

**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 first oxidation base chosen from para-phenylenediamine derivatives, double bases, ortho-aminophenols and heterocyclic bases, at least one second oxidation base chosen from para-aminophenols, at least one meta-aminophenol as coupler 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
5 obtained.

The so-called "permanent" coloration obtained 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
10 of the desired intensity and it must be able to withstand external agents (light, bad weather, washing, permanent-waving, perspiration, rubbing).

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

The oxidation dyeing of keratin fibres is
20 generally carried out in alkaline medium, in the presence of hydrogen peroxide. However, the use of 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
25 keratin fibres, which is not always desirable.

The oxidation dyeing of keratin fibres can 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 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 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 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 combining at least one first oxidation base chosen from para-phenylenediamine derivatives other than para-phenylenediamine, double bases, ortho-aminophenols and heterocyclic bases, at least one second oxidation base chosen from para-aminophenols, at least one meta-aminophenol as coupler and at least one enzyme of 2-electron oxidoreductase type in the presence of at

least one donor for the said enzyme.

This discovery forms the basis of the present invention.

A first subject of the invention is thus a
5 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 first oxidation base chosen from para-
10 phenylenediamine derivatives other than para-
phenylenediamine, double bases, ortho-aminophenols and
heterocyclic bases,
- at least one second oxidation base chosen from para-
aminophenols,
- 15 - at least one meta-aminophenol as coupler,
- at least one enzyme of 2-electron oxidoreductase
type, and
- at least one donor for the said enzyme.

The ready-to-use dye composition in
20 accordance with the invention leads to intense
relatively unselective colorations with excellent
properties of resistance both to atmospheric agents
such as light and bad weather and to perspiration and
the various treatments to which the hair may be
25 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.

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
5 oxidases, pyruvate oxidases and uricases.

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

The 2-electron oxidoreductase(s) can be used in pure crystalline form or in a form diluted in a
15 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) from 0.01 to 20% by weight approximately relative to
20 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.

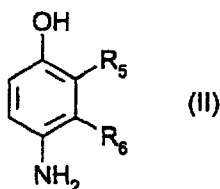
According to the invention, the term donor is understood to refer to the various substrates involved
25 in the functioning of the said 2-electron oxidoreductase(s).

The nature of the donor (or substrate) for the said enzyme varies depending on the nature of the

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
 5 donors for the glycerol oxidases, mention may be made 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
 10 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) from 0.01 to 20% by weight approximately relative to
 15 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.

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



in which:

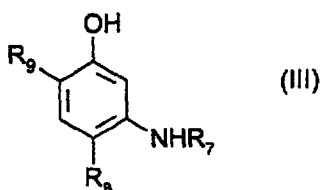
- R_5 represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, (C_1-C_4) alkoxy(C_1-C_4)alkyl, C_1-C_4 aminoalkyl or hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical,
 - 5 - R_6 represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 aminoalkyl, cyano(C_1-C_4)alkyl or (C_1-C_4) alkoxy(C_1-C_4)alkyl radical,
- it being understood that at least one of the radicals R_5
 10 or R_6 represents a hydrogen atom.

Among the para-aminophenols of formula (II) 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, 4-amino-2-(β -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

20 The para-aminophenol(s) which can be used as second oxidation base preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the ready-to-use dye composition in accordance with the invention, and even more preferably
 25 from 0.005 to 6% by weight approximately relative to this weight.

The meta-aminophenol(s) which can be used as coupler in the ready-to-use dye composition in accordance with the invention is (are) preferably chosen

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



in which:

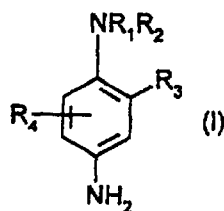
- R_7 represents a hydrogen atom or a C_1 - C_4 alkyl, C_1 - C_4 monohydroxyalkyl or C_2 - C_4 polyhydroxyalkyl radical,
- R_8 represents a hydrogen atom, a C_1 - C_4 alkyl or C_1 - C_4 alkoxy radical or a halogen atom chosen from chlorine, bromine and fluorine,
- R_9 represents a hydrogen atom or a C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 monohydroxyalkyl, C_2 - C_4 polyhydroxyalkyl, C_1 - C_4 monohydroxyalkoxy or C_2 - C_4 polyhydroxyalkoxy radical.

Among the meta-aminophenols of formula (III) above, mention may be made more particularly of meta-aminophenol, 5-amino-2-methoxyphenol, 5-amino-2-(β -hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 5-N-(β -hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol and 5-(γ -hydroxypropylamino)-2-methylphenol, and the addition salts thereof with an acid.

The meta-aminophenol(s) which can be used as coupler preferably represent(s) from 0.0001 to 8% 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.

Among the para-phenylenediamine derivatives which can be used as first oxidation base in the ready-to-use dye composition 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:

- 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;
- R₂ 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 or a C₁-C₄ alkyl radical substituted with a nitrogenous group;
- R₃ represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₁-C₄ hydroxyalkoxy radical, an acetylamino(C₁-C₄)-

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;

5 it being understood that at least one of the radicals R_1 to R_4 is other than a hydrogen atom.

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
10 and ammonium radicals.

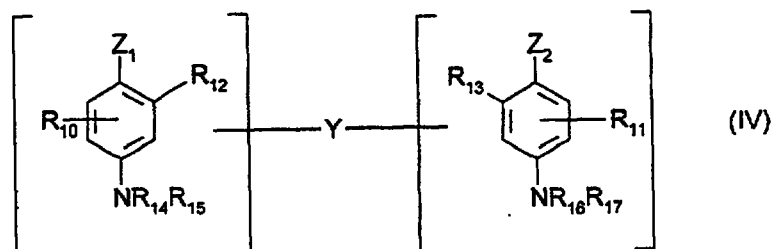
Among the para-phenylenediamine derivatives of formula (I) above, mention may be made more particularly of para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine,
15 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, 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-phenylene-
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diamine, N-(4'-aminophenyl)-para-phenylenediamine,
N-phenyl-para-phenylenediamine, 2- β -hydroxyethyloxy-
para-phenylenediamine, 2- β -acetylaminoethyloxy-para-
phenylenediamine and N-(β -methoxyethyl)-para-
5 phenylenediamine, and the addition salts thereof with an
acid.

Among the para-phenylenediamine derivatives of
formula (I) above, para-toluylenediamine, 2-isopropyl-
para-phenylenediamine, 2- β -hydroxyethyl-para-phenylene-
10 diamine, 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 -acetylaminoethyloxy-para-
15 phenylenediamine and the 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
20 and/or hydroxyl groups.

Among the double bases which can be used as
first oxidation base in the ready-to-use dye
composition in accordance with the invention, mention
may be made in particular of the compounds of formula
25 (IV) below, 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 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 C_1 - C_6 alkoxy radicals;
 - R_{10} and R_{11} 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 polyhydroxyalkyl radical, a C_1 - C_4 aminoalkyl radical or a linker arm Y;
 - R_{12} , R_{13} , R_{14} , R_{15} , R_{16} and R_{17} , 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 (IV) contain only one linker arm Y per molecule.

Among the nitrogenous groups of formula (IV) 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 (IV) above,
5 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)-
10 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
15 acid.

Among these double bases of formula (IV), N,N'-bis(β -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
20 with an acid, are particularly preferred.

Among the ortho-aminophenols which can be used as first oxidation base in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of 2-aminophenol,
25 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

Among the heterocyclic bases which can be

used as first oxidation base in the dye composition in accordance with the invention, mention may be made more particularly of pyridine derivatives, pyrimidine derivatives, pyrazole derivatives and pyrazolo-
5 pyrimidine derivatives, and the addition salts thereof with an acid.

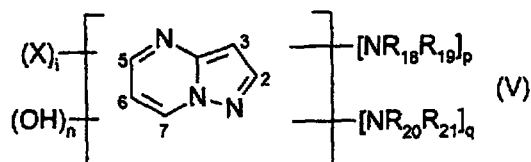
Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB 1,026,978 and GB 1,153,196,
10 such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β -methoxyethyl)amino-3-amino-6-methoxypyridine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

15 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-tetraamino-
20 pyrimidine, 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
25 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-di-
 5 methyl-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-ethyl-3-methylpyrazole, 4,5-diamino-
 10 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-
 15 ethyl)amino-1,3-dimethylpyrazole, 3,4,5-triamino-
 pyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-
 1-methyl-4-methylaminopyrazole and 3,5-diamino-
 4-(β -hydroxyethyl)amino-1-methylpyrazole, and the
 addition salts thereof with an acid.

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



in which:

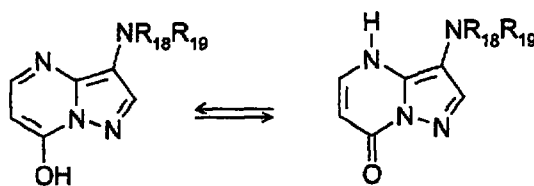
- R_{18} , R_{19} , R_{20} and R_{21} , which may be identical or different, denote a hydrogen atom, a C_1 - C_4 alkyl radical, an aryl radical, a C_1 - C_4 hydroxyalkyl radical, a C_2 - C_4 polyhydroxyalkyl radical, a $(C_1$ - C_4)alkoxy(C_1 - C_4)-alkyl radical, a C_1 - C_4 aminoalkyl radical (it being 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(C_1 - C_4)alkyl- or di[hydroxy(C_1 - C_4)alkyl]amino(C_1 - C_4)alkyl radical;
- the radicals X, 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 aminoalkyl 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 dialkyls to form a 5- or 6-membered carbon-based ring or a heterocycle), a hydroxy(C_1 - C_4)alkyl- or di-[hydroxy(C_1 - C_4)alkyl]amino(C_1 - C_4)alkyl radical, an amino radical, a $(C_1$ - C_4)alkyl- or di[(C_1 - C_4)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;
 - 5 - 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 $NR_{18}R_{19}$ and $NR_{20}R_{21}$ occupy the (2,3); (5,6);
 - 10 (6,7); (3,5) or (3,7) positions;
 - when $p + q$ is equal to 1, then n is equal to 1 and the group $NR_{18}R_{19}$ (or $NR_{20}R_{21}$) 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

15 (V) 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

20 (V) 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;

- 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;
- 5 - 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol;
- 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol;
- 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 10 - 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 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.

15 The pyrazolo[1,5-a]pyrimidines of formula (V) above can be prepared by cyclization starting with an aminopyrazole, according to the syntheses described in the following references:

- EP 628559 Beiersdorf-Lilly.
- 20 - 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,
- 25 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.

The pyrazolo[1,5-a]pyrimidines of formula (V) 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), 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. Higarashi, H. Midorikawa, Bull. Chem. Soc. Japan, 47(2), 476, 1974.

The para-phenylenediamine derivative(s) and/or the double base(s) and/or the ortho-aminophenol(s) and/or the heterocyclic base(s) which can be used as first oxidation base preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the ready-to-use dye composition according to 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 additional couplers other than meta-aminophenols used according to the invention and/or one or more direct dyes, in particular in order to modify the shades or to enrich them with glints.

Among the couplers which can be present

additionally in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of meta-phenylenediamines, meta-diphenols and heterocyclic couplers, and the addition salts thereof with an acid.

When they are present, these additional couplers preferably represent 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 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.

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 or a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently soluble in water. By way of organic solvents, mention may be made, for example, of C₁-C₄ alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether,

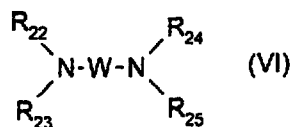
and aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

The solvents can be present in proportions preferably of between 1 and 40% by weight approximately
5 relative to the total weight of the ready-to-use dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the ready-to-use composition in accordance with the invention is chosen such that the
10 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
15 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,
20 tartaric acid, citric acid or lactic acid, and sulphonic acids.

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



in which W is a propylene residue optionally substituted with a hydroxyl group or a C₁-C₄ alkyl radical; R₂₂, R₂₃, R₂₄ and R₂₅, which may be identical or 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 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
5 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 dyes and the 2-electron oxidoreductase(s) are present in the same ready-to-use
10 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
15 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
20 the desired coloration, after which the fibres are 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
25 and even more precisely between 5 and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step which consists in separately storing, on the one hand,

a composition (A) comprising, in a medium which is suitable for dyeing, at least one first oxidation base chosen from para-phenylenediamine derivatives, double bases, ortho-aminophenols and heterocyclic bases, at least one second oxidation base chosen from para-aminophenols, at least one meta-aminophenol as coupler, and, on the other hand, a composition (B) 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.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which comprises composition (A) as defined above and a second compartment of which comprises composition (B) as defined above. These devices can be equipped with means for delivering the 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 scope.

EXAMPLESDYEING EXAMPLES 1 and 2

The ready-to-use dye compositions below were prepared (contents in grams):

5	COMPOSITION	1	2
	2- β -Hydroxyethyl-para-phenylenediamine dihydrochloride (oxidation base)	0.45	0.45.
	para-Aminophenol (oxidation base)	0.1	0.1
	meta-Aminophenol (coupler)	0.1	-
10	2-Methyl-5-aminophenol (coupler)	-	0.13
	Uricase from <i>Arthrobacter globiformis</i> , at 20 international units (I.U.)/mg, sold by the company Sigma	1.5	1.5
	Uric acid	1.5	1.5
15	Common dye support (*)	(*)	(*)
	Demineralized water qs	100 g	100 g

(*): Common dye support:

- Ethanol 20.0 g
- Hydroxyethylcellulose sold under the name
- 20 Natrosol 250 HR[®] by the company Aqualon 1.0 g
- Poly(C₈-C₁₀)alkylglucoside as an aqueous solution containing 60% active material (A.M.) buffered with ammonium citrate (0.5%), sold under the name Oramix CG110[®] by the company
- 25 SEPPIC 8.0 g
- Monoethanolamine qs pH = 9.5

Each of the ready-to-use dye compositions described above was applied to locks of natural grey

hair containing 90% white hairs, for 30 minutes. The hair was then rinsed, washed with a standard shampoo and then dried.

The hair was dyed in the shades given in the
5 table below:

EXAMPLE	Shade obtained
1	Dark pearlescent blonde
2	Dark mahogany blonde

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 that it comprises, in a medium which is suitable for dyeing:
 - at least one first oxidation base chosen from para-phenylenediamine derivatives other than para-phenylenediamine, double bases, ortho-aminophenols and heterocyclic bases,
 - at least one second oxidation base chosen from para-aminophenols,
 - at least one meta-aminophenol as coupler,
 - 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 chosen from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.
3. Composition according to Claim 1 or 2, characterized in that the 2-electron 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



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

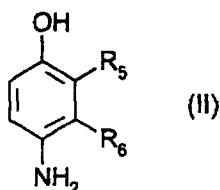
5. Composition according to Claim 4, characterized in that the 2-electron oxidoreductase(s) represent(s) from 0.1 to 5% by weight relative to the total weight of the ready-to-use dye composition.

6. Composition according to Claim 3, 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 para-aminophenols are chosen from the compounds corresponding to formula (II) below, and the addition salts thereof with an acid:



in which:



- R_5 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,
 - 5 - R_6 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, cyano(C_1 - C_4)alkyl or $(C_1$ - C_4)alkoxy(C_1 - C_4)alkyl radical,
- it being understood that at least one of the radicals R_5 or R_6 represents a hydrogen atom.
- 10

10. Composition according to Claim 9, characterized in that the para-aminophenols of formula (II) 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, 4-amino-2-(β -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

15

20

11. Composition according to any one of the preceding claims, characterized in that the para-aminophenol(s) represent(s) from 0.0005 to 12% by weight relative to the total weight of the ready-to-use dye composition.

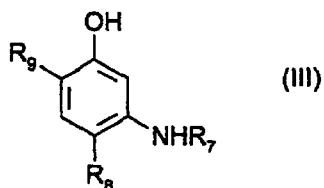
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12. Composition according to Claim 11, characterized in that the para-aminophenol(s) represent(s) from 0.005 to 6% by weight relative to the



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

13. Composition according to any one of the preceding claims, characterized in that the meta-aminophenols are chosen from the compounds of formula (III) below, and the addition salts thereof with an acid:



in which:

- R₇ represents a hydrogen atom or a C₁-C₄ alkyl, C₁-C₄ monohydroxyalkyl or C₂-C₄ polyhydroxyalkyl radical,
- R₈ represents a hydrogen atom, a C₁-C₄ alkyl or C₁-C₄ alkoxy radical or a halogen atom chosen from chlorine, bromine and fluorine,
- R₉ represents a hydrogen atom or a C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ monohydroxyalkyl, C₂-C₄ polyhydroxyalkyl, C₁-C₄ monohydroxyalkoxy or C₂-C₄ polyhydroxyalkoxy radical.

14. Composition according to Claim 13, characterized in that the meta-aminophenols of formula (III) are chosen from meta-aminophenol, 5-amino-2-methoxyphenol, 5-amino-3-(β-hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 5-N-(β-hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-

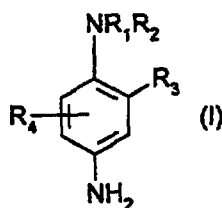


amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol and 5-(γ -hydroxypropylamino)-2-methylphenol and the addition salts thereof with an acid.

5 15. Composition according to any one of the preceding claims, characterised in that the meta-aminophenol(s) represent(s) from 0.0001 to 8% by weight relative to the total weight of the ready-to-use dye composition.

10 16. Composition according to Claim 15, characterized in that the meta-aminophenol(s) represent(s) from 0.005 to 5% by weight relative to the total weight of the dye composition.

15 17. Composition according to any one of the preceding claims, characterized in that the para-phenylenediamine derivatives are chosen from the compounds of formula (I) below, and the addition salts thereof with an acid:



in which:

20 - 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



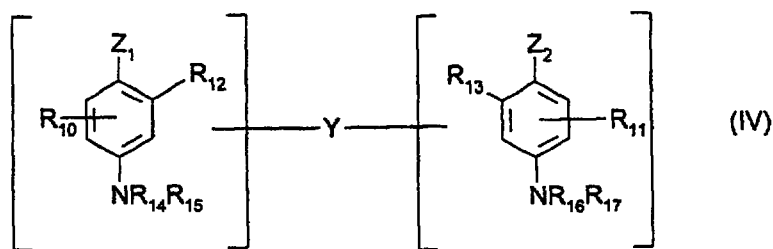
- group, a phenyl radical or a 4'-aminophenyl radical;
- R_2 represents a hydrogen atom, a C_1 - C_4 alkyl radical, a C_1 - C_4 monohydroxyalkyl radical, a C_2 - C_4 polyhydroxyalkyl radical, a $(C_1$ - $C_4)$ alkoxy(C_1 - C_4)alkyl radical or a C_1 - C_4 alkyl radical substituted with a nitrogenous 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;
- it being understood that at least one of the radicals R_1 to R_4 is other than a hydrogen atom.

18. Composition according to Claim 17, characterized in that the para-phenylenediamine derivatives of formula (I) are chosen from 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 -hydroxy-



ethyl)aniline, 2- β -hydroxyethyl-para-phenylenediamine,
 2-fluoro-para-phenylenediamine, 2-isopropyl-para-
 phenylenediamine, N-(β -hydroxypropyl)-para-phenylene-
 diamine, 2-hydroxymethyl-para-phenylenediamine,
 5 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-
 10 phenylenediamine, 2- β -acetylaminioethyloxy-para-
 phenylenediamine and N-(β -methoxyethyl)-para-
 phenylenediamine, and the addition salts thereof with
 an acid.

19. Composition according to any one of the
 15 preceding claims, characterized in that the double
 bases are chosen from the compounds of formula (IV)
 below, and the addition salts thereof with an acid:



in which:

- Z_1 and Z_2 , which may be identical or different,
 20 represent a hydroxyl or $-\text{NH}_2$ 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

5 optionally substituted with one or more hydroxyl or C_1 - C_6 alkoxy radicals;

- R_{10} and R_{11} 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 polyhydroxyalkyl radical, a C_1 - C_4 aminoalkyl

10 radical or a linker arm Y;

- R_{12} , R_{13} , R_{14} , R_{15} , R_{16} and R_{17} , 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 (IV)

15 contain only one linker arm Y per molecule.

20. Composition according to Claim 19, characterized in that the double bases of formula (IV) 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,

20 N,N' -bis(4-aminophenyl)tetramethylenediamine, N,N' -bis(β -hydroxyethyl)- N,N' -bis(4-aminophenyl)-tetramethylenediamine, N,N' -bis(4-methylaminophenyl)-tetramethylenediamine, N,N' -bis(ethyl)- N,N' -bis(4'-

25 amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

21. Composition according to any one of the



preceding claims, characterized in that the ortho-aminophenols are chosen from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an
5 acid.

22. Composition according to any one of the preceding claims, characterized in that the heterocyclic bases are chosen from pyridine derivatives, pyrimidine derivatives, pyrazole
10 derivatives and pyrazolopyrimidine derivatives, and the addition salts thereof with an acid.

23. Composition according to any one of the preceding claims, characterized in that the para-phenylenediamine derivative(s) and/or the double
15 base(s) and/or the ortho-aminophenol(s) and/or the heterocyclic base(s) represent(s) from 0.0005 to 12% by weight relative to the total weight of the ready-to-use dye composition.

24. Composition according to Claim 23,
20 characterized in that the para-phenylenediamine derivative(s) and/or the double base(s) and/or the ortho-aminophenol(s) and/or the heterocyclic base(s) represent(s) from 0.005 to 6% by weight relative to the total weight of the ready-to-use dye composition.

25 25. 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.

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

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

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

29. 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
15 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.

30. Process according to Claim 29, characterized in that it includes a preliminary step
20 which consists in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one first oxidation base chosen from para-phenylenediamine derivatives, double bases, ortho-aminophenols and heterocyclic bases, at
25 least one second oxidation base chosen from para-aminophenols, at least one meta-aminophenol as coupler, and, on the other hand, a composition (B) 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.

- 5 31. Multi-compartment dyeing device or "kit", characterized in that it includes a first compartment comprising composition (A) as defined in Claim 30 and a second compartment comprising composition (B) as defined in Claim 30.

