

**COMPOSITION FOR THE OXIDATION DYEING OF KERATIN
FIBRES AND DYEING PROCESS USING THIS COMPOSITION**

The invention relates to a composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one oxidation base, at least one C₄-C₈ ether of a C₂ glycol and/or at least one C₁-C₈ ether of C₃-C₉ glycol and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme, and to the dyeing process using this composition.

It is known to dye keratin fibres, and in particular human hair, with dye compositions containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic bases, which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation bases, are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise to coloured compounds and dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or colour modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

The so-called "permanent" coloration obtained
5 by means of these oxidation dyes must moreover satisfy a certain number of requirements. Thus, it must have no toxicological drawbacks, it must be able to give shades of the desired intensity and it must be able to withstand external agents (light, bad weather, washing,
10 permanent-waving, perspiration, rubbing).

The dyes must also be able to cover white hair and, lastly, they must be as unselective as possible, i.e. they must give the smallest possible colour differences along the same length of keratin
15 fibre, which may in fact be differently sensitized (i.e. damaged) between its tip and its root.

The oxidation dyeing of keratin fibres is generally carried out in alkaline medium, in the presence of hydrogen peroxide. However, the use of
20 alkaline media in the presence of hydrogen peroxide have the drawback of causing appreciable degradation of the fibres, as well as considerable bleaching of the keratin fibres, which is not always desirable.

The oxidation dyeing of keratin fibres can
25 also be carried out using oxidizing systems other than hydrogen peroxide, such as enzymatic systems. Thus, it has already been proposed to dye keratin fibres, in particular in patent application EP-A-0,310,675, with

compositions comprising an oxidation base and optionally a coupler, in combination with enzymes such as pyranose oxidase, glucose oxidase or uricase, in the presence of a donor for the said enzymes. Although
5 being used under conditions which do not result in a degradation of the keratin fibres which is comparable to that caused by the dyes used in the presence of hydrogen peroxide, these dyeing processes nevertheless lead to colorations which are not entirely
10 satisfactory, in particular as regards their intensity and resistance to the various attacking factors to which the hair may be subjected.

The Applicant has now discovered that it is possible to obtain new dyes, which are capable of
15 leading to intense and chromatic colorations, without giving rise to any significant degradation of the keratin fibres, and which are relatively unselective and show good resistance to the various attacking factors to which the hair may be subjected, by
20 combining at least one oxidation base, at least one C_4 - C_8 ether of a C_2 glycol and/or at least one C_1 - C_8 ether of C_3 - C_9 glycol and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme.

25 This discovery forms the basis of the present invention.

A first subject of the invention is thus a ready-to-use composition for the oxidation dyeing of

keratin fibres, and in particular human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing:

- at least one oxidation base,
- 5 - at least one C₄-C₈ ether of a C₂ glycol and/or at least one C₁-C₈ ether of C₃-C₉ glycol,
- at least one enzyme of 2-electron oxidoreductase type, and
- at least one donor for the said enzyme.

10 The ready-to-use dye composition in accordance with the invention leads to intense, chromatic, relatively unselective colorations with excellent properties of resistance both to atmospheric agents such as light and bad weather and to

15 perspiration and the various treatments to which the hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this ready-to-use dye composition.

20 The 2-electron oxidoreductase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

25 According to the invention, the 2-electron oxidoreductase is preferably chosen from uricases of animal, microbiological or biotechnological origin.

By way of example, mention may be made of

uricase extracted from boar liver, uricase from *Arthrobacter globiformis*, as well as uricase from *Aspergillus flavus*.

The 2-electron oxidoreductase(s) can be used
5 in pure crystalline form or in a form diluted in a diluent which is inert with respect to the said 2-electron oxidoreductase.

The 2-electron oxidoreductase(s) in accordance with the invention preferably represent(s)
10 from 0.01 to 20% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.1 to 5% by weight approximately relative to this weight.

According to the invention, the term donor is
15 understood to refer to the various substrates involved in the functioning of the said 2-electron oxidoreductase(s).

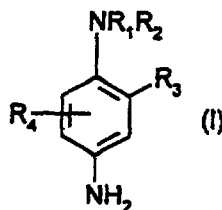
The nature of the donor (or substrate) for the said enzyme varies depending on the nature of the
20 2-electron oxidoreductase used. For example, as donors for the pyranose oxidases, mention may be made of D-glucose, L-sorbose and D-xylose; as a donor for the glucose oxidases, mention may be made of D-glucose; as donors for the glycerol oxidases, mention may be made
25 of glycerol and dihydroxyacetone; as donors for the lactate oxidases, mention may be made of lactic acid and its salts; as donors for the pyruvate oxidases, mention may be made of pyruvic acid and its salts; and

lastly, as donors for the uricases, mention may be made of uric acid and its salts.

The donor(s) (or substrate(s)) used in accordance with the invention preferably represent(s)
5 from 0.01 to 20% by weight approximately relative to the total weight of the ready-to-use dye composition in accordance with the invention, and even more preferably from 0.1 to 5% by approximately relative to this weight.

10 The nature of the oxidation base(s) used in the ready-to-use dye composition is not a critical factor. They can be chosen, in particular, from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

15 Among the para-phenylenediamines which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (I) below, and the addition salts thereof with an acid:



in which:

- 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, a C_1-C_4 alkyl radical substituted with a nitrogenous group, a phenyl radical or a 4'-aminophenyl radical;
- R_2 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 group;
- R_3 represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_1-C_4 hydroxyalkoxy radical, an acetylamino (C_1-C_4) -alkoxy radical, a C_1-C_4 mesylaminoalkoxy radical or a carbamoylamino (C_1-C_4) alkoxy radical,
- R_4 represents a hydrogen or halogen atom or a C_1-C_4 alkyl radical.

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

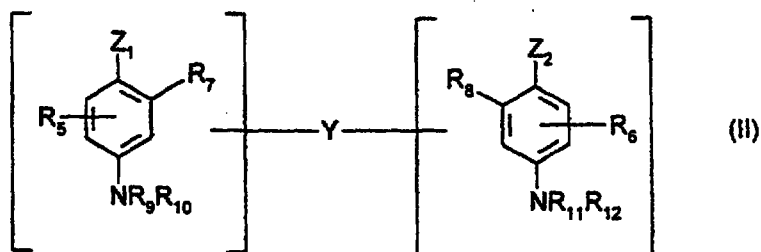
Among the para-phenylenediamines of formula (I) above, mention may be made more particularly of para-phenylenediamine, para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylene-
 5 diamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline,
 10 N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 4-amino-N,N-bis(β -hydroxyethyl)-2-methylaniline, 4-amino-2-chloro-N,N-bis(β -hydroxyethyl)aniline, 2- β -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine,
 15 N-(β -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl- β -hydroxyethyl)-para-phenylenediamine, N-(β,γ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine,
 20 N-phenyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2- β -acetylaminethyloxy-para-phenylenediamine and N-(β -methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

25 Among the para-phenylenediamines of formula (I) above, para-phenylenediamine, para-toluylenediamine, 2-isopropyl-para-phenylenediamine, 2- β -hydroxyethyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine,

2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2- β -acetylaminooethyloxy-para-phenylenediamine and the
 5 addition salts thereof with an acid are most particularly preferred.

According to the invention, the term double bases is understood to refer to the compounds containing at least two aromatic rings bearing amino
 10 and/or hydroxyl groups.

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



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
 20 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;

5 - R₅ and R₆ represent a hydrogen or halogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ aminoalkyl radical or a linker arm Y;

- R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂, which may be identical or
10 different, represent a hydrogen atom, a linker arm Y or a C₁-C₄ alkyl radical;

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

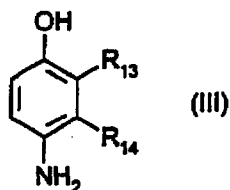
Among the nitrogenous groups of formula (II)
15 above, mention may be made in particular of amino, mono(C₁-C₄)alkylamino, di(C₁-C₄)alkylamino, tri(C₁-C₄)alkylamino, monohydroxy(C₁-C₄)alkylamino, imidazolinium and ammonium radicals.

Among the double bases of formula (II) above,
20 mention may be made more particularly of N,N'-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)-
25 N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)-ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-

3,5-dioxaoctane, and the addition salts thereof with an acid.

Among these double bases of formula (II),
 N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-
 5 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.

Among the para-aminophenols which can be used
 as oxidation bases in the dye compositions in
 10 accordance with the invention, mention may be made in
 particular of the compounds corresponding to formula
 (III) below, and the addition salts thereof with an
 acid:



in which:

- 15 - R_{13} represents a hydrogen or halogen atom or a C_1 - C_4
 alkyl, C_1 - C_4 monohydroxyalkyl, $(C_1$ - 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,
- R_{14} represents a hydrogen or halogen atom or a C_1 - C_4
 20 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,
- it being understood that at least one of the radicals
 R_{13} or R_{14} represents a hydrogen atom.

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

5 2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

10 Among the ortho-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol,
15 and the addition salts thereof with an acid.

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
20 derivatives, pyrazole derivatives and pyrazolopyrimidine derivatives, and the addition salts thereof with an acid.

Among the pyridine derivatives, mention may be made more particularly of the compounds described,
25 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

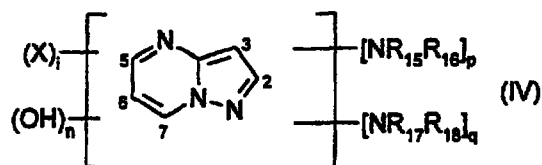
3,4-diaminopyridine, and the addition salts thereof with an acid.

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 applications WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, 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-methylpyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 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-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β -hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-

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

Among the pyrazolopyrimidine derivatives,
 mention may be made more particularly of the
 10 pyrazolo[1,5-a]pyrimidines of formula (IV) below, and
 the addition salts thereof with an acid or with a base
 and the tautomeric forms thereof, when a tautomeric
 equilibrium exists:



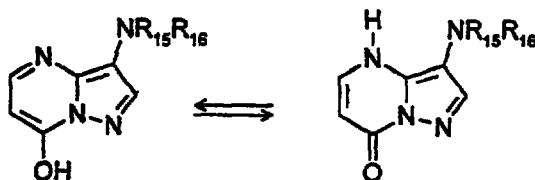
in which:

15 - R_{15} , R_{16} , R_{17} and R_{18} , which may be identical or
 different, denote a hydrogen atom, a C_1 - C_4 alkyl
 radical, an aryl radical, a C_1 - C_4 hydroxyalkyl radical, a
 C_2 - C_4 polyhydroxyalkyl radical, a $(C_1$ - C_4)alkoxy(C_1 - C_4)-
 alkyl radical, a C_1 - C_4 aminoalkyl radical (it being
 20 possible for the amine to be protected with an acetyl,
 ureido or sulphonyl radical), a $(C_1$ - C_4)alkylamino(C_1 - C_4)-
 alkyl radical, a di[(C_1 - C_4)alkyl]amino(C_1 - C_4)alkyl
 radical (it being possible for the dialkyl radicals to
 form a 5- or 6-membered carbon-based ring or a

- heterocycle), a hydroxy(C₁-C₄)alkyl- or di[hydroxy-(C₁-C₄)alkyl]amino(C₁-C₄)alkyl radical;
- the radicals X, which may be identical or different, denote a hydrogen atom, a C₁-C₄ alkyl radical, an aryl radical, a C₁-C₄ hydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a C₁-C₄ aminoalkyl radical, a (C₁-C₄)alkylamino(C₁-C₄)alkyl radical, a di[(C₁-C₄)alkyl]amino(C₁-C₄)alkyl radical (it being possible for the dialkyls to form a 5- or 6-membered carbon-based ring or a heterocycle), a hydroxy(C₁-C₄)alkyl- or di-[hydroxy(C₁-C₄)alkyl]amino(C₁-C₄)alkyl radical, an amino radical, a (C₁-C₄)alkyl- or di[(C₁-C₄)alkyl]amino radical; a halogen atom, a carboxylic acid group, a sulphonic acid group;
- i is equal to 0, 1, 2 or 3;
- p is equal to 0 or 1;
- q is equal to 0 or 1;
- n is equal to 0 or 1;
- with the proviso that:
- the sum p + q is other than 0;
- when p + q is equal to 2, then n is equal to 0 and the groups NR₁₅R₁₆ and NR₁₇R₁₈ occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions;
- when p + q is equal to 1, then n is equal to 1 and the group NR₁₅R₁₆ (or NR₁₇R₁₈) and the OH group occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions.

When the pyrazolo[1,5-a]pyrimidines of formula (IV) above are such that they contain a hydroxyl group

on one of the positions 2, 5 or 7 α to a nitrogen atom, a tautomeric equilibrium exists represented, for example, by the following scheme:



Among the pyrazolo[1,5-a]pyrimidines of formula

- 5 (IV) above, mention may be made in particular of:
- pyrazolo[1,5-a]pyrimidine-3,7-diamine;
 - 2,5-dimethylpyrazolo[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;
 - 10 - 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
 - 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-hydroxy-
 - 15 ethyl)amino]ethanol;
 - 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxy-
 - ethyl)amino]ethanol;
 - 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
 - 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
 - 20 - 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-
 - 3,7-diamine;

and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

The pyrazolo[1,5-a]pyrimidines of formula (IV)

above can be prepared by cyclization starting with an aminopyrazole, according to the syntheses described in the following references:

- EP 628559 Beiersdorf-Lilly.
- 5 - R. Vishdu, H. Navedul, Indian J. Chem., 34b (6), 514, 1995.
- N.S. Ibrahim, K.U. Sadek, F.A. Abdel-Al, Arch. Pharm., 320, 240, 1987.
- R.H. Springer, M.B. Scholten, D.E. O'Brien,
- 10 T. Novinson, J.P. Miller, R.K. Robins, J. Med. Chem., 25, 235, 1982.
- T. Novinson, R.K. Robins, T.R. Matthews, J. Med. Chem., 20, 296, 1977.
- US 3907799 ICN Pharmaceuticals.

15 The pyrazolo[1,5-a]pyrimidines of formula (IV) above can also be prepared by cyclization starting from hydrazine, according to the syntheses described in the following references:

- A. McKillop and R.J. Kobilecki, Heterocycles, 6(9),
- 20 1355, 1977.
- E. Alcade, J. De Mendoza, J.M. Marcia-Marquina, C. Almera, J. Elguero, J. Heterocyclic Chem., 11(3), 423, 1974.
- K. Saito, I. Hori, M. Higashashi, H. Midorikawa, Bull.
- 25 Chem. Soc. Japan, 47(2), 476, 1974.

The oxidation base(s) preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition in accordance

with the invention, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

The ready-to-use dye composition in accordance with the invention can also contain one or more
5 couplers. These couplers can be chosen in particular from meta-phenylenediamines, meta-aminophenols, meta-diphenols, heterocyclic couplers such as, for example, indole derivatives, indoline derivatives, benzimidazole derivatives, benzomorpholine derivatives, sesamol
10 derivatives and pyridine, pyrimidine and pyrazole derivatives, and the addition salts thereof with an acid.

These couplers are chosen more particularly from 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-
15 2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethyloxy)-benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-
20 diaminophenoxy)propane, sesamol, α -naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one and 1-phenyl-3-methyl pyrazole-5-one, and the addition salts thereof
25 with an acid.

When they are present, the coupler(s) preferably represent(s) from 0.0001 to 10% by weight approximately relative to the total weight of the

ready-to-use dye composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

In general, the addition salts with an acid
5 which can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

10 The C_4 - C_8 ether(s) of a C_2 glycol used in the ready-to-use dye composition in accordance with the invention is (are) preferably chosen from C_4 - C_8 alkyl ethers of a C_2 glycol, such as ethylene glycol monobutyl ether and C_6 - C_8 aryl ethers of a C_2 glycol, such as
15 ethylene glycol monophenyl ether and ethylene glycol monobenzyl ether.

The C_1 - C_8 ether(s) of a C_3 - C_9 glycol used in the ready-to-use dye composition in accordance with the invention is (are) preferably chosen from C_1 - C_8 alkyl
20 ethers of a C_3 - C_9 glycol, such as propylene glycol monomethyl ether, propylene glycol monoethyl ether, isopropylene glycol dimethyl ether, diethylene glycol monomethyl ether and monoethyl ether, dipropylene glycol monomethyl ether and tripropylene glycol
25 monomethyl ether, and C_6 - C_8 aryl ethers of a C_3 - C_9 glycol, such as propylene glycol monophenyl ether, propylene glycol monobenzyl ether, diethylene glycol monophenyl ether and diethylene glycol monobenzyl

ether.

The C₄-C₈ ether(s) of a C₂ glycol and/or the C₁-C₈ ether(s) of a C₃-C₉ glycol preferably represent(s) from 1 to 40% by weight approximately relative to the total weight of the ready-to-use dye composition according to the invention, and even more preferably from 5 to 30% by weight approximately relative to this weight.

The ready-to-use dye composition in accordance with the invention can also contain one or more direct dyes, in particular in order to modify the shades or to enrich them with glints.

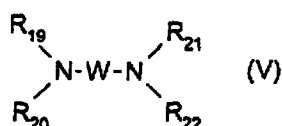
The medium which is suitable for dyeing (or support) for the ready-to-use dye composition in accordance with the invention generally consists of water. The medium which is suitable for dyeing may also contain one or more solvents other than C₄-C₈ ethers of a C₂ glycol and C₁-C₈ ethers of a C₃-C₉ glycol of the invention.

The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the 2-electron oxidoreductase is sufficient. It is generally between 5 and 11 approximately, and preferably between 6.5 and 10 approximately. It can be adjusted to the desired value using acidifying or basifying agents usually used for dyeing keratin fibres.

Among the acidifying agents, mention may be

made, by way of example, of inorganic or organic acids
 such as hydrochloric acid, orthophosphoric acid,
 sulphuric acid, carboxylic acids such as acetic acid,
 tartaric acid, citric acid or lactic acid, and sulphonic
 5 acids.

Among the basifying agents, mention may be made,
 by way of example, of aqueous ammonia, alkaline
 carbonates, alkanolamines such as mono-, di- and
 triethanolamines, 2-methyl-2-aminopropanol and
 10 derivatives thereof, sodium hydroxide, potassium
 hydroxide and the compounds of formula (V) below:



in which W is a propylene residue optionally
 substituted with a hydroxyl group or a C₁-C₄ alkyl
 radical; R₁₉, R₂₀, R₂₁ and R₂₂, which may be identical or
 15 different, represent a hydrogen atom or a C₁-C₄ alkyl or
 C₁-C₄ hydroxyalkyl radical.

The ready-to-use dye composition in accordance
 with the invention can also contain various adjuvants
 used conventionally in compositions for the dyeing of
 20 the hair, such as anionic, cationic, nonionic,
 amphoteric or zwitterionic surfactants or mixtures
 thereof, anionic, cationic, nonionic, amphoteric or
 zwitterionic polymers or mixtures thereof, inorganic or
 organic thickeners, antioxidants, enzymes other than

the 2-electron oxidoreductases used in accordance with the invention, such as, for example, peroxidases, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners such as, for example, silicones which may or may not be volatile or modified, film-forming agents, ceramides, preserving agents and opacifiers.

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

The ready-to-use dye composition in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which may be pressurized, or in any other form which is suitable for dyeing keratin fibres, and in particular human hair. In this case the oxidation dye(s) and the 2-electron oxidoreductase(s) are present in the same ready-to-use composition, and consequently the said composition must be free of gaseous oxygen, so as to avoid any premature oxidation of the oxidation dye(s).

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.

According to this process, at least one ready-to-use dye composition as defined above is applied to the fibres, for a period which is sufficient to develop the desired coloration, after which the fibres are
5 rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is usually between 3 and 60 minutes and even more precisely between 5 and 40 minutes.

10 According to one first specific embodiment of the invention, the process includes a preliminary step which consists in separately storing, on the one hand, a composition (A1) comprising, in a medium which is suitable for dyeing, at least one oxidation base and at
15 least one C₄-C₈ ether of a C₂ glycol and/or at least one C₁-C₈ ether of a C₃-C₉ glycol, and, on the other hand, a composition (B1) comprising, in a medium which is suitable for dyeing, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one
20 donor for the said enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

According to a second specific embodiment of the invention the process includes a first step which
25 consists in separately storing, on the one hand, a composition (A2) comprising, in a medium which is suitable for dyeing, at least one oxidation base, and, on the other hand, a composition (B2) containing, in a

medium which is suitable for dyeing, at least one C₄-C₈ ether of a C₂ glycol and/or at least one C₁-C₈ ether of a C₃-C₉ glycol, and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one
5 donor for the said enzyme, followed by mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-
10 compartment packaging system, a first compartment of which comprises composition (A1) or (A2) as defined above and a second compartment of which comprises composition (B1) or (B2) as defined above. These devices can be equipped with means for delivering the
15 desired mixture onto the hair, such as the devices described in patent FR-2,586,913 in the name of the Applicant.

The examples which follow are intended to illustrate the invention without, however, limiting its
20 scope.

EXAMPLE**DYEING EXAMPLE 1**

The ready-to-use dye composition below was prepared:

5	- para-Phenylenediamine	0.324 g
	- 1,3-Dihydroxybenzene	0.33 g
	- Propylene glycol monomethyl ether	20.0 g
	- Uricase from <i>Arthrobacter globiformis</i> at 20 International Units (I.U.)/mg, sold 10 by the company Sigma	1.5 g
	- Uric acid	1.5 g
	- Hydroxyethylcellulose sold under the name Natrosol 250HR® by the company Aqualon	1.0 g
15	- (C ₈ -C ₁₀)Alkylpolyglucoside as an aqueous solution containing 60% active material (A.M.), buffered with ammonium citrate (0.5%), sold under the name Oramix CG 110® by the company SEPPIC	8.0 g
20	- Monoethanolamine qs	pH = 9.5
	- Demineralized water qs	100.0 g

The ready-to-use dye composition described above was applied to locks of natural grey hair containing 90% white hairs, for 30 minutes. The hair
25 was then rinsed, washed with a standard shampoo and then dried.

The hair was dyed in a matt dark blonde shade.

CLAIMS

1. Ready-to-use composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, characterized in
5 that it comprises, in a medium which is suitable for dyeing:
 - at least one oxidation base,
 - at least one C₄-C₈ ether of a C₂ glycol and/or at least one C₁-C₈ ether of C₃-C₉ glycol,
 - 10 - at least one enzyme of 2-electron oxidoreductase type, and
 - at least one donor for the said enzyme.
2. Composition according to Claim 1, characterized in that the 2-electron oxidoreductase is
15 chosen from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.
3. Composition according to either of Claims 1 and 2, characterized in that the 2-electron
20 oxidoreductase is chosen from uricases of animal, microbiological or biotechnological origin.
4. Composition according to any one of the preceding claims, characterized in that the 2-electron oxidoreductase(s) represent(s) from 0.01 to 20% by
25 weight relative to the total weight of the ready-to-use dye composition.
5. Composition according to Claim 4, characterized in that the 2-electron oxidoreductase(s) represent(s) from 0.1 to 5% by weight relative to the
30 total weight of the ready-to-use dye composition.
6. Composition according to Claim 3,



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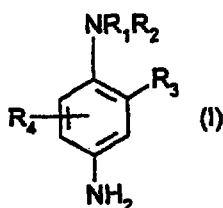
characterized in that the donor (or substrate) for the said 2-electron oxidoreductase is chosen from uric acid and its salts.

7. Composition according to any one of the preceding claims, characterized in that the donor(s) represent(s) from 0.01 to 20% by weight relative to the total weight of the ready-to-use dye composition.

8. Composition according to Claim 7, characterized in that the donor(s) represent(s) from 0.1 to 5% by weight relative to the total weight of the ready-to-use dye composition.

9. Composition according to any one of the preceding claims, characterized in that the oxidation base(s) is (are) chosen from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

10. Composition according to Claim 9, characterized in that the para-phenylenediamines are chosen from the compounds of formula (I) below, and the addition salts thereof with an acid:



in which:

- R₁ represents a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₂-C₄ polyhydroxyalkyl radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical, a C₁-C₄ alkyl radical substituted with a nitrogenous group, a phenyl radical or a 4'-aminophenyl radical;



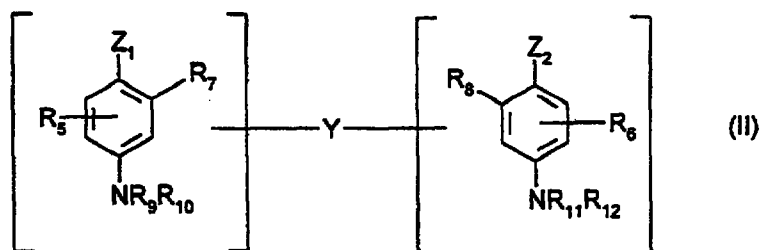
- R_2 represents a hydrogen atom, a C_1 - C_4 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_2 - C_4 polyhydroxyalkyl radical, a $(C_1$ - C_4)alkoxy(C_1 - C_4)alkyl radical or a C_1 - C_4 alkyl radical substituted with a nitrogenous group;
- R_3 represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C_1 - C_4 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_1 - C_4 hydroxyalkoxy radical, an acetylamino(C_1 - C_4)alkoxy radical, a C_1 - C_4 mesylaminoalkoxy radical or a carbamoylamino(C_1 - C_4)alkoxy radical,
- R_4 represents a hydrogen or halogen atom or a C_1 - C_4 alkyl radical.

11. Composition according to Claim 10, characterized in that the para-phenylenediamines of formula (I) are chosen from para-phenylenediamine, para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 4-amino-N,N-bis(β -hydroxyethyl)-2-methylaniline, 4-amino-2-chloro-N,N-bis(β -hydroxyethyl)aniline, 2- β -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl- β -hydroxyethyl)-para-phenylenediamine,



N-(β , γ -dihydroxypropyl)-para-phenylenediamine,
 N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-
 para-phenylenediamine, 2- β -hydroxyethyloxy-para-
 phenylenediamine, 2- β -acetylaminoethyloxy-para-
 5 phenylenediamine and N-(β -methoxyethyl)-para-
 phenylenediamine, and the addition salts thereof with
 an acid.

12. Composition according to Claim 9,
 characterized in that the double bases are chosen from
 10 the compounds of formula (II), and the addition salts
 thereof with an acid:



in which:

- Z_1 and Z_2 , which may be identical or different,
 represent a hydroxyl or $-\text{NH}_2$ radical which may be
 15 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
 20 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
 C_1 - C_6 alkoxy radicals;
- R_5 and R_6 represent a hydrogen or halogen atom, a C_1 - C_4
 25 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_2 - C_4



polyhydroxyalkyl radical, a C₁-C₄ aminoalkyl radical or a linker arm Y;

- R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂, which may be identical or different, represent a hydrogen atom, a linker arm Y or

5 a C₁-C₄ alkyl radical;

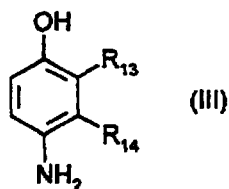
it being understood that the compounds of formula (II) contain only one linker arm Y per molecule.

13. Composition according to Claim 12, characterized in that the double bases of formula (II)

10 are chosen from N,N'-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)-

15 tetramethylenediamine, N,N'-bis(4-methylaminophenyl)-tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

20 14. Composition according to Claim 9, characterized in that the para-aminophenols are chosen from the compounds of formula (III), and the addition salts thereof with an acid:



in which:

25 - R₁₃ represents a hydrogen or halogen atom 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,

- R_{14} represents a hydrogen or halogen atom 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-

5 (C_1-C_4) alkyl radical,

it being understood that at least one of the radicals R_{13} or R_{14} represents a hydrogen atom.

15. Composition according to Claim 14, characterized in that the para-aminophenols of
10 formula (III) are chosen from 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,
15 4-amino-2-(β -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

16. Composition according to Claim 9, characterized in that the ortho-aminophenols are chosen
20 from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

17. Composition according to Claim 9, characterized in that the heterocyclic oxidation bases
25 are chosen from pyridine derivatives, pyrimidine derivatives, pyrazole derivatives and pyrazolo-pyrimidine derivatives, and the addition salts thereof with an acid.

18. Composition according to any one of the
30 preceding claims, characterized in that the oxidation base(s) represent(s) from 0.0005 to 12% by weight



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relative to the total weight of the dye composition.

19. Composition according to Claim 18, characterized in that the oxidation base(s) represent(s) from 0.005 to 6% by weight relative to the
5 total weight of the dye composition.

20. Composition according to any one of the preceding claims, characterized in that it contains one or more couplers chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols, heterocyclic
10 couplers such as, for example, indole derivatives, indoline derivatives, benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives and pyridine, pyrimidine and pyrazole derivatives, and the addition salts thereof with an acid.

21. Composition according to Claim 20, characterized in that the coupler(s) is (are) chosen from 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-
20 dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethyloxy)-benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, sesamol, α -naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-
25 methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazole-5-one and 1-phenyl-3-methyl pyrazole-5-one, and the addition salts thereof with an acid.

22. Composition according to either of
30 Claims 20 and 21, characterized in that the coupler(s) represent(s) from 0.0001 to 10% by weight relative to



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the total weight of the ready-to-use dye composition.

23. Composition according to Claim 22, characterized in that the coupler(s) represent(s) from 0.005 to 5% by weight relative to the total weight of the ready-to-use dye composition.

24. Composition according to any one of the preceding claims, characterized in that the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

25. Composition according to any one of the preceding claims, characterized in that the C₄-C₈ ether(s) of a C₂ glycol is (are) chosen from the C₄-C₈ alkyl ethers of a C₂ glycol and the C₆-C₈ aryl ethers of a C₂ glycol.

26. Composition according to Claim 25, characterized in that the C₄-C₈ ether(s) of a C₂ glycol is (are) chosen from ethylene glycol monobutyl ether, ethylene glycol monophenyl ether and ethylene glycol monobenzyl ether.

27. Composition according to any one of Claims 1 to 24, characterized in that the C₁-C₈ ether(s) of a C₃-C₉ glycol is (are) chosen from C₁-C₈ alkyl ethers of a C₃-C₉ glycol and C₆-C₈ aryl ethers of a C₃-C₉ glycol.

28. Composition according to Claim 27, characterized in that the C₁-C₈ glycol ether(s) of a C₃-C₉ glycol are chosen from propylene glycol monomethyl ether, propylene glycol monoethyl ether, isopropylene glycol dimethyl ether, diethylene glycol monomethyl ether and monoethyl ether, dipropylene glycol monomethyl ether and tripropylene glycol monomethyl



ether, propylene glycol monophenyl ether, propylene glycol monobenzyl ether, diethylene glycol monophenyl ether and diethylene glycol monobenzyl ether.

29. Composition according to any one of the preceding claims, characterized in that the C₄-C₈ ether(s) of a C₂ glycol and/or the C₁-C₈ ether(s) of a C₃-C₉ glycol represent(s) from 1 to 40% by weight relative to the total weight of the ready-to-use dye composition.

30. Composition according to Claim 29, characterized in that the C₄-C₈ ether(s) of a C₂ glycol and/or the C₁-C₈ ether(s) of a C₃-C₉ glycol represent(s) from 5 to 30% by weight relative to the total weight of the ready-to-use dye composition.

31. Composition according to any one of the preceding claims, characterized in that the medium which is suitable for dyeing consists of water or a mixture of water and at least one organic solvent.

32. Composition according to any one of the preceding claims, characterized in that it has a pH of between 5 and 11.

33. Composition according to any one of the preceding claims, characterized in that it contains at least one peroxidase.

34. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that at least one ready-to-use dye composition as defined in any one of the preceding claims is applied to the said fibres, for a period which is sufficient to develop the desired coloration.

35. Process according to Claim 33,



characterized in that it includes a preliminary step which consists in separately storing, on the one hand, a composition (A1) comprising, in a medium which is suitable for dyeing, at least one oxidation base and at least one C₄-C₈ ether of a C₂ glycol and/or at least one C₁-C₈ ether of a C₃-C₉ glycol, and, on the other hand, a composition (B1) comprising, in a medium which is suitable for dyeing, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

36. Process according to Claim 33, characterized in that it includes a first step which consists in separately storing, on the one hand, a composition (A2) comprising, in a medium which is suitable for dyeing, at least one oxidation base, and, on the other hand, a composition (B2) comprising, in a medium which is suitable for dyeing, at least one C₄-C₈ ether of a C₂ glycol and/or at least one C₁-C₈ ether of a C₃-C₉ glycol, and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme, followed by mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

37. Multi-compartment dyeing device or "kit", characterized in that it includes a first compartment comprising composition (A1) as defined in Claim 35 and a second compartment comprising composition (B1) as defined in Claim 35.

38. Multi-compartment dyeing device or



"kit", characterized in that it includes a first compartment comprising composition (A2) as defined in Claim 36 and a second compartment comprising composition (B2) as defined in Claim 36.



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