

**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, para-phenylenediamine as first oxidation base, at least one para-aminophenol as second oxidation base, 2-methyl-5-N-(β -hydroxyethyl)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 obtained.

5 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 of the desired intensity and it must be able to
10 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 possible, i.e. they must give the smallest possible
15 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 generally carried out in alkaline medium, in the
20 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 keratin fibres, which is not always desirable.

25 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 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 para-phenylenediamine as first oxidation base, at least one para-aminophenol as second oxidation base, 2-methyl-5-N-(β -hydroxyethyl)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

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:

- 5 - para-phenylenediamine and/or at least one of the addition salts thereof with an acid, as first oxidation base,
- at least one second oxidation base chosen from para-aminophenols,
- 10 - 2-methyl-5-N-(β -hydroxyethyl)aminophenol and/or at least one of the addition salts thereof with an acid, as coupler,
- at least one enzyme of 2-electron oxidoreductase type, and
- 15 - at least one donor for the said enzyme.

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

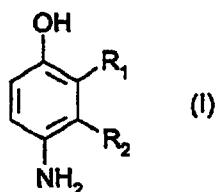
According to the invention, the term donor is understood to refer to the various substrates involved in the functioning of the said 2-electron oxidoreductase(s).

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 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 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 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 as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to formula (I) below, and the addition salts thereof with an acid:



in which:

- R_1 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,

- R₂ represents a hydrogen or halogen atom or a C₁-C₄ alkyl, C₁-C₄ monohydroxyalkyl, C₂-C₄ polyhydroxyalkyl, C₁-C₄ aminoalkyl, C₁-C₄ cyanoalkyl or (C₁-C₄)alkoxy-

5 (C₁-C₄)alkyl radical,

it being understood that at least one of the radicals R₁ or R₂ represents a hydrogen atom.

Among the para-aminophenols of formula (I) above, mention may be made more particularly of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluoro-phenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methyl-phenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β -hydroxyethylaminomethyl)phenol and 4-amino-15 2-fluorophenol, and the addition salts thereof with an acid.

The para-phenylenediamine and/or the addition salt(s) thereof with an acid which can be used as first oxidation base preferably represent(s) from 0.0005 to 20 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 from 0.005 to 6% by weight approximately relative to this weight.

The para-aminophenol(s) which can be used as 25 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 from 0.005 to 6% by weight approximately relative to

this weight.

The 2-methyl-5-N-(β -hydroxyethyl)aminophenol and/or the addition salt(s) thereof with an acid which can be used as coupler preferably represent(s) from
5 0.0001 to 5% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005 to 3% by weight approximately relative to this weight.

The ready-to-use dye composition in accordance
10 with the invention can also contain one or more additional couplers other than 2-methyl-5-N-(β -hydroxyethyl)aminophenol and the addition salts thereof with an acid and/or one or more direct dyes, in particular in order to modify the shades or to enrich
15 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-aminophenols
20 other than 2-methyl-5-N-(β -hydroxyethyl)aminophenol and the addition salts thereof with an acid, meta-diphenols and heterocyclic couplers, and the addition salts thereof with an acid.

When they are present, these additional
25 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 C_1 - C_4 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.

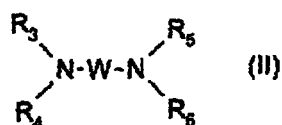
The solvents can be present in proportions preferably of between 1 and 40% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the ready-to-use composition in accordance with the invention is chosen such that the 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 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 derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (II) below:



in which W is a propylene residue optionally substituted with a hydroxyl group or a C₁-C₄ alkyl radical; R₃, R₄, R₅ and R₆, 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
5 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,
10 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-
15 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,
20 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 dyes and the 2-electron oxidoreductase(s) are present in the same
25 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
5 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 rinsed, optionally washed with shampoo, rinsed again and dried.

10 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.

According to one specific embodiment of the
15 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, para-phenylenediamine and/or at least one of the addition salts thereof with an acid,
20 at least one second oxidation base chosen from para-aminophenols, 2-methyl-5-N-(β -hydroxyethyl)aminophenol and/or at least one of the addition salts thereof with an acid as coupler, and, on the other hand, a composition (B) comprising, in a medium which is
25 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
5 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
10 the name of the Applicant.

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

EXAMPLE**DYEING EXAMPLE 1**

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

5	-	para-Phenylenediamine	0.216 g
	-	para-Aminophenol	0.1 g
	-	2-Methyl-5-N-(β -hydroxyethyl)aminophenol	0.18 g
10	-	Uricase from Arthrobacter globiformis at 20 International Units (I.U.)/mg, sold by the company Sigma	1.5 g
	-	Uric acid	1.5 g
	-	Ethanol	20.0 g
15	-	Hydroxyethylcellulose sold under the name Natrosol 250HR® by the company Aqualon	1.0 g
20	-	(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
	-	Monoethanolamine qs	pH = 9.5
25	-	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 was then rinsed, washed with a standard shampoo and

then dried.

The hair was dyed in a dark mahogany 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:

- para-phenylenediamine and/or at least one of the addition salts thereof with an acid, as first oxidation base,
- 10 - at least one second oxidation base chosen from para-aminophenols,
 - 2-methyl-5-N-(β -hydroxyethyl)aminophenol and/or at least one of the addition salts thereof with an acid, as coupler,
- 15 - 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
20 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
25 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.

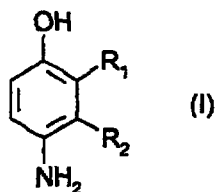
5. Composition according to Claim 4,
5 characterized in that the 2-electron oxidoreductase(s) represent(s) from 0.1 to 5% by weight relative to the total weight of the ready-to-use dye composition.

6. Composition according to Claim 3,
characterized in that the donor (or substrate) for the
10 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
15 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.

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



in which:

- R_1 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_2 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- (C_1-C_4) alkyl radical,

it being understood that at least one of the radicals R_1 or R_2 represents a hydrogen atom.

10. Composition according to Claim 9, characterized in that the para-aminophenols of formula (I) 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.

11. Composition according to any one of the preceding claims, characterized in that the para-phenylenediamine and/or the addition salt(s) thereof with an acid represent from 0.0005 to 12% by weight relative to the total weight of the ready-to-use dye composition.

12. Composition according to Claim 11,



characterized in that the para-phenylenediamine and/or the addition salt(s) thereof with an acid represent from 0.005 to 6% by weight relative to the total weight of the ready-to-use dye composition.

5 13. 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.

10 14. Composition according to Claim 13, 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.

15 15. Composition according to any one of the preceding claims, characterized in that the 2-methyl-5-N-(β -hydroxyethyl)aminophenol and/or the addition salt(s) thereof with an acid represent(s) from 0.0001 to 5% by weight relative to the total weight of the ready-to-use dye composition.

20 16. Composition according to Claim 15, characterized in that the 2-methyl-5-N-(β -hydroxyethyl)aminophenol and/or the addition salt(s) thereof with an acid represent(s) from 0.005 to 3% by weight relative to the total weight of the ready-to-use
25 dye composition.

17. Composition according to any one of the preceding claims, characterized in that it contains one or more couplers other than 2-methyl-5-N-(β -



hydroxyethyl)aminophenol and the addition salts thereof with an acid and/or one or more direct dyes.

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

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

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

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

22. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair,
20 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.

23. Process according to Claim 22,
25 characterized in that it 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, para-phenylenediamine and/or at



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least one of the addition salts thereof with an acid as first oxidation base, at least one second oxidation base chosen from para-aminophenols, 2-methyl-5-N-(β -hydroxyethyl)aminophenol and/or at least one of the addition salts thereof with an acid 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.

24. Multi-compartment dyeing device or "kit", characterized in that it includes a first compartment comprising composition (A) as defined in Claim 23 and a second compartment comprising composition (B) as defined in Claim 23.

