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Keratinous fibre oxidation dyeing composition containing a laccase and dyeing method using same

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<p>(54) Title: KERATINOUS FIBRE OXIDATION DYEING COMPOSITION CONTAINING A LACCASE AND DYEING METHOD USING SAME</p> <p>(54) Titre: COMPOSITION DE TEINTURE D'OXYDATION DES FIBRES KERATINIQUES CONTENANT UNE LACCASE ET PROCEDE DE TEINTURE METTANT EN OEUVRE CETTE COMPOSITION</p> <p>(57) Abstract</p> <p>The invention concerns a ready-to-use composition for oxidation dyeing of keratinous fibres, and in particular human keratinous fibres such as hair comprising, in a suitable dyeing medium, 2-amino 4-N-(β-hydroxyethyl)amino anisole as coupling agent, and at least an enzyme such as laccase, as well as the dyeing method using said composition.</p> <p>(57) Abrégé</p> <p>L'invention a pour objet une composition prête à l'emploi pour la teinture d'oxydation des fibres kératiniques, et en particulier des fibres kératiniques humaines telles que les cheveux comprenant, dans un milieu approprié pour la teinture, au moins une base d'oxydation, du 2-amino 4-N-(β-hydroxyéthyl)amino anisole à titre de coupleur, et au moins une enzyme de type laccase, ainsi que le procédé de teinture mettant en oeuvre cette composition.</p>

COMPOSITION FOR THE OXIDATION DYEING OF KERATINOUS
FIBRES CONTAINING A LACCASE AND DYEING METHOD USING
THIS COMPOSITION

The subject of the invention is a composition
5 for the oxidation dyeing of keratinous fibres, and in
particular of human keratinous fibres such as hair,
comprising, in a medium appropriate for dyeing, at
least one oxidation base, 2-amino-4-N-(β -hydroxy-
ethyl)aminoanisoole as coupler, and at least one enzyme
10 of the laccase type, as well as the dyeing method using
this composition.

It is known to dye keratinous fibres, and in
particular human hair, with dyeing compositions
containing oxidation dye precursors, in particular
15 ortho- and para-phenylenediamines, ortho- or para-
aminophenols, heterocyclic bases generally called
oxidation bases. The oxidation dye precursors,
(oxidation bases), are colourless or weakly coloured
compounds which, combined with oxidizing products, can
20 give rise to dye and coloured compounds 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
25 being chosen in particular from aromatic meta-diamines,
meta-aminophenols, meta-diphenols and certain
heterocyclic compounds.



The variety of molecules used in oxidation bases and couplers allows a rich palette of colours to be obtained.

The so-called "permanent" colour obtained by
5 means of these oxidation dyes should moreover satisfy a number of requirements. Thus, it should have no drawbacks from the toxicological point of view, it should make it possible to obtain shades of the desired intensity and it should exhibit good resistance towards
10 external agents (light, adverse weather conditions, washing, permanent waving, perspiration, rubbing).

The dyes should also make it possible to cover grey hair, and thus should be the least selective possible, that is to say they should make it possible
15 to obtain the smallest possible differences in colour all along the same keratinous fibre, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

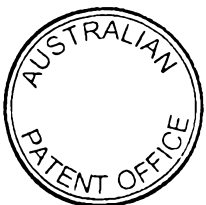
The oxidation dyeing of keratinous fibres is
20 generally carried out in an alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide has the disadvantage of causing substantial degradation of the fibres, as well as decolouring of the keratinous
25 fibres which is not always desirable.

The oxidation dyeing of keratinous fibres can also be carried out with the aid of oxidizing systems different from hydrogen peroxide such as enzymatic



systems. Thus, it has already been proposed in Patent
US 3,251,742, Patent Applications FR-A-2,112,549,
FR-A-2,694,018, EP-A-0,504,005, WO95/07988, WO95/33836,
WO95/33837, WO96/00290, WO97/19998 and WO97/19999 to
5 dye keratinous fibres with compositions comprising at
least one oxidation dye, or at least one melanin
precursor, in combination with enzymes of the laccase
type, the said compositions being brought into contact
with atmospheric oxygen. These dyeing formulations,
10 although used under conditions which do not cause
degradation of the keratinous fibres comparable to that
caused by dyeings carried out in the presence of
hydrogen peroxide, lead to colours which are still
inadequate both from the point of view of homogeneity
15 of the colour distributed along the fibre (unison),
from the point of view of chromaticity (luminosity) and
of the dyeing power.

Now, the applicant has now just discovered
that it is possible to obtain novel dyes which are
20 capable of giving intense and chromatic colours,
without causing significant degradation of the
keratinous fibres, which are not very selective and
which are quite resistant to various attacks to which
the fibres may be subjected, by combining at least one
25 oxidation base, 2-amino-4-N-(β -hydroxyethyl)-
aminoanisoole as coupler, and at least one enzyme of the
laccase type.



This discovery forms the basis of the present invention.

The first subject of the invention is therefore a ready-to-use composition for the oxidation
5 dyeing of keratinous fibres, and in particular human keratinous fibres such as hair, characterized in that it comprises, in a medium appropriate for dyeing:

- at least one oxidation base,
- 2-amino-4-N-(β -hydroxyethyl)aminoanisoole and/or at
10 least one of its addition salts with an acid as coupler,
- at least one enzyme of the laccase type.

The ready-to-use dyeing composition in accordance with the invention gives intense colours
15 which exhibit low selectivity and excellent properties of resistance both to atmospheric agents such as light and adverse weather conditions and to perspiration and various treatments to which the hair may be subjected (washing, permanent deformation).

20 The subject of the invention is also a method for the oxidation dyeing of keratinous fibres using this ready-to-use dyeing composition.

The laccase(s) used in the ready-to-use dye composition in accordance with the invention may be
25 chosen in particular from laccases of plant origin, animal origin, fungal origin (yeasts, moulds, fungi) or bacterial origin, organisms which may be of mono- or pluricellular origin. The laccase(s) used in the ready-



to-use dyeing composition in accordance with the invention can also be obtained by biotechnology.

Among the laccases of plant origin which can be used according to the invention, there may be mentioned the laccases produced by plants which perform chlorophyll synthesis such as those indicated in Patent Application FR-A-2,694,018.

There may be mentioned in particular the laccases present in the extracts of Anacardiaceae such as for example the extracts of *Magnifera indica*, *Schinus molle* or *Pleiogynium timoriense*, in the extracts of Podocarpaceae, *Rosmarinus off.*, *Solanum tuberosum*, *Iris sp.*, *Coffea sp.*, *Daucus carota*, *Vinca minor*, *Persea americana*, *Catharethus roseus*, *Musa sp.*, *Malus pumila*, *Gingko biloba*, *Monotropa hypopithys* (Indian pipe), *Aesculus sp.*, *Acer pseudoplatanus*, *Prunus persica* and *Pistacia palaestina*.

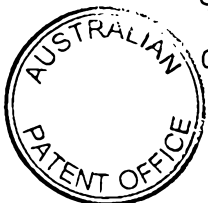
Among the laccases of fungal origin, optionally obtained by biotechnology, which can be used according to the invention, there may be mentioned the laccase(s) derived from *Polyporus versicolor*, *Rhizoctonia praticola* and *Rhus vernicifera* as described for examples in Patent Applications FR-A-2,112,549 and EP-A-504005, the laccases described in Patent Applications W095/07988, W095/33836, W095/33837, W096/00290, W097/19998 and W097/19999, whose content is an integral part of the present description, such as for example the laccase(s) derived



from *Scytalidium*, *Polyporus pinsitus*, *Myceliophthora thermophila*, *Rhizoctonia solani*, *Pyricularia orizae*, and variants thereof. There may also be mentioned the laccase(s) derived from *Trametes versicolor*, *Fomes*
5 *fomentarius*, *Chaetomium thermophile*, *Neurospora crassa*, *Colorius versicol*, *Botrytis cinerea*, *Rigidoporus lignosus*, *Phellinus noxius*, *Pleurotus ostreatus*, *Aspergillus nidulans*, *Podospora anserina*, *Agaricus bisporus*, *Ganoderma lucidum*, *Glomerella cingulata*,
10 *Lactarius piperatus*, *Russula delica*, *Heterobasidion annosum*, *Thelephora terrestris*, *Cladosporium cladosporioides*, *Cerrena unicolor*, *Coriolus hirsutus*, *Ceriporiopsis subvermispora*, *Coprinus cinereus*, *Panaeolus papilionaceus*, *Panaeolus sphinctrinus*,
15 *Schizophyllum commune*, *Dichomitius squalens*, and variants thereof.

The laccases of fungal origin optionally obtained by biotechnology will be preferably chosen.

The enzymatic activity of the laccases used
20 in accordance with the invention and which have syringaldazine among their substrates can be defined from the oxidation of syringaldazine under aerobic conditions. The Lacu unit corresponds to the quantity of enzyme catalysing the conversion of 1 mmol of
25 syringaldazine per minute at a pH of 5.5 and at a temperature of 30°C. The unit U corresponds to the quantity of enzyme producing a delta absorbance of
0.001 per minute, at a wavelength of 530 nm, using



syringaldazine as substrate, at 30°C and at a pH of 6.5. The enzymatic activity of the laccases of the invention can also be defined from the oxidation of para-phenylenediamine. The lacu unit corresponds to the
5 quantity of enzyme producing a delta absorbance of 0.001 per minute, at a wavelength of 496.5 nm, using para-phenylenediamine as substrate (64 mM), at 30°C and at a pH of 5.

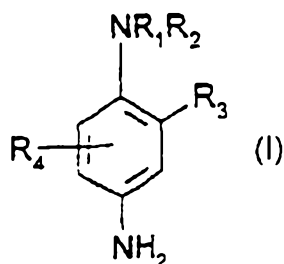
According to the invention, it is preferable
10 to determine the enzymatic activity in lacu units.

The quantity of laccase(s) present in the ready-to-use dyeing composition in accordance with the invention will vary according to the nature of the laccase(s) used. Preferably, the quantity of laccase(s)
15 is between 0.5 and 200 Lacu approximately that is to say between 10,000 and 4×10^6 U units approximately or that is to say between 20 and 2×10^6 lacu units, per 100 g of dyeing composition.

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

Among the para-phenylenediamines which can be
25 used as oxidation base in the dyeing composition in accordance with the invention, there may be mentioned in particular the compounds of the following formula (I) and their addition salts with an acid:

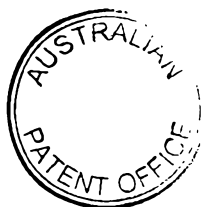




in which:

- R₁ represents a hydrogen atom, a C₁-C₄ alkyl radical, a monohydroxy(C₁-C₄ alkyl) radical, a polyhydroxy-
5 (C₂-C₄ alkyl) radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical, a C₁-C₄ alkyl radical substituted with a nitrogen-containing group, a phenyl radical or a 4'-aminophenyl radical;
- R₂ represents a hydrogen atom, a C₁-C₄ alkyl radical, a monohydroxy(C₁-C₄ alkyl) radical, a
10 polyhydroxy(C₂-C₄ alkyl) radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical or a C₁-C₄ alkyl radical substituted with a nitrogen-containing group;
- R₃ represents a hydrogen atom, a halogen atom such as
15 a chlorine, bromine, iodine or fluorine atom, a C₁-C₄ alkyl radical, a monohydroxy(C₁-C₄ alkyl) radical, a hydroxy(C₁-C₄ alkoxy) radical, an acetylamino(C₁-C₄ alkoxy) radical, a mesylamino(C₁-C₄ alkoxy) radical or a carbamoylamino(C₁-C₄ alkoxy) radical,
- R₄ represents a hydrogen or halogen atom or a C₁-C₄
20 alkyl radical.

Among the nitrogen-containing groups of formula (I) above, there may be mentioned in particular the amino, mono(C₁-C₄)alkylamino, (C₁-C₄)dialkylamino,



(C₁-C₄)trialkylamino, monohydroxy(C₁-C₄)alkylamino, imidazolinium and ammonium radicals.

Among the para-phenylenediamines of formula (I) above, there may be mentioned more particularly

5 para-phenylenediamine, para-tolylenediamine, 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,

10 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-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-

15 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,

20 N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethoxy-para-phenylenediamine, 2-β-acetylaminoethoxy-para-phenylenediamine, N-(β-methoxyethyl)-para-

25 phenylenediamine, and their addition salts with an acid.

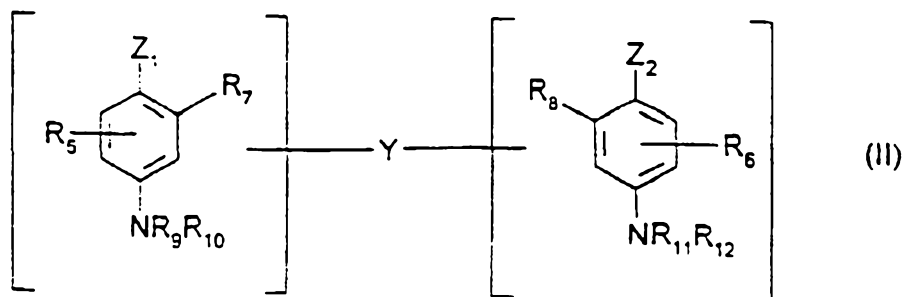
Among the para-phenylenediamines of formula (I) above, there are most particularly preferred para-



phenylenediamine, para-tolylenediamine, 2-isopropyl-
 para-phenylenediamine, 2- β -hydroxyethyl-para-
 phenylenediamine, 2- β -hydroxyethyloxy-para-phenylene-
 diamine, 2,6-dimethyl-para-phenylenediamine,
 5 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-
 phenylenediamine, N,N-bis(β -hydroxyethyl)-para-
 phenylenediamine, 2-chloro-para-phenylenediamine, 2- β -
 acetyl-aminoethyloxy-para-phenylenediamine, and their
 addition salts with an acid.

10 According to the invention, "double bases" is
 understood to mean the compounds containing at least
 two aromatic rings on which amino and/or hydroxyl
 groups are carried.

Among the double bases which can be used as
 15 oxidation bases in the dyeing compositions in
 accordance with the invention, there may be mentioned
 in particular the compounds corresponding to the
 following formula (II), and their addition salts with
 an acid:



20

in which:

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



substituted with a C₁-C₄ alkyl radical or with a linking arm Y;

- the linking arm Y represents a linear or branched alkylene chain comprising from 1 to 14 carbon atoms, which may be interrupted by or which may end with one or more nitrogen-containing groups and/or one or more heteroatoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C₁-C₆ alkoxy radicals;

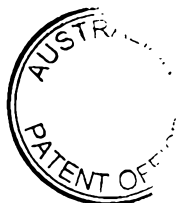
10 - R₅ and R₆ represent a hydrogen or halogen atom, a C₁-C₄ alkyl radical, a monohydroxy(C₁-C₄ alkyl) radical, a polyhydroxy(C₂-C₄ alkyl) radical, an amino(C₁-C₄ alkyl) radical or a linking arm Y;

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

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

Among the nitrogen-containing groups of formula (II) above, there may be mentioned in particular the amino, mono(C₁-C₄)alkylamino, (C₁-C₄)dialkylamino, (C₁-C₄)trialkylamino, monohydroxy(C₁-C₄)alkylamino, imidazolinium and ammonium radicals.

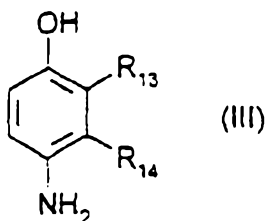
25 Among the double bases of formulae (II) above, there may be mentioned more particularly N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4' -



aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)-
 tetramethylenediamine, N,N'-bis(β -hydroxyethyl)-N,N'-
 bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-
 methylaminophenyl)tetramethylenediamine, N,N'-
 5 bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylene-
 diamine, 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane,
 and their addition salts with an acid.

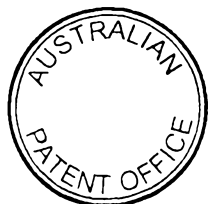
Among these double bases of formula (II),
 N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-
 10 diaminopropanol, 1,8-bis(2,5-diaminophenoxy)-3,5-
 dioxaoctane or one of their addition salts with an acid
 are particularly preferred.

Among the para-aminophenols which can be used
 as oxidation bases in the dyeing compositions in
 15 accordance with the invention, there may be mentioned
 in particular the compounds corresponding to the
 following formula (III), and their addition salts with
 an acid:



20 in which:

- R₁₃ represents a hydrogen or halogen atom, a C₁-C₄
 alkyl, monohydroxy(C₁-C₄ alkyl), (C₁-C₄)alkoxy(C₁-C₄)-
 alkyl, amino(C₁-C₄ alkyl) or hydroxy(C₁-C₄)alkylamino-
 (C₁-C₄ alkyl) radical,



- R₁₄ represents a hydrogen or halogen atom, a C₁-C₄ alkyl, monohydroxy(C₁-C₄ alkyl), polyhydroxy(C₂-C₄ alkyl), amino(C₁-C₄ alkyl), cyano(C₁-C₄ alkyl) or (C₁-C₄)alkoxy(C₁-C₄)alkyl radical,

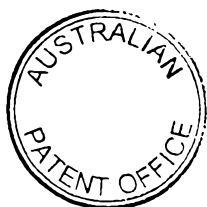
5 it being understood that at least one of the radicals R₁₃ or R₁₄ represents a hydrogen atom.

Among the para-aminophenols of formula (III) above, there may be mentioned more particularly para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-
10 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, 4-amino-2-fluorophenol, and their addition salts with an acid.

15 Among the ortho-aminophenols which can be used as oxidation bases in the dyeing compositions in accordance with the invention, there may be mentioned more particularly 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-
20 aminophenol, and their addition salts with an acid.

Among the heterocyclic bases which can be used as oxidation bases in the dyeing compositions in accordance with the invention, there may be mentioned more particularly pyridine derivatives, pyrimidine
25 derivatives, pyrazole derivatives, pyrazolopyrimidine derivatives, and their addition salts with an acid.

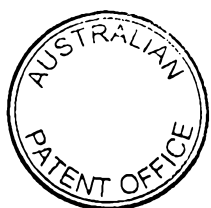
Among the pyridine derivatives, there may be mentioned more particularly the compounds described for



example in Patents GB 1,026,978 and GB 1,153,196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β -methoxyethyl)amino-3-amino-6-methoxypyridine,
5 3,4-diaminopyridine, and their addition salts with an acid.

Among the pyrimidine derivatives, there may be mentioned more particularly the compounds described for example in German Patent DE 2,359,399 or Japanese
10 Patents JP 88-169,571 and JP 91-333,495 or Patent Application WO 96/15765, such as 2,4,5,6-tetra-aminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine, and their
15 addition salts with an acid.

Among the pyrazole derivatives, there may be mentioned more particularly 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
20 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-
25 hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methyl-pyrazole, 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'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylamino-pyrazole, 3,5-diamino-4-(β -hydroxyethyl)amino-1-methylpyrazole, and their addition salts with an acid.

Among the pyrazolopyrimidine derivatives, there may be mentioned more particularly the compounds described in Patent Application FR-A-2,750,048, among which there may be mentioned:

- 15 - 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;
- 20 - 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
- 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol;
- 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol;
- 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol;
- 25 - 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxyethyl)amino]ethanol;
- 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;



- 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

and their addition salts and their tautomeric forms, when a tautomeric equilibrium exists.

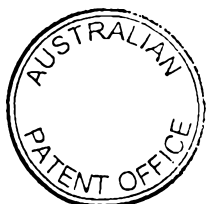
5 The oxidation base(s) preferably represent from 0.0005 to 12% by weight approximately of the total weight of the dyeing composition in accordance with the invention, and still more preferably from 0.005 to 6% by weight approximately of this weight.

10 The 2-amino-4-N-(β -hydroxyethyl)aminoanisole and/or the or its addition salts with an acid preferably represent from 0.0001 to 8% by weight approximately of the total weight of the dyeing composition, and still more preferably from 0.005 to 5%
15 by weight approximately of this weight.

The dyeing composition in accordance with the invention may contain one or more other couplers different from 2-amino-4-N-(β -hydroxyethyl)aminoanisole and/or direct dyes in particular in order to modify the
20 shades or to increase their shimmer.

Among the couplers which can additionally be present in the ready-to-use dyeing composition in accordance with the invention, there may be mentioned in particular meta-phenylenediamines, meta-
25 aminophenols, meta-diphenols, and their addition salts with an acid.

When they are present these additional couplers preferably represent from 0.0001 to 10% by



weight approximately of the total weight of the ready-to-use dyeing composition, and more preferably from 0.005 to 5% by weight approximately of this weight.

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

10 The medium appropriate for dyeing (or carrier) of the ready-to-use dyeing composition in accordance with the invention generally consists of water or of a mixture of water and of at least one organic solvent in order to solubilize the compounds
15 which might not be sufficiently soluble in water.

The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the laccase is sufficient. It is generally between 4 and 11 approximately, and
20 preferably between 6 and 9 approximately. It may be adjusted to the desired value using acidifying or alkalinizing agents normally used in dyeing keratinous fibres.

The ready-to-use dyeing composition in
25 accordance with the invention may also contain various adjuvants conventionally used in hair dyeing compositions, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures

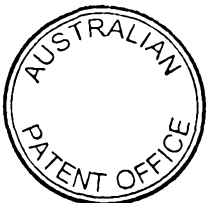


thereof, polymers, antioxidants, enzymes different from the laccases used in accordance with the invention, such as for examples peroxidases or oxidoreductases containing 2 electrons, penetrating agents, 5 sequestering agents, perfumes, buffers, dispersing agents, thickening agents, film-forming agents, preservatives, opacifying agents or vitamins.

Of course, persons skilled in the art will be careful to choose this or these optional additional 10 compounds such that the advantageous properties intrinsically attached to the ready-to-use dyeing composition in accordance with the invention are not, or substantially not, impaired by the addition(s) envisaged.

15 The ready-to-use dyeing composition in accordance with the invention can be provided in various forms, such as in the form of liquids, creams, gels, optionally pressurized, or in any other form appropriate for dyeing keratinous fibres, in particular 20 human hair. In this case, the oxidation dyes and the enzyme(s) of laccase type are present in the same ready-to-use composition, and consequently the said composition should be free of gaseous oxygen, so as to avoid any premature oxidation of the oxidation dye(s).

25 The subject of the invention is also a method of dyeing keratinous fibres, and in particular human keratinous fibres such as hair, using the ready-to-use dyeing composition as defined above.



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

The time necessary for the development of the colour on the keratinous fibres is generally between 3 and 60 minutes and still more precisely 5 and
40 minutes.

10 According to one particular embodiment of the invention, the method comprises a preliminary step consisting in storing in a separate form, on the one hand, a composition (A) comprising, in a medium appropriate for dyeing, at least one oxidation base and
15 2-amino-4-N-(β -hydroxyethyl)aminoanisole and/or at least one of its addition salts with an acid, on the other hand, a composition (B) containing, in a medium appropriate for dyeing, at least one enzyme of the laccase type, and then in mixing them at the time of
20 use before applying this mixture to the keratinous fibres.

Another subject of the invention is a multi-compartment device or dyeing (kit) or any other multi-compartment packaging system in which a first
25 compartment contains the composition (A) as defined above and a second compartment contains a composition (B) as defined above. These devices may be equipped with a means which makes it possible to deliver the



desired mixture to the hair, such as the devices described in Patent FR-2,586,913 in the name of the applicant.

The example which follows is intended to illustrate the invention without limiting the scope as a result.

DYEING EXAMPLE

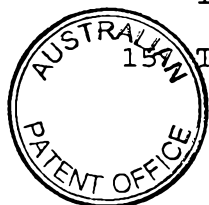
The following dyeing composition was prepared:

10

- para-Phenylenediamine	0.2 g
- 2-Amino-4-N-(β -hydroxyethyl)aminoanisole dihydrochloride	0.25 g
- Laccase derived from <i>Rhus vernicifera</i> containing 180 units/mg sold by the company Sigma	1.8 g
- (C ₈ -C ₁₀)Alkyl polyglucoside in aqueous solution containing 60% of active substance (AS) sold under the name ORAMIX CG110 [®] by the company SEPPIC	8.0 g
- Ethanol	20 g
- pH agent qs	pH 6.5
- Demineralized water qs	100 g

The ready-to-use dyeing composition described above was applied to locks of natural grey hair which is 90% white for 40 minutes, at a temperature of 30°C.

The hair was then rinsed, and then dried.



The hair was dyed in a blue grey shade.

In the dyeing composition described above, Rhus vernicifera laccase at 180 units/mg, sold by the company Sigma can be replaced by 1.0 g of Pyricularia orizae laccase at 100 units/mg sold by the company ICN.

Throughout this specification and the claims, the words "comprise", "comprises" and "comprising" are used in a non-exclusive sense".



CLAIMS

1. Ready-to-use composition for the oxidation dyeing of keratinous fibres, and in particular human keratinous fibres such as hair, 5 characterized in that it comprises, in a medium appropriate for dyeing:

- at least one oxidation base,
- 2-amino-4-N-(β -hydroxyethyl)aminoanisole and/or at least one of its addition salts with an acid as 10 coupler,
- at least one enzyme of the laccase type.

2. Composition according to Claim 1, characterized in that the laccase is chosen from laccases of plant origin, animal origin, fungal origin 15 or bacterial origin and from the laccases obtained by biotechnology.

3. Composition according to either of Claims 1 and 2, characterized in that the laccase is of plant origin and chosen from the laccases present in 20 the extracts of Anacardiaceae, Podocarpaceae, Rosmarinus off., Solanum tuberosum, Iris sp., Coffea sp., Daucus carrota, Vinca minor, Persea americana, Catharethus roseus, Musa sp., Malus pumila, Ginkgo biloba, Monotropa hypopithys (Indian pipe), Aesculus 25 sp., Acer pseudoplatanus, Prunus persica and Pistacia palaestina.



4. Composition according to Claim 1 or 2, characterized in that the laccase is of fungal origin or obtained by biotechnology.

5. Composition according to Claim 4,
5 characterized in that the laccase is chosen from the laccases derived from *Polyporus versicolor*, *Rhizoctonia praticola*, *Rhus vernicifera*, *Scytalidium*, *Polyporus pinsitus*, *Myceliophthora thermophila*, *Rhizoctonia solani*, *Pyricularia orizae*, *Trametes versicolor*, *Fomes*
10 *fomentarius*, *Chaetomium thermophile*, *Neurospora crassa*, *Colorius versicol*, *Botrytis cinerea*, *Rigidoporus lignosus*, *Phellinus noxius*, *Pleurotus ostreatus*, *Aspergillus nidulans*, *Podospora anserina*, *Agaricus bisporus*, *Ganoderma lucidum*, *Glomerella cingulata*,
15 *Lactarius piperatus*, *Russula delica*, *Heterobasidion annosum*, *Thelephora terrestris*, *Cladosporium cladosporioides*, *Cerrena unicolor*, *Coriolus hirsutus*, *Ceriporiopsis subvermispora*, *Coprinus cinereus*, *Panaeolus papilionaceus*, *Panaeolus sphinctrinus*,
20 *Schizophyllum commune*, *Dichomitius squalens*, and of variants thereof.

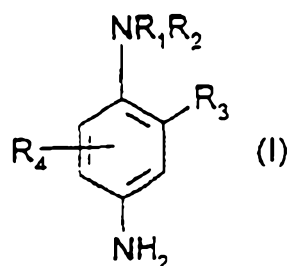
6. Composition according to any one of the preceding claims, characterized in that the quantity of laccase(s) is between 0.5 and 200 Lacu per 100 g of
25 dyeing composition.

7. Composition according to any one of the preceding claims, characterized in that the oxidation base(s) are chosen from para-phenylenediamines, double



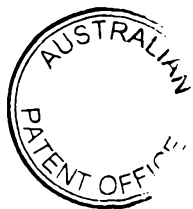
bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

8. Composition according to Claim 7, characterized in that the para-phenylenediamines are
5 chosen from the compounds of formula (I), and their addition salts with an acid:



in which:

- R₁ represents a hydrogen atom, a C₁-C₄ alkyl radical,
10 a monohydroxy(C₁-C₄ alkyl) radical, a polyhydroxy-(C₂-C₄ alkyl) radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical, a C₁-C₄ alkyl radical substituted with a nitrogen-containing group, a phenyl radical or a 4'-aminophenyl radical;
- 15 - R₂ represents a hydrogen atom, a C₁-C₄ alkyl radical, a monohydroxy(C₁-C₄ alkyl) radical, a polyhydroxy(C₂-C₄ alkyl) radical, a (C₁-C₄)alkoxy(C₁-C₄)alkyl radical or a C₁-C₄ alkyl radical substituted with a nitrogen-containing group;
- 20 - R₃ represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C₁-C₄ alkyl radical, a monohydroxy(C₁-C₄ alkyl) radical, a hydroxy(C₁-C₄ alkoxy) radical, an acetylamino(C₁-C₄



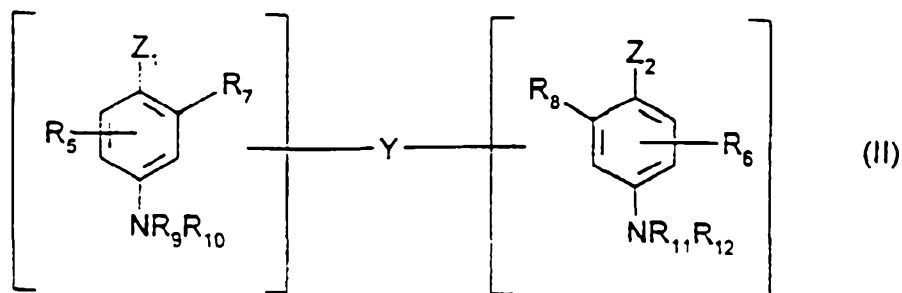
alkoxy) radical, a mesylamino(C₁-C₄ alkoxy) radical or a carbamoylamino(C₁-C₄ alkoxy) radical,
 - R₄ represents a hydrogen or halogen atom or a C₁-C₄ alkyl radical.

5 9. Composition according to Claim 8, characterized in that the para-phenylenediamines of formula (I) are chosen from para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-
 10 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-
 15 phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-
 phenylenediamine, N-(β-hydroxypropyl)-para-
 20 phenylenediamine, 2-hydroxymethyl-para-phenylene-diamine, 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-
 25 phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine, N-(β-methoxyethyl)-para-



phenylenediamine, and their addition salts with an acid.

10. Composition according to Claim 7, characterized in that the double bases are chosen from the compounds of formula (II), and their addition salts with an acid:



in which:

- Z_1 and Z_2 , which are 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 linking arm Y;
- the linking arm Y represents a linear or branched alkylene chain comprising from 1 to 14 carbon atoms, which may be interrupted by or which may end with one or more nitrogen-containing groups and/or one or more heteroatoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C_1 - C_6 alkoxy radicals;
- R_5 and R_6 represent a hydrogen or halogen atom, a C_1 - C_4 alkyl radical, a monohydroxy(C_1 - C_4 alkyl) radical, a polyhydroxy(C_2 - C_4 alkyl) radical, an amino(C_1 - C_4 alkyl) radical or a linking arm Y;

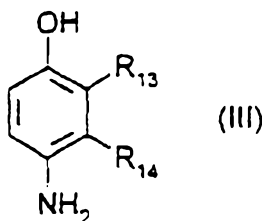


- R₇, R₈, R₉, R₁₀, R₁₁ and R₁₂, which are identical or different, represent a hydrogen atom, a linking arm Y or a C₁-C₄ alkyl radical;

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

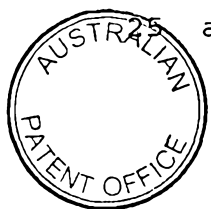
11. Composition according to Claim 10, characterized in that the double bases of formula (II) are chosen from N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine, 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and their addition salts with an acid.

12. Composition according to Claim 7, characterized in that the para-aminophenols are chosen from the compounds of formula (III), and their addition salts with an acid:



in which:

- R₁₃ represents a hydrogen or halogen atom, a C₁-C₄ alkyl, monohydroxy(C₁-C₄ alkyl), (C₁-C₄)alkoxy(C₁-C₄)-



alkyl, amino(C₁-C₄ alkyl) or hydroxy(C₁-C₄)alkylamino-(C₁-C₄ alkyl) radical,

- R₁₄ represents a hydrogen or halogen atom, a C₁-C₄ alkyl, monohydroxy(C₁-C₄ alkyl), polyhydroxy(C₂-C₄ alkyl), amino(C₁-C₄ alkyl), cyano(C₁-C₄ alkyl) or (C₁-C₄)alkoxy(C₁-C₄)alkyl radical, it being understood that at least one of the radicals R₁₃ or R₁₄ represents a hydrogen atom.

13. Composition according to Claim 12, characterized in that the para-aminophenols of 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, 4-amino-2-(β -hydroxyethylaminomethyl)phenol, 4-amino-2-fluorophenol, and their addition salts with an acid.

14. Composition according to Claim 7, characterized in that the ortho-aminophenols are chosen from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol, 5-acetamido-2-aminophenol, and their addition salts with an acid.

15. Composition according to Claim 7, characterized in that the heterocyclic bases are chosen from pyridine derivatives, pyrimidine derivatives, pyrazole derivatives, pyrazolopyrimidine derivatives, and their addition salts with an acid.



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

5 17. Composition according to Claim 16, characterized in that the oxidation base(s) represent from 0.005 to 6% by weight of the total weight of the dyeing composition.

10 18. Composition according to any one of the preceding claims, characterized in that the 2-amino-4-N-(β -hydroxyethyl)aminoanisole and/or the or its addition salts with an acid represent from 0.0001 to 8% by weight of the total weight of the dyeing composition.

15 19. Composition according to Claim 18, characterized in that the 2-amino-4-N-(β -hydroxyethyl)aminoanisole and/or the or its addition salts with an acid represent from 0.005 to 5% by weight of the total weight of the dyeing composition.

20 20. Composition according to any one of the preceding claims, characterized in that it contains one or more other couplers different from 2-amino-4-N-(β -hydroxyethyl)aminoanisole and/or direct dyes.

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



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

5 23. Composition according to any one of the preceding claims, characterized in that it has a pH of between 4 and 11.

24. Method of dyeing keratinous fibres, and in particular human keratinous fibres such as hair,
10 characterized in that at least one ready-to-use dyeing composition as defined in any one of the preceding claims is applied to the said fibres for a sufficient time to develop the desired colour.

25. Method according to Claim 24,
15 characterized in that it comprises a preliminary step consisting in storing in a separate form, on the one hand, a composition (A) comprising, in a medium appropriate for dyeing, at least one oxidation base and 2-amino-4-N-(β -hydroxyethyl)aminoanisoole and/or at
20 least one of its addition salts with an acid and, on the other hand, a composition (B) containing, in a medium appropriate for dyeing, at least one enzyme of laccase [lacuna], and then in mixing them at the time of use before applying this mixture to the keratinous
25 fibres.

26. Multicompartment device or dyeing "kit", characterized in that it comprises a first compartment containing the composition (A) as defined in Claim 25



and a second compartment containing the composition (B) as defined in Claim 25.

27. Ready-to-use compositions or method of dyeing
5 keratinous fibres involving them, substantially as
hereinbefore described with reference to the example.

Dated this 30th day of August 2001

10 L'OREAL

By their Patent Attorneys

GRIFFITH HACK

Fellows Institute of Patent and

Trade Mark Attorneys of Australia

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