated or unsaturated and optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other
  - 25 nitrogen or non-nitrogen heteroatom,
  - \* one quaternary ammonium group -N<sup>+</sup>R'R''R'''<sup>-</sup>, M<sup>-</sup> for which R', R'' and R''' , which are identical or different, represent a hydrogen atom or a C1-C4 alkyl group; and M<sup>-</sup> represents the counterion of the corresponding organic acid, inorganic acid or halide,
  - 30 \* or an optionally cationic 5- or 6-membered heteroaryl group, preferentially imidazolium, optionally substituted with a (C1-C4) alkyl group, preferentially methyl;
  - an acylamino group (-NR-COR') in which the group R is a hydrogen atom or a C1-C4 alkyl group optionally bearing at least one

hydroxyl group and the group R' is a C1-C2 alkyl group;

- a carbamoyl group ((R)<sub>2</sub>N-CO-) in which the groups R, which may be identical or different, represent a hydrogen atom or a C1-C4 alkyl group optionally bearing at least one hydroxyl group;

5           - an alkylsulfonylamino group (R'SO<sub>2</sub>-NR-) in which the group R represents a hydrogen atom or a C1-C4 alkyl group optionally bearing at least one hydroxyl group and the group R' represents a C<sub>i</sub>-C<sub>4</sub> alkyl group, or a phenyl group;

10           - an aminosulfonyl group ((R)<sub>2</sub>N-SO<sub>2</sub>-) in which the groups R, which may be identical or different, represent a hydrogen atom or a C1-C4 alkyl group optionally bearing at least one hydroxyl group;

- a carboxylic group in acid or salified form (preferably with an alkali metal or a substituted or unsubstituted ammonium);

- a cyano group;

15           - a nitro group;

- a carboxyl or glycosylcarbonyl group;

- a phenylcarbonyloxy group optionally substituted by one or more hydroxyl groups;

- a glycosyloxy group; and

20           - a phenyl group optionally substituted by one or more hydroxyl groups.

The term "glycosyl group" means a group originating from a mono- or polysaccharide.

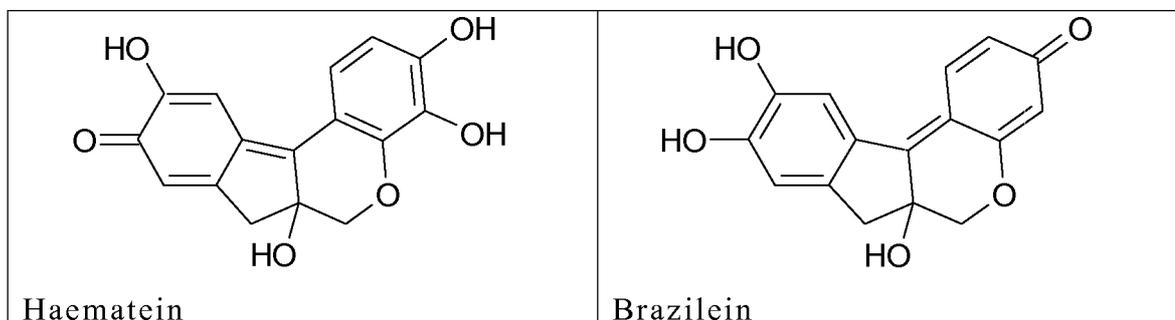
25           Preferably, the alkyl or alkoxy groups of formula (V) are unsubstituted.

According to one particular embodiment of the invention, the dyes of formula (V) comprise a group R<sup>6</sup> which represents a hydroxyl group.

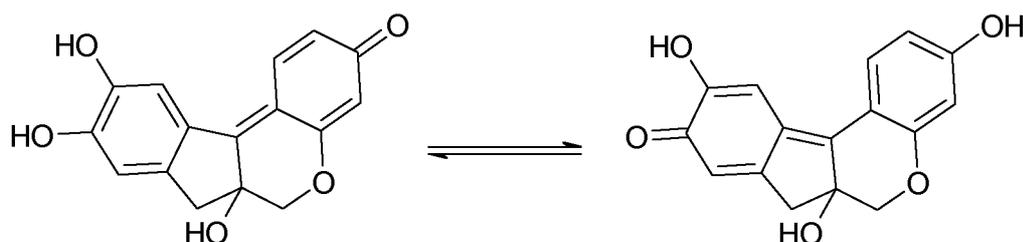
In one preferred variant, X represents a group O=C.

30           Another particular embodiment of the invention relates to the dyes of formula (V), for which the group R<sup>1</sup> represents a hydrogen atom or a hydroxyl group.

More particularly, the dyes of formula (V) are chosen from haematein and brazilein.



Brazilein is a conjugated form of a chroman compound of formula IV-2. The tautomeric structures (Va) and (Vb) illustrated above are found in the scheme below.



Brazilein and haematein or the haematoxylin/haematein and brazilin/brazilein pairings may be obtained synthetically or by extraction of plants known to be rich in these dyes.

The dyes of formula (V) may be used in the form of extracts. Use may be made of the following plant extracts (genus and species): *Haematoxylon campechianum*, *Haematoxylon brasiletto*, *Caesalpinia echinata*, *Caesalpinia sappan*, *Caesalpinia spinosa*, and *Caesalpinia brasiliensis*.

The extracts are obtained by extracting the various plant parts, for instance the root, the wood, the bark or the leaves.

According to one particular embodiment of the invention, the natural dyes of formula (V) are obtained from logwood, pernambuco wood, sappan wood and Brazil wood.

The salts of the dyes of formulae (V) and (VI) of the invention may be salts of cosmetically acceptable acids or bases.

The acids can be inorganic or organic. Preferably, the acid is hydrochloric acid, which results in chlorides.

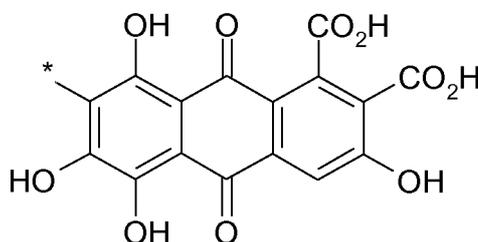
The bases can be inorganic or organic. In particular, the bases are alkali metal hydroxides such as sodium hydroxide, which leads to sodium salts.

Preferably, the dye(s) of formulae (V) and (VI) included in the composition according to the invention are derived from plant extracts. Use may also be made of mixtures of plant extracts.

The natural extracts of the dyes according to the invention may be in the form of powders or liquids. Preferably, the extracts are in powder form.

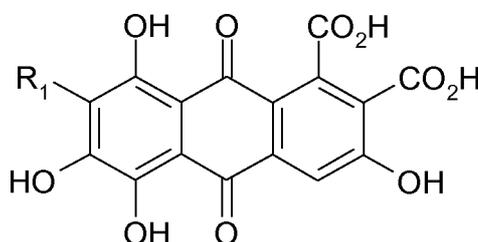
In another variant of the invention, the natural dyes are chosen from laccaic acids.

For the purposes of the present invention, the term "laccaic acid" means a compound having in its structure a unit of the type:



Preferably, the laccaic acids of the invention are of formula (VII) below:

20



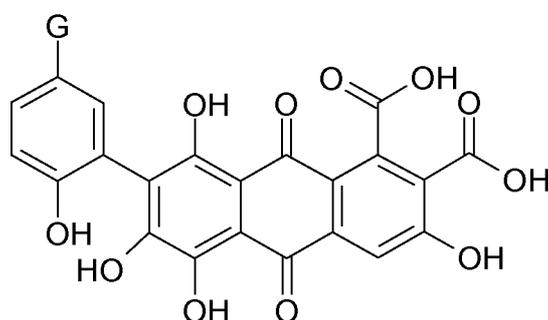
(VII)

with R<sub>i</sub> denoting a phenyl group substituted with at least one hydroxyl group, and preferably with a hydroxyl group that is advantageously in the ortho position relative to the bond attaching it to the fused nuclei.

25

In particular, the phenyl group Ri comprises, besides a hydroxyl group, at least one group -CH<sub>2</sub>R<sub>2</sub>, R<sub>2</sub> denoting an acetamidomethyl (CH<sub>3</sub>CONHCH<sub>2</sub>-), hydroxymethyl (HOCH<sub>2</sub>-) or 2-aminoacetic acid group (HC(=O)C(NH<sub>2</sub>)CH<sub>2</sub>-).

5 Preferentially, the laccaic acids of the invention are chosen from laccaic acids A, B, C and D, or mixtures thereof, and more particularly chosen from A, B and C, or mixtures thereof.



Laccaic acid A G: -CH<sub>2</sub>CH<sub>2</sub>NHC(=O)CH<sub>3</sub>

Laccaic acid B G: -CH<sub>2</sub>CH<sub>2</sub>OH

Laccaic acid C G: -CH<sub>2</sub>CH(NH<sub>2</sub>)C(=O)OH

Laccaic acid D G: -CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

#### Laccaic acid A, B, C and D

10 A laccaic acid according to the invention that may especially be used is the dye CI Natural Red 25, CI 75450, CAS - 60687-93-6, which is often referred to as laccaic acid. This is a dye of natural origin originating from the secretions of an insect, *Coccus laccae* (Lacifer Lacca Kerr), which is generally found on the twigs of certain  
15 trees native to South-East Asia.

CI Natural Red 25 generally contains two major constituents in its composition: laccaic acid A and laccaic acid B. It may also contain a small amount of laccaic acid C.

20 It is obviously also possible to use the purified forms of the laccaic acids of formula (VII).

Even more preferentially, the natural direct dyes are chosen from haematein and brazilein.

If present, the direct dye or dyes may represent from 0.000 1% to 20% by weight, preferably from 0.0 1% to 15% by weight, better still from 0.1% to 10% by weight, relative to the total weight of the expanded dyeing composition (A).

As indicated previously, the expanded dyeing composition (A) according to the invention comprises one or more oxyalkylenated nonionic surfactants.

Examples of oxyalkylenated nonionic surfactants that may be used in the composition used according to the invention are described in, for example, "Handbook of Surfactants" by M.R. PORTER, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178. They are chosen in particular from alcohols, a-diols and alkyl(Ci- C2o)phenols, these compounds being polyethoxylated and/or polypropoxylated and having at least one fatty chain containing, for example, from 8 to 22 carbon atoms, it being possible for the number of ethylene oxide and/or propylene oxide groups to range in particular from 1 to 100.

Mention may also be made of copolymers of ethylene oxide and propylene oxide, oxyethylenated esters of fatty acids and sorbitan, polyoxyalkylenated fatty acid esters and oxyalkylenated alkylpolyglycosides.

Unless otherwise mentioned, a "fatty" compound, as for example a fatty alcohol or a fatty acid, denotes a compound which comprises, in its main chain, at least one linear or branched, saturated or unsaturated hydrocarbon chain, such as alkyl or alkenyl, containing at least 8 carbon atoms, preferably from 8 to 30 carbon atoms, and better still from 10 to 22 carbon atoms.

The oxyalkylenated nonionic surfactant or surfactants particularly preferred in the invention is or are chosen from polyoxyalkylenated, better still polyethoxylated, fatty alcohols, having at least one fatty chain comprising preferably from 8 to 22 carbon

atoms, it being possible for the number of ethylene oxide groups to range in particular from 1 to 100, better still from 1 to 50. Mention may be made, for example, of the compounds with INCI name oleth-30, oleth-20, oleth-10, steareth-2, deceth-3, deceth-5 or laureth-12.

5 The oxyalkylenated nonionic surfactant or surfactants is or are present in an amount which may range from 0.01% to 40% by weight, preferably from 0.1% to 30% by weight and better still from 1% to 20% by weight, relative to the total weight of the expanded dyeing composition (A).

10 The expanded dyeing composition (A) according to the invention may further comprise one or more alkaline agents.

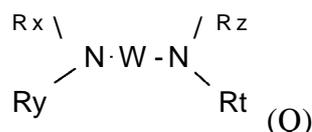
They may be any agent allowing an increase in the pH of the composition in which it is present.

15 The alkaline agent may be a Bronsted-Lowry or Lewis base. It may be inorganic or organic.

In particular, the alkaline agent(s) may be chosen from:

- a) aqueous ammonia,
- b) alkanolamines such as mono-, di- and triethanolamines, isopropanolamine and 2-amino-2-methyl-1-propanol, and also
- 20 derivatives thereof,
- c) oxyethylenated and/or oxypropylenated ethylenediamines,
- d) inorganic or organic hydroxides,
- e) alkali metal silicates such as sodium metasilicates,
- f) amino acids, preferably basic amino acids, such as arginine,
- 25 lysine, ornithine, citrulline and histidine,
- g) carbonates and bicarbonates, particularly of a primary amine, secondary amine or tertiary amine, or of an alkali metal or alkaline-earth metal, or of ammonium, and
- h) the compounds of formula (Q) below:

30



in which W is a Ci-C<sub>6</sub> alkylene residue optionally substituted with a hydroxyl group or a Ci-C<sub>6</sub> alkyl group; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a Ci-C<sub>6</sub> alkyl, Ci-C<sub>6</sub> hydroxyalkyl or Ci-C<sub>6</sub> aminoalkyl group.

5           Examples of such compounds of formula (Q) that may be mentioned include 1,3-diaminopropane, 1,3-diamino-2-propanol, spermine and spermidine.

10           The inorganic or organic hydroxides are preferably chosen from hydroxides of an alkali metal, hydroxides of an alkaline-earth metal, for instance sodium hydroxide or potassium hydroxide, hydroxides of a transition metal, such as hydroxides of metals from groups III, IV, V and VI of the Periodic Table of the Elements, hydroxides of lanthanides or actinides, quaternary ammonium hydroxides and guanidinium hydroxide.

15           The hydroxide may be formed *in situ*, for instance guanidine hydroxide, formed by reacting calcium hydroxide and guanidine carbonate.

20           The alkaline agents which are preferred are chosen in particular from aqueous ammonia, sodium or ammonium carbonate, sodium or ammonium bicarbonate, arginine, an alkanolamine of class b), better still an alkanolamine of class b) such as monoethanolamine.

25           When the alkaline agent or agents is or are present, the amount thereof may vary from 0.1% to 30% by weight, preferably from 0.5% to 20% by weight and better still from 1% to 10% by weight, relative to the total weight of the expanded dyeing composition (A).

          The invention further relates to a ready-to-use composition which results from the extemporaneous mixing of the expanded dyeing composition (A) as described above with an oxidizing composition (B).

30           Compositions (A) and (B) are preferably mixed in an (A)/(B) weight ratio ranging from 0.1 to 5, better still from 0.2 to 2.

          The oxidizing composition (B) comprises one or more oxidizing agents.

The oxidizing agent used in the context of the invention is a chemical oxidizing agent other than atmospheric oxygen.

5 The said oxidizing agent or agents is or are chosen preferably from the group consisting of hydrogen peroxide, urea peroxide, alkali metal bromides or ferricyanides, peroxygenated salts, as for example persulfates, perborates, peracids and precursors thereof, and alkali metal or alkaline-earth metal percarbonates.

Very particularly, the oxidizing agent is hydrogen peroxide.

10 The oxidizing agent or agents may represent from 0.1% to 20% by weight, preferably from 0.1% to 15% by weight and better still from 2% to 12% by weight, relative to the total weight of the oxidizing composition (B).

The oxidizing composition (B) may also be expanded and may further comprise one or more gases.

15 The gas or gases used in the expanded oxidizing compositions is or are preferably air, an inert gas as defined above, or a mixture thereof.

20 The expanded dyeing composition (A) and the oxidizing composition (B) generally comprise water or a mixture of water and at least one organic solvent. Examples of organic solvents that may be mentioned include C<sub>1</sub>-C<sub>4</sub> alcohols, such as ethanol and isopropanol, polyols and polyol ethers, for instance 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, and also aromatic alcohols, for instance benzyl alcohol or phenoxyethanol, and mixtures thereof.

25 If present, the organic solvents represent preferably from 1% to 40% by weight and more preferably still from 5% to 30% by weight, relative to the total weight of the expanded dyeing composition (A) or of the oxidizing composition (B).

30 The expanded dyeing composition (A) according to the invention and/or the oxidizing composition (B) may further comprise one or more cationic polymers, preferably with a cationic charge density of greater than or equal to 4 meq/g.

More preferably still, the cationic charge density is greater than or equal to 5 milliequivalents per gram, and more preferably may vary from 5 to 20 meq/g.

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

The cationic polymers having a cationic charge density of greater than or equal to 4 meq/g that may be used in accordance with the present invention may be chosen from all those already known per se as improving the cosmetic properties of hair treated with detergent  
15 compositions, i.e. especially those described in patent application EP-A-0 337 354 and in French patent applications FR-A-2 270 846, 2 383 660, 2 598 611, 2 470 596 and 2 519 863 .

In general, for the purposes of the present invention, the term "cationic polymer" denotes any polymer comprising cationic groups and/or groups that may be ionized into cationic groups.  
20

The cationic polymers are chosen from those that contain units comprising primary, secondary, tertiary and/or quaternary amine groups that may either form part of the main polymer chain or may be carried by a side substituent directly connected thereto.

25 The cationic polymers used generally have a number-average molecular mass of between 500 and  $5 \times 10^6$  approximately and preferably between  $10^3$  and  $3 \times 10^6$  approximately.

Among the cationic polymers, mention may be made more particularly of polymers of the polyamine, polyaminoamide and polyquaternary ammonium type. These are known products.  
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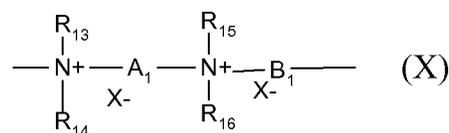
The polymers of polyamine, polyamidoamide and polyquaternary ammonium type that can be used in accordance with the present invention, and that can in particular be mentioned, are

those described in French patents No. 2 505 348 or 2 542 997. Among these polymers, mention may be made of:

- (1) Quaternized or non-quaternized vinylpyrrolidone/dialkylaminoalkyl (meth)acrylate copolymers.
- 5 (2) Polymers composed of piperazinyl units and of divalent alkylene or hydroxyalkylene groups containing straight or branched chains, optionally interrupted by oxygen, sulfur or nitrogen atoms or by aromatic or heterocyclic rings, and also the oxidation and/or quaternization products of these polymers. Such polymers are  
10 described, in particular, in French patents 2 162 025 and 2 280 361.
- (3) Water-soluble polyaminoamides prepared in particular by polycondensation of an acidic compound with a polyamine; these polyaminoamides can be crosslinked by an epihalohydrin, a diepoxide, a dianhydride, an unsaturated dianhydride, a bisunsaturated derivative,  
15 a bishalohydrin, a bisazetidinium, a bishaloacyldiamine or an alkyl bishalide or alternatively by an oligomer resulting from the reaction of a difunctional compound reactive with respect to a bishalohydrin, a bisazetidinium, a bishaloacyldiamine, an alkyl bishalide, an epihalohydrin, a diepoxide or a bisunsaturated derivative; the  
20 crosslinking agent being used in proportions ranging from 0.025 to 0.35 mol per amine group of the polyaminoamide; these polyaminoamides can be alkylated or, if they comprise one or more tertiary amine functions, quaternized. Such polymers are especially described in French patents 2 252 840 and 2 368 508.
- 25 (4) Polyaminoamide derivatives resulting from the condensation of polyalkylene-polyamines with polycarboxylic acids, followed by alkylation with difunctional agents. Mention may be made, for example, of adipic acid/dialkylaminohydroxyalkyldialkylenetriamine  
30 polymers in which the alkyl group comprises from 1 to 4 carbon atoms and preferably denotes methyl, ethyl or propyl. Such polymers are especially described in French patent 1 583 363.
- (5) Polymers obtained by reacting a polyalkylene-polyamine containing two primary amine groups and at least one secondary amine group with a dicarboxylic acid chosen from diglycolic acid and



(7) The diquaternary ammonium polycondensates containing repeating units corresponding to the formula:



5

in which formula (X):

$\text{R}_{13}$ ,  $\text{R}_{14}$ ,  $\text{R}_{15}$  and  $\text{R}_{16}$ , which may be identical or different, represent aliphatic, alicyclic or arylaliphatic groups containing from 1 to 20 carbon atoms or lower hydroxyalkylaliphatic groups, or alternatively  $\text{R}_{13}$ ,  $\text{R}_{14}$ ,  $\text{R}_{15}$  and  $\text{R}_{16}$ , together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally containing a second heteroatom other than nitrogen, or alternatively  $\text{R}_{13}$ ,  $\text{R}_{14}$ ,  $\text{R}_{15}$  and  $\text{R}_{16}$  represent a linear or branched  $\text{C}_1\text{-C}_6$  alkyl group substituted with a nitrile, ester, acyl or amide group or a group  $-\text{CO-O-R}_{17}\text{-D}$  or  $-\text{CO-NH-R}_{17}\text{-D}$  where  $\text{R}_{17}$  is an alkylene group and  $\text{D}$  is a quaternary ammonium group,

15

$\text{A}_1$  and  $\text{B}_1$  represent polymethylene groups containing from 2 to 20 carbon atoms, which may be linear or branched, and saturated or unsaturated, and which may contain, linked to or inserted in the main chain, one or more aromatic rings, or one or more oxygen or sulfur atoms or sulfoxide, sulfone, disulfide, amino, alkylamino, hydroxyl, quaternary ammonium, ureido, amide or ester groups, and

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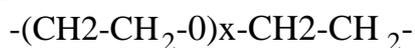
$\text{X}^-$  denotes an anion derived from an inorganic or organic acid,

25

$\text{A}_1$ ,  $\text{R}_{13}$  and  $\text{R}_{15}$  can form, with the two nitrogen atoms to which they are attached, a piperazine ring; in addition, if  $\text{A}_1$  denotes a linear or branched, saturated or unsaturated alkylene or hydroxyalkylene group,  $\text{B}_1$  can also denote a group  $-(\text{CH}_2)_n\text{-CO-D-OC-(CH}_2)_n-$ , in which  $\text{D}$  denotes:

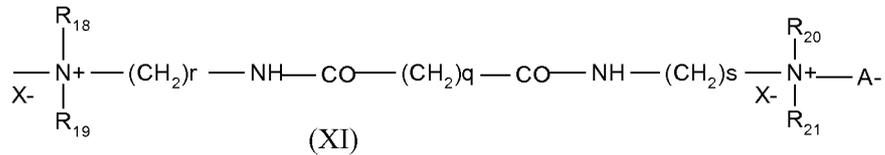
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a) a glycol residue of formula:  $-\text{O-Z-O}-$ , where  $\text{Z}$  denotes a linear or branched hydrocarbon-based group or a group corresponding to one of the following formulae:





(8) Polyquaternary ammonium polycondensates composed of units of formula (XI):



5

in which formula:

R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub> et R<sub>21</sub>, which may be identical or different, represent a hydrogen atom or a methyl, ethyl, propyl, β-hydroxyethyl, β-hydroxypropyl or -CH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>p</sub>OH group, where p is equal to 0 or to an integer between 1 and 6, with the proviso that R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub> and R<sub>21</sub> do not simultaneously represent a hydrogen atom,

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

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

X denotes a halogen atom,

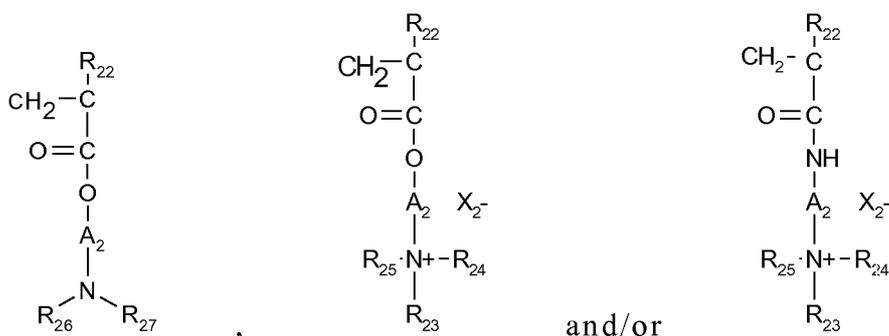
A denotes a dihalide group or preferably represents -CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-.

Such compounds are described especially in patent application EP-A- 122 324.

Mention may be made among these, for example, of the Mirapol<sup>®</sup> A 15, Mirapol<sup>®</sup> AD 1, Mirapol<sup>®</sup> AZ1 and Mirapol<sup>®</sup> 175 products sold by the company Miranol.

(9) Homopolymers or copolymers derived from acrylic or methacrylic acids and comprising units:

25



in which the groups R<sub>22</sub> independently denote H or CH<sub>3</sub>,

the groups A<sub>2</sub> independently denote a linear or branched alkyl group of 1 to 6 carbon atoms or a hydroxyalkyl group of 1 to 4 carbon atoms,

the groups R<sub>23</sub>, R<sub>24</sub> and R<sub>25</sub>, which may be identical or different, independently denote an alkyl group of 1 to 18 carbon atoms or a benzyl group,

the groups R<sub>26</sub> and R<sub>27</sub> represent a hydrogen atom or an alkyl group of 1 to 6 carbon atoms,

X<sub>2</sub><sup>-</sup> denotes an anion, for example methosulfate or halide, such as chloride or bromide.

The comonomer or comonomers that can be used in preparing corresponding copolymers belong to the family of acrylamides, methacrylamides, diacetoneacrylamides, acrylamides and methacrylamides substituted on the nitrogen by lower alkyls, or alkyl esters, acrylic or methacrylic acids, vinylpyrrolidone or vinyl esters.

(10) Quaternary polymers of vinylpyrrolidone and of vinylimidazole.

(11) Crosslinked polymers of methacryloyloxy(C<sub>i</sub>-C<sub>4</sub>)alkyltri(C<sub>i</sub>-C<sub>4</sub>)alkylammonium salts, such as the polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride, or by copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized with methyl chloride, the homo- or copolymerization being followed by crosslinking with an olefinically unsaturated compound, in particular methylenebisacrylamide.

Other cationic polymers that may be used in the context of the invention are polyalkyleneimines, in particular polyethyleneimines, polymers containing vinylpyridine or vinylpyridinium units, condensates of polyamines and of epichlorohydrin, polyquaternary ureylenes and chitin derivatives.

Among all of the cationic polymers which can be used in the context of the present invention, preference is given to employing dialkyldiallylammonium halide homopolymers and copolymers such as Polyquaternium-6, sold for example under the name "MERQUAT® 100" by the company NALCO (LUBRIZOL), polycondensates having repeating diquaternary or polyquaternary ammonium units, more particularly polycondensates composed of repeating units conforming to the formula (a), such as the compound known as Hexadimethrine chloride according to the INCI (CTFA) nomenclature.

As other cationic polymers suitable in the present invention, mention may be made, in particular, of cellulosic polymers, as for example the cellulose ether derivatives that contain quaternary ammonium groups and are described in French patent No. 1 492 597.

It is also possible to mention cellulose copolymers or cellulose derivatives grafted with a water-soluble quaternary ammonium monomer, described especially in patent US 4 131 576, such as hydroxyalkyl celluloses, for instance hydroxymethyl, hydroxyethyl or hydroxypropyl celluloses grafted especially with a methacryloylethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt.

It is also possible to mention cationic guar gum derivatives.

In one particular embodiment, the expanded dyeing composition (A) further comprises one or more cationic polymers having a charge density of greater than or equal to 4 meq/g, as described above.

When the cationic polymer or polymers preferably having a charge density of greater than or equal to 4 meq/g is or are present, their amount varies, for example, from 0.1% to 10% by weight and

preferably from 0.2% to 5% by weight, relative to the total weight of the expanded dyeing composition (A) or oxidizing composition (B).

5 The expanded dyeing composition (A) and/or the oxidizing composition (B) according to the invention may further contain one or more liquid fatty substances, in particular in an amount greater than or equal to 10% by weight, relative to the total weight of the expanded dyeing composition (A) or oxidizing composition (B).

10 The term "fatty substance" means an organic compound that is insoluble in water at standard temperature (25°C) and at atmospheric pressure (760 mmHg, i.e.  $1.013 \times 10^5$  Pa), i.e. with a solubility of less than 5%, preferably of less than 1% and even more preferably of less than 0.1%.

15 The fatty substances are preferably non-siliceous, meaning that their structure does not contain a silicon atom. They generally have in their structure a hydrocarbon chain comprising at least 6 carbon atoms and not comprising any siloxane group.

20 In addition, the fatty substances are generally soluble in organic solvents under the same temperature and pressure conditions, for instance chloroform, ethanol, benzene, liquid petroleum jelly or decamethylcyclopentasiloxane.

25 The liquid fatty substances that may be used in the invention are liquid at ambient temperature (25°C) and under atmospheric pressure (760 mmHg, i.e.  $1.013 \times 10^5$  Pa). They preferably have a viscosity of less than or equal to 2 Pa.s, better still less than or equal to 1 Pa.s, and even better still less than or equal to 0.1 Pa.s at a temperature of 25°C and at a shear rate of  $1 \text{ s}^{-1}$ .

The liquid fatty substances that may be used in the composition according to the invention are generally not oxyalkylenated and preferably do not contain any carboxylic acid COOH functions.

30 The liquid fatty substances are preferably chosen from hydrocarbons, fatty alcohols, fatty esters, fatty ethers, and mixtures thereof.

Even more preferentially, they are chosen from hydrocarbons, fatty alcohols and fatty esters, and mixtures thereof.

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

5 More particularly, the liquid hydrocarbons are chosen from:

- linear or branched, optionally cyclic,  $C_6$ - $C_{16}$  alkanes. Examples that may be mentioned include hexane, undecane, dodecane, tridecane, and isoparaffins, for instance isohexadecane, isododecane and isodecane,

10 - linear or branched hydrocarbons of synthetic, animal or mineral origin, with more than 16 carbon atoms, such as liquid paraffins or liquid petrolatum, polydecenes, hydrogenated polyisobutene such as that sold under the brand name Parleam® by the company NOF Corporation, and squalane.

15 In one preferred variant, the liquid hydrocarbon(s) is (are) chosen from liquid paraffins and liquid petrolatum.

The term "liquid fatty alcohol" is understood to mean a nonglycerolated and nonoxyalkylenated fatty alcohol which is liquid at standard temperature (25°C) and at atmospheric pressure (760 mmHg, i.e.  $1.013 \times 10^5$  Pa).

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

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

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

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

Octyldodecanol is most particularly preferred.

The unsaturated liquid fatty alcohols contain in their structure at least one double or triple bond, and preferably one or more double

bonds. When several double bonds are present, there are preferably 2 or 3 of them, and they may be conjugated or unconjugated.

These unsaturated fatty alcohols may be linear or branched.

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

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

Oleyl alcohol is most particularly preferred.

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

The esters are preferably liquid esters of saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>26</sub> aliphatic mono- or polyacids and of saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>26</sub> aliphatic mono- or polyalcohols, the total number of carbon atoms in the esters being greater than or equal to 10.

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

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

Esters of C<sub>4</sub>-C<sub>22</sub> dicarboxylic or tricarboxylic acids and of C<sub>1</sub>-C<sub>22</sub> alcohols and esters of monocarboxylic, dicarboxylic or tricarboxylic acids and of C<sub>4</sub>-C<sub>26</sub> dihydroxy, trihydroxy, tetrahydroxy or pentahydroxy non-sugar alcohols may also be used.

Mention may be made especially of diethyl sebacate, diisopropyl sebacate, bis(2-ethylhexyl) sebacate, diisopropyl adipate, di-n-propyl adipate, dioctyl adipate, bis(2-ethylhexyl) adipate, diisostearyl adipate, bis(2-ethylhexyl) maleate, triisopropyl citrate,

triisocetyl citrate, triisostearyl citrate, glyceryl trilactate, glyceryl trioctanoate, trioctyldodecyl citrate, trioleyl citrate, neopentyl glycol diheptanoate, and diethylene glycol diisononanoate.

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

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

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

The esters according to this variant may also be chosen from mono-, di-, tri- and tetraesters, and polyesters, and mixtures thereof.

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

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

An example that may be mentioned is the product sold under the name Glucate® DO by the company AMERCHOL, which is a methylglucose dioleate.

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

Among these, mention may be made of plant oils.

As oils of plant origin or synthetic triglycerides that may be  
5 used in the composition of the invention as liquid fatty esters, examples that may be mentioned include:

- triglyceride oils of plant or synthetic origin, such as liquid fatty acid triglycerides containing from 6 to 30 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively, for  
10 example, sunflower oil, corn oil, soybean oil, marrow oil, grapeseed oil, sesame seed oil, hazelnut oil, apricot oil, macadamia oil, arara oil, castor oil, avocado oil, olive oil, rapeseed oil, coconut oil, wheatgerm oil, sweet almond oil, safflower oil, candlenut oil, camelina oil, tamanu oil, babassu oil and pracaxi oil, caprylic/capric acid  
15 triglycerides, for instance those sold by the company STÉARINERIES DUBOIS or those sold under the names Miglyol® 810, 812 and 818 by the company DYNAMIT NOBEL, jojoba oil and shea butter oil.

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

20 Isopropyl myristate and isopropyl palmitate are particularly preferred.

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

The liquid fatty substances are preferably chosen from liquid  
25 paraffins or liquid petrolatum, octyldodecanol, isostearyl alcohol, 2-hexyldecanol, oleyl alcohol, linoleyl alcohol, linolenyl alcohol and undecylenic alcohol, ethyl and isopropyl palmitates, alkyl myristates such as isopropyl or ethyl myristate, isocetyl stearate, 2-ethylhexyl isononanoate, isononyl isononanoate, isodecyl neopentanoate and  
30 isostearyl neopentanoate, and vegetable oils.

More preferably still, the liquid fatty substances are chosen from liquid paraffins or liquid petrolatum.

When the liquid fatty substance or substances is or are present, the amount thereof varies preferably from 10% to 90% by weight,

better still from 20% to 80% by weight, even better still from 30% to 80%, more preferably still from 50% to 80% by weight, relative to the total weight of the expanded dyeing composition (A) or oxidizing composition (B).

5 In one particularly advantageous variant of the invention, the expanded composition (A) comprises one or more liquid fatty substances, particularly in an amount greater than or equal to 10% by weight, relative to the total weight of the expanded dyeing composition (A), preferably chosen from linear or branched  
10 hydrocarbons, of mineral, animal or synthetic origin, with more than 16 carbon atoms, more particularly liquid petrolatum.

The oxidizing composition (B) according to the invention may further comprise one or more anionic, nonionic, cationic or amphoteric surfactants, preferably nonionic surfactants, and even better still  
15 nonionic surfactants which are preferably oxyalkylenated, as described above.

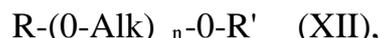
When the preferably nonionic surfactant or surfactants is or are present in the oxidizing composition (B), the amount thereof varies preferably from 0.1% to 30% by weight, better still from 1% to 20%  
20 by weight, relative to the total weight of the oxidizing composition (B).

According to one embodiment, the expanded dyeing composition (A) and/or the oxidizing composition (B) may also comprise a nonionic ether of polyoxyalkylenated fatty alcohols in  
25 addition to the abovementioned oxyalkylenated nonionic surfactant or surfactants.

The term "nonionic ether of polyoxyalkylenated fatty alcohols" is understood to mean an ether derived or resulting from fatty alcohols, i.e. long-chain alcohols, preferably C<sub>8</sub>-C<sub>40</sub> alcohols, which  
30 comprises one or more divalent C<sub>i</sub>-C<sub>6</sub> alkoxy groups:  $-[O-Alk]_p-$ , where p is an integer ranging from 1 to 200 and Alk represents a C<sub>i</sub>-C<sub>6</sub> alkylene group such as ethylene or propylene, preferably ethylene; and in which one of the fatty chains may be substituted, preferably

substituted by one or more hydroxyl groups, including at least one hydroxyl group located in beta position to an ether function.

According to one particular embodiment of the invention, the nonionic ether or ethers of polyalkylenated fatty alcohols are chosen  
5 from the compounds of formula (XII) below:



and also the optical isomers and geometrical isomers thereof;

in which formula (XII):

- 10 - R denotes a saturated or unsaturated, linear or branched C<sub>10</sub>-C<sub>30</sub> hydrocarbon group,
- R' denotes a saturated or unsaturated, linear or branched C<sub>10</sub>-C<sub>30</sub> hydrocarbon group which may be substituted by a hydroxyl group, preferably substituted by the hydroxyl group which is located in β to the ether function,
- 15 - n is an integer ranging from 1 to approximately 100, and
- Alk represents a (C<sub>i</sub>-C<sub>6</sub>) alkylene group which is linear or branched, preferably linear, such as ethylene or propylene, preferably ethylene.

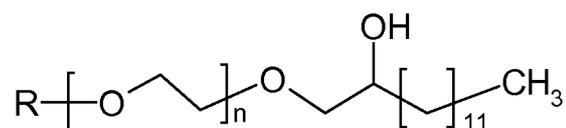
According to one particularly advantageous embodiment of the invention, the group Alk in the formula (XII) represents a group  
20 -CH<sub>2</sub>-CH<sub>2</sub>-.

More particularly, the nonionic ether of formula (XII) is such that R and R', independently of one another, denote a hydrocarbon group which is linear or branched, preferably linear, and is saturated or unsaturated, preferably saturated, this group being C<sub>12</sub>-C<sub>20</sub>,  
25 preferably C<sub>14</sub>-C<sub>18</sub>; R' may be substituted by at least one hydroxyl group, and n denotes an integer greater than or equal to 20, ranging for example from 20 to 100, preferably from 40 to 80.

R and R' preferably denote an alkyl group.

According to a more preferred embodiment, the nonionic ether  
30 of formula (XII) is such that: R denotes a preferably linear C<sub>16</sub>-C<sub>18</sub> alkyl group, and R' denotes a preferably linear C<sub>14</sub> alkyl group which is substituted by an OH group, and n is 60.

The ether of formula (XII) is preferably of the formula below:



where R is a cetyl or stearyl group where  $n = 60$ .

Such a compound is denoted, for example, in the CTFA dictionary under the name Cetareth-60 myristyl glycol or alternatively hydrogenated talloweth-60 myristyl glycol. A Cetareth-60 myristyl glycol is sold, for example, by the company AKZO under the trade name ELFACOS GT 282 S.

In the composition (A) or (B) according to the invention, the nonionic ether or ethers of polyoxyalkylenated fatty alcohols is or are present in a concentration ranging preferably from 0.001% to 10%, more preferably from 0.001% to 5%, by weight, relative to the total weight of the composition of the invention.

The pH of the expanded dyeing composition (A) may vary generally from 3 to 12 approximately, and preferably from 5 to 11 approximately. It may be adjusted to the desired value by means of acidifying or basifying agents customarily used in the dyeing of keratin fibres, or alternatively using standard buffer systems.

Among the acidifying agents, mention may be made, by way of example, of inorganic or organic acids, for instance hydrochloric acid, orthophosphoric acid, sulfuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid and lactic acid, and sulfonic acids.

As far as the basifying agents are concerned, those referred to above may be used.

The pH of the oxidizing composition varies preferably from 1.5 to 8.5, more preferably from 2 to 7 and better still from 2 to 4.

The expanded dyeing composition (A) and/or the oxidizing composition (B) may also comprise various adjuvants which are conventionally used in compositions for the colouring or lightening of hair, such as anionic, nonionic or amphoteric polymers or mixtures thereof; associative polymers; antioxidants; penetrants; sequestrants such as etidronic acid or pentasodium pentetate; fragrances;

dispersants; film-formers; ceramides; preservatives; opacifiers, and polyols, more particularly polyols with molecular weights of less than 500.

Amphoteric polymers include, in particular, the polymers comprising as monomers at least one monomer derived from a vinyl compound carrying a carboxyl group, such as, more particularly, acrylic acid, methacrylic acid, maleic acid, alpha-chloroacrylic acid, and at least one basic monomer derived from a substituted vinyl compound containing at least one basic atom, chosen in particular from the following:

a) dialkylaminoalkyl methacrylates, dialkylaminoalkyl acrylates, dialkylaminoalkylmethacrylamides and dialkylaminoalkylacrylamides. Such compounds are described in patent US 3 836 537.

b) trialkylaminoalkyl methacrylate salts and trialkylaminoalkyl acrylate salts, and salts of trialkylaminoalkylmethacrylamide and of trialkylaminoalkylacrylamide. Mention may in particular be made of the acrylic acid/acrylamidopropyltrimethylammonium chloride copolymer available from the company Stockhausen under the name Polymere W3794. Mention may also be made of the acrylic acid/acrylamidopropyltrimethyl ammonium/ chloride/acrylamide copolymers available from the company Nalco under the names Merquat 200 1 and Merquat 2003 .

The associative polymers may be anionic, cationic, amphoteric or nonionic, preferably nonionic and cationic. For the purposes of the present invention, the term "associative polymers" means water-soluble polymers that are capable, in an aqueous medium, of reversibly combining with each other or with other molecules. Their chemical structure comprises at least one hydrophilic region and at least one hydrophobic region characterized by at least one  $C_8-C_{30}$  fatty chain.

Mention may be made more particularly of the nonionic associative polymers chosen from polyether polyurethanes having hydrophilic and hydrophobic sequences, nonionic cellulose derivatives

comprising at least one fatty chain, and cationic associative polymers, chosen from quaternized cellulose derivatives comprising at least one fatty chain.

5 Polyols with a molecular mass of less than 500 include sorbitol, glucose, fructose, xylose, trehalose, sucrose, maltose, lactose, polyethylene glycols and C<sub>3</sub>-C<sub>8</sub> diols or triols, particularly butanediol.

Preference is given to non-etherified polyols and non-esterified polyols.

10 Particularly preferred polyols are glycerol and 1,2-propylene glycol, and preferably glycerol.

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

15 Preferably, the expanded compositions of the invention are not conditioned in a pressurized container.

Another subject of the invention is a method for dyeing keratin fibres, employing an expanded dyeing composition (A) and an oxidizing composition (B) as defined above.

20 The method of oxidation-colouring keratin fibres involves applying the expanded dyeing composition (A) and the optionally expanded oxidizing composition (B), as described above, to the keratin fibres, sequentially or simultaneously.

25 In a first variant of the method according to the invention, the expanded dyeing composition (A) is mixed at the time of use with the oxidizing composition (B), and the resulting mixture is then applied to the keratin fibres.

In a second variant of the method according to the invention, the expanded dyeing composition (A) is applied to the keratin fibres before or after the oxidizing composition (B).

30 The method may be repeated several times in order to obtain the desired coloration.

The compositions described previously are applied to wet or dry keratin fibres.

The composition(s) are usually left in place on the fibres for a time generally ranging from 1 minute to 1 hour and preferably from 5 minutes to 30 minutes.

5 The temperature during the method is conventionally between 20 and 80°C, preferably between 20 and 60°C.

After the treatment, the human keratin fibres are advantageously rinsed with water. They may optionally be washed with a shampoo, followed by rinsing with water, before being dried or left to dry.

10 Another subject of the invention concerns a multi-compartment device, or a kit for dyeing keratin fibres, comprising at least two compartments:

- a first compartment containing an expanded dyeing composition (A) as described above; and
- 15 - a second compartment containing an oxidizing composition (B) as described above.

In a first variant of the invention, only the dyeing composition (A) is expanded.

20 In a second variant of the invention, the two compositions (A) and (B) are expanded.

According to one variant of the invention, the kit also comprises an additional compartment containing an additional composition comprising one or more treating agents.

25 The compositions of the kit are packaged in separate compartments, which may be optionally accompanied by suitable identical or different application means, such as fine brushes, coarse brushes or sponges.

30 The abovementioned kit may also be equipped with means allowing the delivery to the hair of the desired mixture, such as, for example, the device described in patent FR 2 586 913.

The examples that follow are given purely as illustrations of the present invention.

**EXAMPLES**Example 1

5 A base dyeing composition, referred to hereinafter as dyeing composition 1, is prepared from the ingredients indicated in the table below. The amounts indicated are expressed in % by weight of active substance relative to the total weight of the dyeing composition 1.

Dyeing composition 1:

	% by weight
Fragrance	0.5
Stearamide MEA	4.8
Oleic acid	3
Cetyl hydroxyethylcellulose	0.45
p-Aminophenol	0.159
Ammonium hydroxide	2.057
Titanium dioxide CI 77891	0.3
Ethanolamine	6.51
1-Hydroxyethyl 4,5-diaminopyrazole sulfate	1.4
Polyquaternium-6	2
4-Amino-2-hydroxytoluene	1.12
Stearic acid	0.1
EDTA	0.2
Hexadimethrine chloride	1.2
Oleth-30	1.5
Sodium sulfite	0.5
5-Amino-6-chloro-o-cresol	0.19
Erythorbic acid	0.5
Hydroxypropyl methylcellulose	0.191
PEG-40 stearate	1.8
Steareth-2	5.5
C20-22 alcohols	3
2,5-Diaminotoluene	0.297
Water	q. s. 100

5 Dyeing composition 1 is expanded using a Minimondomix expander from the company HAAS. Dyeing composition 1 is metered using a diaphragm pump to the aerating head; at the same time, the inert gas, in the present case nitrogen, is metered by means of a volumetric flowmeter. Both arrive perpendicularly in the part of the

aerator upstream of the rotor. By combining the flow of dyeing composition 1 and nitrogen with the actuation of the rotor, mixing takes place continuously and regularly, to give, at the outlet of the device, the dyeing composition 2.

5           At a constant flow rate of dyeing composition 1, the degree of expansion may easily be adapted depending on the volume of nitrogen introduced in the Minimondomix.

Dyeing composition 2 is composed of 60 g of dyeing composition 1 and 40 g of nitrogen.

10           Dyeing composition 2 has the appearance of an oily, aerated cream (of chocolate mousse type).

At the time of use, 10 g of dyeing composition 2 are mixed with 15 g of oxidizing composition (INOA® oxidizing agent, containing 6% of H<sub>2</sub>O<sub>2</sub>/pH 2.2). Mixing is performed very easily. The mixture is subsequently applied to the locks at 10 g of mixture per gram of hair. Application is easy. The mixture is left to act for 30 minutes.

15           The original appearance of the dyeing cream is retained on mixing with the oxidizing composition.

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

This produces an intense reddish, light brown colour.

Similar results are obtained when the nitrogen is replaced by carbon dioxide or argon.

25

### Example 2

A base dyeing composition, referred to hereinafter as dyeing composition 1, is prepared from the ingredients indicated in the table below. The amounts indicated are expressed in % by weight of active substance relative to the total weight of the dyeing composition 1.

30

Dyeing composition 1:

	% by weight
Fragrance	0.5
Stearamide MEA	4.8
Oleic acid	3
Cetyl hydroxyethylcellulose	0.45
p-Aminophenol	0.0994
Ammonium hydroxide	2.8805
Titanium dioxide CI 77891	0.3
Ethanolamine	5.3
Polyquaternium-6	2
4-Amino-2-hydroxytoluene	0.42
2-Methyl-5-hydroxyethylaminophenol	0.17
Stearic acid	0.1
EDTA	0.2
Hexadimethrine chloride	1.2
Oleth-30	1.5
Sodium sulfite	0.5
5-Amino-6-chloro-o-cresol	0.16
2,3-Diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one dimethanesulfonate	1.5
Erythorbic acid	0.5
Hydroxypropyl methylcellulose	0.191
PEG-40 stearate	1.8
Steareth-2	5.5
C20-22 alcohols	3
Water	q.s. 100

5 The procedure employed is the same as in Example 1, to give dyeing composition 2, with nitrogen.

Dyeing composition 2 has the appearance of an oily, aerated cream (of chocolate mousse type).

At the time of use, 10 g of dyeing composition 2 are mixed with 15 g of oxidizing composition (INOA® oxidizing agent, containing 6% of H<sub>2</sub>O<sub>2</sub>/pH 2.2). Mixing is performed very easily. The mixture is subsequently applied to the locks at 10 g of mixture per gram of hair. Application is easy. The mixture is left to act for 30 minutes.

The original appearance of the dyeing cream is retained on mixing with the oxidizing composition.

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

The hair coloration is evaluated visually. An intense coppery blonde colour is obtained.

Similar results are obtained when the nitrogen is replaced by carbon dioxide or argon.

### Example 3

A base dyeing composition, referred to hereinafter as dyeing composition 1, is prepared from the ingredients indicated in the table below. The amounts indicated are expressed in % by weight of active substance relative to the total weight of the dyeing composition 1.

Dyeing composition 1:

	% by weight
Fragrance	0.5
2-[(3-Aminopyrazolo[1,5-a]pyridin-2-yl)oxy]ethanol hydrochloride	1.7
Stearamide MEA	4.8
Oleic acid	3
Cetyl hydroxyethylcellulose	0.45
p-Aminophenol	0.159
Ammonium hydroxide	2.0575
Titanium dioxide CI 77891	0.3
Ethanolamine	7.1
Polyquaternium-6	2
4-Amino-2-hydroxytoluene	1.15
Stearic acid	0.1
EDTA	0.2
Hexadimethrine chloride	1.2
Oleth-30	1.5
Polyglyceryl-2 oleyl ether	1.5
Sodium sulfite	0.5
5-Amino-6-chloro-o-cresol	0.25
Erythorbic acid	0.5
Hydroxypropylmethylcellulose	0.191
PEG-40 stearate	1.8
Steareth-2	5.5
C20-22 alcohols	3
2,5-Diaminotoluene	0.2376
Water	q.s. 100

5 The procedure employed is the same as in Example 1, to give dyeing composition 2, with nitrogen.

Dyeing composition 2 has the appearance of an oily, aerated cream (of chocolate mousse type).

At the time of use, 10 g of dyeing composition 2 are mixed with 15 g of oxidizing composition (INOA® oxidizing agent, containing 6% of H<sub>2</sub>O<sub>2</sub>/pH 2.2). Mixing is performed very easily. The mixture is subsequently applied to the locks at 10 g of mixture per gram of hair. Application is easy. The mixture is left to act for 30 minutes.

The original appearance of the dyeing cream is retained on mixing with the oxidizing composition.

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

The hair coloration is evaluated visually. A pearly red brown colour is obtained.

Similar results are obtained when the nitrogen is replaced by carbon dioxide or argon.

#### Example 4

A base dyeing composition, referred to hereinafter as dyeing composition 1, is prepared from the ingredients indicated in the table below. The amounts indicated are expressed in % by weight of active substance relative to the total weight of the dyeing composition 1.

Dyeing composition 1:

	% by weight
Resorcinol	0.67
Ethanolamine	4.28
Hydroxybenzomorpholine	0.033
Ascorbic acid	0.12
Glycerol	5
m-Aminophenol	0.12
EDTA	0.2
2,4-Diaminophenoxyethanol HCl	0.02
Deceth-5	1.08
Sodium metabisulfite	0.22
Liquid paraffin	60
Carbomer	0.098
Oleth-10	1
Oleth-20	4
C20-22 alcohols	4.6
2,5-Diaminotoluene	0.7623
Cetyl palmitate	2
Cetareth-60 myristyl glycol	0.01
Water	q.s. for 100

5 Dyeing composition 1 is expanded by means of a  
 Minimondomix expander from the company HAAS, with introduction  
 of nitrogen. Dyeing composition 1 is metered by means of a diaphragm  
 pump to the aeration head; at the same time, the inert gas, in the  
 present case nitrogen, is metered by means of a volumetric flowmeter.  
 The two arrive perpendicularly in the part of the aerator upstream of  
 10 the rotor. By combining the flow of dyeing composition 1 and nitrogen  
 with the actuation of the rotor, mixing is carried out continuously and  
 regularly, to give the dyeing composition 2 at the outlet of the device.

At a constant rate of dyeing composition 1, the degree of expansion can be easily adapted depending on the volume of nitrogen introduced into the Minimondomix.

5 Dyeing composition 2 is composed of 60 g of dyeing composition 1 and 40 g of nitrogen.

Dyeing composition 2 has the appearance of an oily, aerated cream (of chocolate mousse type).

10 At the time of use, 10 g of dyeing composition 2 are mixed with 15 g of oxidizing composition (INOA® oxidizing agent, containing 6% of  $H_2O_2$ /pH 2.2). Mixing is performed very easily. The mixture is subsequently applied to the locks at 10 g of mixture per gram of hair. Application is easy. The mixture is left to act for 30 minutes.

15 The original appearance of the dyeing cream is retained on mixing with the oxidizing composition.

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

The hair coloration is evaluated visually. A light brown colour is obtained.

20 Similar results are obtained when the nitrogen is replaced by carbon dioxide or argon.

#### Example 5

25 A base dyeing composition, referred to hereinafter as dyeing composition 1, is prepared from the ingredients indicated in the table below. The amounts indicated are expressed in % by weight of active substance relative to the total weight of the dyeing composition 1.

Dyeing composition 1:

	% by weight
Fragrance	0.5
Resorcinol	0.132
Titanium dioxide CI 77891	0.1
Pentasodium pentetate	0.8
Ethanolamine	5.45
Lauric acid	3
Polyquaternium-6	2.4
2-Oleamido-1,3-octadecanediol	0.01
Propylene glycol	10
m-Aminophenol	0.131
2-Methylresorcinol	0.893
Glycol distearate	2
2,4-Diaminophenoxyethanol HCl	0.058
Deceth-3	9
Cetearyl alcohol	11.5
Sodium metasilicate	1
Hexadimethrine chloride	1.2
Laureth-12	7
Silica dimethyl silylate	1.2
Oleth-30	4
Sodium metabisulfite	0.7
Erythorbic acid	0.3
Carbomer	0.392
2,5-Diaminotoluene	1.188
Water	q.s. 100

5 Dyeing composition 1 is expanded by means of a Minimondomix expander from the company HAAS. Dyeing composition 1 is metered by means of a diaphragm pump to the aeration head; at the same time, the inert gas, in the present case

nitrogen, is metered by means of a volumetric flowmeter. The two arrive perpendicularly in the part of the aerator upstream of the rotor. By combining the flow of dyeing composition 1 and nitrogen with the actuation of the rotor, mixing is carried out continuously and regularly, to give the dyeing composition 2 at the outlet of the device.

5 At a constant rate of dyeing composition 1, the degree of expansion can be easily adapted depending on the volume of nitrogen introduced into the Minimondomix.

10 Dyeing composition 2 is composed of 60 g of dyeing composition 1 and 40 g of nitrogen.

Dyeing composition 2 has the appearance of an oily, aerated cream (of chocolate mousse type).

15 At the time of use, 10 g of dyeing composition 2 are mixed with 15 g of oxidizing composition (INOA® oxidizing agent, containing 6% of  $H_2O_2$ /pH 2.2). Mixing is performed very easily. The mixture is subsequently applied to the locks at 10 g of mixture per gram of hair. Application is easy. The mixture is left to act for 30 minutes.

20 The original appearance of the dyeing cream is retained on mixing with the oxidizing composition.

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

A light brown colour is obtained.

25 Similar results are obtained when the nitrogen is replaced by carbon dioxide or argon.

## CLAIMS

1. Expanded dyeing composition comprising:

- 5 - from 30 to 70 % by weight relative to the total weight of the expanded dyeing composition, of one or more inert gases,
- one or more oxidation dyes and
- one or more oxyalkylenated nonionic surfactants.

2. Composition according to Claim 1, characterized in that the inert gas or gases is or are chosen from nitrogen, carbon dioxide,  
10 nitrogen oxides, noble gases and mixtures thereof, preferably from nitrogen, argon and mixtures thereof.

3. Composition according to Claim 1 or 2, characterized in that the inert gas or gases is or are present in an amount ranging from 30% to 60% by weight and more preferably from 30% to 50% by  
15 weight, relative to the total weight of the expanded dyeing composition.

4. Composition according to any one of the preceding claims, characterized in that it has a density of less than  $0.95 \text{ g/cm}^3$ , ranging advantageously from  $0.2$  to  $0.9 \text{ g/cm}^3$  and preferably from  $0.3$  to  
20  $0.8 \text{ g/cm}^3$ , this density being measured at a temperature of approximately  $20^\circ\text{C}$  and at atmospheric pressure.

5. Composition according to any one of the preceding claims, characterized in that the inert gas or gases represents or represent from 10% to 500% of the volume of the unexpanded dyeing composition,  
25 preferably from 30% to 200%, more preferably from 35% to 150% and better still from 40% to 140%.

6. Composition according to any one of the preceding claims, characterized in that the oxidation dyes are chosen from oxidation bases, and preferably from para-phenylenediamines,  
30 bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols, heterocyclic bases and addition salts thereof, optionally in combination with one or more couplers, preferably chosen from meta-

phenylenediamines, meta-aminophenols, meta-diphenols, naphthalenic couplers, heterocyclic couplers and also the addition salts thereof.

5 7. Composition according to any one of the preceding claims, characterized in that it further comprises one or more direct dyes, preferably chosen from synthetic direct dyes and natural direct dyes.

10 8. Composition according to any one of the preceding claims, characterized in that the oxidation dye or dyes represents or represent from 0.000 1% to 20% by weight, preferably from 0.0 1% to 15% by weight, better still from 0.1% to 10% by weight, relative to the total weight of the expanded dyeing composition.

15 9. Composition according to any one of the preceding claims, characterized in that the oxyalkylenated nonionic surfactant or surfactants is or are chosen from polyoxyalkylenated, better still polyethoxylated, fatty alcohols having at least one fatty chain comprising preferably from 8 to 22 carbon atoms, it being possible for the number of ethylene oxide groups to range in particular from 1 to 100, better still from 1 to 50.

20 10. Composition according to any one of the preceding claims, characterized in that the oxyalkylenated nonionic surfactant or surfactants is or are present in an amount ranging from 0.1% to 30% by weight and preferably from 1% to 20% by weight, relative to the total weight of the expanded dyeing composition (A).

25 11. Composition according to any one of the preceding claims, characterized in that it comprises one or more alkaline agents, preferably in an amount ranging from 0.1% to 30% by weight, better still from 0.5% to 20% by weight, and even better from 1% to 10% by weight, relative to the total weight of the expanded dyeing composition.

30 12. Ready-to-use composition resulting from the extemporaneous mixing of an expanded dyeing composition (A) according to any one of the preceding claims with an oxidizing composition (B) comprising one or more oxidizing agents, preferably in an (A)/(B) weight ratio ranging from 0.1 to 5, better still from 0.2 to 2.

13. Composition according to Claim 12, characterized in that the oxidizing agent or agents is or are chosen from hydrogen peroxide, urea peroxide, alkali metal bromides or ferricyanides, peroxygenated salts, better still is hydrogen peroxide, and is or are preferably present  
5 in an amount ranging from 0.1% to 20% by weight, more particularly from 0.1%, to 15% by weight, better still from 2% to 12% by weight, relative to the total weight of the oxidizing composition (B).

14. Composition according to any one of Claims 1 to 13, characterized in that the expanded dyeing composition (A) and/or the  
10 oxidizing composition (B) comprise(s) one or more cationic polymers preferably with a charge density of greater than or equal to 4 meq/g, preferably in an amount ranging from 0.1% to 10% by weight and more preferably from 0.2% to 5% by weight relative to the weight of the expanded dyeing composition (A) or oxidizing composition (B).

15. Composition according to any one of Claims 1 to 14, characterized in that the expanded dyeing composition (A) and/or the oxidizing composition (B) comprise(s) one or more liquid fatty substances, preferably in an amount greater than or equal to 10% by weight, relative to the total weight of the expanded dyeing  
20 composition (A) or oxidizing composition (B).

16. Method for dyeing keratin fibres, employing an expanded dyeing composition (A) as defined in any one of Claims 1 to 11, 14 and 15, and an oxidizing composition (B) as defined in any one of Claims 12 to 15.

25 17. Kit for the oxidation dyeing of keratin fibres, comprising at least two compartments:

- a first compartment containing a dyeing composition (A) as defined in any one of Claims 1 to 11, 14 and 15; and
- a second compartment containing an oxidizing composition (B) as  
30 defined in any one of Claims 12 to 15.

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2014/073176

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. A61Q5/06 A61Q5/10 A61K8/04 A61K8/39 A61K8/86  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
 Minimum documentation searched (classification system followed by classification symbols)  
 A61K A61Q

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

Electronic data base consulted during the international search (name of data base and, where 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.
X	FR 2 989 587 A1 (OREAL [FR] ) 25 October 2013 (2013-10-25)	1-17
Y	page 2, line 24 - page 3, line 4 page 24, line 30 - page 26, line 24 page 38, line 2 - line 28 example	1-17
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X	FR 2 989 586 A1 (OREAL [FR] ) 25 October 2013 (2013-10-25)	1-17
Y	page 2, line 23 - page 3, line 10 page 27, line 8 - page 29, line 3 page 41, line 21 - page 41, line 23 example	1-17
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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  
 "E" earlier application or patent but published on or after the international filing date  
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 "O" document referring to an oral disclosure, use, exhibition or other means  
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 "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  
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 "&" document member of the same patent family

Date of the actual completion of the international search <b>13 January 2015</b>	Date of mailing of the international search report <b>26/01/2015</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <b>Simon , Frederic</b>
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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/073176

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 989 584 A1 (OREAL [FR]) 25 October 2013 (2013-10-25)	1-17
Y	page 2, line 22 - page 3, line 8 page 27, line 8 - page 24, line 22 page 22, line 27 - page 24, line 22 example	1-17
Y	----- US 2010/236570 A1 (FUJINUMA HIROYUKI [JP] ET AL) 23 September 2010 (2010-09-23) examples paragraphs [0053], [0054], [0064], [0065] -----	1-17

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Information on patent family members

International application No

PCT/EP2014/073176

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