Title: DYE COMPOSITION COMPRISING A SECONDARY PARA-PHENYLENEDIAMINE OXIDATION BASE AND A 4-AMINOINDOLE COUPLER

Abstract: The present invention relates to a composition for dyeing keratin fibres, comprising, in a medium that is suitable for dyeing keratin fibres: at least one oxidation base chosen from the compounds of Formula (I), and the addition salts thereof, solvates thereof and solvates of the salts thereof; and - at least one coupler chosen from the compounds of Formula (II), and the addition salts thereof, solvates thereof and solvates of the salts thereof. The composition of the present invention makes it possible in particular to obtain colorations with varied shades, which are strong and/or chromatic, powerful, aesthetic, sparingly selective and resistant to the various attacking factors to which the hair may be subjected.
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DYE COMPOSITION COMPRISING A SECONDARY PARA-
PHENYLENEDIAMINE OXIDATION BASE AND A 4-AMINOINDOLE COUPLER

The invention relates to a dye composition comprising at least one oxidation base of secondary para-phenylenediamine type and at least one coupler of 4-aminindole type of given formulae, and also to the dyeing process using this composition.

It is known practice to dye keratin fibres and in particular human hair with dye compositions containing oxidation dye precursors, which are generally known as oxidation bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are colorless or weakly colored compounds, which, when combined with oxidizing products, may give rise to colored compounds by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases may be varied by combining them with couplers or coloration modifiers, the latter being chosen especially from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds such as indole compounds.

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

The "permanent" coloration obtained by virtue of these oxidation dyes is required, moreover, to meet a certain number of demands. Thus it should have no toxicological drawbacks, it should allow shades to be obtained in the desired intensity, and it should show good resistance to external agents such as light, bad weather, washing, permanent waving treatments, perspiration and rubbing.

The dyes should also allow grey hair to be covered and, finally, they should be as unselective as possible, i.e. they should produce the smallest possible differences in coloration along the same keratin fibre, which in general is differently sensitized (i.e. damaged) between its end and its root.

It is already known practice to use oxidation bases of the para-phenylenediamine type in the field of dyeing keratin fibres, especially 2-[[2-(4-aminophenylamino)ethyl]-[(2-hydroxyethyl)amino]ethanol. In particular, such a base is disclosed in documents EP 1 580 184 and EP 0 055 386.

It is also known practice, in documents EP 0 425 345 and WO 92/18093, to use oxidation dyes of aminindole type, and in particular 7-methyl-1 H-indol-4-amine and 7-ethyl-1 H-indol-4-amine for dyeing keratin fibres, and in particular the hair.
However, the prior art dye compositions lead to colorations that are not entirely satisfactory in terms of intensity, chromaticity, selectivity and fastness with respect to external agents.

The aim of the present invention is to obtain a hair dye composition that has improved dyeing properties in terms of intensity and/or chromaticity and/or selectivity and/or resistance to external agents.

This aim is achieved with the present invention, one subject of which is a composition for dyeing keratin fibres, comprising, in a cosmetically acceptable medium:

- at least one oxidation base chosen from the compounds of formula (I) and the addition salts thereof, solvates thereof and solvates of the salts thereof:

\[
\text{NH}_2 \quad \text{CH}_3 \\
\text{NH} - (\text{CH}_2)_x \text{N} \quad \text{R}_1 \\
\text{R}_2
\]

(I)

in which:

- \( x \) is equal to 2 or 3;
- \( R_1 \) and \( R_2 \) represent a hydroxyethyl radical or form, together with the nitrogen to which they are attached, an imidazole heterocycle; and

- at least one coupler chosen from the 4-aminoindole derivatives of formula (II), and also the addition salts thereof, solvates thereof and solvates of the salts thereof:

\[
\text{R}_1 \text{N} \text{R} '_4 \\
\text{R}_2 \text{R} '_3
\]

(II)

in which:

- \( \text{R} '_1 \) represents:
- a hydrogen atom;
- a linear or branched saturated C₁⁻C₆ alkyl radical, optionally interrupted with an oxygen atom or a radical NR'₇, optionally substituted with a radical chosen from OH and NR'₇R'₈;

R'₂ and R'₃, which may be identical or different, represent:
- a hydrogen atom;
a C₁⁻C₆ and preferably C₁⁻C₄ alkyl radical, optionally substituted with one or more hydroxyl radicals;
- a C₁⁻C₆ alkyl carboxylate radical;
a carboxyl radical;
a radical CONR'₇R'₈;

R'₄ and R'₅, which may be identical or different, represent:
- a hydrogen atom;
a C₁⁻C₆ alkyl radical;

R'₆ represents:
- a halogen;
a linear or branched C₁⁻C₁₀ alkyl radical, optionally interrupted with a heteroatom chosen from O or a radical NR'₉, and/or optionally substituted with one or more radicals, which may be identical or different, chosen from OH and NR'₇R'₈;
a C₁⁻C₁₀ alkyl carboxylate radical;
a radical CONR'₇R'₈;
a C₁⁻C₁₀ alkoxy radical or a C₁⁻C₁₀ (poly)hydroxyalkoxy radical;
a (poly)(Ci-Cio)alkoxy(CrCio)alkyloxy radical;
a radical O-Ak-NR'₉R'₁₀ with Ak = linear C₁⁻C₈ or branched C₃⁻C₈ divalent alkylene radical, optionally interrupted with one or more oxygen atoms and/or groups NR'₇;

R'₇ and R'₈, which may be identical or different, represent:
- a hydrogen atom;
a C₁⁻C₈ alkyl radical optionally substituted with one or more hydroxyl radicals;

R'₉ and R'₁₀, which may be identical or different, represent a linear or branched, saturated or unsaturated C₁⁻C₄ alkyl;

R'₉ and R'₁₀ may form, with the nitrogen that bears them, a saturated or unsaturated 5- to 8-membered heterocycle, one of the chain members possibly
being an oxygen atom or a radical NR'n with R'n = H or C₁₋₄ alkyl, optionally substituted with one or more radicals chosen from OH and NR'yRV

A subject of the invention is also a dyeing process using this composition.

Another subject of the invention is the use of the composition of the present invention for dyeing keratin fibres, and in particular human keratin fibres such as the hair.

The invention also relates to multi-compartment devices comprising compositions using at least one oxidation base chosen from the compounds of formula (I), addition salts thereof, solvates thereof and solvates of the salts thereof, and at least one coupler chosen from the compounds of formula (II) as defined previously, and also the addition salts thereof, solvates thereof and solvates of the salts thereof.

The composition of the present invention makes it possible in particular to obtain a composition for dyeing keratin fibres that is suitable for use in oxidation dyeing and that can produce colorations in varied shades, which are strong or chromatic, powerful, aesthetic, sparingly selective, and resistant to the various attacking factors to which the hair may be subjected, such as shampoo, sweat, permanent reshaping and light. In particular, the composition according to the invention leads to very powerful fundamental shades.

In the context of the present invention, the term "at least one" is equivalent to "one or more".

The present invention also covers the mesomeric forms and the stereoisomers of the various oxidation dyes of the invention.

It should be noted that, in the text hereinbelow, unless otherwise indicated, the limits of a range of values are included in that range.

According to one particular embodiment of the invention, in formula (I), R₁ and R₂ form, together with the nitrogen to which they are attached, an imidazole heterocycle.

According to an even more particular embodiment, the compound of formula (I) is N₄-[3-(1 H-imidazol-1-yl)propyl]-2-methylenzene-1,4-diamine.

According to another particular embodiment of the invention, in formula (I), R₁ and R₂ represent a hydroxyethyl radical.

According to an even more particular embodiment, the compound of formula (I) is 2,2'-((2-[4-amino-3-methylphenyl]aminoethyl)imino)diethanol.

The compounds of formula (I) as defined previously may be in the form of addition salts chosen especially from addition salts with an acid such as the
hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

They may also be in the form of solvates, for example a hydrate or a solvate of a linear or branched alcohol such as ethanol or isopropanol.

According to one particular embodiment of the invention, in formula (II), $R'_1$ represents a hydrogen atom or a saturated $C_1$-$C_4$ alkyl radical optionally substituted with a hydroxyl radical.

According to another particular embodiment, $R'_2$ and $R'_3$, which may be identical or different, represent a hydrogen atom; a $C_1$-$C_4$ alkyl radical optionally substituted with one or more hydroxyl radicals; a carboxyl radical; a $C_1$-$C_4$ alkyl carboxylate radical; a radical $CONR_5'R_6R_7$, preferably $CONH_2$. Preferably, $R'_2$ and $R'_3$, which may be identical or different, represent a hydrogen atom; a $C_1$-$C_4$ alkyl radical optionally substituted with one or more hydroxyl radicals.

According to another particular embodiment, $R'_4$ and $R'_5$ are identical and represent a hydrogen atom.

According to another particular embodiment, $R'_6$ represents a linear or branched $C_1$-$C_6$ alkyl radical; a carboxyl radical; a $C_1$-$C_6$ alkyl carboxylate; a carboxamide radical; a $(C_1$-$C_6)$alkoxy$(C_1$-$C_6)$alkyloxy radical; a $C_1$-$C_6$ alkoxy or hydroxy$(CrC_6)$alkyloxy radical; a radical $O-Ak-NR'_9R'_10$ with $Ak$ = linear $C_1$-$C_6$ or branched $C_3$-$C_6$ divalent alkyene radical optionally interrupted with a radical $NR'_7$. Preferably, $R'_6$ represents a linear or branched $C_1$-$C_6$ alkyl radical; a $(C_1$-$C_6)$alkoxy$(CrC_6)$alkyloxy radical; a $C_1$-$C_6$ alkoxy or hydroxy$(CrC_6)$alkyloxy radical; a radical $O-Ak-NR'_9R'_10$ with $Ak$ = linear $C_1$-$C_6$ or branched $C_3$-$C_6$ divalent alkyene radical optionally interrupted with a radical $NR'_7$.

According to one particular embodiment, the compounds in accordance with the invention are chosen from the 4-aminoindole derivatives of formula (II'), and also the addition salts thereof, solvates thereof and solvates of the salts thereof:
R represents:
- a hydrogen atom;
- a saturated C\textsubscript{1}-C\textsubscript{4} alkyl radical optionally substituted with a hydroxyl radical;

5 R'\textsubscript{2} and R'\textsubscript{3}, which may be identical or different, represent:
- a hydrogen atom;
- a C\textsubscript{1}-C\textsubscript{4} alkyl radical optionally substituted with one or more hydroxyl radicals, preferably optionally substituted with a hydroxyl radical;
- a carboxyl radical;
- a C\textsubscript{1}-C\textsubscript{4} alkyl carboxylate radical;
- a radical CON'R'yR's, preferably a carboxamide radical CONH\textsubscript{2};

R'\textsubscript{4} and R'\textsubscript{5} represent a hydrogen atom;
R'\textsubscript{6} represents:
- a linear or branched C\textsubscript{1}-C\textsubscript{6} alkyl radical;
- a carboxyl radical;
- a C\textsubscript{1}-C\textsubscript{6} alkyl carboxylate;
- a carboxamide radical;
- a (Cl-C\textsubscript{6})alkoxy(C\textsubscript{1}-C\textsubscript{6})alkyloxy radical;
- a C\textsubscript{1}-C\textsubscript{6} alkoxy radical or a C\textsubscript{1}-C\textsubscript{6} hydroxyalkoxy radical;
- a radical O-Ak-NR'\textsubscript{9}R'\textsubscript{0} with Ak = linear C\textsubscript{1}-C\textsubscript{6} or branched C\textsubscript{3}-C\textsubscript{6} divalent alkyylene radical, optionally interrupted with one or more oxygen atoms and/or groups NR'\textsubscript{7};

R'\textsubscript{7} and R'\textsubscript{8} represent a hydrogen atom or a C\textsubscript{1}-C\textsubscript{6} alkyl radical optionally substituted with a hydroxyl radical;

25 R'\textsubscript{9} and R'\textsubscript{10}, which may be identical or different, represent a saturated linear C\textsubscript{1}-C\textsubscript{4} alkyl radical or an unsaturated linear C\textsubscript{2}-C\textsubscript{4} alkyl radical;
R'\textsubscript{9} and R'\textsubscript{10} may form, with the nitrogen that bears them, a saturated or unsaturated 5- to 8-membered heterocycle, one of the chain members possibly being an oxygen atom or a radical NR'n with R'n = H or C\textsubscript{1}-C\textsubscript{4} alkyl, optionally substituted with OH.

The derivatives of formula (II) may optionally be salified with strong mineral acids, for instance HCl, HBr, HI, H\textsubscript{2}SO\textsubscript{4} or H\textsubscript{3}PO\textsubscript{4}, or organic acids, for instance acetic acid, lactic acid, tartaric acid, citric acid, succinic acid, benzenesulfonic acid, para-toluenesulfonic acid, formic acid or methanesulfonic acid.
The derivatives of formula (II) may also be in the form of solvates, for example a hydrate or a solvate of a linear or branched alcohol such as ethanol or isopropanol.

As examples of derivatives of formula (II), mention may be made of the compounds presented below:

- 2,3-dimethyl-7-(propan-2-yl)-1H-indol-4-amine
- 7-ethyl-2,3-dimethyl-1H-indol-4-amine
- 2,3,7-trimethyl-1H-indol-4-amine
- 3-ethyl-2,7-dimethyl-1H-indol-4-amine
- 7-ethyl-2,3-dimethyl-1H-indol-4-amine
- 3,7-diethyl-2-methyl-1H-indol-4-amine
- 2,3-dimethyl-7-(propan-2-yl)-1H-indol-4-amine
- 3-ethyl-2-methyl-7-(propan-2-yl)-1H-indol-4-amine
amine

7-ethyl-1,2,3-trimethyl-1H-indol-4-amine

3,7-diethyl-1,2-dimethyl-1H-indol-4-amine

2-(4-amino-7-ethyl-2,3-dimethyl-1H-indol-1-yl)ethanol

2-(4-amino-3,7-diethyl-2-methyl-1H-indol-1-yl)ethanol

1,2,3-trimethyl-7-(propan-2-yl)-1 H-indol-4-amine

3-ethyl-1,2-dimethyl-7-(propan-2-yl)-1 H-indol-4-amine
2-(4-amino-3-ethyl-7-methoxy-2-methyl-1H-indol-7-ethoxy-2,3-dimethyl-1H-indol-4-amine-yl)ethanol

7-ethoxy-3-ethyl-2-methyl-1H-indol-4-amine

7-ethoxy-3-ethyl-1,2-dimethyl-1H-indol-4-amine

7-ethoxy-1,2,3-trimethyl-1H-indol-4-amine

12-(4-amino-7-ethoxy-2,3-dimethyl-1H-indol-1-yl)ethanol

7-ethoxy-2,3-dimethyl-1H-indol-4-amine
2-(4-amino-7-ethoxy-3-ethyl-2-methyl-1H-indol-1-yl)ethanol

2-[(4-amino-2,3-dimethyl-1H-indol-7-yl)oxy]ethanol

2-[(4-amino-1,2,3-trimethyl-1H-indol-7-yl)oxy]ethanol

2-[[4-amino-1,2,3-trimethyl-1H-indol-7-yl]oxy]ethanol

2-[4-amino-7-(2-hydroxyethoxy)-2,3-dimethyl-1H-indol-1-yl]ethanol

7-[2-(dimethylamino)ethoxy]-2,3-dimethyl-1H-indol-4-amine

7-[2-(dimethylamino)ethoxy]-1,2,3-trimethyl-1H-indol-4-amine
2-{4-amino-7-[2-(dimethylamino)ethoxy]-2,3-dimethyl-1H-indol-1-yl}ethanol

2,3-dimethyl-7-[2-(pyrrolidin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(piperidin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(morpholin-4-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(4-methylpiperazin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(morpholin-4-yl)ethoxy]-1H-indol-4-amine
2-(4-{2-[(4-amino-2,3-dimethyl-1H-indol-7-methyl-1H-indol-4-amine)]yl)oxy}ethyl)piperazin-1-yl)ethanol

7-[2-(dimethylamino)ethoxy]-3-ethyl-2-methyl-1H-indol-4-amine

3-ethyl-2-methyl-7-[2-(piperidin-1-yl)ethoxy]-1H-indol-4-amine

3-ethyl-2-methyl-7-[2-(pyrrolidin-1-yl)ethoxy]-1H-indol-4-amine

3-ethyl-2-methyl-7-[2-(pyrrolidin-1-yl)ethoxy]-1H-indol-4-amine

2-[4-amino-7-(2-hydroxyethoxy)-1H-indol-1-]
indol-4-amine

2-[(4-amino-1H-indol-7-yl)oxy]ethanol

7-[(2-[piperidin-1-yl]ethoxy]-1 H-indol-4-amine

7-[(2-[morpholin-4-yl]ethoxy]-1 H-indol-4-amine
7-{[2-(4-methylpiperazin-1-yl)ethoxy]-1'H-indol-2-(4-{2-[(4-amino-1'H-indol-7-yl)oxy]ethyl}piperazin-1-yl)ethanol

7-{[2-(dimethylamino)ethoxy]-1'H-indol-4-amine

7-{[2-(1'H-imidazol-1-yl)ethoxy]-1'H-indol-4-amine

7-{[2-(1'H-imidazol-1-yl)ethoxy]-2,3-dimethyl-2,3-dimethyl-7-{[2-(1'H-pyrrol-1-yl)ethoxy]-1'H-indol-4-amine

7-{[2-(1'H-imidazol-1-yl)ethoxy]-1'H-indol-4-amine

2,3-dimethyl-7-{[2-(1'H-pyrrol-1-yl)ethoxy]-1'H-indol-4-amine
ethyl 4-amino-3-methyl-7-(propan-2-yl)-1H-indole-2-carboxylate

4-amino-7-(propan-2-yl)-1H-indole-2-carboxylic acid

7-(2-methoxyethoxy)-1H-indol-4-amine

27-(2-methoxyethoxy)-2,3-dimethyl-1H-indol-4-amine

7-(2-[[2-(piperidin-1-yl)ethyl]amino]ethoxy)-1H-indol-4-amine

2,3-dimethyl-7-(2-[[2-(pyrrolidin-1-yl)ethyl]amino]ethoxy)-1H-indol-4-amine
N'-{2-[(4-amino-1H-indol-7-yl)oxy]ethyl}-N,N-dimethylethane-1,2-diamine

N'-{2-[(4-amino-2,3-dimethyl-1H-indol-7-yl)oxy]ethyl}-N,N-dimethylethane-1,2-diamine

4-amino-3,7-dimethyl-1H-indole-2-carboxamide

4-amino-1H-indole-7-carboxylic acid

4-amino-2,3-dimethyl-1H-indole-7-carboxylic acid

methyl 4-amino-2,3-dimethyl-1H-indole-7-carboxylate
-methyl-1H-indol-4-amine

7-ethyl-1H-indol-4-amine

4-amino-2,3-dimethyl-1H-indole-7-carboxamide

4-amino-1H-indole-7-carboxamide

2-(4-amino-7-methyl-1H-indol-3-yl)ethanol

3-(4-amino-7-methyl-1H-indol-3-yl)propan-1-ol

2-(4-amino-2,7-dimethyl-1H-indol-3-yl)ethanol

3-(4-amino-2,7-dimethyl-1H-indol-3-yl)propan-1-ol

7-methyl-1H-indol-4-amine

7-ethyl-1H-indol-4-amine
Among these compounds, the derivatives of formula (II) that are particularly preferred are the following:

- 2,3-dimethyl-7-(propan-2-yl)-1\(H\)-indol-4-amine
- 7-ethyl-2,3-dimethyl-1\(H\)-indol-4-amine
- 2,3,7-trimethyl-1\(H\)-indol-4-amine
- 3-ethyl-2,7-dimethyl-1\(H\)-indol-4-amine
- 7-ethyl-2,3-dimethyl-1\(H\)-indol-4-amine
- 3,7-diethyl-2-methyl-1\(H\)-indol-4-amine
- 2,3-dimethyl-7-(propan-2-yl)-1\(H\)-indol-4-amine
- 3-ethyl-2-methyl-7-(propan-2-yl)-1\(H\)-indol-4-amine
7-ethyl-1,2,3-trimethyl-1H-indol-4-amine
3,7-diethyl-1,2-dimethyl-1H-indol-4-amine
2-(4-amino-7-ethyl-2,3-dimethyl-1H-indol-1-yl)ethanol
2-(4-amino-3,7-diethyl-2-methyl-1H-indol-1-yl)ethanol
1,2,3-trimethyl-7-(propan-2-yl)-1H-indol-4-amine
2-[4-amino-2,3-dimethyl-7-(propan-2-yl)-1H-indol-1-yl]ethanol
7-methoxy-2,3-dimethyl-1H-indol-4-amine
7-methoxy-1,2,3-trimethyl-1H-indol-4-amine
2-(4-amino-3-ethyl-7-methoxy-2-methyl-1H-indol-7-ethoxy-2,3-dimethyl-1H-indol-4-amine-yl)ethanol

7-ethoxy-2,3-dimethyl-1H-indol-4-amine

7-ethoxy-1,2,3-trimethyl-1H-indol-4-amine

12-(4-amino-7-ethoxy-2,3-dimethyl-1H-indol-1-yl)ethanol

2-[(4-amino-2,3-dimethyl-1H-indol-7-yl)oxy]ethanol

2-[(4-amino-1,2,3-trimethyl-1H-indol-7-yl)oxy]ethanol
2-[4-amino-7-(2-hydroxyethoxy)-2,3-dimethyl-1H-indol-1-yl]ethanol

7-[2-(dimethylamino)ethoxy]-2,3-dimethyl-1H-indol-4-amine

7-[2-(dimethylamino)ethoxy]-1,2,3-trimethyl-1H-indol-4-amine

2-[4-amino-7-[2-(dimethylamino)ethoxy]-2,3-dimethyl-1H-indol-1-yl]ethanol

2,3-dimethyl-7-[2-(pyrrolidin-1-yl)ethoxy]-1H-indol-4-amine
2,3-dimethyl-7-[2-(piperidin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(morpholin-4-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(4-methylpiperazin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(morpholin-4-yl)ethoxy]-1H-indol-4-amine

2-(4-{2-[(4-amino-2,3-dimethyl-1H-indol-7-yl)ethoxy]carboxamido}-1-piperazinyl)ethanol
yl)oxyethyl)piperazin-1-yl)ethanol

2-[4-amino-7-(2-hydroxyethoxy)-1H-indol-1-yl]ethanol

7-[2-(piperidin-1-yl)ethoxy]-1 H-indol-4-amine

7-[2-(morpholin-4-yl)ethoxy]-1 H-indol-4-amine
1H-indol-4-amine

7-(2-methoxyethoxy)-1H-indol-4-amine

27-(2-methoxyethoxy)-2,3-dimethyl-1H-indol-4-amine

2-(4-amino-7-methyl-1H-indol-3-yl)ethanol

3-(4-amino-7-methyl-1H-indol-3-yl)propan-1-ol

7-methyl-1H-indol-4-amine

7-ethyl-1H-indol-4-amine
The compounds of formula (I), the compounds of formula (II), and the addition salts thereof, solvates thereof and solvates the salts thereof are in general each present in an amount of between 0.001% and 10% by weight approximately and preferably between 0.005% and 6% by weight relative to the total weight of the dye composition.

The dye composition of the invention may optionally comprise one or more additional oxidation bases conventionally used for dyeing keratin fibres, other than the compounds of formula (I) or the addition salts thereof, solvates thereof and solvates of the salts thereof.

By way of example, these additional oxidation bases are chosen from para-phenylenediamines other than the compounds of formula (I), the addition salts thereof, solvates thereof and solvates of the salts thereof, bis(phenyl)alkylenediamines, para-aminophenols, bis-para-aminophenols, ortho-aminophenols and heterocyclic bases, the addition salts thereof, solvates thereof and solvates of the salts thereof.

Among the para-phenylenediamines, examples that may be mentioned include para-phenylenediamine, para-toluenediamine, 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-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis$\beta$-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis$\beta$-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis$\beta$-hydroxyethyl)amino-2-chloroaniline, 2$\beta$-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-$\beta$-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-$\beta$-hydroxyethyl)-para-phenylenediamine, N-$\beta$-di hydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2$\beta$-hydroxyethoxy-para-phenylenediamine, 2$\beta$-acetylaminoethoxy-para-phenylenediamine, N-(β-methoxyethyl)-para-phenylenediamine, 4-aminophenylpyrrolidine, 2-thi enyl-para-phenylenediamine, 2$\beta$-hydroxyethy lamino-5-aminotoluene and 3-hydroxy-1-(4'-aminophenyl)pyrrolidine, and the addition salts thereof with an acid, solvates thereof and solvates of the salts thereof.
Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-toluenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2^-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^-acetylaminoethylxy-para-phenylenediamine, and the addition salts thereof with an acid, solvates thereof and solvates of the salts thereof are particularly preferred.

Among the bis(phenyl)alkylenediamines, examples that may be mentioned include 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^-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 and 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane, and the addition salts thereof with an acid, solvates thereof and solvates of the salts thereof.

Among the para-aminophenols, examples that may be mentioned include 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^-hydroxyethylaminomethyl)phenol, 4-amino-2-fluorophenol, 1-hydroxy-4-methylaminobenzene and 2-2'-methylenebis-4-aminophenol, and the addition salts thereof with an acid, solvates thereof and solvates of the salts thereof.

Among the ortho-aminophenols, examples that may be mentioned include 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid, solvates thereof and solvates of the salts thereof.

Among the heterocyclic bases, examples that may be mentioned include pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Among the pyridine derivatives that may be mentioned are the compounds described, for example, in patents GB 1 026 978 and GB 1 153 196, for instance 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2^-methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid, solvates thereof and solvates of the salts thereof.
Other pyridine oxidation bases that are useful in the present invention are the 3-aminopyrazolo[1,5-a]pyridine oxidation bases or the addition salts thereof described, for example, in patent application FR 2 801 308. Examples that may be mentioned include pyrazolo[1,5-a]pyrid-3-ylamine, 2-acetylamino pyrazolo[1,5-a]pyrid-3-ylamine, 2-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine, (3-aminopyrazolo[1,5-a]pyrid-7-yl)methanol, 2-(3-aminopyrazolo[1,5-a]pyrid-5-yl)ethanol, 2-(3-aminopyrazolo[1,5-a]pyrid-7-yl)ethanol, (3-aminopyrazolo[1,5-a]pyrid-2-yl)methanol, 3,6-diaminopyrazolo[1,5-a]pyridine, 3,4-diaminopyrazolo[1,5-a]pyridine, pyrazolo[1,5-a]pyridine-3,7-diamine, 7-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine, pyrazolo[1,5-a]pyridine-3,5-diamine, 5-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine, 2-[(3-aminopyrazolo[1,5-a]pyrid-5-yl)(2-hydroxyethyl)amino]ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrid-7-yl)(2-hydroxyethyl)amino]ethanol, 3-aminopyrazolo[1,5-a]pyridin-5-ol, 3-aminopyrazolo[1,5-a]pyridin-6-ol and 3-aminopyrazolo[1,5-a]pyridin-7-ol, and the addition salts thereof, solvates thereof and solvates of the salts thereof.

Among the pyrimidine derivatives that may be mentioned are the compounds described, for example, in patents DE 2 359 399; JP 88-169 571; JP 05-63124; EP 0 770 375 or patent application WO 96/15765, for instance 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, pyrazolopyrimidine derivatives such as those mentioned in patent application FR-A-2 750 048, and among which mention may be made 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, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-5-yl)(2-hydroxyethyl)amino]ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5-N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 3-amino-5-methyl-7-imidazolylpropaminopyrazolo[1,5-a]pyrimidine, and the addition salts thereof with an acid, solvates thereof and solvates of the salts thereof.
Examples of diaminopyrazole bases that may be mentioned include the compounds described in patents DE-A-38 43 892 and DE-A-41 33 957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE-A-195 43 988, for instance 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(2-hydroxyethyl)pyrazole, 5, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-^-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 and 4-amino-5-(2'-aminoethyl)amino-1 ,3-dimethylpyrazole, the addition salts thereof, solvates thereof and solvates of the salts thereof.

Mention may also be made of the diaminopyrazolinones described in patent application FR 2 886 137 and in particular 2,3-diamino-6,7-dihydro-1 H,5H-pyrazol-1-one, salts thereof, solvates thereof and solvates of salts thereof.

The additional oxidation base(s) are each generally present in an amount of between 0.001% and 10% by weight and preferably between 0.005% and 6% by weight relative to the total weight of the dye composition.

The dye composition according to the invention may also contain one or more additional couplers conventionally used for the dyeing keratin fibres, other than the couplers that are useful in the present invention or the addition salts thereof with an acid. Among these couplers, mention may be made especially of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers other than the compounds of formula (II), the addition salts thereof, solvates thereof and solvates of the salts thereof.

Examples of couplers that may be mentioned include 2-methyl 5-aminophenol, 5-N-^-hydroxyethyl)amino-2-methylphenol, 6-chloro-2-methyl-5-aminophenol, 2,4-dichloro-3-aminophenol, 5-amino-4-chloro-o-cresol, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1^-hydroxyethyloxy)benzene, 2-amino-4^-hydroxyethylamino)-1-methoxybenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1-β-hydroxyethylaminobenzene, 3,4-methylenedioxynaphthalene, oc-naphthol, 2-methyl-1-naphthol, 1,5-dihydroxynaphthalene, 2,7-naphthalenediol, 1-acetoxy-2-methylnaphthalene, 6-
hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 3,5-diamino-2,6-
dimethoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 3-amino-2-methylamino-6-
methoxypyridine, 1-N-(β-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-
bis(β-hydroxyethylamino)toluene and 3-methyl-1-phenyl-5-pyrazolone, the addition
salts thereof with an acid, solvates thereof and solvates of the salts thereof.

The preferred additional couplers are chosen from 2-methyl-5-
aminophenol, 5-N-^-hydroxyethyl)amino-2-methylphenol and 6-chloro-2-methyl-5-
aminophenol.

The additional coupler(s) are each generally present in an amount of between
0.001 % and 10% by weight and preferably between 0.005% and 6% by weight
relative to the total weight of the dye composition.

In general, the addition salts of the additional oxidation bases and additional
couplers that may be used in the context of the invention are especially chosen
from addition salts with an acid, such as hydrochlorides, hydrobromides, sulfates,
citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates
and acetates, and the addition salts with a base such as sodium hydroxide, potassium
hydroxide, ammonia, amines or alkanolamines.

According to one particular embodiment of the invention, the composition
comprises at least one additional coupler chosen from the compounds of formula
(III) below, and the addition salts thereof, solvates thereof and solvates of the salts
thereof:

\[
\begin{array}{c}
\text{R}_{3}^{\prime} \\
\text{R}_{2}^{\prime} \\
\text{R}_{4}^{\prime} \\
\text{NH} \\
\text{R}_{1}^{\prime}
\end{array}
\]  

in which:
\begin{align*}
\text{R}_{1}^{\prime} & \text{ represents a hydrogen atom or a C}_{1}\text{-C}_{4} \text{ hydroxyalkyl radical;} \\
\text{R}_{2}^{\prime} & \text{ represents an amino radical or a hydroxyl radical;} \\
\text{R}_{3}^{\prime} & \text{ represents a C}_{1}\text{-C}_{4} \text{ alkyl radical or a C}_{1}\text{-C}_{4} \text{ hydroxyalkyl radical;} \\
\text{R}_{4}^{\prime} & \text{ represents a hydrogen atom or a halogen atom, for example a fluorine,} \\
& \text{chlorine, bromine or iodine atom.}
\end{align*}

According to one particular embodiment of the invention, \( \text{R}_{1}^{\prime} \) represents a
hydrogen atom.

According to another particular embodiment of the invention, \( \text{R}_{2}^{\prime} \) represents a
hydroxyl radical.
According to another particular embodiment of the invention, R"\textsubscript{3} represents a C\textsubscript{1}-C\textsubscript{4} alkyl radical. Preferably, R"\textsubscript{3} represents a methyl radical.

According to another particular embodiment of the invention, R"\textsubscript{4} represents a halogen atom. Preferably, R"\textsubscript{4} represents a chlorine atom.

According to one preferred embodiment, the composition in accordance with the invention comprises 2-chloro-6-methyl-3-aminophenol as additional coupler.

The dye composition in accordance with the invention may also contain one or more direct dyes that may be chosen especially from nitrobenzene dyes, azo direct dyes and methine direct dyes. These direct dyes may be of nonionic, anionic or cationic nature. They may be synthetic or of natural origin.

The medium that is suitable for dyeing, also known as the dye support, generally comprises water or a mixture of water and of one or more organic solvents, for instance C\textsubscript{1}-C\textsubscript{4} lower alkanols such as ethanol and isopropanol, polyols, for instance propylene glycol, dipropylene glycol or glycerol, and polyols, for instance dipropylene glycol monomethyl ether.

The solvent(s) are generally present in proportions that may be between 1% and 40% by weight approximately and even more preferentially between 3% and 30% by weight approximately relative to the total weight of the dye composition.

The dye composition in accordance with the invention may also contain various adjuvants conventionally used in hair dye compositions, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, mineral or organic thickeners, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersants, conditioning agents, for instance volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents and opacifiers.

The above adjuvants are generally present in an amount, for each of them, of between 0.01% and 20% by weight relative to the weight of the composition.

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

The pH of the dye composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 11 approximately.
It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres, or alternatively using standard buffer systems.

Among the acidifying agents that may be mentioned, for example, are mineral or organic acids, for instance hydrochloric acid, (ortho)phosphoric acid or sulfuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid and lactic acid, and sulfonic acids.

Among the basifying agents, examples that may be mentioned include aqueous ammonia, alkali metal carbonates, sodium metasilicate, sodium silicate, alkanolamines such as monoethanolamine, diethanolamine, triethanolamine and derivatives thereof, for example monoethanolamine, aminomethylpropanol, triethanolamine, sodium hydroxide, potassium hydroxide, sodium pyrrolidinecarboxylate, and the compounds of formula (IV) below:

\[
\begin{array}{c}
\text{R}_a \ \text{N}: \text{W} - \text{N} \\
\text{R}_b & \text{R}_c & \text{R}_d
\end{array}
\] (IV)

in which W is a propylene residue optionally substituted with a hydroxyl group or a \(\text{C}_1-\text{C}_4\) alkyl radical; \(\text{R}_a, \text{R}_b, \text{R}_c\) and \(\text{R}_d\), which may be identical or different, represent a hydrogen atom or a \(\text{C}_1-\text{C}_4\) alkyl or \(\text{C}_1-\text{C}_4\) hydroxyalkyl radical.

The composition according to the invention may comprise one or more oxidizing agents.

The oxidizing agents are those conventionally used for the oxidation dyeing of keratin fibres, for example hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulfates, peracids and oxidase enzymes, among which mention may be made of peroxidases, two-electron oxidoreductases such as uricases, and four-electron oxygenases, for instance laccases. Hydrogen peroxide is particularly preferred.

The composition with or without oxidizing agent according to the invention may be in various forms, such as in the form of liquids, creams or gels, or in any other form that is suitable for dyeing keratin fibres, and especially human hair.

It may result from the mixing at the time of use of several compositions.

In one particular variant, it results from the mixing of two compositions, one comprising at least one oxidation base chosen from the compounds of formula (I), addition salts thereof, solvates thereof and solvates of the salts thereof, and at least one coupler chosen from the compounds of formula (II), and also the addition
salts thereof, solvates thereof and solvates of the salts thereof, and another composition comprising at least one oxidizing agent as described previously.

The composition of the invention is thus applied to the hair for the dyeing of keratin fibres, either in unmodified form or in the presence of at least one oxidizing agent for the dyeing of keratin fibres.

The process of the present invention is a process in which the composition free of oxidizing agent according to the present invention as defined previously is applied to the fibres in the presence of an oxidizing agent for a time that is sufficient to develop the desired coloration. The colour may be revealed at acidic, neutral or alkaline pH, and the oxidizing agent may be added to the composition of the invention right at the time of use, or it may be used starting with an oxidizing composition containing it, which is applied simultaneously with or sequentially to the composition of the invention.

According to one particular embodiment, the composition free of oxidizing agent according to the present invention is mixed, preferably at the time of use, with a composition containing, in a suitable dyeing medium, at least one oxidizing agent. The mixture obtained is then applied to the keratin fibres. After a contact time of 3 to 50 minutes approximately and preferably 5 to 30 minutes approximately, the keratin fibres are rinsed, optionally washed with shampoo, rinsed again and then dried.

The oxidizing agents are those described previously.

The oxidizing composition may also contain various adjuvants conventionally used in compositions for dyeing the hair and as defined above.

The pH of the oxidizing composition containing the oxidizing agent is such that, after mixing with the dye composition, the pH of the resulting composition applied to the keratin fibres preferably ranges between 3 and 12 approximately and even more preferentially between 5 and 11. It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres and as defined previously.

A subject of the invention is also a multi-compartment dyeing device or "kit" in which a first compartment contains the dye composition free of oxidizing agent of the present invention defined above, comprising at least one oxidation base chosen from the compounds of formula (I), the addition salts thereof, solvates thereof and solvates of the salts thereof, and at least one coupler chosen from the compounds of formula (II), and also the addition salts thereof, solvates thereof and
solvates of the salts thereof, and a second compartment containing at least one oxidizing agent.

A second device is formed from a first compartment containing a composition comprising at least one oxidation base chosen from the compounds of formula (I), addition salts thereof, solvates thereof and solvates of the salts thereof, and a second compartment containing a composition comprising at least one coupler chosen from the compounds of formula (II) as defined previously, and also the addition salts thereof, solvates thereof and solvates of the salts thereof.

A third device may optionally comprise the two compartments of the second device plus a third compartment containing a composition comprising at least one oxidizing agent.

This device may be equipped with a means for dispensing the desired mixture on the hair, such as the devices described in patent FR-2 586 913 in the name of the Applicant.

According to a second particular embodiment, the synthesis of the compounds of formula (II) is performed according to the following scheme:

![Chemical Structures](image)

in which:
Pg is a protecting group for the amine function chosen from those mentioned in the publication *Protective Groups in Organic Synthesis*, T.W. Greene, P.G.M. Wutz, John Wiley & Sons, 2nd Ed, 1991; X denotes a halogen atom such as a fluorine, chlorine, bromine or iodine atom.

According to another particular embodiment, the synthesis of the compounds of formula (II) is performed according to the following scheme:

![Chemical structures](image)

The compounds (2) are obtained from the protected amines (1) via a cyclization reaction of Bischler type performed in a dipolar solvent such as DMF, NMP, acetonitrile or THF, or in an alcohol such as ethanol, for example, optionally in the presence of an organic or mineral base such as triethylamine, ethyldiisopropylamine, sodium hydroxide or potassium hydroxide, with 0.5 to 1 or more equivalents of carbonyl halide $R_2$-CO-CHX-$R_3$ for 1 to 24 hours at a temperature ranging from 20°C to the reflux temperature of the solvent. The cyclization reactions of (3) to lead to (4), or of (5) to lead to (6), or of (7) to lead to (8), or of (9) to lead to (10), or of (11) to lead to (I), are performed in the same manner.

The alkylation of compounds (4) is performed with at least one equivalent of alkyl halide $R_1$-X in a solvent such as THF or acetonitrile or dioxane or ethyl
acetate, in the presence of an organic or mineral base such as triethylamine, ethyldiisopropylamine, sodium hydroxide or potassium hydroxide, for 15 minutes to 24 hours at a temperature ranging from 15°C to the reflux temperature of the solvent and leads to compounds (6). The alkylation of compounds (2) to give compounds (8), or of (9) to give (11), or of (10) to give (1), is performed according to an identical protocol.

The reduction of the nitro group of the compounds (4) and (6) is performed under standard conditions, for example by performing a hydrogenation reaction under heterogeneous catalysis in the presence of a catalyst such as Pd/C, Pd(II)/C or Ni/Ra, or alternatively by performing a reduction reaction with a metal, for example with zinc, iron or tin (see Advanced Organic Chemistry, 3rd Edition, J. March, 1985, Wiley Interscience and Reduction in Organic Chemistry, M. Hudlicky, 1983, Ellis Horwood Series Chemical Science).

The cleavage of the protecting group Pg may be performed in acidic or basic medium in a very conventional manner, depending on their nature (see Protective Groups for Organic Synthesis, T.W. Greene, P.G.M. Wutz, John Wiley & Sons, 2nd Ed, 1991).

When compounds (9) are not commercially available, they may be obtained, for example, from the diamines (12) or (13).

The examples that follow serve to illustrate the invention without, however, being limiting in nature.

EXAMPLES

EXAMPLES OF SYNTHESIS

Example 1: synthesis of 2,3,7-trimethyl-1H-indol-4-amine hydrochloride
Step 1: synthesis of N-(2,3,7-trimethyl-1H-indol-4-yl)acetamide

5 g (30 mmol) of N-(3-amino-4-methylphenyl)acetamide are placed in 12 ml of dimethylformamide in a 25 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer, and 3.24 ml (30 mmol) of 3-bromo-2-butanone are added dropwise. The mixture is then maintained at 100°C for 8 hours until the starting material has totally disappeared. The reaction medium is cooled and then poured into a mixture of ice and water. The gummy precipitate formed is taken up in dichloromethane. The organic phase is then washed with water, after which it is dried over sodium sulfate, and the solvents are then removed on a rotary evaporator under vacuum. The crude product thus obtained is purified by flash chromatography on a column of silica (eluent: dichloromethane) to give, after removal of the solvent, 1.4 g of a beige-coloured powder corresponding to the expected product (yield = 21.2%).

The NMR analyses (H 400 MHz and 13C 100.61 MHz DMSO-d6) are in accordance with the expected structure. The analysis by mass spectrometry confirms the structure of the expected compound C13H16N2O. The quasi-molecular ions [M+H]+, [M+Na]+, [M-H]- of the expected molecule are mainly detected.

Step 2: Synthesis of 2,3,7-trimethyl-1H-indol-4-amine

1.4 g (30 mmol) of N-(2,3,7-trimethyl-1H-indol-4-yl)acetamide are placed in 8 ml of a 50% solution of HCl in isopropanol in a 25 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer. The medium is refluxed for 48 hours.
The solvent is then removed under vacuum on a rotary evaporator to give 1.15 g of a grey powder corresponding to the expected compound (yield = 64%).

The analysis by mass spectrometry confirms the expected structure CnH14N2. The quasi-molecular ions [M+H]+, [M+Na]+, [M-H]- of the expected molecule are mainly detected.

**Example 2:** synthesis of 2,3-dimethyl-7-(propan-2-yl)-1H-indol-4-amine hydrochloride

Step 1: synthesis of N-[2,3-dimethyl-7-(propan-2-yl)-1H-indol-4-yl]acetamide

6.7 g (34.8 mmol) of N-[3-amino-4-(1-methylethyl)phenyl]acetamide are placed in 20 ml of dimethylformamide in a 25 ml three-necked flask equipped with a condenser, a thermometer and a magnetic stirrer, and 1.4 ml (13 mmol) of 3-bromo-2-butanone are then added dropwise.

The medium is then maintained at 100°C for 48 hours, and is then cooled and poured into a mixture of ice and water, with stirring.

The precipitate formed is filtered off and washed thoroughly with water, and then dried under vacuum in the presence of a desiccant.

The crude product thus obtained is purified by flash chromatography on a column of silica (eluent: 95/5 dichloromethane/methanol) to give, after removal of the solvent, 2.87 g of a brown powder corresponding to the expected product (yield = 51%).

The NMR analyses (1H 400 MHz and 13C 100.61 MHz DMSO-d6) are in accordance with the expected structure.
The analysis by mass spectrometry confirms the structure of the expected compound \( \text{C}_{15}\text{H}_{20}\text{N}_{2}\text{O} \). The quasi-molecular ions \([\text{M}+\text{H}]^+, [\text{M}+\text{Na}]^+, [\text{M}-\text{H}]^-\) of the expected molecule are mainly detected.

Step 2: Synthesis of 2,3-dimethyl-7-(propan-2-yl)-1H-indol-4-amine hydrochloride

This compound is obtained according to a protocol identical to that described for Example 1, replacing the 6N HCl isopropanol solution with 6 ml of a 37.5% hydrochloric acid solution. For this example, the reaction of 2.87 g of N-[2,3-dimethyl-7-(propan-2-yl)-1 H-indol-4-yl]acetamide leads to 2.8 g of a powder corresponding to the expected product (yield = 89%).

The NMR analyses (\(^1\text{H}\) 400 MHz and \(^{13}\text{C}\) 100.61 MHz DMSO-d\(_6\)) are in accordance with the expected structure.

The analysis by mass spectrometry confirms the structure of the expected compound \( \text{C}_{13}\text{H}_{18}\text{N}_{2} \). The quasi-molecular ions \([\text{M}+\text{H}]^+, [\text{M}+\text{Na}]^+, [\text{M}-\text{H}]^-\) of the expected molecule are mainly detected.

**EXAMPLES OF DYEING**

<table>
<thead>
<tr>
<th>Composition C1 below was prepared:</th>
<th>C1</th>
</tr>
</thead>
<tbody>
<tr>
<td>N4-[3-(1 H-imidazol-1-yl)propyl]-2-methylbenzene-1,4-diamine trihydrochloride</td>
<td>0.01 mol</td>
</tr>
<tr>
<td>7-Methyl-1 H-indol-4-amine</td>
<td>0.0075 mol</td>
</tr>
<tr>
<td>6-Chloro 2-methyl 5-aminophenol</td>
<td>0.0025 mol</td>
</tr>
<tr>
<td>Oleyl alcohol polyglycerolated with 2 mol of glycerol</td>
<td>4 g AM</td>
</tr>
<tr>
<td>Oleyl alcohol polyglycerolated with 4 mol of glycerol (78% AM)</td>
<td>6 g AM</td>
</tr>
</tbody>
</table>
Oleic acid 3 g
Oleylamine 2 OE sold under the name Ethomeen 012 by the company Akzo 7 g AM
Diethylenetriaminepentaacetic acid (EDTA) 3 g AM
Oleyl alcohol 5 g
Diethylaminopropyl laurylaminosuccinate, sodium salt, at 55% AM 3 g AM
Propylene glycol 9.5 g
Ethyl alcohol 5 g
Hexylene glycol 9.3 g
Sodium metabisulfite as an aqueous solution containing 35% AM 0.455 g AM
Ammonium acetate 0.8 g
Antioxidant, sequestrant qs
Fragrance, preservative qs
Aqueous ammonia containing 20% NH₃ 10.2 g
Demineralized water qs 100 g

AM : Active Material

**Mode of application**
The composition was diluted extemporaneously with 1 times its own weight of 20-volumes aqueous hydrogen peroxide solution.
The mixture was then applied to locks of grey hair containing 90% white hairs, at a rate of 10 g of mixture per 1 g of hair. After a leave-on time of 30 minutes at room temperature (25°C), the hair was then rinsed, washed with a standard shampoo and dried.

**Results**
The hair coloration was evaluated visually.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tone depth</th>
<th>Tint</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Chestnut brown</td>
<td>Ash-blue</td>
</tr>
</tbody>
</table>

**Compositions**
Composition C2 below was prepared:

| C2 | N4-[3-(1 H-imidazol-1-yl)propyl]-2-methylbenzene-1,4-diamine | 0.01 mol |
Mode of application
The composition was diluted extemporaneously with 1 times its own weight of 20-volumes aqueous hydrogen peroxide solution.
The mixture was then applied to locks of grey hair containing 90% white hairs, at a rate of 10 g of mixture per 1 g of hair. After a leave-on time of 30 minutes at room temperature (25°C), the hair was then rinsed, washed with a standard shampoo and dried.

Results
The hair coloration was evaluated visually.
<table>
<thead>
<tr>
<th>Composition</th>
<th>Tone depth</th>
<th>Tint</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>Chestnut brown</td>
<td>Ash-blue</td>
</tr>
</tbody>
</table>

Composition C3 below was prepared:

<table>
<thead>
<tr>
<th></th>
<th>C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2'-(2-[(4-amino-3-methylphenyl)amino]ethyl)iminodiethanol trihydrochloride</td>
<td>0.01 mol</td>
</tr>
<tr>
<td>7-Methyl-1H-indol-4-amine</td>
<td>0.0075 mol</td>
</tr>
<tr>
<td>6-Chloro 2-methyl 5-aminophenol</td>
<td>0.0025 mol</td>
</tr>
<tr>
<td>Oleyl alcohol polyglycerolated with 2 mol of glycerol</td>
<td>4 g AM</td>
</tr>
<tr>
<td>Oleyl alcohol polyglycerolated with 4 mol of glycerol (78% AM)</td>
<td>6 g AM</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>3 g</td>
</tr>
<tr>
<td>Oleylamine 2 OE sold under the name Ethomeen 012 by the company Akzo</td>
<td>7 g AM</td>
</tr>
<tr>
<td>Diethylaminopropyl laurylaminosuccinate, sodium salt, at 55% AM</td>
<td>3 g AM</td>
</tr>
<tr>
<td>Oleyl alcohol</td>
<td>5 g</td>
</tr>
<tr>
<td>(50% linear 70/30 C13/C15)alkyl ether carboxylic acid monoethanolamide (2 OE)</td>
<td>10 g AM</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>9.5 g</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>5 g</td>
</tr>
<tr>
<td>Hexylene glycol</td>
<td>9.3 g</td>
</tr>
<tr>
<td>Sodium metabisulfite as an aqueous solution containing 35% AM</td>
<td>0.455 g AM</td>
</tr>
<tr>
<td>Ammonium acetate</td>
<td>0.8 g</td>
</tr>
<tr>
<td>Antioxidant, sequestrant</td>
<td>qs</td>
</tr>
<tr>
<td>Fragrance, preservative</td>
<td>qs</td>
</tr>
<tr>
<td>Aqueous ammonia containing 20% NH₃</td>
<td>10.2 g</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>qs100 g</td>
</tr>
</tbody>
</table>

AM : Active Material

5 Mode of application
The composition was diluted extemporaneously with 1 times its own weight of 20-volumes aqueous hydrogen peroxide solution.
The mixture was then applied to locks of grey hair containing 90% white hairs, at a rate of 10 g of mixture per 1 g of hair. After a leave-on time of 30 minutes at room temperature (25°C), the hair was then rinsed, washed with a standard shampoo and dried.

Results

The hair coloration was evaluated visually.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tone depth</th>
<th>Tint</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3</td>
<td>Chestnut brown</td>
<td>Iridescent ash</td>
</tr>
</tbody>
</table>

Composition C4 below was prepared:

<table>
<thead>
<tr>
<th></th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2'-(2-[4-amino-3-methylphenyl)(amino]ethyl]imino)diethanol trihydrochloride</td>
<td>0.01 mol</td>
</tr>
<tr>
<td>2,3,7-trimethyl-1 H-indol-4-amine hydrochloride</td>
<td>0.0075 mol</td>
</tr>
<tr>
<td>6-Chloro 2-methyl 5-aminophenol</td>
<td>0.0025 mol</td>
</tr>
<tr>
<td>Oleyl alcohol polyglycerolated with 2 mol of glycerol</td>
<td>4 g AM</td>
</tr>
<tr>
<td>Oleyl alcohol polyglycerolated with 4 mol of glycerol (78% AM)</td>
<td>6 g AM</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>3 g</td>
</tr>
<tr>
<td>Oleylamine 2 OE sold under the name Ethomeen 012 by the company Akzo</td>
<td>7 g AM</td>
</tr>
<tr>
<td>Diethylaminopropyl laurylaminosuccinate, sodium salt, at 55% AM</td>
<td>3 g AM</td>
</tr>
<tr>
<td>Oleyl alcohol</td>
<td>5 g</td>
</tr>
<tr>
<td>(50% linear 70/30 C13/C15)alkyl ether carboxylic acid monoethanolamide (2 OE)</td>
<td>10 g AM</td>
</tr>
<tr>
<td>Propylene glycol</td>
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<td>5 g</td>
</tr>
<tr>
<td>Hexylene glycol</td>
<td>9.3 g</td>
</tr>
<tr>
<td>Sodium metabisulfite as an aqueous solution containing 35% AM</td>
<td>0.455 g AM</td>
</tr>
<tr>
<td>Ammonium acetate</td>
<td>0.8 g</td>
</tr>
<tr>
<td>Antioxidant, sequestrant</td>
<td>qs</td>
</tr>
<tr>
<td>Fragrance, preservative</td>
<td>qs</td>
</tr>
</tbody>
</table>
Aqueous ammonia containing 20% NH₃ | 10.2 g
---|---
Demineralized water | qs100 g

AM : Active Material

**Mode of application**
The composition was diluted extemporaneously with 1 times its own weight of 20-volumes aqueous hydrogen peroxide solution.
The mixture was then applied to locks of grey hair containing 90% white hairs, at a rate of 10 g of mixture per 1 g of hair. After a leave-on time of 30 minutes at room temperature (25°C), the hair was then rinsed, washed with a standard shampoo and dried.

**Results**
The hair coloration was evaluated visually.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tone depth</th>
<th>Tint</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>Chestnut brown</td>
<td>Iridescent ash</td>
</tr>
</tbody>
</table>
CLAIMS

1. Composition for dyeing keratin fibres, comprising, in a medium that is suitable for dyeing keratin fibres:
- at least one oxidation base chosen from the compounds of formula (I) and the addition salts thereof, solvates thereof and solvates of the salts thereof:

![Formula I](image)

in which:
- \( x \) is equal to 2 or 3;
- \( R_1 \) and \( R_2 \) represent a hydroxyethyl radical or form, together with the nitrogen to which they are attached, an imidazole heterocycle;
- at least one coupler chosen from the compounds of formula (II) and the addition salts thereof, solvates thereof and solvates of the salts thereof:

![Formula II](image)

in which:
- \( R'_1 \) represents:
  - a hydrogen atom;
  - a linear or branched saturated \( C_1-C_6 \) alkyl radical, optionally interrupted with an oxygen atom or a radical \( NR'_7 \), optionally substituted with a radical chosen from \( OH \) and \( NR'_7 R'_8 \);
- \( R'_2 \) and \( R'_3 \), which may be identical or different, represent:
  - a hydrogen atom;
  - a \( C_1-C_6 \) and preferably \( C_1-C_4 \) alkyl radical, optionally substituted with one or more hydroxyl radicals;
  - a \( C_1-C_6 \) alkyl carboxylate radical;
  - a carboxyl radical;
- a radical CON'R'R';
R'R' which may be identical or different, represent:
- a hydrogen atom;
- a C1-C6 alkyl radical;
5 R'6 represents:
- a halogen;
- a linear or branched C1-C10 alkyl radical, optionally interrupted with a heteroatom chosen from O or a radical NR'R', and/or optionally substituted with one or more radicals, which may be identical or different, chosen from
10 OH and NR'R'R';
- a carboxyl radical;
- a C1-C6 alkyl carboxylate radical;
- a radical CON'R'R';
- a C1-C6 alkoxy radical or a C1-C6(alkoxy)hydroxyalkoxy radical;
15 - a (alkoxy)alkyl radical or a C1-C6(alkoxy)alkyl radical;
- a radical O-Ak-NR'R'R' with Ak = linear C1-C8 or branched C3-C8 divalent alkylene radical, optionally interrupted with one or more oxygen atoms and/or groups NR'R';
R'R' and R'R' which may be identical or different, represent:
20 - a hydrogen atom;
- a C1-C8 alkyl radical optionally substituted with one or more hydroxyl radicals;
R'8 and R'8, which may be identical or different, represent a linear or branched, saturated or unsaturated C1-C4 alkyl;
25 R'8 and R'8, may form, with the nitrogen that bears them, a saturated or unsaturated 5- to 8-membered heterocycle, one of the chain members possibly being an oxygen atom or a radical NR'n with R'n = H or C1-C4 alkyl, optionally substituted with one or more radicals chosen from OH and NR'R'.

2. Composition according to Claim 1, in which, in formula (I), R1 and R2 form, together with the nitrogen to which they are attached, an imidazole heterocycle.

3. Composition according to Claim 2, in which the compound of formula (I) is N4-[3-(1 H-imidazol-1-yl)propyl]-2-methylbenzene-1,4-diamine.

4. Composition according to Claim 1, in which, in formula (I), R1 and R2 represent a hydroxyethyl radical.

5. Composition according to Claim 4, in which the compound of formula (I) is 2,2'-([(4-amino-3-methylphenyl)amino]ethyl)imino)diethanol.
6. Composition according to any one of Claims 1 to 5, in which, in formula (II), \( R'_{1} \) represents a hydrogen atom or a saturated \( \text{C}_{1}-\text{C}_{4} \) alkyl radical optionally substituted with a hydroxyl radical.

7. Composition according to any one of Claims 1 to 6, in which, in formula (II), \( R'_{2} \) and \( R'_{3} \), which may be identical or different, represent a hydrogen atom; a \( \text{Ci-C}_{4} \) alkyl radical optionally substituted with one or more hydroxyl radicals; a carboxyl radical; a \( \text{C}_{1}-\text{C}_{4} \) alkyl carboxylate radical; a radical \( \text{CONR'}_{7}R'_{8} \).

8. Composition according to any one of Claims 1 to 7, in which, in formula (II), \( R'_{4} \) and \( R'_{5} \) are identical and represent a hydrogen atom.

9. Composition according to any one of Claims 1 to 8, in which, in formula (II), \( R'_{6} \) represents a linear or branched \( \text{C}_{1}-\text{C}_{6} \) alkyl radical; a carboxyl radical; a \( \text{C}_{1}-\text{C}_{6} \) alkyl carboxylate; a carboxamide radical; a \((\text{Ci-C}_{6})\text{alkoxy(}\text{Ci-C}_{6}\text{)}\)alkyloxy radical; a \( \text{Ci-C}_{6} \) alkoxy or hydroxy(\( \text{CrC}_{6} \))alkyloxy radical; a radical \( \text{O-Ak-NR'}_{9}R'_{10} \) with \( \text{Ak} \) = linear \( \text{C}_{1}-\text{C}_{6} \) or branched \( \text{C}_{3}-\text{C}_{6} \) divalent alkylene radical optionally interrupted with a radical \( \text{NR'}_{7} \).

10. Composition according to any one of Claims 1 to 9, in which the 4-aminoindole derivatives are chosen from the derivatives of formula (II') and the addition salts thereof, solvates thereof and solvates of the salts thereof:

![Diagram](image)

(II')

in which:

\( R'_{1} \) represents:
- a hydrogen atom;
- a saturated \( \text{C}_{1}-\text{C}_{4} \) alkyl radical optionally substituted with a hydroxyl radical;

\( R'_{2} \) and \( R'_{3} \), which may be identical or different, represent:
- a hydrogen atom;
- a \( \text{Ci-C}_{6} \) alkyl radical optionally substituted with one or more hydroxyl radicals;
- a carboxyl radical;
- a \text{C}1-\text{C}4 alkyl carboxylate radical;
- a radical CONR'yR's, preferably a carboxamide radical CONH$_2$;

R'$_4$ and R'$_5$ represent a hydrogen atom;

R'$_6$ represents:
- a linear or branched \text{C}1-\text{C}6 alkyl radical;
- a carboxyl radical;
- a \text{C}1-\text{C}6 alkyl carboxylate;
- a carboxamide radical;
- a \text{(C}1-\text{C}6 \text{)alkoxy(C}1-\text{C}6 \text{)alkyloxy} radical;

- a \text{C}1-\text{C}6 alkoxy radical or a \text{C}1-\text{C}6 hydroxyalkoxy radical;
- a radical O-Ak-NR'$_9$R'$_0$ with Ak = linear \text{C}1-\text{C}6 or branched \text{C}3-\text{C}6 divalent alkylene radical, optionally interrupted with a radical NR'$_7$;

R'$_7$ and R'$_8$ represent a hydrogen atom or a \text{C}1-\text{C}6 alkyl radical optionally substituted with a hydroxyl radical;

R'$_g$ and R'$_i$$_o$, which may be identical or different, represent a saturated linear \text{C}1-\text{C}4 alkyl radical or an unsaturated linear \text{C}2-\text{C}4 alkyl radical;

R'$_g$ and R'$_i$$_o$ may form, with the nitrogen that bears them, a saturated or unsaturated 5- to 8-membered heterocycle; one of the chain members possibly being an oxygen atom or a radical NR'n with R'n = H or \text{C}1-\text{C}4 alkyl, optionally substituted with OH.

11. Composition according to any one of Claims 1 to 10, in which the 4-aminooindole derivatives are chosen from:

\begin{align*}
\text{2,3-dimethyl-7-(propan-2-yl)-1 H-indol-4-amine} & \quad \text{7-ethyl-2,3-dimethyl-1 H-indol-4-amine} \\
\text{2,3,7-trimethyl-1 H-indol-4-amine} & \quad \text{3-ethyl-2,7-dimethyl-1 H-indol-4-amine}
\end{align*}
7-ethyl-2,3-dimethyl-1H-indol-4-amine

3,7-diethyl-2-methyl-1H-indol-4-amine

2,3-dimethyl-7-(propan-2-yl)-1H-indol-4-amine

3-ethyl-2-methyl-7-(propan-2-yl)-1H-indol-4-amine

7-ethyl-1,2-(4-amino-7-ethyl-2,3-dimethyl-1H-indol-1-yl)ethanol

3,7-diethyl-1,2-dimethyl-1H-indol-4-amine

2-(4-amino-7-ethyl-2,3-dimethyl-1H-indol-1-yl)ethanol

2-(4-amino-3,7-diethyl-2-methyl-1H-indol-1-yl)ethanol

1,2,3-trimethyl-7-(propan-2-yl)-1H-indol-4-amine

3-ethyl-1,2-dimethyl-7-(propan-2-yl)-1H-indol-4-amine
2-[4-amino-2,3-dimethyl-7-(propan-2-yl)-1\textsubscript{H}-indol-1-yl]ethanol

7-methoxy-2,3-dimethyl-1\textsubscript{H}-indol-4-amine

2-(4-amino-7-methoxy-2,3-dimethyl-1\textsubscript{H}-indol-1-yl)ethanol

3-ethyl-7-methoxy-1,2-dimethyl-1\textsubscript{H}-indol-4-amine

2-[4-amino-3-ethyl-2-methyl-7-(propan-2-yl)-1\textsubscript{H}-indol-1-yl]ethanol

7-methoxy-1,2,3-trimethyl-1\textsubscript{H}-indol-4-amine

3-ethyl-7-methoxy-2-methyl-1\textsubscript{H}-indol-4-amine

3-ethyl-7-methoxy-1,2-dimethyl-1\textsubscript{H}-indol-4-amine

3-ethyl-7-methoxy-1,2-dimethyl-1\textsubscript{H}-indol-4-amine
2-(4-amino-3-ethyl-7-methoxy-2-methyl-1H-indol-1-yl)ethanol

7-ethoxy-2,3-dimethyl-1H-indol-4-amine

7-ethoxy-1,2,3-trimethyl-1H-indol-4-amine

12-(4-amino-7-ethoxy-2,3-dimethyl-1H-indol-1-yl)ethanol

7-ethoxy-3-ethyl-2-methyl-1H-indol-4-amine

7-ethoxy-3-ethyl-1,2-dimethyl-1H-indol-4-amine

2-(4-amino-7-ethoxy-3-ethyl-2-methyl-1H-indol-1-yl)ethanol

2-[(4-amino-2,3-dimethyl-1H-indol-7-yl)oxy]ethanol
2,3-dimethyl-7-[2-(piperidin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(4-methylpiperazin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(4-methylpiperazin-1-yl)ethoxy]-1H-indol-4-amine

2,3-dimethyl-7-[2-(morpholin-4-yl)ethoxy]-1H-indol-4-amine

2-[(4-[(4-amino-2,3-dimethyl-1H-indol-7-methyl-1H-indol-4-amine)yloxy]ethyl)piperazin-1-yl]ethanol

7-[2-(dimethylamino)ethoxy]-3-ethyl-2-methyl-1H-indol-4-amine
3-ethyl-2-methyl-7-[2-(piperidin-1-yl)ethoxy]-1H-indol-4-amine

3-ethyl-2-methyl-7-[2-(morpholin-4-yl)ethoxy]-1H-indol-4-amine

3-ethyl-2-methyl-7-[2-(pyrrolidin-1-yl)ethoxy]-1H-indol-4-amine

2-[4-amino-7-(2-hydroxyethoxy)-1H-indol-1-yl]ethanol

2-[(4-amino-1H-indol-7-yl)oxy]ethanol
7-[(2-piperidin-1-yl)ethoxy]-1H-indol-4-amine

7-[(2-morpholin-4-yl)ethoxy]-1H-indol-4-amine

7-[(2-(4-methylpiperazin-1-yl)ethoxy]-1H-indol-2-(4-[(2-[(4-amino-1H-indol-7-4-amine

2-(4-{2-[(4-amino-1H-indol-7-yl)oxy]ethyl}piperazin-1-yl)ethanol

7-[(2-(dimethylamino)ethoxy]-1H-indol-4-amine

7-[(2-(1H-imidazol-1-yl)ethoxy]-1H-indol-4-amine
amine

7-[2-(1H-imidazol-1-yl)ethoxy]-2,3-dimethyl-1H-indol-4-amine

2,3-dimethyl-7-[2-(1H-pyrrol-1-yl)ethoxy]-1H-indol-4-amine

ethyl 4-amino-3-methyl-7-(propan-2-yl)-1 H-indole-2-carboxylate

4-amino-7-(propan-2-yl)-1 H-indole-2-carboxylic acid
4-amino-3,7-dimethyl-1H-indole-2-carboxamide

4-amino-1H-indole-7-carboxylic acid

4-amino-2,3-dimethyl-1H-indole-7-carboxylic acid

methyl 4-amino-2,3-dimethyl-1H-indole-7-carboxylate

4-amino-2,3-dimethyl-1H-indole-7-carboxamide

4-amino-1H-indole-7-carboxamide
7-methyl-1H-indol-4-amine
7-ethyl-1H-indol-4-amine
and the addition salts thereof, solvates thereof and solvates of the salts thereof.

12. Composition according to any one of Claims 1 to 11, also comprising at least one additional coupler chosen from the compounds of formula (III) and the addition salts thereof, solvates thereof and solvates of the salts thereof:

![Chemical Structure]

in which:
R"1 represents a hydrogen atom or a C_1-C_4 hydroxyalkyl radical;
R"2 represents an amino radical or a hydroxyl radical;
R"3 represents a C_1-C_4 alkyl radical or a C_1-C_4 hydroxyalkyl radical;
R"4 represents a hydrogen atom or a halogen atom.

13. Composition according to Claim 12, in which the compound of formula (III) is 2-chloro-6-methyl-3-aminophenol.

14. Composition according to any one of Claims 1 to 13, comprising at least one oxidizing agent.

15. Composition according to Claim 14, in which the oxidizing agent(s) are chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, peracids and oxidase enzymes, and preferably hydrogen peroxide.

16. Process for dyeing keratin fibres, in which the composition as defined in any one of Claims 1 to 13 is applied to the keratin fibres in the presence of at least one oxidizing agent for a time that is sufficient to develop the desired coloration.

17. Multi-compartment device in which a first compartment contains a dye composition as defined in any one of Claims 1 to 13 and a second compartment contains at least one oxidizing agent.