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 Composition for the oxidation dyeing of keratin fibres,
 comprising a mono- or polyglycerolated fatty alcohol and a
 particular polyol
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- (71) Applicant(s) L'Oreal
- (72) Inventor(s)
 Millequant, Jean-Marie; Vuarier, Patricia
- (74) Agent/Attorney
 Griffith Hack, 509 St Kilda Road, Melbourne, VIC, 3004
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ABSTRACT

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES, COMPRISING A MONO- OR POLYGLYCEROLATED FATTY ALCOHOL AND A PARTICULAR POLYOL

The invention relates to a composition for the oxidation dyeing of keratin fibres, in particular of human keratin fibres and more particularly the hair, comprising, in a medium that is suitable for dyeing and that is free of glycerol and of cationic synthetic thickening polymer comprising at least one fatty chain, at least one oxidation dye, at least one mono- or polyglycerolated fatty alcohol and at least one particular polyol.

The invention also relates to the dyeing processes and devices using the said composition.

AUSTRALIA Patents Act 1990

COMPLETE SPECIFICATION STANDARD PATENT

Applicant(s):

L'OREAL

Invention Title:

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN
FIBRES, COMPRISING A MONO- OR POLYGLYCEROLATED FATTY
ALCOHOL AND A PARTICULAR POLYOL

The following statement is a full description of this invention, including the best method of performing it known to me/us:

COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES,

COMPRISING A MONO- OR POLYGLYCEROLATED FATTY ALCOHOL

AND A PARTICULAR POLYOL

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The present invention relates to a composition for the oxidation dyeing of keratin fibres, in particular of human keratin fibres and more particularly the hair, comprising, in a medium that is suitable for dyeing and that is free of glycerol and of cationic synthetic thickening polymer comprising at least one fatty chain, at least one oxidation dye, at least one mono- or polyglycerolated fatty alcohol and at least one particular polyol.

15 It is known practice to dye keratin fibres, and in particular human hair, with dye compositions containing oxidation dye precursors, generally known as "oxidation bases", in particular ortho- or paraphenylenediamines, ortho- or para-aminophenols and 20 heterocyclic bases.

Oxidation dye precursors are compounds which are initially uncoloured or only weakly coloured and which develop their dyeing power on the hair in the presence of oxidizing agents leading to the formation of coloured compounds. The formation of these coloured compounds results either from an oxidative condensation of the "oxidation bases" with themselves or from an oxidative condensation of the "oxidation bases" with

coloration modifiers, or "couplers", which are generally present in the dye compositions used in oxidation dyeing and are represented more particularly by meta-phenylenediamines, meta-aminophenols and meta-5 diphenols, and certain heterocyclic compounds.

The variety of molecules used, which consist on the one hand of the "oxidation bases" and on the other hand of the "couplers", allows a very wide range of colours to be obtained.

These oxidation bases and these couplers are formulated in vehicles that allow them to be applied to keratin fibres after mixing with an oxidizing agent.

These vehicles are generally aqueous and
usually comprise one or more surfactants, in particular
nonionic surfactants, optionally combined with one or
more solvents.

However, the Applicant has found that the systems mentioned above are not able to produce shades that are entirely satisfactory in terms of strength,

20 chromaticity or staying power. The Applicant has in particular found that the dye compositions of the prior art cannot achieve a sufficient strength on sensitized hair.

After considerable research conducted in this

25 matter, the Applicant has now discovered that it is
possible to obtain oxidation dye compositions that
produce strong and chromatic (luminous) shades with
good staying power with respect to chemical agents

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(shampoo, permanent-waving agents, etc.) or natural
agents (light, perspiration, etc.), thus giving a
satisfactory strength on sensitized hair, by
introducing into the dye composition at least one monoor polyglycerolated fatty alcohol and at least one
particular polyol.

 $\label{eq:these discoveries} \mbox{ form the basis of the }$ present invention.

One subject of the present invention is thus

10 a composition for the oxidation dyeing of keratin
fibres, in particular of human keratin fibres and more
particularly the hair, comprising, in a medium that is
suitable for dyeing, at least one oxidation dye, and
characterized in that:

15 - (a) it comprises at least one mono- or polyglycerolated fatty alcohol and at least one polyol of formula (Ia) below:

$$R_1 \xrightarrow{R_2} [A]_m \xrightarrow{R_3} R_4 \qquad (Ia)$$

20

in which:

 R_1 , R_2 , R_3 and R_4 denote, independently of each other, a hydrogen atom, a $C_1\text{--}C_6$ alkyl radical or a $C_1\text{--}C_6$ mono- or polyhydroxyalkyl radical;

25 A denotes a linear or branched alkylene radical containing a number of carbon atoms "n" ranging from 1

to 18, and optionally interrupted with a number of oxygen atoms "z" ranging from 0 to 9; m denotes 0 or 1;

it being understood that the total number of carbon $5 \quad \text{atoms contained both in the radical A and in all of the} \\ \text{substituents } R_1 \text{ to } R_4 \text{ is greater than or equal to 2,} \\ \text{and in that the molecular weight of the polyol ranges:} \\$

from 95 to 500,

if m is equal to 0, or if m and n are equal to 1,

10 and

if m is equal to 1 with A linear and n is equal to 2 with z equal to 0,

from 140 to 500,

if n is greater than or equal to 2, and $\mbox{if m is equal to 1 with n equal to 2 and z other}$ than 0,

from 90 to 500,

20 if m is equal to 1 with n other than 1 or 2 and z equal to 0, or $\\ \text{if m is equal to 1 with A branched, and n equal to} \\ 2 \text{ and z equal to 0,}$

and

25 - (b) it contains no glycerol and no cationic synthetic thickening polymer comprising at least one fatty chain.

Another subject of the invention relates to a ready-to-use composition for the oxidation dyeing of

keratin fibres, which comprises, in a medium that is suitable for dyeing, at least one composition as described above and at least one oxidizing agent.

For the purposes of the present invention,

5 the expression "ready-to-use composition" means the
composition intended to be applied immediately to the
keratin fibres, i.e. it may be stored in unmodified
form before use, or may result from the extemporaneous
mixing of two or more compositions.

10 The invention is also directed towards a process for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, which consists in applying to the fibres a composition (A) containing, in a medium that is suitable for 15 dyeing, at least one oxidation dye in combination with at least one mono- or polyglycerolated fatty alcohol and at least one polyol of formula (I) and containing no glycerol and no cationic synthetic thickening polymer comprising at least one fatty chain, the colour 20 being developed at alkaline, neutral or acidic pH with the aid of a composition (B) containing at least one oxidizing agent, which is mixed with composition (A) just at the time of use, or which is applied sequentially without intermediate rinsing.

25 A subject of the invention is also a multicompartment dyeing device or "kit" for the oxidation dyeing of keratin fibres, in particular of human keratin fibres and more particularly the hair, which comprises at least one first compartment containing a composition free of glycerol and of cationic synthetic thickening polymer comprising at least one fatty chain, comprising at least one oxidation dye, at least one 5 mono- or polyglycerolated fatty alcohol and at least one polyol of formula (Ia), and a second compartment

However, other characteristics, aspects, objects and advantages of the invention will emerge even more clearly on reading the description and the examples that follow.

containing an oxidizing agent.

The expression "mono- or polyglycerolated fatty alcohol" means any compound of formula (IIa) below:

15

$$RO - CH2-CH(CH2OH) - O - H$$
 (IIa)

in which:

R represents a saturated or unsaturated, linear or
20 branched radical containing from 8 to 40 carbon atoms
and preferably from 10 to 30 carbon atoms;
n represents a number ranging from 1 to 30 and
preferably from 1 to 10.

Compounds of this type that may be mentioned
25 include lauryl alcohol containing 4 mol of glycerol

(INCI name: polyglyceryl-4 lauryl ether), oleyl alcohol
containing 4 mol of glycerol (INCI name: polyglyceryl-4

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oleyl ether), oleyl alcohol containing 2 mol of glycerol (INCI name: polyglyceryl-2 oleyl ether), cetearyl alcohol containing 2 mol of glycerol, cetearyl alcohol containing 6 mol of glycerol, oleocetyl alcohol containing 6 mol of glycerol and octadecanol containing 6 mol of glycerol.

The fatty alcohol may represent a mixture of fatty alcohols in the same respect that the value of n represents a random value, which means that several

10 species of polyglycerolated fatty alcohol may coexist in the form of a mixture in a commercial product.

The mono- or polyglycerolated fatty
alcohol(s) represent(s) from about 0.01% to about 30%,
preferably from about 0.05% to about 20% and more

15 preferably from about 0.1% to about 15% relative to the total weight of the composition.

Among the polyols of formula (Ia), and in which m=0, mention may be made especially of pinacol (2,3-dimethyl-2,3-butanediol) and 1,2,3-butanetriol.

Among the polyols of formula (Ia) that are preferred are those for which, in formula (Ia), m=1 and R_1 to R_4 denote, independently of each other, a hydrogen atom or a C_1 - C_6 alkyl radical.

Among the said preferred polyols of formula

25 (Ia) that may be mentioned are polyethylene glycols
such as, for example, the product known as PEG-6 in the
CTFA publication (International Cosmetic Ingredient
Dictionary, Seventh Edition).

It is also preferred to use one or more polyols of formula (Ia) for which m=1, R_1 to R_4 denote, independently of each other, a hydrogen atom or a C_1 - C_6 alkyl radical, and which have a molecular weight 5 of less than 200.

Polyols of this type are chosen especially from 3-methyl-1,3,5-pentanetriol, 1,2,4-butanetriol, 1,5-pentanediol, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, neopentyl glycol (2,2-dimethyl-1,3-propanediol), isoprene glycol (3-methyl-1,3-butanediol) and hexylene glycol (2-methyl-2,4-pentanediol). The ones that are most particularly preferred according to the invention are hexylene glycol, neopentyl glycol and 3-methyl-1,5-pentanediol.

The polyol(s) of formula (Ia) represent(s) from about 0.1% to about 40%, preferably from about 0.5% to about 30% and more preferably from about 1% to about 20% relative to the total weight of the composition.

The oxidation dyes that may be used according to the invention are chosen from oxidation bases and/or couplers.

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Preferably, the compositions according to the invention contain at least one oxidation base.

The oxidation bases that may be used in the context of the present invention are chosen from those conventionally known in oxidation dyeing, and among which mention may be made in particular of the ortho-

and para-phenylenediamines, double bases, ortho- and para-aminophenols and heterocyclic bases below, and also the addition salts thereof with an acid.

Mention may be made in particular of:

5 - (I) the para-phenylenediamines of formula (II) below, and the addition salts thereof with an acid:

10 in which:

15

 R_1 represents a hydrogen atom, a C_1 - C_4 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_2 - C_4 polyhydroxyalkyl radical, a $(C_1$ - $C_4)$ alkoxy $(C_1$ - $C_4)$ alkyl radical or a C_1 - C_4 alkyl radical substituted with a nitrogenous, phenyl or 4'-aminophenyl group;

 R_2 represents a hydrogen atom, a $C_1\text{-}C_4$ alkyl radical, a $C_1\text{-}C_4 \text{ monohydroxyalkyl radical, a } C_2\text{-}C_4 \text{ polyhydroxy-}$ alkyl radical, a $(C_1\text{-}C_4) \text{ alkoxy} (C_1\text{-}C_4) \text{ alkyl radical or}$ a $C_1\text{-}C_4$ alkyl radical substituted with a nitrogenous

20 group;

 R_1 and R_2 may also form, with the nitrogen atom which bears them, a 5- or 6-membered nitrogenous heterocycle optionally substituted with one or more alkyl, hydroxyl or ureido groups;

 R_3 represents a hydrogen atom, a halogen atom such as a chlorine atom, a C_1 - C_4 alkyl radical, a sulpho radical, a carboxy radical, a C_1 - C_4 monohydroxyalkyl radical, a C_1 - C_4 hydroxyalkoxy radical, an acetylamino(C_1 - C_4) alkoxy radical, a mesylamino(C_1 - C_4) - alkoxy radical or a carbamoylamino(C_1 - C_4) alkoxy radical,

 R_4 represents a hydrogen or halogen atom or a $C_1\text{--}C_4$ alkyl radical.

Among the nitrogenous groups of formula (II) above, mention may be made in particular of amino, $mono\left(C_1-C_4\right)alkylamino, \ di\left(C_1-C_4\right)alkylamino, \ tri\left(C_1-C_4\right)-alkylamino, \ monohydroxy\left(C_1-C_4\right)alkylamino, \ imidazolinium and ammonium radicals.$

Among the para-phenylenediamines of formula

(II) above, mention may be made more particularly of para-phenylenediamine, para-tolylenediamine, 2-chloropara-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine,

20 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-paraphenylenediamine, N,N-dimethyl-para-phenylenediamine,
N,N-diethyl-para-phenylenediamine, N,N-dipropyl-paraphenylenediamine, 4-amino-N,N-diethyl-3-methylaniline,
N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N25 bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-

hydroxyethyl)amino-2-chloroaniline, 2- β -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β -hydroxypropyl)-

para-phenylenediamine, 2-hydroxymethyl-paraphenylenediamine, N,N-dimethyl-3-methyl-paraphenylenediamine, N,N-(ethyl-β-hydroxyethyl)-paraphenylenediamine, N-(β,γ-dihydroxypropyl)-para5 phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-βacetylaminoethyloxy-para-phenylenediamine,
N-(β-methoxyethyl)-para-phenylenediamine and 2-methyl10 1-N-β-hydroxyethyl-para-phenylenediamine, and the
addition salts thereof with an acid.

Among the para-phenylenediamines of formula

(II) above, para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2-β
15 hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-paraphenylenediamine, 2,6-diethyl-para-phenylenediamine,

2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine and 2-chloro-para
20 phenylenediamine, and the addition salts thereof with
an acid are most particularly preferred.

-(II) According to the invention, the term double bases
is understood to refer to compounds containing at least

Among the double bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular

two aromatic nuclei bearing amino and/or hydroxyl

25 groups.

of the compounds corresponding to formula (III) below, and the addition salts thereof with an acid:

5

in which:

- Z_1 and Z_2 , which may be identical or different, represent a hydroxyl or -NH $_2$ radical which may be substituted with a C_1 - C_4 alkyl radical or with a linker

10 arm Y;

- the linker arm Y represents a linear or branched alkylene chain containing from 1 to 14 carbon atoms, which may be interrupted by or terminated with one or more nitrogenous groups and/or one or more hetero atoms
- 15 such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C_1 - C_6 alkoxy radicals;
 - R_5 and R_6 represent a hydrogen or halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4
- 20 polyhydroxyalkyl radical, a C_1 - C_4 aminoalkyl radical or a linker arm Y;
 - R_7 , R_8 , R_9 , R_{10} , R_{11} and R_{12} , which may be identical or different, represent a hydrogen atom, a linker arm Y or a C_1 - C_4 alkyl radical;

it being understood that the compounds of formula (III) contain only one linker arm Y per molecule.

Among the nitrogenous groups of formula (III) above, mention may be made in particular of amino, $\label{eq:continuous} 5 \text{ mono}(C_1-C_4) \text{ alkylamino, } \text{ di}(C_1-C_4) \text{ alkylamino, } \text{ tri}(C_1-C_4) \text{ alkylamino, } \text{ monohydroxy}(C_1-C_4) \text{ alkylamino, } \text{ imidazolinium } \text{ and ammonium radicals.}$

Among the double bases of formula (III)

above, mention may be made more particularly of N,N'
10 bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3
diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'
aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)
tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'
bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4
15 methylaminophenyl)tetramethylenediamine, N,N'-bis
(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenedi
amine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane,

and the addition salts thereof with an acid.

Among these double bases of formula (III), $20 \quad N,N'-bis(\beta-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, or one of the addition salts thereof with an acid, are particularly preferred.$

-(III) The para-aminophenols corresponding to formula

25 (IV) below, and the addition salts thereof with an acid:

in which:

R₁₃ represents a hydrogen atom, a halogen atom, such as
fluorine, or a C₁-C₄ alkyl, C₁-C₄ monohydroxyalkyl,
 (C₁-C₄) alkoxy(C₁-C₄) alkyl, C₁-C₄ aminoalkyl or
 hydroxy(C₁-C₄) alkylamino(C₁-C₄) alkyl radical,
 R₁₄ represents a hydrogen atom, a halogen atom, such as
 fluorine, or a C₁-C₄ alkyl, C₁-C₄ monohydroxyalkyl, C₂-C₄
10 polyhydroxyalkyl, C₁-C₄ aminoalkyl, C₁-C₄ cyanoalkyl or
 (C₁-C₄) alkoxy(C₁-C₄) alkyl radical.

Among the para-aminophenols of formula (IV) above, mention may be made more particularly of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-

- fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol and 4-amino-2-(β -hydroxyethylaminomethyl)phenol, and the addition salts thereof with an acid.
- 20 -(IV) The ortho-aminophenols which can be used as oxidation bases in the context of the present invention are chosen in particular from 2-aminophenol, 2-amino-1-hydroxy-5-methylbenzene, 2-amino-1-hydroxy-6-methylbenzene and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

-(V) Among the heterocyclic bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of pyridine derivatives, pyrimidine 5 derivatives and pyrazole derivatives, and the addition salts thereof with an acid.

Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

- Among the pyrimidine derivatives, mention may be made more particularly of the compounds described, for example, in German patent DE 2 359 399 or Japanese patents JP 88-169 571 and JP 91-10659 or patent application WO 96/15765, such as 2,4,5,6-
- tetraaminopyrimidine, 4-hydroxy-2,5,6triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6triaminopyrimidine, and pyrazolopyrimidine derivatives such as those mentioned in patent application FR-A-
- 25 2 750 048 and among which mention may be made of pyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,5-dimethyl-pyrazolo[1,5-a]pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-

a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol; 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol; 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol; 2-[(7-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol; 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine; 2,5,x1-diamine and 3-amino-5-methyl-7-imidazolylpropylaminopyrazolo[1,5-a]pyrimidine, and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists, and the addition salts thereof with an acid.

Among the pyrazole derivatives, mention may be made more particularly of the compounds described in patents DE 3 843 892, DE 4 133 957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988, such as 4,5-diamino-1-methyl-pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethyl-pyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methyl-pyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-(β-hydrox

diamino-1-(β-hydroxyethyl)pyrazole, 4,5-diamino-1ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-15 methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5triaminopyrazole, 3,5-diamino-1-methyl-4-methylamino-1methylpyrazole, and the addition salts thereof with an acid.

According to the present invention, the oxidation bases preferably represent from 0.0005% to 12% by weight approximately relative to the total weight of the composition and even more preferably from 0.005% to 8% by weight approximately relative to this weight.

The couplers which may be used in the dye

composition according to the invention are those
conventionally used in oxidation dye compositions, that
is to say meta-aminophenols, meta-phenylenediamines,
meta-diphenols, naphthols and heterocyclic couplers
such as, for example, indole derivatives, indoline

derivatives, sesamol and its derivatives, pyridine
derivatives, pyrazolotriazole derivatives, pyrazolones,
indazoles, benzimidazoles, benzothiazoles,

benzoxazoles, 1,3-benzodioxoles and quinolines, and the addition salts thereof with an acid.

These couplers are chosen more particularly from 2,4-diamino-1-(β-hydroxyethyloxy)benzene, 2
5 methyl-5-aminophenol, 5-N-(β-hydroxyethyl)amino-2methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2-amino-4-(β-hydroxyethylamino)-1methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4
10 diaminophenoxy)propane, sesamol, 1-amino-2-methoxy-4,5methylenedioxybenzene, α-naphthol, 6-hydroxyindole, 4hydroxyindole, 4-hydroxy-N-methylindole, 6hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1H-3methylpyrazol-5-one, 1-phenyl-3-methylpyrazolo[3,2-c]1,2,4-triazole and 2,6-dimethylpyrazolo[1,5-b]-1,2,4triazole, and the addition salts thereof with an acid.

When they are present, these couplers preferably represent from 0.0001% to 10% by weight 20 approximately relative to the total weight of the composition, and even more preferably from 0.005% to 5% by weight approximately.

In general, the addition salts with an acid of the oxidation bases and couplers are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

In addition to the oxidation dyes defined above, the composition according to the invention may

also contain direct dyes to enrich the shades with glints. In this case, these direct dyes may be chosen in particular from neutral, cationic or anionic nitro, azo or anthraquinone dyes, in a weight proportion from 5 about 0.001% to 20% and preferably from 0.01% to 10% relative to the total weight of the composition.

In the ready-to-use composition according to the invention, composition (A) and/or composition (B) may also more particularly contain at least one

10 cationic or amphoteric polymer.

Cationic polymers

For the purposes of the present invention,
the expression "cationic polymer" denotes any polymer
containing cationic groups and/or groups which may be
ionized into cationic groups.

The cationic polymers which may be used in accordance with the present invention may be chosen from any of those already known per se as improving the cosmetic properties of the hair, namely, in particular, those described in patent application EP-A-337 354 and in French patents FR-2 270 846, 2 383 660, 2 598 611, 2 470 596 and 2 519 863.

The cationic polymers that are preferred are chosen from those containing units comprising primary,

25 secondary, tertiary and/or quaternary amine groups, which may either form part of the main polymer chain or may be borne by a side substituent directly attached thereto.

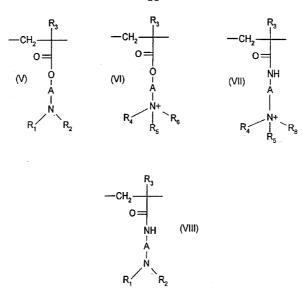
The cationic polymers used generally have a number-average molecular mass of between 500 and 5 \times 10^6 approximately and preferably between 10^3 and 3 \times 10^6 approximately.

Among the cationic polymers which may be mentioned more particularly are polymers of the polyamine, polyamino amide and polyquaternary ammonium type.

These are known products. They are described

10 in particular in French patents 2 505 348 and
2 542 997. Among the said polymers, mention may be made
of:

- (1) homopolymers or copolymers derived from acrylic or methacrylic esters or amides and comprising at least
- 15 one of the units of formula (V), (VI), (VII) or (VIII) below:



in which:

 R_3 , which may be identical or different, denote a

- 5 hydrogen atom or a CH₃ radical; A, which may be identical or different, represent a linear or branched alkyl group of 1 to 6 carbon atoms, preferably 2 or 3 carbon atoms, or a hydroxyalkyl group of 1 to 4 carbon atoms;
- 10 R_4 , R_5 and R_6 , which may be identical or different, represent an alkyl group containing from 1 to 18 carbon atoms or a benzyl radical and preferably an alkyl group containing from 1 to 6 carbon atoms;

 R_1 and R_2 , which may be identical or different,

15 represent hydrogen or an alkyl group containing from $\hat{1}$ to 6 carbon atoms, and preferably methyl or ethyl;

X denotes an anion derived from an inorganic or organic acid, such as a methosulphate anion or a halide such as chloride or bromide.

The polymers of family (1) can also contain

5 one or more units derived from comonomers which may be chosen from the family of acrylamides, methacrylamides, diacetoneacrylamides, acrylamides and methacrylamides substituted on the nitrogen with lower (C₁-C₄) alkyls, acrylic or methacrylic acids or esters thereof,

10 vinyllactams such as vinylpyrrolidone or

vinylcaprolactam, and vinyl esters.
Thus, among these polymers of family (1),

- mention may be made of:
- 15 methacrylate quaternized with dimethyl sulphate or with a dimethyl halide, such as the product sold under the name Hercofloc by the company Hercules,

- copolymers of acrylamide and of dimethylaminoethyl

- the copolymers of acrylamide and of methacryloyloxy-ethyltrimethylammonium chloride described, for example,
- 20 in patent application EP-A-080 976 and sold under the name Bina Quat P 100 by the company Ciba Geigy,
 - the copolymer of acrylamide and of methacryloyloxyethyltrimethylammonium methosulphate sold under the name Reten by the company Hercules,
- 25 quaternized or non-quaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers, such as the products sold under the name "Gafquat" by the company ISP, such as, for example,

- "Gafquat 734" or "Gafquat 755", or alternatively the products known as "Copolymer 845, 958 and 937". These polymers are described in detail in French patents 2 077 143 and 2 393 573,
- 5 dimethylaminoethyl methacrylate/vinylcaprolactam/vinylpyrrolidone terpolymers, such as the product sold under the name Gaffix VC 713 by the company ISP,
 - vinylpyrrolidone/methacrylamidopropyldimethylamine copolymers sold in particular under the name Styleze
- 10 CC 10 by ISP, and
 - quaternized vinylpyrrolidone/dimethylaminopropylmethacrylamide copolymers such as the product sold under the name "Gafquat HS 100" by the company ISP.
 - (2) The cellulose ether derivatives containing
- 15 quaternary ammonium groups, described in French patent
 1 492 597, and in particular the polymers sold under
 the names "JR" (JR 400, JR 125 and JR 30M) or "LR"
 (LR 400, or LR 30M) by the company Union Carbide
 Corporation. These polymers are also defined in the
- 20 CTFA dictionary as quaternary ammoniums of hydroxyethylcellulose which has reacted with an epoxide substituted with a trimethylammonium group.
 - (3) Cationic cellulose derivatives such as cellulose copolymers or cellulose derivatives grafted with a
- 25 water-soluble monomer of quaternary ammonium, and described in particular in US patent 4 131 576, such as hydroxyalkylcelluloses, for instance hydroxymethyl-, hydroxyethyl- or hydroxypropylcelluloses grafted, in

particular, with a methacryloyloxyethyltrimethylammonium, methacrylamidopropyltrimethylammonium or dimethyldiallylammonium salt.

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

- (4) The cationic polysaccharides described more particularly in US patents 3 589 578 and 4 031 307,
- such as guar gums containing cationic trialkylammonium groups. Guar gums modified with a salt (e.g. chloride) of 2,3-epoxypropyltrimethylammonium are used, for example.

Such products are sold in particular under

- 15 the trade names Jaguar C13 S, Jaguar C 15, Jaguar C 17 or Jaguar C162 by the company Meyhall.
 - (5) Polymers consisting of piperazinyl units and of divalent alkylene or hydroxyalkylene radicals containing straight or branched chains, optionally
- 20 interrupted by oxygen, sulphur or nitrogen atoms or by aromatic or heterocyclic rings, and also the oxidation and/or quaternization products of these polymers. Such polymers are described, in particular, in French patents 2 162 025 and 2 280 361.
- 25 (6) Water-soluble polyamino amides prepared in particular by polycondensation of an acidic compound with a polyamine; these polyamino amides can be crosslinked with an epihalohydrin, a diepoxide, a

dianhydride, an unsaturated dianhydride, a
bis-unsaturated derivative, a bis-halohydrin, a
bis-azetidinium, a bis-haloacyldiamine, a bis-alkyl
halide or alternatively with an oligomer resulting from

5 the reaction of a difunctional compound which is
reactive with a bis-halohydrin, a bis-azetidinium, a
bis-haloacyldiamine, a bis-alkyl halide, an
epihalohydrin, a diepoxide or a bis-unsaturated
derivative; the crosslinking agent being used in

10 proportions ranging from 0.025 to 0.35 mol per amine
group of the polyamino amide; these polyamino amides
can be alkylated or, if they contain one or more
tertiary amine functions, they can be quaternized. Such
polymers are described, in particular, in French

- (7) The polyamino amide 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 polymers in which the alkyl radical contains from 1 to 4 carbon atoms and preferably denotes methyl, ethyl or propyl. Such polymers are described in particular in French patent 1 583 363.
- 25 Among these derivatives, mention may be made more particularly of the adipic acid/dimethylamino-hydroxypropyl/diethylenetriamine polymers sold under

the name "Cartaretine F, F4 or F8" by the company Sandoz.

- (8) The polymers obtained by reaction of a polyalkylene polyamine containing two primary amine 5 groups and at least one secondary amine group with a dicarboxylic acid chosen from diglycolic acid and saturated aliphatic dicarboxylic acids having from 3 to 8 carbon atoms. The molar ratio between the polyalkylene polyamine and the dicarboxylic acid is 10 between 0.8:1 and 1.4:1; the polyamino amide resulting therefrom is reacted with epichlorohydrin in a molar ratio of epichlorohydrin relative to the secondary amine group of the polyamino amide of between 0.5:1 and 1.8:1. Such polymers are described in particular in
- Polymers of this type are sold in particular under the name "Hercosett 57" by the company Hercules Inc. or alternatively under the name "PD 170" or "Delsette 101" by the company Hercules in the case of the adipic acid/epoxypropyl/diethylenetriamine copolymer.
 - (9) Cyclopolymers of alkyldiallylamine or of dialkyldiallylammonium, such as the homopolymers or copolymers containing, as main constituent of the
- 25 chain, units corresponding to formula (IX) or (X):

in which formulae k and t are equal to 0 or 1, the sum k + t being equal to 1; R_9 denotes a hydrogen atom or a 5 methyl radical; $\ensuremath{R_7}$ and $\ensuremath{R_8}\textsubscript{,}$ independently of each other, denote an alkyl group having from 1 to 6 carbon atoms, a hydroxyalkyl group in which the alkyl group preferably has 1 to 5 carbon atoms, a lower $C_1\text{--}C_4$ amidoalkyl group, or $\ensuremath{R_7}$ and $\ensuremath{R_8}$ can denote, together with 10 the nitrogen atom to which they are attached, heterocyclic groups such as piperidyl or morpholinyl; $\ensuremath{R_{7}}$ and $R_{\theta}\text{, independently of each other, preferably denote$ an alkyl group having from 1 to 4 carbon atoms; Y^- is an anion such as bromide, chloride, acetate, borate, 15 citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate. These polymers are described in particular in French patent 2 080 759 and in its Certificate of Addition 2 190 406.

Among the polymers defined above, mention may 20 be made more particularly of the dimethyldiallyl-

ammonium chloride homopolymer sold under the name
"Merquat 100" by the company Calgon (and its homologues
of low weight-average molecular mass) and copolymers of
diallyldimethylammonium chloride and of acrylamide,
5 sold under the name "Merquat 550".

(10) The quaternary diammonium polymer containing repeating units corresponding to the formula:

10

in which formula (XI):

R₁₀, R₁₁, R₁₂ and R₁₃, which may be identical or different, represent aliphatic, alicyclic or arylaliphatic radicals containing from 1 to 20 carbon atoms or lower hydroxyalkylaliphatic radicals, or alternatively R₁₀, R₁₁, R₁₂ and R₁₃, together or separately, constitute, with the nitrogen atoms to which they are attached, heterocycles optionally containing a second hetero atom other than nitrogen, or alternatively R₁₀, R₁₁, R₁₂ and R₁₃ represent a linear or branched C₁-C₆ alkyl radical substituted with a nitrile, ester, acyl or amide group or a group -CO-O-R₁₄-D or -CO-NH-R₁₄-D where R₁₄ is an alkylene and D is a quaternary ammonium group;

25 A_1 and B_1 represent polymethylene groups containing from 2 to 20 carbon atoms which may be linear or branched,

saturated or unsaturated, and which may contain, linked to or intercalated in the main chain, one or more aromatic rings or one or more oxygen or sulphur atoms or sulphoxide, sulphone, disulphide, amino, alkylamino,

5 hydroxyl, quaternary ammonium, ureido, amide or ester groups, and

 \mathbf{X}^{-} denotes an anion derived from a mineral or organic acid;

 A_1 , R_{10} and R_{12} can form, with the two nitrogen atoms to which they are attached, a piperazine ring; in addition, if A_1 denotes a linear or branched, saturated or unsaturated alkylene or hydroxyalkylene radical, B_1 can also denote a group $-(CH_2)_n-CO-D-OC-(CH_2)_n-$ in which D denotes:

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

 $-(CH_2-CH_2-O)_x-CH_2-CH_2-$

 $-[CH_2-CH(CH_3)-O]_y-CH_2-CH(CH_3)-$

where x and y denote an integer from 1 to 4, representing a defined and unique degree of polymerization or any number from 1 to 4 representing an average degree of polymerization;

- 25 b) a bis-secondary diamine residue such as a piperazine derivative;
 - c) a bis-primary diamine residue of formula:
 -NH-Y-NH-, where Y denotes a linear or branched

hydrocarbon-based radical, or alternatively the divalent radical

 $-CH_2-CH_2-S-S-CH_2-CH_2-;$

d) a ureylene group of formula: -NH-CO-NH-. Preferably, X is an anion such as chloride or bromide.

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

Polymers of this type are described in

10 particular in French patents 2 320 330, 2 270 846,
2 316 271, 2 336 434 and 2 413 907 and US patents
2 273 780, 2 375 853, 2 388 614, 2 454 547, 3 206 462,
2 261 002, 2 271 378, 3 874 870, 4 001 432, 3 929 990,
3 966 904, 4 005 193, 4 025 617, 4 025 627, 4 025 653,

15 4 026 945 and 4 027 020.

It is more particularly possible to use polymers which consist of repeating units corresponding to formula (XII) below:

20

in which R_{10} , R_{11} , R_{12} and R_{13} , which may be identical or different, denote an alkyl or hydroxyalkyl radical containing from 1 to 4 carbon atoms approximately, n and p are integers ranging from 2 to 20 approximately,

and \mathbf{X}^{-} is an anion derived from a mineral or organic acid.

(11) Polyquaternary ammonium polymers consisting of
repeating units of formula (XIII):

5

in which p denotes an integer ranging from 1 to 6 approximately, D may be nothing or may represent a $10 \quad \text{group } -(\text{CH}_2)_r - \text{CO- in which r denotes a number equal to 4}$ or 7, X^- is an anion.

Such polymers may be prepared according to the processes described in US patents Nos. 4 157 388, 4 702 906 and 4 719 282. They are described in

15 particular in patent application EP-A-122 324.

Among these products, mention may be made, for example, of "Mirapol A 15", "Mirapol AD1", "Mirapol AZ1" and "Mirapol 175" sold by the company Miranol.

- 20 (12) Quaternary polymers of vinylpyrrolidone and of vinylimidazole, such as, for example, the products sold under the names Luviquat FC 905, FC 550 and FC 370 by the company BASF.
 - (13) Polyamines such as Polyquart H sold by Henkel,
- 25 which are given under the reference name "Polyethylene glycol (15) tallow polyamine" in the CTFA dictionary.

(14) Crosslinked methacryloyloxy(C1-C4)alkyltri- (C_1-C_4) alkylammonium salt polymers such as the polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized with methyl chloride, or by 5 copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized with methyl chloride, the homo- or copolymerization being followed by crosslinking with a compound containing olefinic unsaturation, in particular methylenebisacrylamide. A 10 crosslinked acrylamide/methacryloyloxyethyltrimethylammonium chloride copolymer (20/80 by weight) in the form of a dispersion containing 50% by weight of the said copolymer in mineral oil can be used more particularly. This dispersion is sold under the name 15 "Salcare® SC 92" by the company Allied Colloids. A ${\tt crosslinked}\ {\tt methacryloyloxyethyltrimethylammonium}$ chloride homopolymer containing about 50% by weight of the homopolymer in mineral oil or in a liquid ester can also be used. These dispersions are sold under the 20 names "Salcare" SC 95" and "Salcare" SC 96" by the company Allied Colloids.

Other cationic polymers which can be used in the context of the invention are polyalkyleneimines, in particular polyethyleneimines, polymers containing

25 vinylpyridine or vinylpyridinium units, condensates of polyamines and of epichlorohydrin, quaternary polyureylenes and chitin derivatives.

Among all the cationic polymers which may be used in the context of the present invention, it is preferred to use the polymers of families (1), (9), (10), (11) and (14) and even more preferably the 5 polymers consisting of repeating units of formulae (W) and (U) below:

$$\begin{array}{c|c} CH_3 & CH_3 \\ & | \\ \hline - \underbrace{ \begin{bmatrix} N_2^* & (CH_2)_3 & -N_2^* & (CH_2)_6 \\ CH_3 & CH_3 \end{bmatrix}}_{ \begin{array}{c} CH_3 \\ \end{array} } (W)$$

and in particular those whose weight-average molar mass, determined by gel permeation chromatography, is between 9500 and 9900;

$$\begin{array}{c|c} CH_3 & C_2H_5\\ & | & \\ \hline - \begin{array}{c|c} N^{\underline{+}} & (CH_2)_3 & -N^{\underline{+}} & (CH_2)_3 \\ & | & Br \end{array} \end{array} \qquad \text{(U)}$$

$$\begin{array}{c|c} CH_3 & C_2H_5 \end{array}$$

15

and in particular those whose weight-average molar mass, determined by gel permeation chromatography, is about 1200.

The concentration of cationic polymer in the composition according to the present invention may range from 0.01% to 10% by weight relative to the total weight of the composition, preferably from 0.05% to 5% and even more preferably from 0.1% to 3%.

Amphoteric polymers

amine groups.

The amphoteric polymers which may be used in accordance with the present invention may be chosen from polymers comprising units K and M randomly 5 distributed in the polymer chain, in which K denotes a unit derived from a monomer comprising at least one basic nitrogen atom and M denotes a unit derived from an acidic monomer comprising one or more carboxylic or sulphonic groups, or alternatively K and M may denote 10 groups derived from zwitterionic carboxybetaine or sulphobetaine monomers; K and M may also denote a cationic polymer chain comprising primary, secondary, tertiary or quaternary amine groups, in which at least one of the amine groups 15 bears a carboxylic or sulphonic group linked via a hydrocarbon-based radical, or alternatively K and M $\,$ form part of a chain of a polymer containing an α,β dicarboxylic ethylene unit in which one of the

The amphoteric polymers corresponding to the above definition which are more particularly preferred are chosen from the following polymers:

carboxylic groups has been made to react with a

20 polyamine comprising one or more primary or secondary

25 (1) polymers resulting from the copolymerization of a monomer derived from a vinyl compound bearing a carboxylic group such as, more particularly, acrylic acid, methacrylic acid, maleic acid, α-chloroacrylic acid, and a basic monomer derived from a substituted vinyl compound containing at least one basic atom, such as, more particularly, dialkylaminoalkyl methacrylate and acrylate, dialkylaminoalkylmethacrylamide and

5 -acrylamide. Such compounds are described in US patent 3 836 537.

Mention may also be made of the sodium acrylate/acrylamidopropyltrimethylammonium chloride copolymer sold under the name Polyquart KE 3033 by the 10 company Henkel.

The vinyl compound may also be a dialkyldiallylammonium salt such as dimethyldiallylammonium chloride. The copolymers of acrylic acid and of the latter monomer are sold under the names Merquat

- 15 280, Merquat 295 and Merquat Plus 3330 by the company Calgon.
 - (2) polymers containing units derived from:
 - a) at least one monomer chosen from acrylamides and methacrylamides substituted on the nitrogen with an
- 20 alkyl radical,
 - b) at least one acidic comonomer containing one or more reactive carboxylic groups, and
 - c) at least one basic comonomer such as esterscontaining primary, secondary, tertiary and quaternary
- amine substituents of acrylic and methacrylic acids and the product of quaternization of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

The N-substituted acrylamides or

methacrylamides which are more particularly preferred
according to the invention are groups in which the
alkyl radicals contain from 2 to 12 carbon atoms and
5 more particularly N-ethylacrylamide, N-tertbutylacrylamide, N-tert-octylacrylamide,
N-octylacrylamide, N-decylacrylamide,
N-dodecylacrylamide and the corresponding
methacrylamides.

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

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

15

The copolymers whose CTFA (4th edition, 1991)
name is octylacrylamide/acrylates/butylaminoethyl

methacrylate copolymer such as the products sold under
the name Amphomer or Lovocryl 47 by the company
National Starch are particularly used.

(3) crosslinked and alkylated polyamino amides partially or totally derived from polyamino amides of 25 general formula:

$$-[-co-R_{19}-co-z-]-$$
 (XIV)

in which R_{19} represents a divalent radical derived from a saturated dicarboxylic acid, a mono- or dicarboxylic aliphatic acid containing an ethylenic double bond, an ester of a lower alkanol, having 1 to 6 carbon atoms,

- of these acids or a radical derived from the addition of any one of the said acids to a bis(primary) or bis(secondary) amine, and Z denotes a bis(primary), mono- or bis(secondary) polyalkylene-polyamine radical and preferably represents:
- 10 a) in proportions of from 60 to 100 mol%, the radical

$$- \underbrace{N - \left(CH_2\right)_x - \underbrace{N - \left(DH_2\right)_x}_{p} \qquad (XV)$$

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

15 p = 2

from piperazine:

this radical being derived from diethylenetriamine,
from triethylenetetraamine or from dipropylenetriamine;
b) in proportions of from 0 to 40 mol%, the radical
(XV) above in which x = 2 and p = 1 and which is
derived from ethylenediamine, or the radical derived

_N__N__

25 c) in proportions of from 0 to 20 mol%, the $-{\rm NH-(CH_2)_6-NH-\ radical\ derived\ from}$ hexamethylenediamine, these polyamino amines being

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

The saturated carboxylic acids are preferably chosen from acids having 6 to 10 carbon atoms, such as adipic acid, 2,2,4-trimethyladipic acid and 2,4,4-trimethyladipic acid and acids containing an ethylenic double bond such as, for example, acrylic acid, methacrylic acid and itaconic acid.

The alkane sultones used in the alkylation are preferably propane sultone or butane sultone, and the salts of the alkylating agents are preferably the sodium or potassium salts.

(4) polymers containing zwitterionic units of formula:

20

15

$$R_{20} = \begin{bmatrix} R_{21} \\ C \\ R_{20} \end{bmatrix} y \begin{bmatrix} R_{23} \\ N_{1}^{+} \\ N_{2}^{+} \end{bmatrix} (CH_{2})_{2} = \ddot{C} - O^{-}$$
 (XVI)

in which R_{20} denotes a polymerizable unsaturated group such as an acrylate, methacrylate, acrylamide or 25 methacrylamide group, y and z represent an integer from 1 to 3, R_{21} and R_{22} represent a hydrogen atom, methyl,

ethyl or propyl, R_{23} and R_{24} represent a hydrogen atom or an alkyl radical such that the sum of the carbon atoms in R_{23} and R_{24} does not exceed 10.

The polymers comprising such units can also

5 contain units derived from non-zwitterionic monomers

such as dimethyl or diethylaminoethyl acrylate or

methacrylate or alkyl acrylates or methacrylates,

acrylamides or methacrylamides or vinyl acetate.

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

(5) polymers derived from chitosan containing monomer 15 units corresponding to formulae (XVII), (XVIII) and (XIX) below:

20 the unit (XVII) being present in proportions of between 0 and 30%, the unit (XVIII) in proportions of between 5% and 50% and the unit (XIX) in proportions of between

30% and 90%, it being understood that, in this unit (XIX), R_{25} represents a radical of formula:

5

in which q denotes zero or 1;

if q = 0, R₂₆, R₂₇ and R₂₈, which may be identical or

different, each represent a hydrogen atom, a methyl,

hydroxyl, acetoxy or amino residue, a monoalkylamine

10 residue or a dialkylamine residue which are optionally

interrupted by one or more nitrogen atoms and/or

optionally substituted with one or more amine,

hydroxyl, carboxyl, alkylthio or sulphonic groups, an

alkylthio residue in which the alkyl group bears an

15 amino residue, at least one of the radicals R₂₆, R₂₇ and

R₂₈ being, in this case, a hydrogen atom;

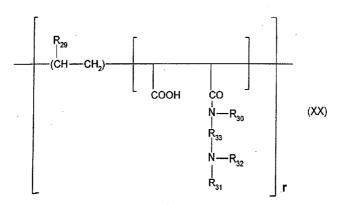
or, if q = 1, R₂₆, R₂₇ and R₂₈ each represent a hydrogen

atom, and also the salts formed by these compounds with

bases or acids.

- 20 (6) polymers derived from the N-carboxyalkylation of chitosan, such as N-carboxymethylchitosan or N-carboxybutylchitosan sold under the name "Evalsan" by the company Jan Dekker.
- (7) polymers corresponding to the general formula (XX)

 25 as described, for example, in French patent 1 400 366:



in which R₂₉ represents a hydrogen atom, a CH₃O, CH₃CH₂O or phenyl radical, R₃₀ denotes hydrogen or a lower alkyl radical such as methyl or ethyl, R₃₁ denotes hydrogen or a lower alkyl radical such as methyl or ethyl, R₃₂ denotes a lower alkyl radical such as methyl or ethyl or a radical corresponding to the formula: -R₃₃-N(R₃₁)₂, R₃₃ representing a -CH₂-CH₂-, -CH₂-CH₂- or

10 $-CH_2-CH(CH_3)-$ group, R_{31} having the meanings mentioned above,

and also the higher homologues of these radicals and containing up to 6 carbon atoms, $\,$

 \boldsymbol{r} is such that the molecular weight is between 500 and

- 15 $\,$ 6 000 000 and preferably between 1000 and 1 000 000.
 - (8) amphoteric polymers of the type -D-X-D-X- chosen from:
 - a) polymers obtained by the action of chloroacetic acid or sodium chloroacetate on compounds containing at
- 20 least one unit of formula:

42

$$-D-X-D-X-D-$$
 (XXI)

(XXII)

where D denotes a radical

5

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

- 10 chain, which is unsubstituted or substituted with hydroxyl groups and which can contain, in addition to the oxygen, nitrogen and sulphur atoms, 1 to 3 aromatic and/or heterocyclic rings; the oxygen, nitrogen and sulphur atoms being present in the form of ether,
- thioether, sulphoxide, sulphone, sulphonium, alkylamine or alkenylamine groups, hydroxyl, benzylamine, amine oxide, quaternary ammonium, amide, imide, alcohol, ester and/or urethane groups;
 - b) polymers of formula:

20 -D-X-D-X-

where D denotes a radical

25 and X denotes the symbol E or E' and at least once E'; E having the meaning given above and E' being a

divalent radical which is an alkylene radical with a straight or branched chain having up to 7 carbon atoms in the main chain, which is unsubstituted or substituted with one or more hydroxyl radicals and containing one or more nitrogen atoms, the nitrogen atom being substituted with an alkyl chain which is optionally interrupted by an oxygen atom and necessarily containing one or more carboxyl functions or one or more hydroxyl functions and betainized by reaction with chloroacetic acid or sodium

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

chloroacetate.

The amphoteric polymers that are particularly preferred according to the invention are those of 20 family (1).

According to the invention, the amphoteric polymer(s) may represent from 0.01% to 10% by weight, preferably from 0.05% to 5% by weight and even more preferably from 0.1% to 3% by weight relative to the total weight of the composition.

The ready-to-use composition according to the invention preferably comprises one or more additional

surfactants in the dye composition (A) and/or in the oxidizing composition (B).

The additional surfactant(s) may be chosen, without discrimination, alone or as mixtures, from 5 anionic, amphoteric, nonionic, zwitterionic and cationic surfactants.

The additional surfactants that are suitable for carrying out the present invention are especially the following:

10 (i) Anionic surfactant(s):

By way of example of anionic surfactants
which can be used, alone or as mixtures, in the context
of the present invention, mention may be made in
particular (nonlimiting list) of salts (in particular
alkali metal salts, especially sodium salts, ammonium
salts, amine salts, amino alcohol salts or magnesium
salts) of the following compounds: alkyl sulphates,
alkyl ether sulphates, alkylamido ether sulphates,
alkylarylpolyether sulphates, monoglyceride sulphates;
alkyl sulphonates, alkyl phosphates, alkylamide
sulphonates, paraffin sulphonates, α-olefin
sulphosuccinates, (C₆-C₂₄) alkyl ether sulphosuccinates,
(C₆-C₂₄) alkylamide sulphosuccinates; (C₆-C₂₄) alkyl
sulphoacetates; (C₆-C₂₄) acyl sarcosinates; and

 (C_6-C_{24}) acyl glutamates. It is also possible to use (C_6-C_{24}) alkylpolyglycoside carboxylic esters such as alkylglucoside citrates, alkylpolyglycoside tartrates

and alkylpolyglycoside sulphosuccinates,
alkylsulphosuccinamates; acyl isethionates and N-acyl
taurates, the alkyl or acyl radical of all of these
different compounds preferably containing from 12 to 20
carbon atoms and the aryl radical preferably denoting a
phenyl or benzyl group. Among the anionic surfactants
which can also be used, mention may also be made of
fatty acid salts such as oleic, ricinoleic, palmitic
and stearic acid salts, coconut oil acid or
hydrogenated coconut oil acid; acyl lactylates in which
the acyl radical contains 8 to 20 carbon atoms. It is
also possible to use alkyl D-galactoside uronic acids
and their salts, polyoxyalkylenated (C₆-C₂₄)alkyl ether
carboxylic acids, polyoxyalkylenated (C₆-C₂₄)alkylaryl

 (C_6-C_{24}) alkylamido ether carboxylic acids and their salts, in particular those containing from 2 to 50 alkylene oxide groups, in particular ethylene oxide groups, and mixtures thereof.

15 ether carboxylic acids, polyoxyalkylenated

20 (ii) Nonionic surfactant(s):

The nonionic surfactants are, themselves also, compounds that are well known per se (see in particular in this respect "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178) and their nature is not a critical factor in the context of the present invention. Thus, they can be chosen in particular from (non-limiting list) polyethoxylated or

polypropoxylated, alkylphenols, alpha-diols or alcohols, having a fatty chain containing, for example, 8 to 18 carbon atoms, it being possible for the number of ethylene oxide or propylene oxide groups to range in 5 particular from 2 to 50. Mention may also be made of copolymers of ethylene oxide and of propylene oxide, condensates of ethylene oxide and of propylene oxide with fatty alcohols; polyethoxylated fatty amides preferably having from 2 to 30 mol of ethylene oxide, 10 polyglycerolated fatty amides containing on average 1 to 5, and in particular 1.5 to 4, glycerol groups; polyethoxylated fatty amines preferably having 2 to 30 mol of ethylene oxide; oxyethylenated fatty acid esters of sorbitan having from 2 to 30 mol of ethylene 15 oxide; fatty acid esters of sucrose, fatty acid esters of polyethylene glycol, alkylpolyglycosides, Nalkylglucamine derivatives, and amine oxides such as $(C_{10}-C_{14})$ alkylamine oxides or N-acylaminopropylmorpholine oxides. It will be noted that alkylpolyglycosides are 20 nonionic surfactants that are particularly suitable within the context of the present invention, as are ethoxylated fatty alcohols.

(iii) Amphoteric or zwitterionic surfactant(s):

The amphoteric or zwitterionic surfactants,

25 the nature of which is not a critical factor in the context of the present invention, can be, in particular (nonlimiting list), aliphatic secondary or tertiary amine derivatives in which the aliphatic radical is a linear or branched chain containing 8 to 18 carbon atoms and containing at least one water-solubilizing anionic group (for example carboxylate, sulphonate, sulphate, phosphate or phosphonate); mention may also be made of (C_8-C_{20}) alkylbetaines, sulphobetaines, (C_8-C_{20}) alkylamido (C_1-C_6) alkylbetaines or (C_8-C_{20}) alkylamido (C_1-C_6) alkylsulphobetaines.

Among the amine derivatives, mention may be made of the products sold under the name Miranol, as 10 described in US patents 2 528 378 and 2 781 354 and classified in the CTFA dictionary, 3rd edition, 1982, under the names Amphocarboxyglycinates and Amphocarboxypropionates, with the respective structures:

15 R_{34} -CONHCH₂CH₂-N(R₃₅)(R₃₆)(CH₂COO⁻) in which: R₃₄ denotes an alkyl radical of an acid R₃₄-COOH present in hydrolysed coconut oil, a heptyl, nonyl or undecyl radical, R₃₅ denotes a betahydroxyethyl group and R₃₆ denotes a carboxymethyl

20 group;

and

 R_{34}' -CONHCH₂CH₂-N(B)(C)

in which:

B represents $-CH_2CH_2OX'$, C represents $-(CH_2)_z-Y'$, with

25 z = 1 or 2,

 $\rm X'$ denotes the $\rm -CH_2CH_2-COOH$ group or a hydrogen atom, $\rm Y'$ denotes -COOH or the -CH_2-CHOH-SO_3H radical,

 R_{34} , denotes an alkyl radical of an acid R_{37} -COOH present in coconut oil or in hydrolysed linseed oil, an alkyl radical, in particular a C_7 , C_9 , C_{11} or C_{13} alkyl radical, a C_{17} alkyl radical and its iso form, or an 5 unsaturated C_{17} radical.

These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names Disodium Cocoamphodiacetate, Disodium Lauroamphodiacetate, Disodium Caprylamphodiacetate, Disodium

- 10 Capryloamphodiacetate, Disodium Cocoamphodipropionate,
 Disodium Lauroamphopropionate, Disodium
 Caprylamphodipropionate, Disodium
 Caprylamphodipropionate, Lauroamphodipropionic acid and
 Cocoamphodipropionic acid.
- By way of example, mention may be made of the coccoamphodiacetate sold under the trade name Miranol®

 C2M concentrate by the company Rhodia Chimie.

(iv) Cationic surfactants:

Among the cationic surfactants, mention may

20 be made in particular (non-limiting list) of: salts of
optionally polyoxyalkylenated primary, secondary or
tertiary fatty amines; quaternary ammonium salts such
as tetraalkylammonium, alkylamidoalkyltrialkylammonium,
trialkylbenzylammonium, trialkylhydroxyalkylammonium or

25 alkylpyridinium chlorides or bromides; imidazoline

The amounts of the additional surfactants present in the composition according to the invention

derivatives; or amine oxides of cationic nature.

can range from 0.01% to 40% and preferably from 0.1% to 30% relative to the total weight of the composition.

The ready-to-use composition according to the invention can also contain in the dye composition (A)

5 and/or the oxidizing composition (B) agents for adjusting the rheology, such as cellulosic thickeners (hydroxyethylcellulose, hydroxypropylcellulose, carboxymethylcellulose, etc.), guar gum and its derivatives (hydroxypropyl guar, etc.), gums of

10 microbial origin (xanthan gum, scleroglucan gum, etc.), synthetic thickeners not containing a fatty chain, such as crosslinked homopolymers of acrylic acid or of acrylamidopropanesulphonic acid and synthetic thickeners comprising at least one fatty chain.

The thickening polymers comprising at least one fatty chain are of nonionic, anionic or amphoteric type.

15

Among the thickening polymers comprising at least one fatty chain and of anionic type, mention may 20 be made of:

- -(I) those comprising at least one hydrophilic unit and at least one fatty-chain allyl ether unit, more particularly those in which the hydrophilic unit consists of an ethylenic unsaturated anionic monomer,
- 25 even more particularly a vinylcarboxylic acid and most particularly an acrylic acid, a methacrylic acid or mixtures thereof, and in which the fatty-chain allyl

ether unit corresponds to the monomer of formula (XXIII) below:

 $CH_2 = CR'CH_2OB_nR$ (XXIII)

in which R' denotes H or CH₃, B denotes an ethyleneoxy

5 radical, n is zero or denotes an integer ranging from 1
to 100, R denotes a hydrocarbon-based radical chosen
from alkyl, arylalkyl, aryl, alkylaryl and cycloalkyl
radicals, containing from 8 to 30 carbon atoms,
preferably 10 to 24 carbon atoms and even more

10 particularly from 12 to 18 carbon atoms. A unit of
formula (XXIII) which is more particularly preferred is
a unit in which R' denotes H, n is equal to 10 and R
denotes a stearyl (C₁₀) radical.

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

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

Among the latter polymers, those most particularly preferred are crosslinked terpolymers of methacrylic acid, of ethyl acrylate and of polyethylene glycol (10 EO) stearyl ether (Steareth-10), in

- 5 particular those sold by the company Allied Colloids under the names Salcare SC 80 and Salcare SC 90, which are aqueous 30% emulsions of a crosslinked terpolymer of methacrylic acid, of ethyl acrylate and of steareth-10 allyl ether (40/50/10).
- 10 -(II) those comprising at least one hydrophilic unit of unsaturated olefinic carboxylic acid type, and at least one hydrophobic unit of $(C_{10}-C_{30})$ alkyl ester of unsaturated carboxylic acid type.

Preferably, these polymers are chosen from

15 those in which the hydrophilic unit of unsaturated olefinic carboxylic acid type corresponds to the monomer of formula (XXIV) below:

$$CH_2 = C - C - OH \qquad (XXIV)$$

$$R_1 = 0$$

20

in which R_1 denotes H or CH_3 or C_2H_5 , that is to say acrylic acid, methacrylic acid or ethacrylic acid units, and of which the hydrophobic unit of $(C_{10}-C_{30})$ alkyl ester of unsaturated carboxylic acid type 25 corresponds to the monomer of formula (XXV) below:

$$CH_2 = C - C - OR_3 \qquad (XXV)$$

$$R_2 = 0$$

in which R_2 denotes H or CH_3 or C_2H_5 (that is to say acrylate, methacrylate or ethacrylate units) and 5 preferably H (acrylate units) or CH_3 (methacrylate units), R_3 denoting a C_{10} - C_{30} and preferably C_{12} - C_{22} alkyl radical.

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

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

Among the fatty-chain anionic thickening polymers of this type which will be used more

20 particularly are polymers formed from a monomer blend comprising:

- (i) essentially acrylic acid,
- (ii) an ester of formula (XXV) described above in which $\rm R_2$ denotes H or CH_3, $\rm R_3$ denoting an alkyl radical

copolymerizable polyethylenic unsaturated monomer, for

25 containing from 12 to 22 carbon atoms,
 (iii) and a crosslinking agent, which is a well-known

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

Among fatty-chain anionic thickening polymers

5 of this type which will be used more particularly are
those consisting of from 95% to 60% by weight of
acrylic acid (hydrophilic unit), 4% to 40% by weight of
C10-C30 alkyl acrylate (hydrophobic unit) and 0% to 6% by
weight of crosslinking polymerizable monomer, or

10 alternatively those consisting of from 98% to 96% by
weight of acrylic acid (hydrophilic unit), 1% to 4% by
weight of C10-C30 alkyl acrylate (hydrophobic unit) and
0.1% to 0.6% by weight of crosslinking polymerizable
monomer such as those described above.

- 15 Among the said above polymers, those most particularly preferred according to the present invention are the products sold by the company Goodrich under the trade names Pemulen TR1, Pemulen TR2 and Carbopol 1382, and even more preferentially Pemulen
 20 TR1, and the product sold by the company S.E.P.P.I.C
- -(III) maleic anhydride/ C_{30} - C_{38} α -olefin/alkyl maleate terpolymers, such as the product (maleic anhydride/ C_{30} - C_{38} α -olefin/isopropyl maleate copolymer) sold under the name Performa V 1608 by the company
- 25 sold under the name Performa V 1608 by the company Newphase Technologies.
 - -(IV) acrylic terpolymers comprising:

under the name Coatex SX.

- (a) about 20% to 70% by weight of a carboxylic acid containing α,β -monoethylenic unsaturation,
- (b) about 20% to 80% by weight of a non-surfactant monomer containing $\alpha,\beta\mbox{-monoethylenic}$ unsaturation other
- 5 than (a),
 - (c) about 0.5% to 60% by weight of a nonionic monourethane which is the product of reaction of a monohydric surfactant with a monoisocyanate containing monoethylenic unsaturation,
- such as those described in patent application

 EP-A-0 173 109 and more particularly the terpolymer

 described in Example 3, namely a methacrylic

 acid/methyl acrylate/behenyl dimethyl-metaisopropenylbenzylisocyanate ethoxylated (40 EO)
- 15 terpolymer, as an aqueous 25% dispersion. -(V) copolymers comprising among their monomers a carboxylic acid containing α,β -monoethylenic unsaturation and an ester of a carboxylic acid containing α,β -monoethylenic unsaturation and of an
- 20 oxyalkylenated fatty alcohol.

Preferentially, these compounds also comprise as monomer an ester of a carboxylic acid containing $\alpha,\beta\text{-monoethylenic unsaturation and of a C_1-C_4 alcohol.}$

An example of a compound of this type which

25 may be mentioned is Aculyn 22 sold by the company Rohm & Haas, which is a methacrylic acid/ethyl acrylate/stearyl methacrylate oxyalkylenated terpolymer.

The fatty-chain thickening polymers of nonionic type which are used according to the invention are preferably chosen from:

- -(1) celluloses modified with groups comprising at
- 5 least one fatty chain;

examples which may be mentioned include:

- hydroxyethylcelluloses modified with groups comprising at least one fatty chain, such as alkyl, arylalkyl or alkylaryl groups, or mixtures thereof, and
 in which the alkyl groups are preferably C₈-C₂₂, for instance the product Natrosol Plus Grade 330 CS (C₁₆ alkyls) sold by the company Aqualon, or the product Bermocoll EHM 100 sold by the company Berol Nobel,
- those modified with alkylphenyl polyalkylene
 glycol ether groups, such as the product Amercell
 Polymer HM-1500 (nonylphenyl polyethylene glycol (15)
 ether) sold by the company Amerchol.
 - -(2) hydroxypropylguars modified with groups comprising at least one fatty chain, such as the product Esaflor
- 20 HM 22 (C_{22} alkyl chain) sold by the company Lamberti, and the products RE210-18 (C_{14} alkyl chain) and RE205-1 (C_{20} alkyl chain) sold by the company Rhône-Poulenc.
 - -(3) copolymers of vinylpyrrolidone and of fatty-chain hydrophobic monomers;
- 25 examples which may be mentioned include:
 - the products Antaron V216 or Ganex V216 (vinylpyrrolidone/hexadecene copolymer) sold by the company I.S.P.

- the products Antaron V220 or Ganex V220 (vinylpyrrolidone/eicosene copolymer) sold by the company I.S.P.
- -(4) copolymers of C₁-C₆ alkyl methacrylates or 5 acrylates and of amphiphilic monomers comprising at least one fatty chain, such as, for example, the oxyethylenated methyl acrylate/stearyl acrylate copolymer sold by the company Goldschmidt under the name Antil 208.
- 10 -(5) copolymers of hydrophilic methacrylates or acrylates and of hydrophobic monomers comprising at least one fatty chain, such as, for example, the polyethylene glycol methacrylate/lauryl methacrylate copolymer.
- 15 -(6) polyether polyurethanes comprising in their chain both hydrophilic blocks usually of polyoxyethylenated nature and hydrophobic blocks which may be aliphatic sequences alone and/or cycloaliphatic and/or aromatic sequences.
- 20 -(7) polymers with an aminoplast ether skeleton containing at least one fatty chain, such as the Pure Thix compounds sold by the company Sud-Chemie.

Preferably, the polyether polyurethanes comprise at least two hydrocarbon-based lipophilic chains containing from 6 to 30 carbon atoms, separated by a hydrophilic block, the hydrocarbon-based chains possibly being pendent chains, or chains at the end of the hydrophilic block. In particular, it is possible

for one or more pendent chains to be included. In addition, the polymer may comprise a triblock copolymer whose hydrophilic block is a polyoxyethylenated hydrocarbon-based chain at one end or at both ends of a hydrophilic block.

The polyether polyurethanes may be multiblock, in particular in triblock form. Hydrophobic blocks may be at each end of the chain (for example: triblock copolymer with a hydrophilic central block) or distributed both at the ends and in the chain (for example: multiblock copolymer). These same polymers may also be graft polymers or starburst polymers.

The nonionic fatty-chain polyether
polyurethanes may be [lacuna] comprising from 50 to
15 1000 oxyethylene groups. The nonionic polyether
polyurethanes comprise a urethane linkage between the
hydrophilic blocks, whence arises the name.

By extension, also included among the nonionic fatty-chain polyether polyurethanes are those

20 in which the hydrophilic blocks are linked to the lipophilic blocks via other chemical bonds.

As examples of nonionic fatty-chain polyether polyurethanes which may be used in the invention, use may also be made of Rheolate 205 containing a urea

25 function, sold by the company Rheox, or Rheolate 208, 204 or 212, and also Acrysol RM 184, Aculyn 44 and Aculyn 46 from the company Rohm & Haas [Aculyn 46 is a polycondensate of polyethylene glycol containing 150 or

180 mol of ethylene oxide, of stearyl alcohol and of methylenebis(4-cyclohexyl isocyanate) (SMDI), at 15% by weight in a matrix of maltodextrin (4%) and water (81%); Aculyn 44 is a polycondensate of polyethylene glycol containing 150 or 180 mol of ethylene oxide, of decyl alcohol and of methylenebis(4-cyclohexyl isocyanate) (SMDI), at 35% by weight in a mixture of propylene glycol (39%) and water (26%)].

Mention may also be made of the product $10 \quad \text{Elfacos T210 containing a C_{12-14} alkyl chain, and the} \\ \quad \text{product Elfacos T212 containing a C_{18} alkyl chain, from $Akzo.}$

The product DW 1206B from Rohm & Haas containing a C_{20} alkyl chain and urethane linkage, sold 15 at a solids content of 20% in water, may also be used.

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

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

Rohm & Haas may also be used.

The fatty-chain thickening polymers of amphoteric type used in the present invention comprise

at least one fatty chain containing from 8 to 30 carbon atoms, and may be chosen, for example, from polymers derived from polyaspartic acid comprising at least one fatty chain containing from 8 to 30 carbon atoms, such

5 as those:

- described and prepared in patent application
 EP 0 767 191, the content of which forms an integral part of the present invention. Such polymers are prepared, in a known manner, by reacting
 10 polysuccinimide (PSI) with fatty-chain (C₈-C₂₄) amines, in a solvent medium, in the presence or absence of a basic catalyst such as, for example, aliphatic tertiary amines, followed by amphoterization of the product obtained by reacting with a haloorganic acid.

15 Among the C₈-C₂₄ fatty-chain amines that are reacted with PSI, mention may be made especially of octylamine, nonylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, octadecylamine, eicosyldecylamine, octynylamine, decenylamine, dodecenylamine, tetradecenylamine, hexadecenylamine, octadecenylamine and eicosenylamine.

Examples of such polymers are prepared by reacting PSI with n-laurylamine or n-stearylamine in the presence of N,N-dimethyl-1,3-propanediamine as basic catalyst, followed by amphoterization of the product obtained by reaction with potassium monochloroacetate. These polymers are prepared with further details on pages 13 to 20 (lines 1-4) and in

Examples 1 to 5 on pages 28 to 34 (lines 1-4) of the said patent application EP-0 767 191.

- described and prepared in patent application EP-0 884 344, the content of which forms an integral 5 part of the present invention. Such polymers are prepared by reacting ammonia gas with a C_8 - C_{24} alkyl or alkenyl monomaleate, in a solvent medium, under reduced pressure and at a temperature of 120-140°C for 4 to 6 hours.

The C_8-C_{24} alkyl or alkenyl radicals may be chosen especially from the following linear or branched radicals: decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, oleyl.

Examples of such polymers comprise polymers

15 containing aspartic acid units and decyl aspartate
units, polymers containing aspartic acid units and
dodecyl aspartate units, polymers containing aspartic
acid units and cetyl aspartate units, polymers
containing aspartic acid units and stearyl aspartate

20 units, and polymers containing aspartic acid units and
n-decylaspartamide units, described in Examples 1 to 6
of the said patent application.
- described and prepared in patent application
EP-0 959 094, the content of which forms an integral

25 part of the present invention. Such polymers are prepared by reacting, in a solvent medium, ammonia gas with a hydrophobic maleic acid monoamide, polyoxyalkylenated and modified with a linear or branched $C_8\!-\!C_{30}$ alkyl or alkenyl chain, optionally as a mixture with a maleic acid monoester.

An example of a polymer thus prepared is described in Example 2, page 11 of the said patent 5 application.

- described and prepared in patent application
 EP-0 959 090, the content of which forms an integral part of the present invention. Such hydrophobic modified polymers of high molecular weight are obtained
 from maleic acid derivatives and ammonia gas and di- or polyfunctional alcohols or amines.

Examples of copolymers containing aspartic acid and cetyl aspartate units or containing aspartic acid and cetyl aspartate units are given, respectively,

15 in Examples 3 and 5 of the said patent application.

- or those described and prepared in patent application EP-0 959 091, the content of which forms an integral part of the present invention. Such hydrophobic modified polymers are prepared from maleic acid

20 monoester or monoamide and ammonia gas.

Examples of such polymers are given in Examples 1, 2, 3 and 5 of the said patent application.

Preferably, according to the present invention, the amphoteric polymers comprising at least 25 one fatty chain containing from 8 to 30 carbon atoms are chosen from those comprising at least one non-cyclic cationic unit. The ones that are even more particularly preferred are those prepared from or

comprising 1 to 20 mol% of monomer comprising a fatty chain, preferably 1.5 to 15 mol% and even more particularly 1.5 to 6 mol% relative to the total number of moles of monomers.

The said preferred fatty-chain amphoteric polymers according to the invention comprise, or are prepared by copolymerizing:

. 1) at least one monomer of formula (Ib) or (Ic):

10

$$R_{1} - P_{1} = \begin{bmatrix} C - Z - (C_{n}H_{2n}) & & & \\ & &$$

in which R_1 and R_2 , which may be identical or different, represent a hydrogen atom or a methyl radical, $R_3,\ R_4$

- and R_5 , which may be identical or different, represent a linear or branched alkyl radical containing from 1 to 30 carbon atoms,
 - $\ensuremath{\mathbf{Z}}$ represents an NH group or an oxygen atom, $\ensuremath{\mathbf{n}}$ is an integer from 2 to 5,
- 20 A is an anion derived from an organic or mineral acid, such as a methosulphate anion or a halide such as chloride or bromide;
 - 2) at least one monomer of formula (IIb)

 R_6 -CH=CR $_7$ -COOH (IIb)

in which R_6 and R_7 , which may be identical or different, represent a hydrogen atom or a methyl radical; and

5 3) at least one monomer of formula (IIIa): $R_6\text{-}CH\text{-}CR_7\text{-}COXR_8 \qquad \text{(IIIa)} \label{eq:R6}$

in which R_6 and R_7 , which may be identical or different, represent a hydrogen atom or a methyl radical, X denotes an oxygen or nitrogen atom and R_8 denotes a

- 10 linear or branched alkyl radical containing from 1 to
 30 carbon atoms;
 - at least one of the monomers of formula (Ib), (Ic) or (IIIa) comprising at least one fatty chain.

The monomers of formulae (Ib) and (Ic) of the
15 present invention are preferably chosen from the group
consisting of:

- dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate,
- diethylaminoethyl methacrylate, diethylaminoethyl
- 20 acrylate,
 - dimethylaminopropyl methacrylate, dimethylaminopropyl acrylate,
 - dimethylaminopropylmethacrylamide,
 dimethylaminopropylacrylamide,
- 25 these monomers optionally being quaternized, for example with a C_1-C_4 alkyl halide or a C_1-C_4 dialkyl sulphate.

More particularly, the monomer of formula (Ib) is chosen from acrylamidopropyltrimethylammonium chloride and methacrylamidopropyltrimethylammonium chloride.

The monomers of formula (IIb) of the present invention are preferably chosen from the group consisting of acrylic acid, methacrylic acid, crotonic acid and 2-methylcrotonic acid. More particularly, the monomer of formula (IIb) is acrylic acid.

The monomers of formula (IIIa) of the present invention are preferably chosen from the group consisting of $C_{12}\text{-}C_{22}$ and more particularly $C_{16}\text{-}C_{18}$ alkyl acrylates or methacrylates.

The monomers constituting the fatty-chain

15 amphoteric polymers of the invention are preferably already neutralized and/or quaternized.

The ratio of the number of cationic charges/anionic charges is preferably equal to about 1.

The fatty-chain amphoteric polymers according

20 to the invention preferably comprise from 1 mol% to

10 mol% of the monomer comprising a fatty chain

(monomer of formula (Ib), (Ic) or (IIIa)), and

preferably from 1.5 mol% to 6 mol%.

The weight-average molecular weights of the 25 fatty-chain amphoteric polymers according to the invention may range from 500 to 50 000 000 and are preferably between 10 000 and 5 000 000.

The fatty-chain amphoteric polymers according to the invention may also contain other monomers such as nonionic monomers and in particular such as $C_1\text{-}C_4$ alkyl acrylates or methacrylates.

Fatty-chain amphoteric polymers according to the invention are described and prepared, for example, in patent application WO 98/44012.

Among the fatty-chain amphoteric polymers according to the invention, the ones that are preferred are acrylic acid/(meth)acrylamidopropyltrimethyl-ammonium chloride/stearyl methacrylate terpolymers.

It is preferred to use a fatty-chain thickening polymer of nonionic type in the oxidation dye composition according to the invention.

15 The thickening polymers are preferably used in an amount that can range from about 0.01% to about 10% by weight relative to the total weight of the dye composition. More preferably, this amount ranges from about 0.1% to about 5% by weight.

20 The medium for the composition that is suitable for dyeing is preferably an aqueous medium consisting of water and can advantageously contain cosmetically acceptable organic solvents other than the polyol(s) of the invention including, more

25 particularly, other polyols, for instance propylene glycol, alcohols such as ethyl alcohol, isopropyl alcohol, benzyl alcohol and phenylethyl alcohol, or glycol ethers such as, for example, ethylene glycol monomethyl, monoethyl or monobutyl ether, propylene glycol monomethyl ether, and also diethylene glycol alkyl ethers such as, for example, diethylene glycol monoethyl ether or monobutyl ether, in concentrations ranging from about 0.5% to about 20% and preferably between about 2% and 10% by weight relative to the total weight of the composition.

The composition according to the invention may also contain an effective amount of other agents,

10 known previously elsewhere in oxidation dyeing, such as various common adjuvants, for instance sequestering agents such as EDTA and etidronic acid, UV screening agents, waxes, volatile or non-volatile, cyclic or linear or branched silicones, which are optionally organomodified (in particular with amine groups), preserving agents, ceramides, pseudoceramides, plant, mineral or synthetic oils, vitamins or provitamins, for instance panthenol, opacifiers, etc.

The said composition may also contain

reducing agents or antioxidants. These agents may be chosen in particular from sodium sulphite, thioglycolic acid, thiolactic acid, sodium bisulphite, dehydroascorbic acid, hydroquinone, 2-methylhydroquinone, tert-butylhydroquinone and homogentisic acid,

and, in this case, they are generally present in amounts ranging from about 0.05% to 3% by weight relative to the total weight of the composition.

The composition according to the invention can also contain one or more fatty alcohols, these fatty alcohols being introduced in pure form or as a mixture. Among these, mention may be made more

5 particularly of lauryl alcohol, cetyl alcohol, stearyl alcohol and oleyl alcohol and mixtures thereof. These additional fatty alcohols can represent from 0.001% to 20% by weight approximately relative to the total weight of the composition.

Needless to say, a person skilled in the art will take care to select the optional additional compound(s) mentioned above such that the advantageous properties intrinsically associated with the ready-to-use composition according to the invention are not, or are not substantially, adversely affected by the envisaged addition(s).

In the oxidizing composition (B), the oxidizing agent is preferably chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, and persalts such as perborates and persulphates. It is particularly preferred to use hydrogen peroxide. This oxidizing agent advantageously consists of an aqueous hydrogen peroxide solution whose titre may range, more particularly, from about 1 to 40 volumes and even more preferably from about 5 to 40 volumes.

Oxidizing agents which may also be used are one or more redox enzymes such as laccases, peroxidases

and 2-electron oxidoreductases (such as uricase), where appropriate in the presence of their respective donor or co-factor.

The pH of the dye composition (A) or of the foready-to-use composition applied to the keratin fibres [composition resulting from mixing together the dye composition (A) and the oxidizing composition (B)] is generally between 4 and 12. It is preferably between 6 and 11 and may be adjusted to the desired value using acidifying or basifying agents that are well known in the prior art in the dyeing of keratin fibres.

Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkali metal carbonates, alkanolamines such as

15 monoethanolamine, diethanolamine and triethanolamine and derivatives thereof, oxyethylenated and/or oxypropylenated hydroxyalkylamines and ethylenediamines, sodium hydroxide, potassium hydroxide and the compounds of formula (XXVI) below:

20

$$\begin{array}{c|c} R_{38} & N-R-N & R_{40} \\ \hline R_{20} & R_{41} \end{array} (XXVI)$$

in which R is a propylene residue optionally substituted with a hydroxyl group or a C_1 - C_4 alkyl 25 radical; R_{38} , R_{39} , R_{40} and R_{41} , which may be identical or different, represent a hydrogen atom, a C_1 - C_4 alkyl radical or a C_1 - C_4 hydroxyalkyl radical.

The acidifying agents are conventionally, for example, mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid, carboxylic acids, for instance tartaric acid, citric acid or 5 lactic acid, or sulphonic acids.

The dyeing process according to the invention preferably consists in applying the ready-to-use composition, prepared extemporaneously at the time of use from compositions (A) and (B) described above, to 10 wet or dry keratin fibres, and in leaving the composition to act for an exposure time preferably ranging from 1 to 60 minutes approximately, and more preferably from 10 to 45 minutes approximately, in rinsing the fibres and then in optionally washing them $\,$ 15 $\,$ with shampoo, rinsing them again and then drying them. Concrete examples illustrating the invention

are given below without, however, being limiting in

EXAMPLES

20 Example 1

nature.

The following composition was prepared: Dye composition:

(expressed in grams)

| Oleyl alcohol | 6 |
|--|---|
| Oleic acid | 3 |
| Oleyl alcohol polyglycerolated with 2 mol of | 6 |

| glycerol | |
|--|-------|
| Oleyl alcohol polyglycerolated with 6 mol of | 6 |
| glycerol | |
| Diethylaminopropyl laurylaminosuccinamate, | 3 |
| sodium salt | |
| Oleylamine oxyethylenated with 2 mol of ethylene | 7 |
| oxide | |
| Alkyl ether carboxylic acid monoethanolamide | 10 |
| containing 2 mol of ethylene oxide | |
| Ammonium acetate | 0.8 |
| Hexylene glycol | 20 |
| Reducing agents, antioxidants | 0.915 |
| Sequestering agent | 1 |
| 1,3-Dihydroxybenzene (resorcinol) | 0.085 |
| para-Phenylenediamine | 0.27 |
| 5-N-(β-Hydroxyethyl)amino-2-methylphenol | 0.16 |
| 2-Methyl-5-aminophenol | 1.12 |
| para-Aminophenol | 0.2 |
| 6-Hydroxyindole | 0.045 |
| Fragrance | qs |
| Aqueous ammonia (containing 20.5% ammonia) | 10.2 |
| Demineralized water qs | 100 |

The dye composition was mixed, at the time of use, in a plastic bowl and for 2 minutes, with an oxidizing composition having a titre of 20 volumes of

aqueous hydrogen peroxide solution, at a rate of 1 part of dye composition per 1 part of oxidizing composition.

The mixture obtained was applied to locks of hair containing 90% grey hairs, and was left in place 5 for 30 minutes.

The locks were then rinsed with water, washed with shampoo, rinsed again with water and then dried and disentangled.

A particularly strong dark red-blond shade

10 was then obtained on hair sensitized with a permanent
wave.

Example 2

 $\label{eq:definition} \mbox{The following composition was prepared:} $$ \mbox{ \underline{Dye composition}:} $$$

15 (expressed in grams)

| Oleyl alcohol | 4 |
|--|------|
| Oleic acid | 5 |
| Oleyl alcohol polyglycerolated with 2 mol of | 4 |
| glycerol | |
| Lauryl alcohol polyglycerolated with 4 mol of | 3.6 |
| glycerol | |
| Rapeseed acid amide oxyethylenated with 4 mol of | 7.99 |
| ethylene oxide | |
| Oleylamine oxyethylenated with 2 mol of ethylene | 4 . |
| oxide | |
| Decyl alcohol oxyethylenated with 3 mol of | 2.7 |

| ethylene oxide | |
|--|-------|
| Ethyl alcohol | 7.45 |
| 3-Methyl-1,5-pentanediol | 15 |
| Reducing agents, antioxidants | 0.63 |
| Sequestering agent | 1 |
| 1,3-Dihydroxybenzene (resorcinol) | 0.49 |
| para-Phenylenediamine | 0.50 |
| 1,3-Dihydroxy-2-methylbenzene | 0.17 |
| 3-Methyl-1-phenyl-5-pyrazolone | 0.15 |
| 2,4-Diamino-1-(β-hydroxyethyloxy)benzene | 0.049 |
| dihydrochloride | |
| Pure monoethanolamine | 2 |
| Fragrance | qs |
| Aqueous ammonia (containing 20.5% ammonia) | 10 |
| Demineralized water qs | 100 |

The dye composition was mixed, at the time of use, in a plastic bowl and for 2 minutes, with an oxidizing composition having a titre of 20 volumes of aqueous hydrogen peroxide solution, at a rate of 1 part of dye composition per 1 part of oxidizing composition.

The mixture obtained was applied to locks of hair containing 90% grey hairs, and was left in place for 30 minutes.

The locks were then rinsed with water, washed with shampoo, rinsed again with water and then dried and disentangled.

A light chestnut shade was then obtained.

Example 3

The following composition was prepared:

Dye composition:

5 (expressed in grams)

| Oleic acid | 3 |
|---|-------|
| Oleyl alcohol polyglycerolated with 4 mol of | 5.46 |
| glycerol | |
| Lauryl alcohol polyglycerolated with 1.5 mol of | 5 |
| glycerol | |
| Alkyl(70/30 C13/C15 - 50% linear) ether | 5 |
| carboxylic acid monoethanolamide oxyethylenated | |
| with 2 mol of ethylene oxide | |
| Decyl alcohol oxyethylenated with 5 mol of | 5.4 |
| ethylene oxide | |
| Ethyl alcohol | 6.52 |
| 2,2-Dimethyl-1,3-propanediol (neopentyl glycol) | 12 |
| Reducing agents, antioxidants | 0.774 |
| Sequestering agent | 1.2 |
| 6-Hydroxybenzomorpholine | 3.018 |
| para-Phenylenediamine | 2.39 |
| 1,3-Dihydroxy-2-methylbenzene | 0.165 |
| 3-Methyl-1-phenyl-5-pyrazolone | 0.15 |
| 2,4-Diamino-1-(β-hydroxyethyloxy)benzene | 0.196 |
| dihydrochloride | |
| Pure monoethanolamine | 2 |

| Fragrance | qs |
|--|-----|
| Aqueous ammonia (containing 20.5% ammonia) | 12 |
| Demineralized water qs | 100 |

The dye composition was mixed, at the time of use, in a plastic bowl and for 2 minutes, with an oxidizing composition having a titre of 20 volumes of aqueous hydrogen peroxide solution, at a rate of 1 part of dye composition per 1 part of oxidizing composition.

The mixture obtained was applied to locks of hair containing 90% grey hairs, and was left in place for 30 minutes.

The locks were then rinsed with water, washed with shampoo, rinsed again with water and then dried and disentangled.

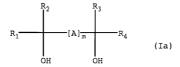
A black shade was then obtained.

For the purposes of this specification it will be clearly understood that the word "comprising" means "including but not limited to", and that the word "comprises" has a corresponding meaning.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

- Composition for the oxidation dyeing of human keratin fibres, comprising, in a medium that is suitable for dyeing, at least one oxidation dye, and characterized in that:
 - (a) it comprises at least one mono- or polyglycerolated fatty alcohol and at least one polyol of formula (Ia) below:



10

in which:

 $R_1,\ R_2,\ R_3$ and R_4 denote, independently of each other, a hydrogen atom, a $C_1\text{--}C_6$ alkyl radical or a $C_1\text{--}C_6$ mono- or polyhydroxyalkyl radical;

- A denotes a linear or branched alkylene radical containing a number of carbon atoms "n" ranging from 1 to 18, and optionally interrupted with a number of oxygen atoms "z" ranging from 0 to 9; m denotes 0 or 1;
- 20 it being understood that the total number of carbon atoms contained both in the radical A and in all of the substituents R_1 to R_4 is greater than or equal to 2, and in that the molecular weight of the polyol ranges: from 95 to 500,

25

if m is equal to 0, or if m and n are equal to 1, and $\frac{1}{2} \left(\frac{1}{2} \right) = \frac{1}{2} \left(\frac{1}{2} \right) \left(\frac{1}{2}$

if m is equal to 1 with A linear and n is equal to 2 with z equal to 0,

5

from 140 to 500, $\\ \\ \text{if n is greater than or equal to 2, and} \\ \\ \text{if m is equal to 1 with n equal to 2 and z other} \\ \\ \text{than 0,} \\$

10

15

from 90 to 500,

if m is equal to 1 with n other than 1 or 2 and z

equal to 0, or

if m is equal to 1 with A branched, and n equal to
2 and z equal to 0,

and

- (b) it contains no glycerol and no cationic synthetic thickening polymer comprising at least one fatty chain.
 - 2. Composition according to Claim 1,
- 20 characterized in that the mono- or polyglycerolated fatty alcohol is of formula (IIa) below:

$$RO = \begin{bmatrix} -CH_2-CH(CH_2OH) - O \end{bmatrix} \frac{1}{n} H$$
 (lla)

25 in which:

R represents a saturated or unsaturated, linear or branched radical containing from 8 to 40 carbon atoms;

n is a number ranging from 1 to 30.

- \$3.\$ Composition according to Claim 2, characterized in that, in formula (IIa), R contains from $10\ \text{to}\ 30\ \text{carbon}$ atoms.
- 4. Composition according to Claim 2, characterized in that, in formula (IIa), n is a number ranging from 1 to 10.
- Composition according to any one of the preceding claims, characterized in that the mono- or
 polyglycerolated fatty alcohol(s) represent(s) from 0.01% to 30% by weight relative to the total weight of the composition.
- 6. Composition according to Claim 5, characterized in that the mono- or polyglycerolated fatty alcohol(s) represent(s) from 0.05% to 20% by weight relative to the total weight of the composition.
- 7. Composition according to Claim 6, characterized in that the mono- or polyglycerolated fatty alcohol(s) represent(s) from 0.1% to 15% by weight relative to the total weight of the composition.
- 8. Composition according to any one of the preceding claims, characterized in that the polyol is a compound of formula (Ia) in which m=1 and R_1 to R_4 denote, independently of each other, a hydrogen atom or a $R_1 = 1$ 25 $R_2 = 1$ 26 alkyl radical.
 - 9. Composition according to Claim 8, characterized in that the polyol of formula (Ia) is a polyethylene glycol.
- 10. Composition according to Claim 8,30 characterized in that the polyol of formula (Ia) has a molecular weight of less than 200.
- 11. Composition according to Claim 10,
 characterized in that the polyol of formula (Ia) is chosen
 from 3-methyl-1,3,5-pentanetriol, 1,2,4-butanetriol, 1,5 pentanediol, 2-methyl-1,3-propanediol, 3-methyl-1,5 pentanediol, neopentyl glycol (2,2-dimethyl-1,3-

- propanediol), isoprene glycol (3-methyl-1,3-butanediol)
 and hexylene glycol (2-methyl-2,4-pentanediol).
- 12. Composition according to Claim 11,
 characterized in that the polyol of formula (Ia) is chosen
 5 from hexylene glycol, neopentyl glycol and 3-methyl-1,5 pentanediol.
- 13. Composition according to any one of the preceding claims, characterized in that the polyol(s) of formula (Ia) represent(s) from 0.1% to 40% relative to the total weight of the composition.
 - 14. Composition according to Claim 13, characterized in that the polyol(s) of formula (Ia) represent(s) from 0.5% to 30% relative to the total weight of the composition.
- 15. Composition according to Claim 14, characterized in that the polyol(s) of formula (Ia) represent(s) from 1% to 20% relative to the total weight of the composition.
- 16. Composition according to any one of the 20 preceding claims, characterized in that the oxidation dye is chosen from oxidation bases and couplers.
 - 17. Composition according to Claim 16, characterized in that it contains at least one oxidation base.
- 25
 18. Composition according to Claim 16 or 17, characterized in that the oxidation bases are chosen from ortho- or para-phenylenediamines, double bases, ortho- or para-aminophenols and heterocyclic bases, and also the addition salts of these compounds with an acid.
- 19. Composition according to Claim 18, characterized in that the para-phenylenediamines are chosen from the compounds of formula (II) below:

$$R_4$$
 R_3
 R_3
 R_4
 R_3

in which:

- 5 R_1 represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4) alkyl radical or a C_1-C_4 alkyl radical substituted with a nitrogenous, phenyl or 4'-aminophenyl group;
- 10 R₂ represents a hydrogen atom, a C_1 - C_4 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_2 - C_4 polyhydroxyalkyl radical, a $(C_1$ - $C_4)$ alkyl radical or a C_1 - C_4 alkyl radical substituted with a nitrogenous group;
- 15 R_1 and R_2 may also form, with the nitrogen atom which bears them, a 5- or 6-membered nitrogenous heterocycle optionally substituted with one or more alkyl, hydroxyl or ureido groups;
- R_3 represents a hydrogen atom, a halogen atom such as a chlorine atom, a C_1 - C_4 alkyl radical, a sulpho radical, a carboxy radical, a C_1 - C_4 monohydroxyalkyl radical, a C_1 - C_4 hydroxyalkoxy radical, an acetylamino(C_1 - C_4) alkoxy radical, a mesylamino(C_1 - C_4) alkoxy radical or a carbamoylamino(C_1 - C_4) alkoxy

25 radical,

 $\ensuremath{R_4}$ represents a hydrogen or halogen atom or a $\ensuremath{C_1\text{--}C_4}$ alkyl radical.

20. Composition according to Claim 18, characterized in that the double bases are chosen from the 5 compounds of structure (III) below:

in which:

- Z_1 and Z_2 , which may be identical or different, represent a hydroxyl or -NH₂ radical which may be substituted with a C_1 - C_4 alkyl radical or with a linker arm Y;
- the linker arm Y represents a linear or branched alkylene chain containing from 1 to 14 carbon atoms, which may be interrupted by or terminated with one or more
 nitrogenous groups and/or one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C₁-C₆ alkoxy radicals;
- R_5 and R_6 represent a hydrogen or halogen atom, a C_1 - C_4 20 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_2 - C_4 polyhydroxylalkyl radical, a C_1 - C_4 aminoalkyl radical or a linker arm Y;
- R_7 , R_8 , R_9 , R_{10} , R_{11} and R_{12} , which may be identical or different, represent a hydrogen atom, a linker arm Y or a 25 C_1 - C_4 alkyl radical;
 - it being understood that the compounds of formula (III) contain only one linker arm Y per molecule.

- $21. \quad \text{Composition according to Claim 19 or 20,} \\ \text{characterized in that the nitrogenous groups are chosen} \\ \text{from amino, mono}(C_1-C_4)\text{alkylamino, di}(C_1-C_4)\text{alkylamino,} \\ \text{tri}(C_1-C_4)\text{alkylamino, monohydroxy}(C_1-C_4)\text{alkylamino,} \\ \text{5} \\ \text{imidazolinium and ammonium radicals.} \\$
 - 22. Composition according to Claim 18, characterized in that the para-aminophenols are chosen from the compounds of structure (IV) below:

$$\bigcap_{NH_2}^{OH} R_{13}$$

10 in which:

 R_{13} represents a hydrogen atom, a halogen atom, such as fluorine, or a C_1-C_4 alkyl, C_1-C_4 monohydroxylalkyl, (C_1-C_4) alkoxy(C_1-C_4) alkyl, C_1-C_4 aminoalkyl or hydroxy(C_1-C_4) alkylamino(C_1-C_4) alkyl radical,

- 15 R_{14} represents a hydrogen atom, a halogen atom, such as fluorine, or a C_1 - C_4 alkyl, C_1 - C_4 monohydroxyalkyl, C_2 - C_4 polyhydroxyalkyl, C_1 - C_4 aminoalkyl, C_1 - C_4 cyanoalkyl or $(C_1$ - $C_4)$ alkoxy $(C_1$ - $C_4)$ alkyl radical.
- 23. Composition according to Claim 18,
 20 characterized in that the heterocyclic bases are chosen
 from pyridine derivatives, pyrimidine derivatives,
 including pyrazolopyrimidines, and pyrazole derivatives.
- 24. Composition according to any one of Claims 16 to 23, characterized in that the oxidation bases are 25 present in concentrations ranging from 0.0005% to 12% by weight relative to the total weight of the composition.
 - 25. Composition according to Claim 16, characterized in that the couplers are chosen from metaphenylenediamines, meta-aminophenols, meta-diphenols and

heterocyclic couplers, and the addition salts of these compounds with an acid.

- 26. Composition according to Claim 16 or 25, characterized in that the couplers are present in5 concentrations ranging from 0.0001% to 10% by weight relative to the total weight of the composition.
- 27. Composition according to Claim 18 or 25, characterized in that the addition salts with an acid of the oxidation bases and couplers are chosen from the
 10 hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.
 - 28. Composition according to any one of the preceding claims, characterized in that it also contains direct dyes.
- 29. Composition according to any one of the preceding claims, characterized in that it also contains at least one reducing agent, in amounts ranging from 0.05 % to 3% by weight relative to the total weight of the composition.
- 20 30. Composition according to any one of the preceding claims, characterized in that it contains one or more additional fatty alcohols.
- 31. Composition according to Claim 30, characterized in that the fatty alcohol(s) represent(s)25 from 0.001% to 20% by weight relative to the total weight of the composition.
 - 32. Ready-to-use composition for the oxidation dyeing of human keratin fibres, characterized in that it is obtained by mixing a composition (A) as defined in any one of Claims 1 to 31 and a composition (B) containing at least one oxidizing agent.
 - 33. Composition according to Claim 32, characterized in that the oxidizing agent is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, persalts, redox enzymes such as laccases, peroxidases and 2-electron oxidoreductases, where

appropriate in the presence of their respective donor or co-factor.

- 34. Composition according to Claim 33,characterized in that the oxidizing agent is hydrogenperoxide.
 - 35. Composition according to Claim 34, characterized in that the oxidizing agent is an aqueous hydrogen peroxide solution with a titre ranging from 1 to 40 volumes.
- 10 36. Composition according any one of the preceding claims, characterized in that it is has a pH ranging from 4 to 12.
- 37. Composition according to any one of Claims 1 to 32 and according to Claim 36, characterized in that 15 composition (A) and/or composition (B) contains at least one cationic or amphoteric polymer.
- 38. Composition according to Claim 37, characterized in that the cationic polymer is a polyquaternary ammonium consisting of repeating units corresponding to formula (W) below:

39. Composition according to Claim 37, characterized in that the cationic polymer is a25 polyquaternary ammonium consisting of repeating units corresponding to formula (U) below:

$$\begin{array}{c|cccc} CH_3 & C_2H_5 & & \\ \hline & & & & \\ \hline & N_{-}^{+}(CH_2)_3 & N_{-}^{+}(CH_2)_3 & \\ & & & & \\ \hline & Br & & & \\ CH_3 & & C_2H_5 & \\ \end{array} \tag{U}$$

- 40. Composition according to Claim 37, characterized in that the amphoteric polymer is a copolymer comprising at least acrylic acid and a dimethyldiallylammonium salt as monomer.
 - 41. Composition according to any one of Claims 37 to 40, characterized in that the cationic or amphoteric polymer(s) represent(s) from 0.01% to 10% by weight relative to the total weight of the composition.
- 10 42. Composition according to any one of Claims 1 to 32 and according to Claim 36, characterized in that composition (A) and/or composition (B) contains at least one additional surfactant chosen from anionic, cationic, nonionic and amphoteric surfactants.
- 15 43. Composition according to Claim 38, characterized in that the additional surfactants represent 0.01% to 40% of the total weight of the composition.
- 44. Composition according to any one of Claims
 1 to 32 and according to Claim 36, characterized in that
 20 composition (A) and/or composition (B) contains a
 thickener chosen from cellulose derivatives, guar
 derivatives, gums or microbial origin, synthetic
 thickeners not comprising a fatty chain and synthetic
 thickeners of nonionic, anionic or amphoteric nature
 25 comprising a fatty chain.
 - 45. Composition according to Claim 44, characterized in that the thickening polymer(s) is (are) present in a proporation of from 0.01% to 10% by weight relative to the total weight of the composition.
- 30 46. Process for dyeing human keratin fibres, characterized in that it consists in applying to the

fibres a dye composition (A) as defined in any one of Claims 1 to 31 and 36 to 45, and in developing the colour in alkaline, neutral or acidic medium with the aid of a composition (B) containing at least one oxidizing agent, 5 the said composition (B) being defined in any one of Claims 32 to 45 and added to composition (A) just at the time of use, or applied sequentially without intermediate rinsing.

- 47. Multi-compartment device or "kit" for the

 10 oxidation dyeing of keratin fibres, characterized in that
 it comprises at least two compartments, one of which
 contains a composition (A) as defined in any one of Claims
 1 to 31 and 36 to 45, and another of which contains a
 composition (B) comprising an oxidizing agent and as

 15 defined in any one of Claims 32 to 45.
 - 48. Compositions, processes involving said compositions or kits comprising said compositions, substantially as herein described with reference to the accompanying examples.

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Dated this 10th day of September 2004 L'OREAL

By their Patent Attorneys

25 GRIFFITH HACK

Fellows Institute of Patent and Trade Mark Attorneys of Australia