



(51) International Patent Classification:

A61K 8/41 (2006.01)

A61Q 5/10 (2006.01)

C07C 211/51 (2006.01)

C07D 211/00 (2006.01)

EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/EP2019/062831

(22) International Filing Date:

17 May 2019 (17.05.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1854108

17 May 2018 (17.05.2018)

FR

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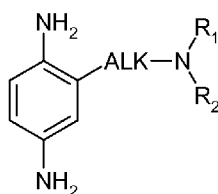
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

Published:

— with international search report (Art. 21(3))

(54) Title: PARA-PHENYLENEDIAMINE BASES MONOSUBSTITUTED IN POSITION 2 WITH AN AMINOALKYL CHAIN AND USE THEREOF FOR THE OXIDATION DYEING OF KERATIN FIBRES



(I)

(57) Abstract: The present invention relates to novel para-phenylenediamine compounds substituted in position 2 with an aminoalkyl chain (Formula (I)). The present invention is used in the field of the dyeing of keratin fibres and more particularly the dyeing of keratin fibres, especially of human keratin fibres such as the hair.

**para-Phenylenediamine bases monosubstituted in position 2 with an aminoalkyl chain
and use thereof for the oxidation dyeing of keratin fibres**

5 The present invention relates to para-phenylenediamine compounds substituted in position 2 with an aminoalkyl chain.

 The present invention is used in the field of the dyeing of keratin fibres and more particularly the dyeing especially of human keratin fibres such as the hair.

10 It is already known from the prior art that para-phenylenediamine bases play an important role in the process of hair dyeing. They are colourless or weakly coloured oxidation dye precursors which, in the presence of oxidizing compounds, are transformed into coloured compounds.

 By combining an oxidation dye precursor with oxidizing compounds and dyeing couplers, a rich, broad range of colours is obtained.

15 "Permanent" dyeing is characterized by the use of dye precursors in the presence of oxidizing compounds. In order to be considered as efficient dyeing, said dyeing needs to satisfy certain criteria. It must make it possible to obtain shades in the desired intensity with colour differences, between the end and the root of a same lock (also known as the selectivity), which are as small as possible.

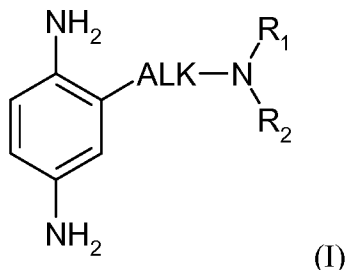
20 The colouring must also be resistant over time and must not become degraded in the presence of external agents such as washing, light, bad weather, rubbing and perspiration.

 However, the dyeing results obtained are not always very satisfactory, especially in terms of colour build-up, selectivity, chromaticity, intensity and/or
25 persistence in particular with respect to successive shampooing, or resistance to light or to perspiration.

 There is thus a real need to propose colourings that have better dyeing properties, especially in terms of chromaticity, selectivity, power and fastness, and which are also capable of leading to a wide range of colours.

30 This aim is achieved by the present invention, one subject of which is especially a composition (A) comprising, in a medium that is suitable for dyeing keratin fibres, in particular human keratin fibres such as the hair:

- one or more oxidation bases chosen from the compounds of formula (I), and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates:



in which formula (I):

- ALK represents a linear or branched alkylene chain including from 3 to 8 carbon atoms, optionally substituted with one or more identical or different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy;
- R₁ and R₂, which may be identical or different, represent:
 - a hydrogen atom;
 - a (C₁-C₆)alkylcarbonyl group such as acetyl;
 - a linear or branched (C₁-C₈)alkyl group;
 - optionally substituted with one or more identical or different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy, iii) acylamino, iv) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (C₁-C₈)alkyl group, optionally interrupted with one or more additional heteroatoms and/or groups, which may be identical or different, chosen from -O-, -S-, -NH-, -S(O)-, -S(O)₂-, -C(O)- and/or -C(S)-, and/or optionally substituted with one or more identical or different radicals chosen from the hydroxyl radical, the C₁-C₆ alkoxy radical, v) aromatic or non-aromatic (hetero)cycle, such as phenyl, and vi) -C(X)-NR'₃R'₄ with R'₃ and R'₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a radical NR'₃ with R'₃ as

defined previously; preferentially, R'₃ and R'₄ represent a hydrogen atom and X denotes NR'₃; and/or

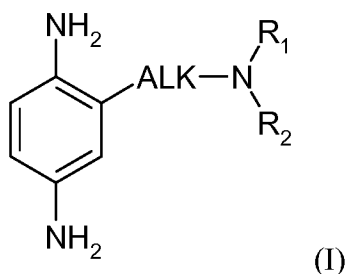
- optionally interrupted with one or more additional heteroatoms and/or groups, which may be identical or different, chosen from -O-, -S-, -NH-, -S(O)-, -S(O)₂-, -C(O)- and/or -C(S)-; and

- one or more coupling agents.

This composition according to the invention makes it possible to obtain better dyeing properties, and especially better solubility, colour build-up, chromaticity, fastness and selectivity. It also affords access to a wide range of light, natural and dark colours.

It has also been observed that the keratin fibre colourings obtained with the composition of the invention are particularly persistent with respect to external agents (washing, light, bad weather, friction, perspiration), and especially persistent for at least four shampoo washes.

Another subject of the present invention is compounds of formula (I) below, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates:



in which formula (I):

- ALK represents a linear or branched alkylene chain including from 3 to 8 carbon atoms, optionally substituted with one or more identical or different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy;
- R₁ and R₂, which may be identical or different, represent:
 - a hydrogen atom;
 - a (C₁-C₆)alkylcarbonyl group such as acetyl;

- a linear or branched (C₁-C₈)alkyl group;
 - optionally substituted with one or more identical or different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy, iii) acylamino, iv) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (C₁-C₈)alkyl group, optionally interrupted with one or more additional heteroatoms and/or groups, which may be identical or different, chosen from -O-, -S-, -NH-, -S(O)-, -S(O)₂-, -C(O)- and/or -C(S)-, and/or optionally substituted with one or more identical or different radicals chosen from the hydroxyl radical, the C₁-C₆ alkoxy radical, v) aromatic or non-aromatic (hetero)cycle, such as phenyl, and vi) -C(X)-NR'₃R'₄ with R'₃ and R'₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a radical NR'₃ with R'₃ as defined previously; preferentially, R'₃ and R'₄ represent a hydrogen atom and X denotes NR'₃; and/or
 - optionally interrupted with one or more additional heteroatoms and/or groups, which may be identical or different, chosen from -O-, -S-, -NH-, -S(O)-, -S(O)₂-, -C(O)- and/or -C(S)-.

The invention also relates to the use of one or more compounds of formula (I) for dyeing keratin fibres, in particular human keratin fibres such as the hair.

The present invention also relates to a composition for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising, in a suitable dyeing medium, one or more compounds of formula (I).

In particular, the invention relates to the use of said composition for dyeing keratin fibres, in particular human keratin fibres such as the hair.

The invention also relates to a process for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step of applying to said fibres the dye composition according to the invention in the presence of one or more chemical oxidizing agents for a time that is sufficient to obtain the desired colouring, after which the resulting fibres are rinsed, optionally washed with shampoo, rinsed again and dried or left to dry.

Another subject of the present invention concerns a multi-compartment dyeing device or kit comprising a first compartment containing a dye composition as described above and a second compartment containing one or more chemical oxidizing agents. The multi-compartment device is thus suitable for performing the dyeing process according to the invention.

Other characteristics, aspects, subjects and advantages of the present invention will emerge even more clearly on reading the description and the examples that follow.

- For the purposes of the invention, unless otherwise indicated:
- the limits of a range of values are included in that range, in particular in the expressions "between... and ..." and "ranging from ... to ...";
 - the expression "at least one" used in the present description is equivalent to the expression "one or more", and may be replaced therewith;
 - according to the present patent application, the term "keratin fibres" denotes human keratin fibres and more particularly the hair;
 - the term "*alkyl*" denotes a linear or branched, saturated or unsaturated hydrocarbon-based group, comprising from 1 to 8 carbon atoms; preferably, the alkyl group is saturated, in particular, the alkyl group is a saturated C₁-C₆ group such as methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *tert*-butyl, 2-butyl, *n*-pentyl, 2-pentyl, 3-pentyl or *n*-hexyl;
 - the term "*alkoxy*" denotes an alkyl-oxy group with alkyl as defined previously, preferably methoxy or ethoxy, in particular methoxy;
 - the term "(hydroxy)alkyl" denotes an alkyl group as defined previously or a hydroxyalkyl group with alkyl as defined previously;
 - the term "*alkylene*" corresponds to a linear or branched divalent C₃-C₈ hydrocarbon-based group of general formula C_nH_{2n} with $3 \leq n \leq 8$, in particular C₃-C₆; preferably C₃-C₄ such as propylene;
 - the term "*acylamino*" corresponds to a group (-NR-C(O)-R') in which the radical R is a hydrogen atom or a C₁-C₄ alkyl radical optionally bearing at least one hydroxyl group and the radical R' is a C₁-C₂ alkyl radical such as methyl;

- the term "*(hetero)cycle*" corresponds to a cyclic radical or to an aromatic or non-aromatic, monocyclic or bicyclic, preferably monocyclic, 5- to 10-membered, preferably 5- to 8-membered heterocyclic radical; said (*hetero*)cycle being optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) linear or branched C₁-C₄ (hydroxy)alkyl; v) hydroxyl; vii) C₁-C₄ alkoxy; viii) amino -NH₂, one or more ring members of said "*(hetero)cycle*" possibly denoting a heteroatom such as O, S or N or a carbonyl diradical -CO-.

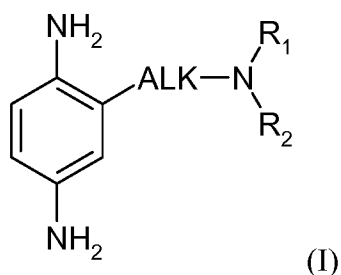
It is understood that, for the purposes of the invention, a heterocyclic radical comprises one or more heteroatoms chosen, for example, from an oxygen atom, a nitrogen atom, a sulfur atom, in particular a nitrogen atom and optionally a nitrogen or oxygen atom.

For the purposes of the invention, the term "*(hetero)cycle*" in particular denotes a phenyl radical or a heterocyclic radical such as a pyrrolidinyl, piperidyl, morpholinyl radical;

- the term "*addition salts with organic or mineral acids*" more particularly means salts chosen from a salt derived from i) hydrochloric acid HCl, ii) hydrobromic acid HBr, iii) sulfuric acid H₂SO₄, iv) alkylsulfonic acids: Alk-S(O)₂OH such as methylsulfonic acid and ethylsulfonic acid; v) arylsulfonic acids: Ar-S(O)₂OH such as benzenesulfonic acid and toluenesulfonic acid; vi) citric acid; vii) succinic acid; viii) tartaric acid; ix) lactic acid; x) alkoxysulfinic acids: Alk-O-S(O)OH such as methoxysulfinic acid and ethoxysulfinic acid; xi) aryloxysulfinic acids such as tolueneoxysulfinic acid and phenoxy sulfinic acid; xii) phosphoric acid H₃PO₄; xiii) acetic acid CH₃C(O)OH; xiv) triflic acid CF₃SO₃H; and xv) tetrafluoroboric acid HBF₄; preferably, the acid salts according to the invention are salts of mineral acids such as hydrochloric acid salts.

Compounds of formula (I)

One subject of the present invention relates to the compounds of formula (I) below:



with ALK, R₁ and R₂ as defined previously.

The addition salts with organic or mineral acids, the optical isomers, the geometrical isomers, the tautomers, and the solvates such as hydrates, of the compounds of formula (I) are also included in the subject of the invention.

Preferably, ALK is unsubstituted.

More preferentially, ALK represents an unsubstituted linear C₃-C₆ alkylene chain; more preferentially unsubstituted linear C₃-C₅; even more preferentially unsubstituted linear C₃-C₄; better still unsubstituted linear C₃ such as propylene -(CH₂)₃-.

Preferably, R₁ and R₂, which may be identical or different, represent:

- a hydrogen atom;
- a linear or branched (C₁-C₈)alkyl group;
 - optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy such as methoxy, iii) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (hydroxy)(C₁-C₄)alkyl group, iv) aromatic or non-aromatic (hetero)cycle, such as phenyl, pyrrolidinyl, morpholinyl, piperidyl, and v) -C(X)-NR₃R₄ with R₃ and R₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom, or a group NR₃ with R₃ as defined previously; preferentially, R₃ and R₄ represent a hydrogen atom and X denotes NR₃; and/or
 - optionally interrupted with a heteroatom chosen from -O-, -S-, -NH-, preferably with an oxygen atom -O-.

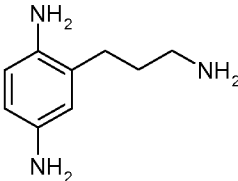
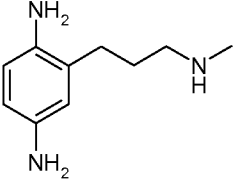
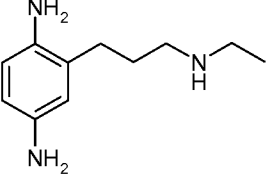
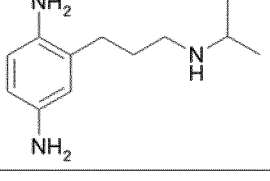
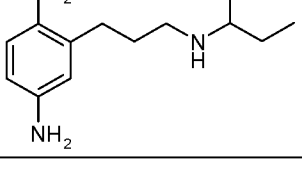
More preferentially, R₁ is different from R₂, and R₁ represents a hydrogen atom or a linear (C₁-C₄)alkyl group, even more preferentially a hydrogen atom or a methyl group or an ethyl group, better still a hydrogen atom.

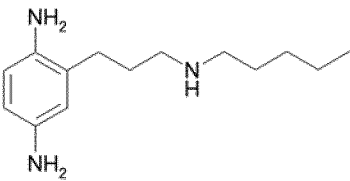
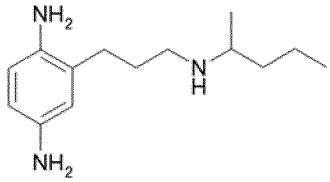
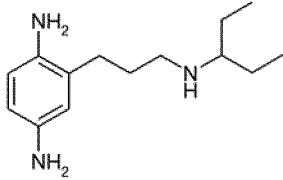
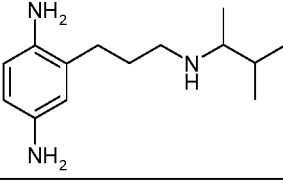
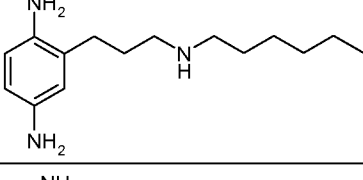
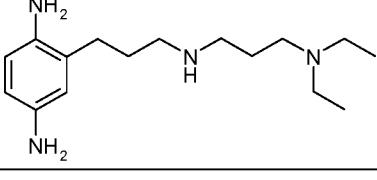
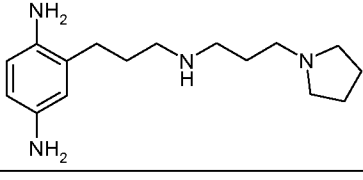
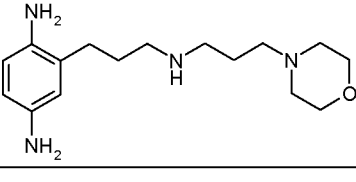
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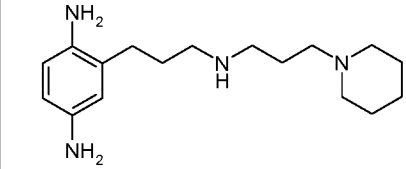
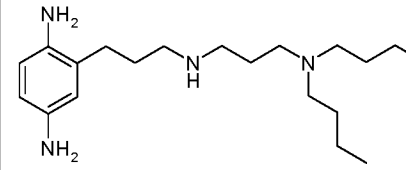
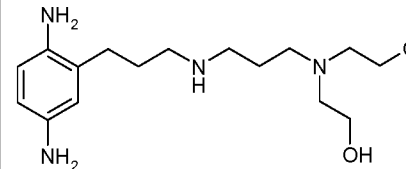
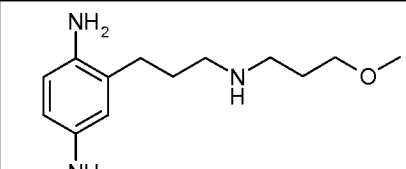
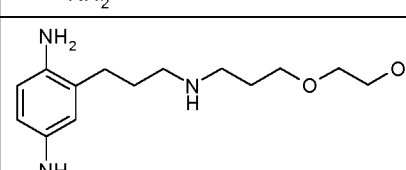
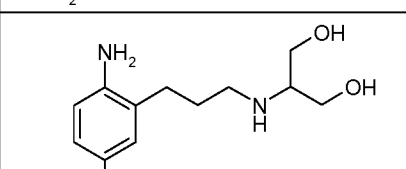
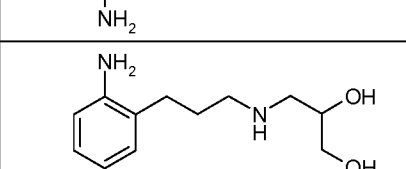
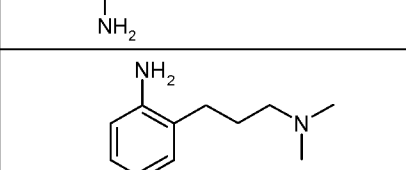
Even more preferentially, the compound(s) of formula (I) are chosen from compounds (1) to (36) as described in table 1 below, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates:

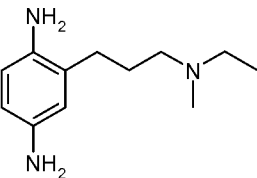
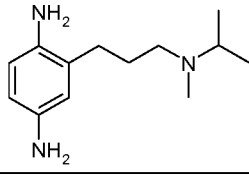
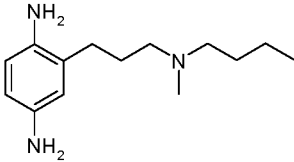
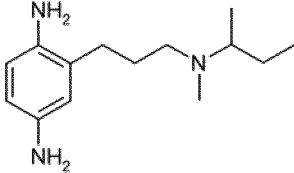
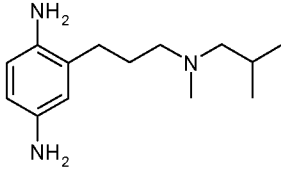
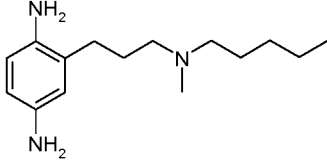
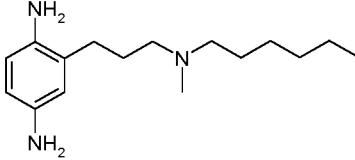
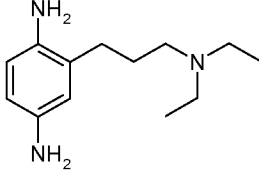
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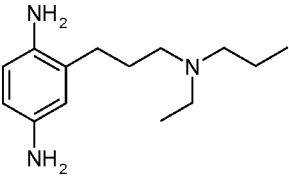
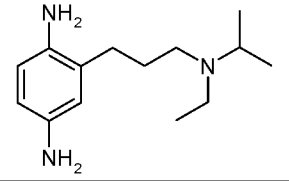
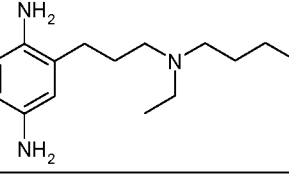
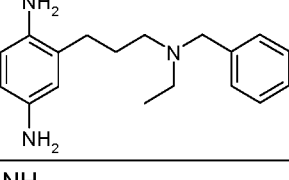
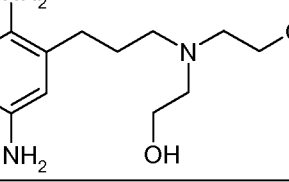
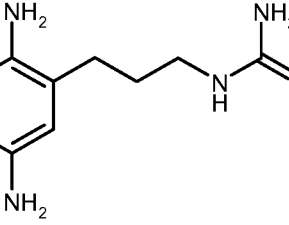
Table 1:

	Structures	Chemical name
Compound 1		2-(3-aminopropyl)benzene-1,4-diamine
Compound 2		2-[3-(methylamino)propyl]benzene-1,4-diamine
Compound 3		2-[3-(ethylamino)propyl]benzene-1,4-diamine
Compound 4		2-[3-(propan-2-ylamino)propyl]benzene-1,4-diamine
Compound 5		2-[3-(butan-2-ylamino)propyl]benzene-1,4-diamine

Compound 6		2-[3-(pentylamino)propyl]benzene-1,4-diamine
Compound 7		2-[3-(pentan-2-ylamino)propyl]benzene-1,4-diamine
Compound 8		2-[3-(pentan-3-ylamino)propyl]benzene-1,4-diamine
Compound 9		2-{3-[(3-methylbutan-2-yl)amino]propyl}benzene-1,4-diamine
Compound 10		2-[3-(hexylamino)propyl]benzene-1,4-diamine
Compound 11		2-(3-{3-(diethylamino)propyl}amino)propylbenzene-1,4-diamine
Compound 12		2-(3-{3-(pyrrolidin-1-yl)propyl}amino)propylbenzene-1,4-diamine
Compound 13		2-(3-{3-(morpholin-4-yl)propyl}amino)propylbenzene-1,4-diamine

Compound 14		2-(3-{{[3-(piperidin-1-yl)propyl]amino}propyl)benzene-1,4-diamine
Compound 15		2-(3-{{[3-(dibutylamino)propyl]amino}propyl)benzene-1,4-diamine
Compound 16		2,2'-[(3-{{[3-(2,5-diaminophenyl)propyl]amino}propyl)imino]diethanol
Compound 18		2-{3-[(3-methoxypropyl)amino]propyl}benzene-1,4-diamine
Compound 19		2-(3-{{[3-(2-methoxyethoxy)propyl]amino}propyl)benzene-1,4-diamine
Compound 20		2-{[3-(2,5-diaminophenyl)propyl]amino}propane-1,3-diol
Compound 21		3-{[3-(2,5-diaminophenyl)propyl]amino}propane-1,2-diol
Compound 22		2-[3-(dimethylamino)propyl]benzene-1,4-diamine

Compound 23		2-{3-[ethyl(methyl)amino]propyl}benzene-1,4-diamine
Compound 24		2-{3-[methyl(propan-2-yl)amino]propyl}benzene-1,4-diamine
Compound 25		2-{3-[butyl(methyl)amino]propyl}benzene-1,4-diamine
Compound 26		2-{3-[butan-2-yl(methyl)amino]propyl}benzene-1,4-diamine
Compound 27		2-{3-[methyl(2-methylpropyl)amino]propyl}benzene-1,4-diamine
Compound 28		2-{3-[methyl(pentyl)amino]propyl}benzene-1,4-diamine
Compound 29		2-{3-[hexyl(methyl)amino]propyl}benzene-1,4-diamine
Compound 30		2-[3-(diethylamino)propyl]benzene-1,4-diamine

Compound 31		2-{3-[ethyl(propyl)amino]propyl}benzene-1,4-diamine
Compound 32		2-{3-[ethyl(propan-2-yl)amino]propyl}benzene-1,4-diamine
Compound 33		2-{3-[butyl(ethyl)amino]propyl}benzene-1,4-diamine
Compound 34		2-{3-[benzyl(ethyl)amino]propyl}benzene-1,4-diamine
Compound 35		2,2'-{[3-(2,5-diaminophenyl)propyl]imino}diethanol
Compound 36		1-[3-(2,5-diaminophenyl)propyl]guanidine

More preferentially, R₁ and R₂, which may be identical or different, represent:

- a hydrogen atom;
- a linear or branched (C₁-C₄)alkyl group, optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₄ alkoxy such as methoxy, and iii) -C(X)-NR'₃R'₄ with R'₃ and R'₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom, or a group NR'₃ with R'₃ as

defined previously; preferentially, R'₃ and R'₄ represent a hydrogen atom and X denotes NR'₃.

Thus, the compounds of formula (I) are chosen in particular from compounds
5 20, 21, 30, 35 and 36 described in table 1 mentioned previously, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates.

According to a particular embodiment of the invention, R₁ and R₂ are
10 identical;
preferably, according to this embodiment, R₁ and R₂ each represent a hydrogen atom or a linear (C₁-C₄)alkyl group:

- optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₄ alkoxy such
15 as methoxy, iii) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (hydroxy)(C₁-C₄)alkyl group; and/or
- optionally interrupted with a heteroatom chosen from -O-, -S-, -NH-, preferably with an oxygen atom -O-.

Thus, the compounds of formula (I) are chosen in particular from compounds
20 1, 22, 30 and 35 described in table 1 mentioned previously, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates.

More preferentially, according to this embodiment, R₁ and R₂, which are
25 identical, each represent a hydrogen atom or a linear (hydroxy)(C₁-C₄)alkyl group, even more preferentially a methyl group, or an ethyl group or a hydroxyethyl group. In particular, the compounds of formula (I) are chosen from compounds 30 and 35 described in table 1 mentioned previously, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof,
30 the tautomers thereof, and the solvates thereof such as hydrates.

According to another embodiment of the invention, R₁ is different from R₂.

Preferably, according to this embodiment, R₁ represents a hydrogen atom or a linear (C₁-C₄)alkyl group optionally substituted with one or more radicals, which

may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy such as methoxy;

and R₂, which is different from R₁, represents a hydrogen atom or a linear or branched (C₁-C₆) alkyl group:

- 5 ▪ optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy such as methoxy, iii) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (hydroxy)(C₁-C₄)alkyl group, iv) aromatic or non-aromatic (hetero)cycle, such as phenyl, pyrrolidinyl, morpholinyl, piperidyl, and v) -C(X)-NR₃R₄ with R₃ and R₄,
10 which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a group NR₃ with R₃ as defined previously; preferentially, R₃ and R₄ represent a hydrogen atom and X denotes NR₃; in particular, X denotes NH; and/or
15 ▪ optionally interrupted with a heteroatom chosen from -O-, -S-, -NH-, preferably with an oxygen atom -O-.

Thus, according to this embodiment, the compounds of formula (I) are chosen in particular from compounds 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 19, 20, 21, 23, 24, 25, 26, 27, 28, 29, 31, 32, 33, 34 and 36 as described in table 1 above, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates.

More preferentially, according to this embodiment, R₁, which is different from R₂, represents a hydrogen atom or a linear (C₁-C₄)alkyl group, in particular a
25 hydrogen atom or a methyl group or an ethyl group, even more particularly a hydrogen atom.

Preferably, according to this embodiment, R₂, which is different from R₁, represents a linear or branched (C₁-C₄)alkyl group, optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₄ alkoxy such as methoxy, and iii) -C(X)-NR₃R₄ with R₃ and R₄,
30 which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a group NR₃ with R₃ as defined previously; preferentially, R₃ and R₄ represent a hydrogen atom and X denotes NR₃.

According to another particular embodiment of the invention, R₁ is different from R₂, and R₂ represents a group from among: i) (C₁-C₆)alkyl optionally substituted with one or more groups chosen from a) hydroxyl, b) (di)(C₁-C₄)alkylamino, c) (di)hydroxy(C₁-C₄)alkylamino, and d) 5- or 6-membered saturated heterocycle such as pyrrolino, piperazino, piperidino or morpholino, ii) (C₁-C₄)alkoxy(C₁-C₄)alkyl, iii) (C₁-C₄)alkoxy(C₁-C₄)alkoxy(C₁-C₄)alkyl, iii) aryl(C₁-C₄)alkyl such as benzyl, iv) -C(NH)-NH₂.

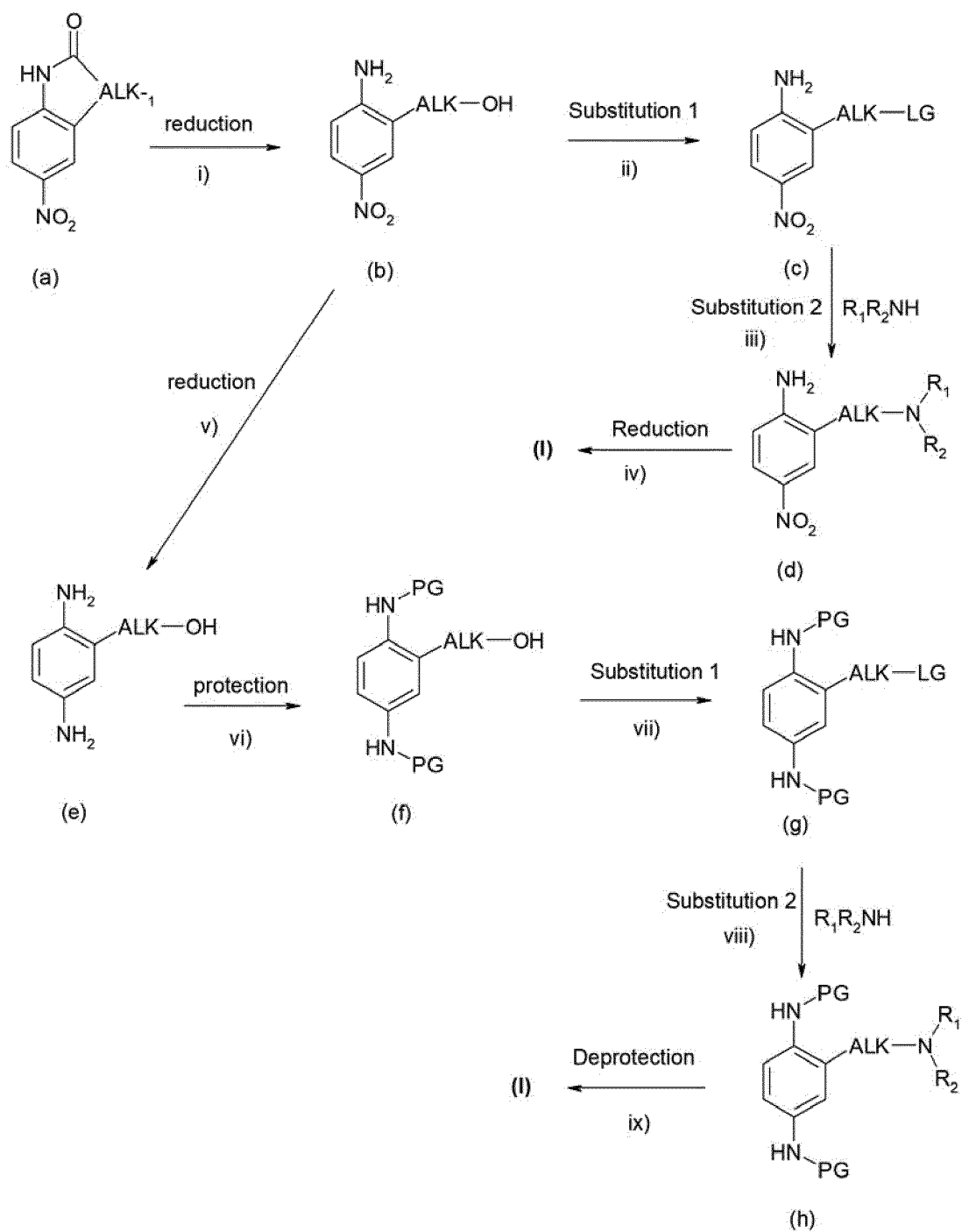
More preferentially, R₂ represents i) a (C₁-C₆)alkyl group optionally substituted with one or more hydroxyl groups.

Thus, according to this embodiment, more particularly, the compounds of formula (I) are chosen from compounds 20, 21 and 36 as described in table 1 above, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates; and, even more particularly, R₁, which is different from R₂, and the compounds of formula (I) denote compound 20 as described in table 1 above, and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates.

A subject of the invention is also the use of one or more compounds of formula (I), and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates, as defined previously, as an oxidation base for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair.

Process for preparing the compounds of formula (I)

A subject of the invention is also a process for preparing the compounds of formula (I) as defined above, according to the following chemical synthetic scheme, from compounds of formula (a) or from any of the compounds (b), (c), (d), (e), (f), (g) or (h):



in which scheme:

- R_1 and R_2 are as defined previously,
- ALK is as defined previously,
- ALK-_1 represents a linear or branched alkylene chain including from 2 to 7 carbon atoms, optionally substituted with one or more identical or

different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy,

- LG (leaving group) represents a nucleofugal group such as halogen, tosyl or triflate,

5 - PG (protecting group) representing a protecting group which withstands the reaction conditions of the entire synthesis up to the deprotection step;

the process consisting:

10 * either, in a first step i), in reducing the bicyclic amido derivative (a) to give the 4-nitroaniline compound substituted in alpha to the amino with a hydroxy-ALK group (b); preferably, this step is performed in a polar protic or aprotic organic solvent such as a (C₁-C₆)alkanol, in particular methanol or tetrahydrofuran (THF), in the presence of a reducing agent chosen in particular from borohydrides of an alkaline agent such as NaBH₄; and then, in a second step ii), in transforming the hydroxyl group
15 of compound (b) into a nucleofugal leaving group LG such as halogen, triflate, tosylate, mesylate, for example *via* a (C₁-C₆)alkylsulfonyl halide such as methanesulfonyl chloride, step ii) performed in particular in a polar or non-polar protic solvent such as THF, preferably in the presence of an alkaline agent such as *N,N*-diisopropylethylamine (DIPEA); and then, in a third step iii), in substituting the
20 nucleofugal group LG with an amine N(H)R₁R₂ with R₁ and R₂ as defined previously, preferably in alkaline medium; and then, in a fourth step iv), in reducing the nitro compound (d) in particular by catalytic hydrogenation preferably with palladium, nickel, zinc, iron or tin preferably on graphite, such as Pd(II)/C, to give the compound of formula (I) of the invention;

25 * or, after the first step i), in a second step v), in reducing the 4-nitroaniline derivative substituted in alpha to the amino with a hydroxy-ALK group (b), preferably by catalytic hydrogenation to give the 1,4-phenylenediamine compound substituted in alpha to the amino with a hydroxy-ALK group (e), and then, in a third step vi), in protecting the amino groups with a protecting group in particular via a reagent such as
30 R-C(Y_a)-Y_a-C(Y_a)-R' with R and R', which may be identical or different, representing a (C₁-C₆)alkyl group, and Y_a, which may be identical or different, representing an oxygen or sulfur atom; preferably, said reagent is acetic anhydride; followed by steps vii) and viii) of substitutions 1 and 2 under the same conditions as during steps ii) and iii) to give compounds (c) and (d), respectively, and compound (h) is then deprotected,

in particular in a preferably polar protic organic solvent, more preferentially in the presence of one or more mineral or organic acids, more preferentially mineral acids such as hydrochloric acid, to give the compound of formula (I) as defined previously.

5 Composition

Another subject of the present invention relates to a composition (A) comprising, in a medium that is suitable for dyeing keratin fibres, in particular human keratin fibres such as the hair, one or more oxidation bases chosen from the compounds of formula (I), and also the addition salts thereof with organic or mineral acids, the
10 optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates, as defined previously, and mixtures thereof, and one or more coupling agents.

The compound(s) of formula (I) present in composition (A) have the same preferences and the same embodiments as the compounds of formula (I) according to
15 the invention described previously.

Preferably, the compound(s) of formula (I), and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the geometrical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates, as defined previously, are present in composition (A) according to the invention in a total content
20 ranging from 0.1% to 20% by weight, more preferentially in a content ranging from 0.1% to 5% by weight relative to the total weight of composition (A).

The medium that is suitable for dyeing, also known as the dye support, is cosmetically acceptable. By way of example, said medium generally comprises water
25 or a mixture of water and of one or more solvents, for instance C₁-C₄ lower alkanols such as ethanol and isopropanol, polyols, for instance propylene glycol, dipropylene glycol or glycerol, and polyol ethers, 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%
30 by weight approximately relative to the total weight of the dye composition.

For the purposes of the invention, the solvent(s) are in liquid form at room temperature (25°C) and at atmospheric pressure.

Composition (A) according to the invention comprises one or more coupling agents or "couplers".

Preferably, the coupling agent(s) are chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers, the addition salts thereof, and mixtures thereof.

More preferentially, the coupling agent(s) are chosen from 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethoxy)benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1- β -hydroxyethylamino-3,4-methylenedioxybenzene, α -naphthol, 2-methyl-1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-(β -hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-bis(β -hydroxyethylamino)toluene, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one, 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-1,2,4-triazole, 6-methylpyrazolo[1,5-a]benzimidazole, 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 3-amino-2-chloro-6-methylphenol, the corresponding addition salts thereof with an acid, and mixtures thereof.

Preferably, the total content of coupling agent(s) in composition (A) is between 0.001% and 10% by weight, more preferentially between 0.005% and 5% by weight, relative to the total weight of composition (A).

Composition (A) according to the invention may optionally also comprise one or more additional oxidation bases other than the compounds of formula (I) described previously.

Preferably, the additional oxidation base(s) other than the compounds of formula (I) described previously are chosen from para-phenylenediamines other than the compounds of formula (I) described previously, bis(phenyl)alkylenediamines, ortho-aminophenols, heterocyclic bases, the corresponding addition salts, and mixtures thereof.

Among the para-phenylenediamines other than the compounds of formula (I) described previously, mention may be made especially of para-phenylenediamine (PPD), para-toluenediamine (PTD), 2-chloro-1,4-phenylenediamine, 2,3-dimethyl-1,4-phenylenediamine, 2,6-dimethyl-1,4-phenylenediamine, 2,6-diethyl-1,4-phenylenediamine, 2,5-dimethyl-1,4-phenylenediamine, N,N-dimethyl-1,4-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β -hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β -hydroxyethyl)amino-2-chloroaniline, 2- β -hydroxyethyl-1,4-phenylenediamine, 2-methoxymethyl-1,4-phenylenediamine, 2-fluoro-1,4-phenylenediamine, 2-isopropyl-1,4-phenylenediamine, N-(β -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-1,4-phenylenediamine, N,N-dimethyl-3-methyl-1,4-phenylenediamine, N-ethyl-N-(β -hydroxyethyl)-para-phenylenediamine, N-(β,γ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- β -hydroxyethoxy-1,4-phenylenediamine, 2- β -acetylaminoethoxy-1,4-phenylenediamine, N-(β -methoxyethyl)-para-phenylenediamine, 4-aminophenylpyrrolidine, 2-thienyl-1,4-phenylenediamine, 2- β -hydroxyethylamino-5-aminotoluene and 3-hydroxy-1-(4'-aminophenyl)pyrrolidine, and the corresponding addition salts with an acid, and mixtures thereof.

More preferentially, the para-phenylenediamines other than the compounds of formula (I) described previously are chosen from PPD, PTD, N,N-bis(β -hydroxyethyl)-para-phenylenediamine, 2- β -hydroxyethyl-1,4-phenylenediamine, 2-methoxyoxyethyl-1,4-phenylenediamine, 2-isopropoxyethyl-1,4-phenylenediamine, 2-isopropyl-para-phenylenediamine, 2- β -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2- β -acetylaminooxyethyl-para-phenylenediamine, the corresponding addition salts thereof with an acid, and mixtures thereof.

30 Among the bis(phenyl)alkylenediamines, mention may be made especially of N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β -hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β -hydroxyethyl)-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, the corresponding addition salts, and mixtures thereof.

Among the ortho-aminophenols, mention may be made especially of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, the corresponding addition salts, and mixtures thereof.

Among the heterocyclic bases, mention may be made especially of pyridine, pyrimidine and pyrazole derivatives, and mixtures thereof.

Other pyridine oxidation bases that may be mentioned are the 3-aminopyrazolo[1,5-a]pyridine oxidation bases or the corresponding addition salts described, for example, in patent application FR 2 801 308. Examples that may be mentioned include 2-acetylaminopyrazolo[1,5-a]pyrid-3-ylamine, 2-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine, 2-methoxypyrazolo[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, 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-4-ol, 3-aminopyrazolo[1,5-a]pyridin-6-ol, 3-aminopyrazolo[1,5-a]pyridin-7-ol, 2-b-hydroxyethoxy-3-aminopyrazolo[1,5-a]pyridine; 2-(4-dimethylpiperazinium-1-yl)-3-aminopyrazolo[1,5-a]pyridine; and the corresponding addition salts.

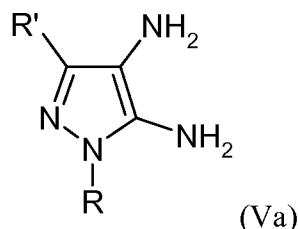
More particularly, the additional oxidation bases in the present invention may be chosen from 3-aminopyrazolo[1,5-a]pyridines and preferably substituted on carbon atom 2 with:

- a) a (di)(C₁-C₆)(alkyl)amino group, said alkyl group possibly being substituted with at least one hydroxyl, amino or imidazolium group;
- b) an optionally cationic 5- to 7-membered heterocycloalkyl group containing from 1 to 3 heteroatoms, optionally substituted with one or more (C₁-C₆)alkyl groups, such as a di(C₁-C₄)alkylpiperazinium or imidazolium group; or
- c) a (C₁-C₆)alkoxy group optionally substituted with one or more hydroxyl groups, such as a β-hydroxyalkoxy group, and the corresponding addition salts.

According to a particular embodiment of the invention, the additional oxidation bases other than the compounds of formula (I) described previously are

chosen from pyrazoles and preferably 4,5-diaminopyrazoles optionally substituted in position 1 and/or 3 with a (C₁-C₁₀)alkyl, (poly)hydroxy(C₁-C₁₀)alkyl, (di)(C₁-C₄)(alkyl)amino(C₁-C₁₀)alkyl or heterocyclo(C₁-C₁₀)alkyl group.

In particular, the pyrazoles are chosen from the compounds of formula (Va) below:

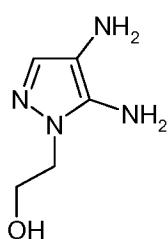


and also the addition salts thereof with organic or mineral acids, the tautomers thereof, and the solvates thereof such as hydrates:

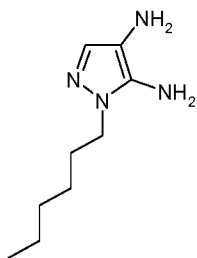
in which formula (Va):

- R represents a (C₁-C₁₀)alkyl group optionally substituted with one or more hydroxyl groups,
- R' represents a hydrogen atom or a (C₁-C₄)alkyl group optionally substituted with a hydroxyl or amino group; preferably, R' represents a (C₁-C₄)alkyl group such as methyl.

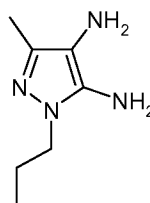
Preferably, the heterocyclic bases are chosen from the bases of formula (Va) in which R' represents a hydrogen atom or methyl, and R represents an ethyl, β-hydroxyethyl or *n*-hexyl group. The heterocyclic bases are chosen from compounds (Va1) to (Va4) below, and also the organic or mineral acid salts thereof, and the solvates thereof such as hydrates:



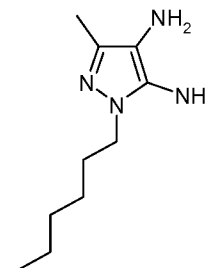
(Va1)



(Va2)



(Va3)



(Va4)

Among the pyrimidine derivatives that may be mentioned are the compounds described, for example, in patents DE 2359399; JP 88-169571; JP 05-63124; EP 0770375 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-

dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists, and mixtures thereof.

5 Preferably, when the additional oxidation base(s) other than the compounds of formula (I) are present in composition (A), the total content of additional oxidation base(s) other than the compounds of formula (I) is between 0.001% and 10% by weight, more preferentially between 0.005% and 5% by weight, relative to the total weight of composition (A).

10 In general, the addition salts of the additional oxidation bases other than the compounds of formula (I) and coupling agents that may be used in the context of the invention are chosen in particular from the addition salts with an acid such as the hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

15 Composition (A) according to the invention may also optionally comprise one or more direct dyes that may be chosen especially from nitrobenzene dyes, azo direct dyes, methine direct dyes, and mixtures thereof. These direct dyes may be of nonionic, anionic or cationic nature.

20 Preferably, when the direct dye(s) are present in composition (A), the total content of direct dye(s) is between 0.001% and 10% by weight, more preferentially between 0.005% and 5% by weight, relative to the total weight of composition (A).

25 Composition (A) according to the invention may optionally also comprise one or more chemical oxidizing agents.

The term "*chemical oxidizing agent*" means chemical oxidizing agents other than atmospheric oxygen.

30 Preferably, the chemical oxidizing agent(s) are chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulfates, in particular sodium persulfate, potassium persulfate and ammonium persulfate, peracids and oxidase enzymes (with the optional cofactors thereof) such as peroxidases, 2-electron oxidoreductases such as uricases and 4-electron oxygenases such as laccases, and mixtures thereof; preferentially, the chemical oxidizing agent(s) are chosen from hydrogen peroxide, persalts, and mixtures thereof.

Preferably, when the chemical oxidizing agent(s) are present in composition (A), the total content of the chemical oxidizing agent(s) is between 1% and 50% by weight, more preferentially between 3% and 30% by weight, and even more preferentially between 5% and 20% by weight, relative to the total weight of composition (A).

Composition (A) according to the invention may also optionally comprise one or more adjuvants preferably chosen from anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers and/or mixtures thereof, mineral or organic thickeners, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, antioxidants, penetrants, sequestrants, fragrances, buffers, dispersants, conditioning agents, for instance volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preservatives and opacifiers.

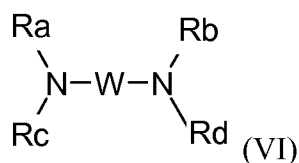
Preferably, when the above adjuvant(s) are present in composition (A), the adjuvant(s) are generally present in an amount, for each of them, of between 0.01% and 20% by weight, relative to the weight of composition (A).

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 (A) in accordance with the invention are not, or are not substantially, adversely affected by the envisaged addition(s).

The pH of the dye composition (A) 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, examples that may be mentioned include mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid or sulfuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid or lactic acid, and sulfonic acids.

Among the basifying agents, examples that may be mentioned include aqueous ammonia, alkali metal carbonates, (C₁-C₆)alkanolamines, such as mono-, di- and triethanolamines and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VI) below:



in which W is a (C₁-C₁₀)alkylene group such as propylene, optionally substituted with one or more hydroxyl groups; Ra, Rb, Rc and Rd, which may be identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical.

The dye composition (A) 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, in particular human keratin fibres and especially the hair.

A subject of the invention is also the use of composition (A) as defined previously, for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair.

Process for dyeing keratin fibres

Another subject of the present invention relates to a process for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one step (i) of applying to said keratin fibres a composition (A) as defined previously, optionally in the presence of a composition (B) containing one or more chemical oxidizing agents such as those described previously, different from composition (A).

Composition (A) as defined previously may be used in the presence simultaneously with or sequentially to a different composition (B) comprising one or more chemical oxidizing agents such as those described previously.

According to a preferred embodiment of the invention, the process according to the invention is a process for dyeing keratin fibres, comprising at least one step (i) of applying to the keratin fibres a composition (M) resulting from the extemporaneous mixing of:

- a composition (A) as defined previously; and
- a different composition (B) comprising one or more chemical oxidizing agents.

According to another preferred embodiment of the invention, the process according to the invention is a process for dyeing keratin fibres, comprising:

- at least one step (i) of applying to said keratin fibres a composition (A) as defined previously;
 - 5 - at least one step (ii) of applying to said keratin fibres a different composition (B) comprising one or more chemical oxidizing agents;
- it being understood that steps (i) and (ii) of application to said keratin fibres are performed sequentially.

10 Preferably, according to this embodiment, step(s) (i) of application to the keratin fibres are performed before step(s) (ii).

For the purposes of the present invention, the term "sequentially" means that the different composition (B) is applied before or after composition (A), i.e. as a pretreatment or a post-treatment.

15 According to one variant of the invention, the process according to the invention is a process for dyeing keratin fibres, comprising:

- at least one step (i) of applying to said keratin fibres a composition (A) as defined previously;
- 20 - at least one step (ii) of applying to said keratin fibres a different composition (B) comprising one or more chemical oxidizing agents;

it being understood that steps (i) and (ii) of application to said keratin fibres are performed simultaneously.

25 The embodiment according to which the keratin fibre treatment process according to the invention comprises at least one step (i) of applying to the keratin fibres a composition (M) resulting from the extemporaneous mixing of a composition (A) and of a different composition (B) is advantageously preferred.

30 The keratin fibre treatment process according to the present invention may optionally comprise additional steps, for example a step comprising a leave-on time after application and/or rinsing and/or drying.

The composition(s) may be applied to wet or dry hair, and preferably to wet or moist hair. The process of the invention may especially comprise a step of washing

the hair before applying the composition(s) described previously. It may also comprise a washing step after the application of the composition(s) described previously.

According to one embodiment of the invention, the process consists in applying to the keratin fibres an effective amount of the composition(s) according to the invention, optionally massaging the fibres, optionally leaving the composition to stand on the fibres, and rinsing.

The leave-on time of composition(s) (A) and/or (B) and/or (M) on the keratin fibres may be between a few seconds and 60 minutes and preferably between 30 seconds and 30 minutes. The composition used in the keratin fibre treatment process according to the present invention is generally rinsed out with water.

An optional step of drying the keratin fibres may be performed.

Device

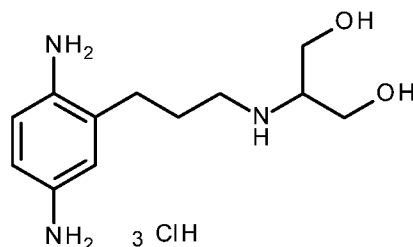
A subject of the invention is also a multi-compartment dyeing device or “kit” comprising:

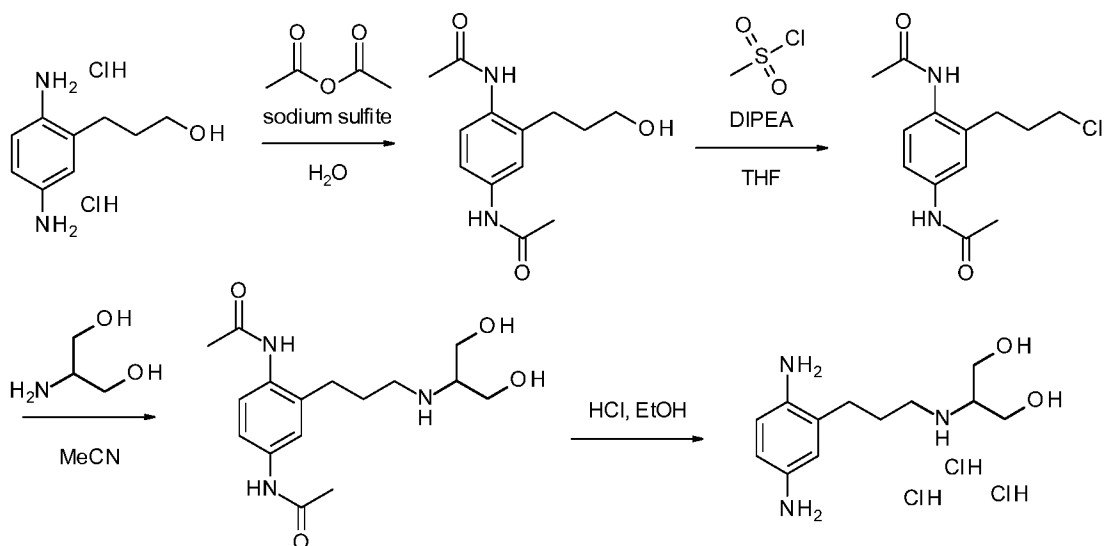
- a first compartment containing a composition (A) according to the invention as defined previously; and
- a second compartment containing one or more chemical oxidizing agents as defined previously.

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

25 **EXAMPLES:**

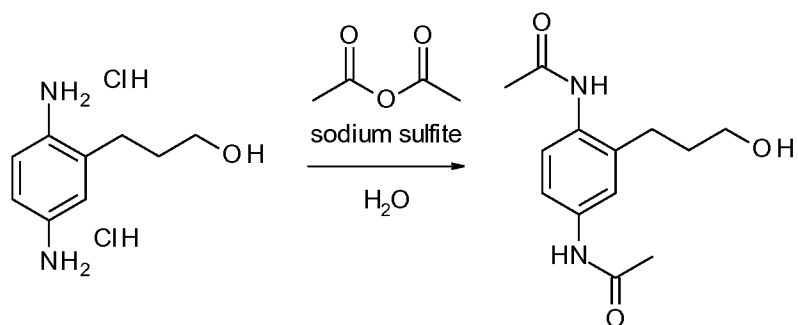
Example 1: synthesis of 2-[[3-(2,5-diaminophenyl)propyl]amino}propane-1,3-diol trihydrochloride



General synthetic scheme

1.1 Preparation of the intermediate N,N'-[2-(3-chloropropyl)benzene-1,4-diyl]diacetamide.

- 5 N,N'-[2-(3-Chloropropyl)benzene-1,4-diyl]diacetamide is synthesized in two steps as described below.

Step 1:

- 10 The synthesis of N,N'-[2-(3-hydroxypropyl)benzene-1,4-diyl]diacetamide is performed starting with 3-(2,5-diaminophenyl)propan-1-ol dihydrochloride.

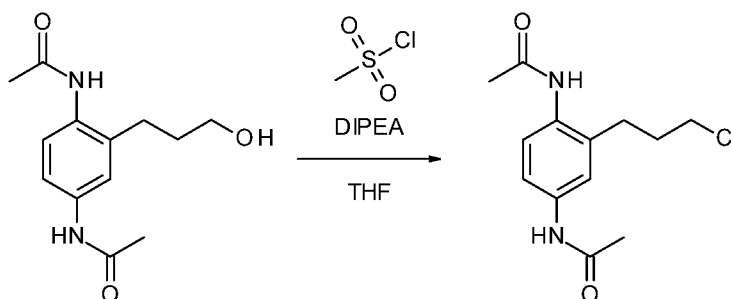
- 7.45 g of 3-(2,5-diaminophenyl)propan-1-ol dihydrochloride are placed in 45 ml of water in a 250 ml three-necked flask equipped with a thermometer and a magnetic bar, and a solution of 6.22 g of sodium sulfite in 20 ml of water are then added with stirring. On cooling, 10 ml of acetic anhydride are added dropwise and the mixture is
- 15

stirred at room temperature for 3 hours (monitoring by TLC, eluting with 90/10 EtOAc/MeOH). The reaction medium is transferred into a flask containing 50 ml of n-BuOH. After stirring and separation of the two phases, the aqueous phase is extracted twice with n-BuOH. The combined organic phases are washed once with water, and then
5 once with saturated NaCl solution, and then dried over anhydrous magnesium sulfate, before being concentrated under reduced pressure to give a white powder, which is washed with hot ethyl acetate to give the expected N,N'-[2-(3-hydroxypropyl)benzene-1,4-diyl]diacetamide in the form of a white powder.

10 The reaction medium (suspension) is filtered and a portion of the product is obtained in the form of a white powder after washing and drying.

The filtrate is transferred into a separating funnel and is extracted several times with EtOAc. The combined organic phases are dried and then concentrated under reduced pressure, and dried, to give another portion of the product in the form of a white
15 powder.

Step 2:

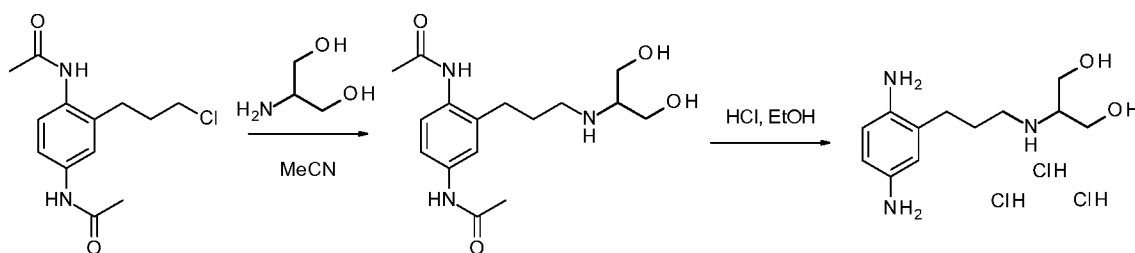


20 The synthesis of the intermediate N,N'-[2-(3-chloropropyl)benzene-1,4-diyl]diacetamide is performed starting with N,N'-[2-(3-hydroxypropyl)benzene-1,4-diyl]diacetamide.

60 g of N,N'-[2-(3-hydroxypropyl)benzene-1,4-diyl]diacetamide are placed in 1150 ml of anhydrous THF (milky suspension) in a three-necked flask equipped with a thermometer, a dropping funnel and a magnetic bar, and 50 ml of N,N-diisopropylethylamine in 30 ml of anhydrous THF are then added with stirring. On
25

cooling, 23 ml of methanesulfonyl chloride are added dropwise over 1 hour, and stirring is then continued at room temperature, before maintaining at reflux until TLC monitoring (80/20 EtOAc/MeOH) indicates that the reaction is complete. After cooling, the reaction medium is transferred into a water/EtOAc mixture and the insoluble material formed, corresponding to a portion of the expected product, is filtered off, washed and dried. The filtrate is evaporated under reduced pressure and the residue is purified by flash chromatography on silica gel (eluent: 5/95 ~10/90 MeOH/EtOAc). After removing the solvent, another portion of the product is obtained in the form of a white powder.

1.2 Synthesis of 2-{[3-(2,5-diaminophenyl)propyl]amino}propane-1,3-diol trihydrochloride



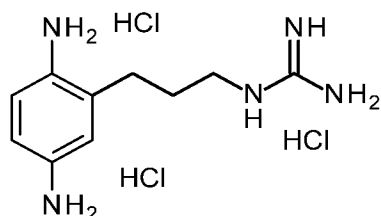
15 g of N,N'-[2-(3-chloropropyl)benzene-1,4-diyl]diacetamide are placed in 150 ml of acetonitrile in a three-necked flask equipped with a condenser, a thermometer and a magnetic bar, and 6.1 g of serinol are then added. After refluxing for 35 hours, the supernatant is separated from the precipitate, which is purified on a column, eluting with a CH₂Cl₂/MeOH gradient (5/95 ~10/90). 9 g of N,N'-(2-{3-[(1,3-dihydroxypropan-2-yl)amino]propyl}benzene-1,4-diyl)diacetamide are obtained in the form of a pale pink oil.

9 g of the product obtained previously are introduced cautiously into 50 ml of ethanol and 50 ml of 37% hydrochloric acid in a three-necked flask equipped with a condenser, a thermometer and a magnetic bar. After refluxing for 3 hours 30 minutes, the reaction medium is evaporated under reduced pressure. The residue is taken up in isopropanol and the mixture is concentrated to dryness under reduced pressure. The residue is taken up in ethanol and the mixture is stirred at 45°C and then filtered while hot, before placing in a desiccator. This operation is repeated several times, and the desired 2-{[3-(2,5-diaminophenyl)propyl]amino}propane-1,3-diol trihydrochloride is obtained in the form of a beige-coloured powder.

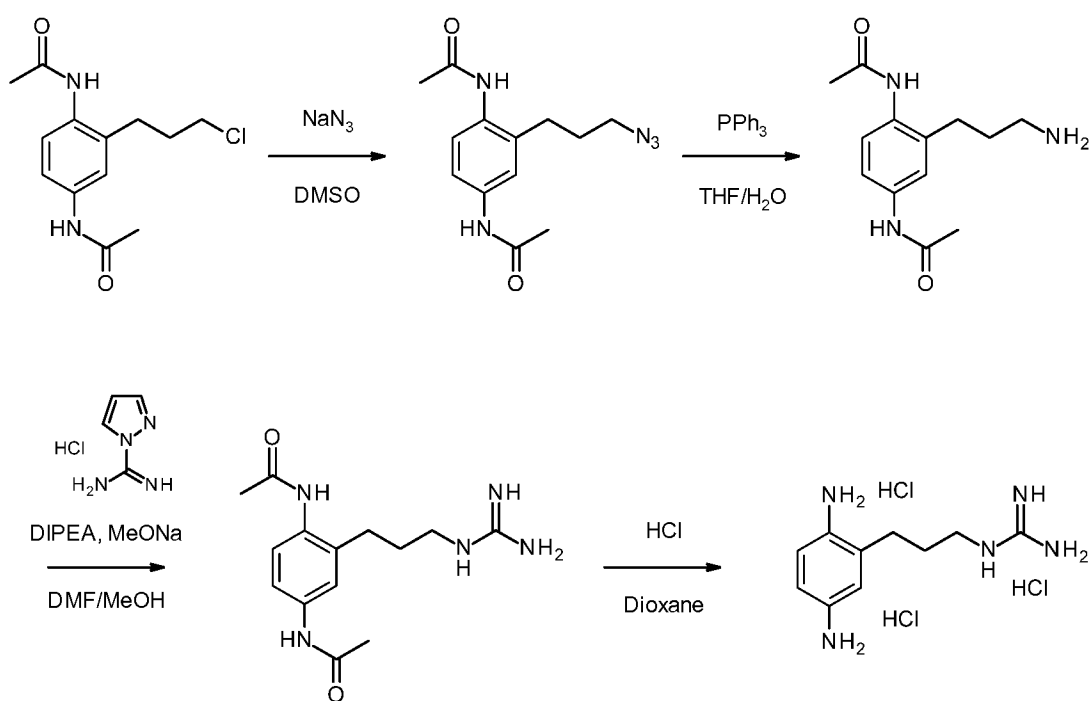
The NMR and mass analyses confirm the structure of the expected product.

Example 2: Synthesis of 1-[3-(2,5-diaminophenyl)propyl]guanidine trihydrochloride

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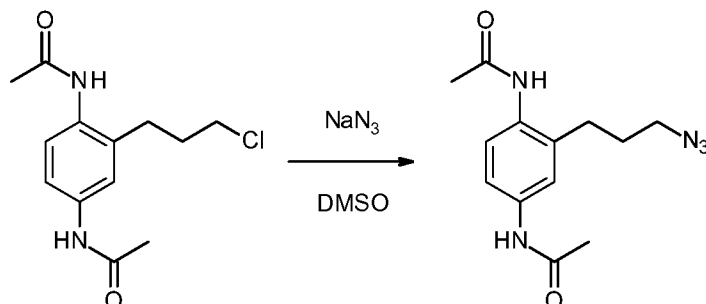
General synthetic scheme



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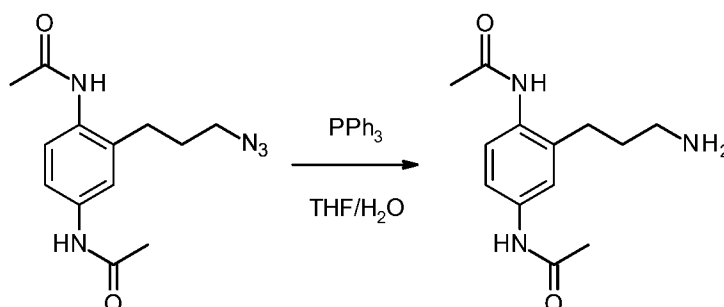
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2.1 Preparation of N,N'-[2-(3-azidopropyl)benzene-1,4-diyl]diacetamide intermediate



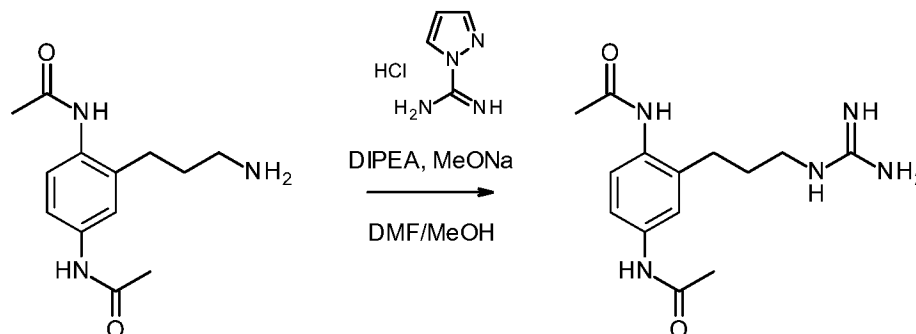
In a 50mL round bottom flask were introduced 3.0g N,N'-[2-(3-chloropropyl)benzene-1,4-diyl]diacetamide and 1.6g NaN₃. The synthesis of the N,N'-[2-(3-chloropropyl)benzene-1,4-diyl]diacetamide has been previously described in point 1.1 of example 1 above. The mixture was heated at 65°C for 2hours to finish the reaction. The mixture was left to return at room temperature (i.e. RT, 25°C) and 50mL of water was added. The mixture was extracted 3 times with ethyl acetate (EtOAc) and the organic layer was washed with brine and dried over anhydrous magnesium sulfate (MgSO₄). The organic layer was evaporated to afford the N,N'-[2-(3-azidopropyl)benzene-1,4-diyl]diacetamide as a beige solid.

2.2 Preparation of N,N'-[2-(3-aminopropyl)benzene-1,4-diyl]diacetamide intermediate



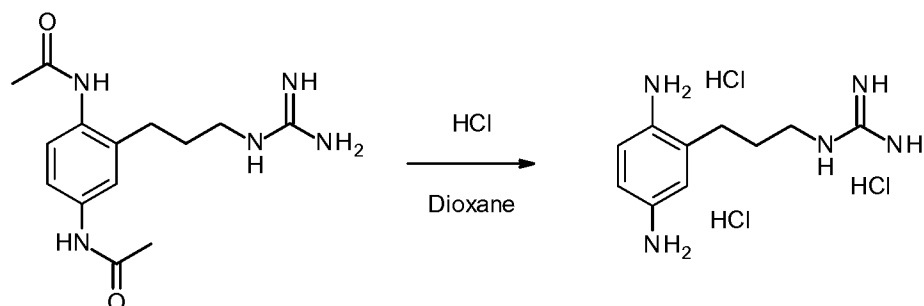
In a 250mL round bottom flask was introduced 3.2g N,N'-[2-(3-azidopropyl)benzene-1,4-diyl]diacetamide with 22ml THF and water. The mixture was degazed with N₂ for 10min. Then 3.6g PPh₃ was added and the mixture was heated to 50°C for 2h30min. THF was removed by evaporation and 30mL of water was added and the mixture was filtered on a sintered glass to remove the P(O)Ph₃ and PPh₃. The aqueous filtrate was evaporated to dryness to afford the N,N'-[2-(3-aminopropyl)benzene-1,4-diyl]diacetamide as a beige solid.

2.3 Preparation of N,N'-[2-(3-guanidylpropyl)benzene-1,4-diyl]diacetamide intermediate



Into a solution of 24ml DMF/DIPEA 3:1 (5mL/mmol) was added 2.3 g of N,N'-[2-(3-aminopropyl)benzene-1,4-diyl]diacetamide and 4.7g 1H-pyrazole-1-carboxamidine hydrochloride under N₂ atmosphere. The mixture was stirred at RT for overnight. Then Et₂O was added and the resulting oil was isolated and washed twice with Et₂O. The oil containing the guanidine salt was dissolved in 26ml MeOH. Then 10ml sodium methoxide was added and the mixture was stirred at RT for 1 hour. Then the precipitate was filtered and the filtrate was evaporated to afford the N,N'-[2-(3-guanidylpropyl)benzene-1,4-diyl]diacetamide as an orange solid.

2.4 Preparation of 1-[3-(2,5-diaminophenyl)propyl]guanidine trihydrochloride



In a 50mL round bottom flask was introduced 1.8g of N,N'-[2-(3-guanidylpropyl)benzene-1,4-diyl]diacetamide and 9ml HCl/Dioxane 4N. The mixture was heated at 65°C for overnight. Then the mixture was left 24h at 65°C for a total complexation of the reaction. The mixture was evaporated to dryness and taken with 25mL of EtOH, heated for 1 hour at 50°C and filtered at 50°C on a sintered glass. The off-white precipitated was dried under vacuum to give the target compound 1-[3-(2,5-diaminophenyl)propyl]guanidine trihydrochloride.

The NMR and mass spectrometry analyses confirm the structure of the expected product.

Example 3: dyeing

The dye compositions (A) and (B) according to the invention are prepared from the
5 following ingredients and amounts:

Ingredients	Composition (A)	Composition (B)
Oxidation base: 2-[[3-(2,5-diaminophenyl)propyl]amino}propane-1,3- diol trihydrochloride (example 1)	0.05 mmol	-
Oxidation base: 1-[3-(2,5-diaminophenyl)propyl]guanidine trihydrochloride (example 2)	-	0.05 mmol
Oxidation coupler: 3,4-dihydro-2H-1,4-benzoxazin-6-ol	0.05 mmol	
Water	7.0 mL	
Ethanol	2.0 mL	
Aqueous ammonia containing 20% NH ₃	1.0 mL	
6-Volume aqueous hydrogen peroxide solution	1.0 mL	-
20-Volume aqueous hydrogen peroxide solution	-	1.0mL

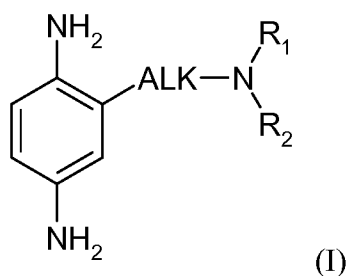
Compositions (A) and (B) are each applied to a 1 g lock of natural Caucasian
hair containing 90% white hairs, distinct from each other. After a leave-on time of 30
minutes at 27°C, the lock is rinsed, washed with a standard shampoo, rinsed again and
then dried.
10

The lock thus treated with composition (A) has an ash-yellow colouring, and
the lock treated with composition (B) has a brown colouring.

CLAIMS

1. Composition (A) comprising, in a medium that is suitable for dyeing keratin fibres, in particular human keratin fibres such as the hair:

- 5 - one or more oxidation bases chosen from the compounds of formula (I), and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates:



in which formula (I):

- 10
- ALK represents a linear or branched alkylene chain including from 3 to 8 carbon atoms, optionally substituted with one or more identical or different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy;
 - 15
 - R₁ and R₂, which may be identical or different, represent:
 - a hydrogen atom;
 - a (C₁-C₆)alkylcarbonyl group such as acetyl;
 - a linear or branched (C₁-C₈)alkyl group;
 - optionally substituted with one or more identical or different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy, iii) acylamino, iv) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (C₁-C₈)alkyl group, optionally interrupted with one or more additional heteroatoms and/or groups, which may be identical or different, chosen from -O-, -S-, -NH-, -S(O)-, -S(O)₂-, -C(O)- and/or -C(S)-, and/or optionally substituted with one or more identical or different radicals chosen from the hydroxyl radical, the C₁-C₆ alkoxy radical, v) aromatic or non-aromatic (hetero)cycle, such as phenyl, and vi) -C(X)-
 - 20
 - 25

NR₃R₄ with R₃ and R₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a radical NR₃ with R₃ as defined previously; preferentially, R₃ and R₄ represent a hydrogen atom and X denotes NR₃; and/or

- optionally interrupted with one or more additional heteroatoms and/or groups, which may be identical or different, chosen from -O-, -S-, -NH-, -S(O)-, -S(O)₂-, -C(O)- and/or -C(S)-;
- one or more coupling agents.

2. Composition according to the preceding claim, characterized in that ALK represents an unsubstituted linear C₃-C₆ alkylene chain, preferably unsubstituted linear C₃-C₅, more preferentially unsubstituted linear C₃-C₄, even more preferentially unsubstituted linear C₃ such as propylene -(CH₂)₃-.

3. Composition according to either of the preceding claims, characterized in that R₁ and R₂, which may be identical or different, represent:

- a hydrogen atom;
- a linear or branched (C₁-C₈)alkyl group;

- optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy such as methoxy, iii) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (hydroxy)(C₁-C₄)alkyl group, iv) aromatic or non-aromatic (hetero)cycle, such as phenyl, pyrrolidinyl, morpholinyl, piperidyl, and v) -C(X)-NR₃R₄ with R₃ and R₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a group NR₃ with R₃ as defined previously; preferentially, R₃ and R₄ represent a hydrogen atom and X denotes NR₃; and/or
- optionally interrupted with a heteroatom chosen from -O-, -S-, -NH-, preferably with an oxygen atom -O-.

4. Composition according to the preceding claim, characterized in that R_1 and R_2 , which may be identical or different, represent:

- a hydrogen atom;
- a linear or branched (C₁-C₄)alkyl group, optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₄ alkoxy such as methoxy, and iii) -C(X)-NR'₃R'₄ with R'₃ and R'₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a group NR'₃ with R'₃ as defined previously; preferentially, R'₃ and R'₄ represent a hydrogen atom and X denotes NR'₃.

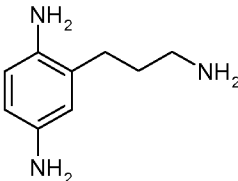
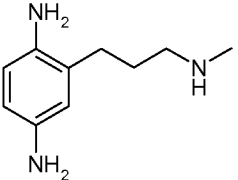
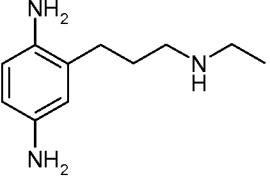
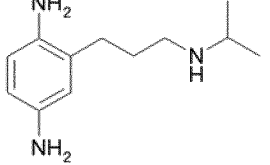
5. Composition according to any one of Claims 1 to 3, characterized in that R_1 represents a hydrogen atom or a linear (C₁-C₄)alkyl group optionally substituted with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy such as methoxy; and R_2 , which is different from R_1 , represents a hydrogen atom or a linear or branched (C₁-C₆) alkyl group:

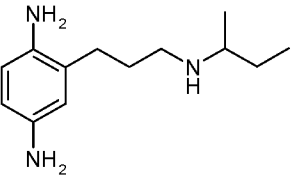
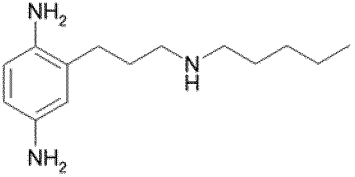
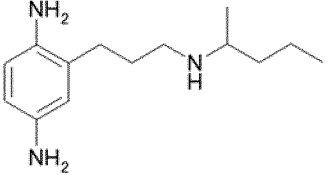
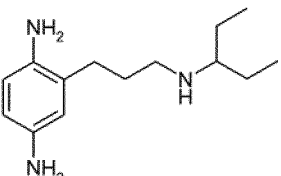
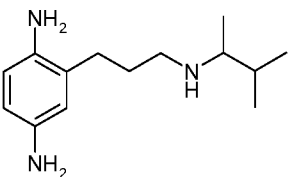
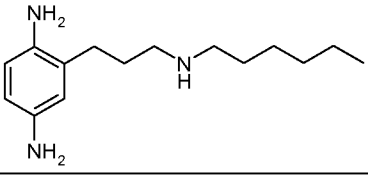
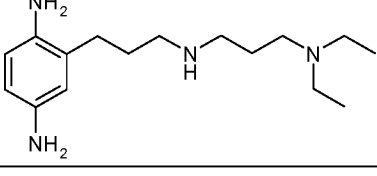
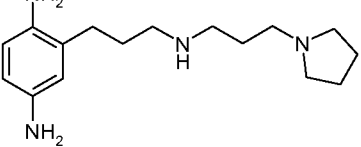
- optionally substituted with one or more radicals, which may be identical or different, chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy such as methoxy, iii) amino -NR₃R₄ in which R₃ and R₄, which may be identical or different, represent a hydrogen atom or a linear or branched (hydroxy)(C₁-C₄)alkyl group, iv) aromatic or non-aromatic (hetero)cycle, such as phenyl, pyrrolidinyl, morpholinyl, piperidyl, and v) -C(X)-NR'₃R'₄ with R'₃ and R'₄, which may be identical or different, representing a hydrogen atom or a (C₁-C₄)alkyl group, and X representing an oxygen or sulfur atom or a group NR'₃ with R'₃ as defined previously; preferentially, R'₃ and R'₄ represent a hydrogen atom and X denotes NR'₃; in particular, X denotes NH; and/or
- optionally interrupted with a heteroatom chosen from -O-, -S-, -NH-, preferably with an oxygen atom -O-.

6. Composition according to any one of Claims 1 to 3, characterized in that R_1 is different from R_2 , and R_1 represents a hydrogen atom or a linear (C₁-C₄)alkyl group, even more preferentially a hydrogen atom or a methyl group or an ethyl group, better still a hydrogen atom.

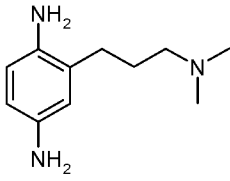
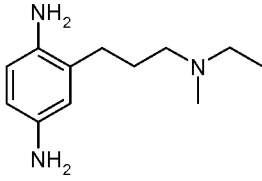
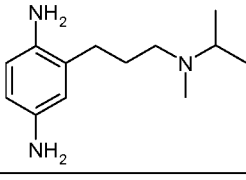
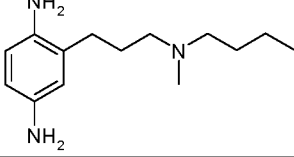
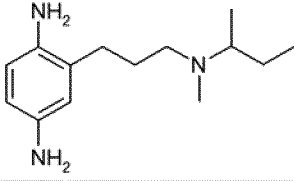
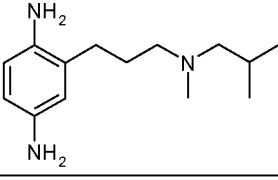
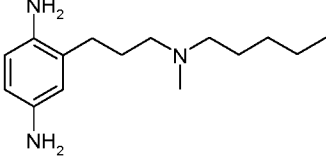
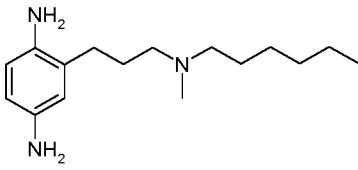
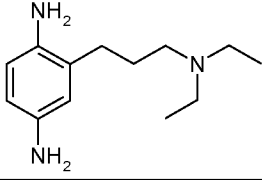
7. Composition according to any one of Claims 1 to 3 or 6, characterized in that R₁ is different from R₂, and R₂ represents a group from among: i) (C₁-C₆)alkyl optionally substituted with one or more groups chosen from a) hydroxyl, b) (di)(C₁-C₄)alkylamino, c) (di)hydroxy(C₁-C₄)alkylamino, and d) 5- or 6-membered saturated heterocycle such as pyrrolino, piperazino, piperidino or morpholino, ii) (C₁-C₄)alkoxy(C₁-C₄)alkyl, iii) (C₁-C₄)alkoxy(C₁-C₄)alkoxy(C₁-C₄)alkyl, iii) aryl(C₁-C₄)alkyl such as benzyl, iv) -C(NH)-NH₂;
 more preferentially, R₂ represents i) a (C₁-C₆)alkyl group optionally substituted with one or more hydroxyl groups.

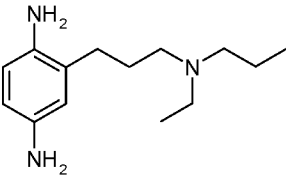
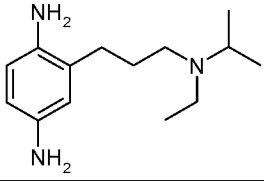
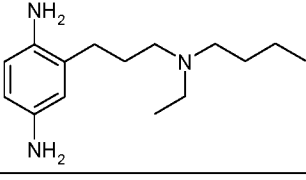
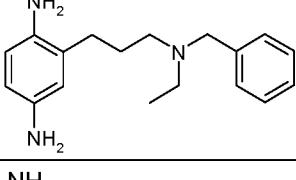
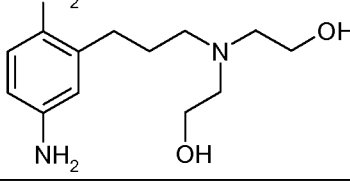
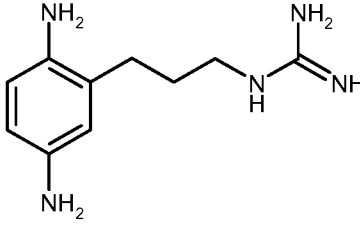
8. Composition according to any one of the preceding claims, characterized in that the oxidation base(s) are chosen from compounds (1) to (36), and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates:

	Structures	Chemical name
Compound 1		2-(3-aminopropyl)benzene-1,4-diamine
Compound 2		2-[3-(methylamino)propyl]benzene-1,4-diamine
Compound 3		2-[3-(ethylamino)propyl]benzene-1,4-diamine
Compound 4		2-[3-(propan-2-ylamino)propyl]benzene-1,4-diamine

Compound 5		2-[3-(butan-2-ylamino)propyl]benzene-1,4-diamine
Compound 6		2-[3-(pentylamino)propyl]benzene-1,4-diamine
Compound 7		2-[3-(pentan-2-ylamino)propyl]benzene-1,4-diamine
Compound 8		2-[3-(pentan-3-ylamino)propyl]benzene-1,4-diamine
Compound 9		2-{3-[(3-methylbutan-2-yl)amino]propyl}benzene-1,4-diamine
Compound 10		2-[3-(hexylamino)propyl]benzene-1,4-diamine
Compound 11		2-(3-{3-(diethylamino)propyl}amino)propylbenzene-1,4-diamine
Compound 12		2-(3-{3-(pyrrolidin-1-yl)propyl}amino)propylbenzene-1,4-diamine

Compound 13		2-(3-{{3-(morpholin-4-yl)propyl}amino}propyl)benzene-1,4-diamine
Compound 14		2-(3-{{3-(piperidin-1-yl)propyl}amino}propyl)benzene-1,4-diamine
Compound 15		2-(3-{{3-(dibutylamino)propyl}amino}propyl)benzene-1,4-diamine
Compound 16		2,2'-[3-{{3-(2,5-diaminophenyl)propyl}amino}propyl]imino]diethanol
Compound 18		2-{3-[(3-methoxypropyl)amino]propyl}benzene-1,4-diamine
Compound 19		2-(3-{{3-(2-methoxyethoxy)propyl}amino}propyl)benzene-1,4-diamine
Compound 20		2-{3-[(2,5-diaminophenyl)propyl]amino}propane-1,3-diol
Compound 21		3-{3-[(2,5-diaminophenyl)propyl]amino}propane-1,2-diol

Compound 22		2-[3-(dimethylamino)propyl]benzene-1,4-diamine
Compound 23		2-[3-(ethyl(methyl)amino)propyl]benzene-1,4-diamine
Compound 24		2-[3-(methyl(propan-2-yl)amino)propyl]benzene-1,4-diamine
Compound 25		2-[3-(butyl(methyl)amino)propyl]benzene-1,4-diamine
Compound 26		2-[3-(butan-2-yl(methyl)amino)propyl]benzene-1,4-diamine
Compound 27		2-[3-(methyl(2-methylpropyl)amino)propyl]benzene-1,4-diamine
Compound 28		2-[3-(methyl(pentyl)amino)propyl]benzene-1,4-diamine
Compound 29		2-[3-(hexyl(methyl)amino)propyl]benzene-1,4-diamine
Compound 30		2-[3-(diethylamino)propyl]benzene-1,4-diamine

Compound 31		2-{3-[ethyl(propyl)amino]propyl}benzene-1,4-diamine
Compound 32		2-{3-[ethyl(propan-2-yl)amino]propyl}benzene-1,4-diamine
Compound 33		2-{3-[butyl(ethyl)amino]propyl}benzene-1,4-diamine
Compound 34		2-{3-[benzyl(ethyl)amino]propyl}benzene-1,4-diamine
Compound 35		2,2'-{[3-(2,5-diaminophenyl)propyl]imino}diethanol
Compound 36		1-[3-(2,5-diaminophenyl)propyl]guanidine

9. Composition according to any one of the preceding claims, characterized in that the coupling agent(s) are chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers, heterocyclic couplers, the addition salts thereof, and mixtures thereof; preferably, the coupling agent(s) are chosen from 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β -hydroxyethoxy)benzene, 2-amino-4-(β -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1- β -hydroxyethylamino-3,4-methylenedioxybenzene, α -naphthol, 2-methyl-

1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-(β -hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-bis(β -hydroxyethylamino)toluene, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one, 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-1,2,4-triazole, 6-methylpyrazolo[1,5-a]benzimidazole, 2-methyl-5-aminophenol, 5-N-(β -hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 3-amino-2-chloro-6-methylphenol, the corresponding addition salts thereof with an acid, and mixtures thereof.

10. Composition according to any one of the preceding claims, characterized in that it comprises one or more chemical oxidizing agents; preferably, the chemical oxidizing agent(s) are chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulfates, in particular sodium persulfate, potassium persulfate and ammonium persulfate, peracids, and oxidase enzymes (with the possible cofactors thereof), for instance peroxidases, 2-electron oxidoreductases such as uricases, and 4-electron oxygenases, for instance laccases, and mixtures thereof; preferentially, the chemical oxidizing agent(s) are chosen from hydrogen peroxide, persalts, and mixtures thereof.

11. Use of one or more compounds of formula (I), and also the addition salts thereof with organic or mineral acids, the optical isomers thereof, the tautomers thereof, and the solvates thereof such as hydrates, as defined according to any one of claims 1 to 8, as an oxidation base for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair.

12. Process for dyeing keratin fibres, in particular human keratin fibres such as the hair, characterized in that it comprises at least one step (i) of applying to said keratin fibres a composition (A) as defined according to any one of Claims 1 to 10, optionally in the presence of a different composition (B) containing one or more chemical oxidizing agents as defined according to Claim 10.

13. Process for dyeing keratin fibres according to the preceding claim, characterized in that it comprises at least one step (i) of applying to the keratin fibres a composition (M) resulting from the extemporaneous mixing of:

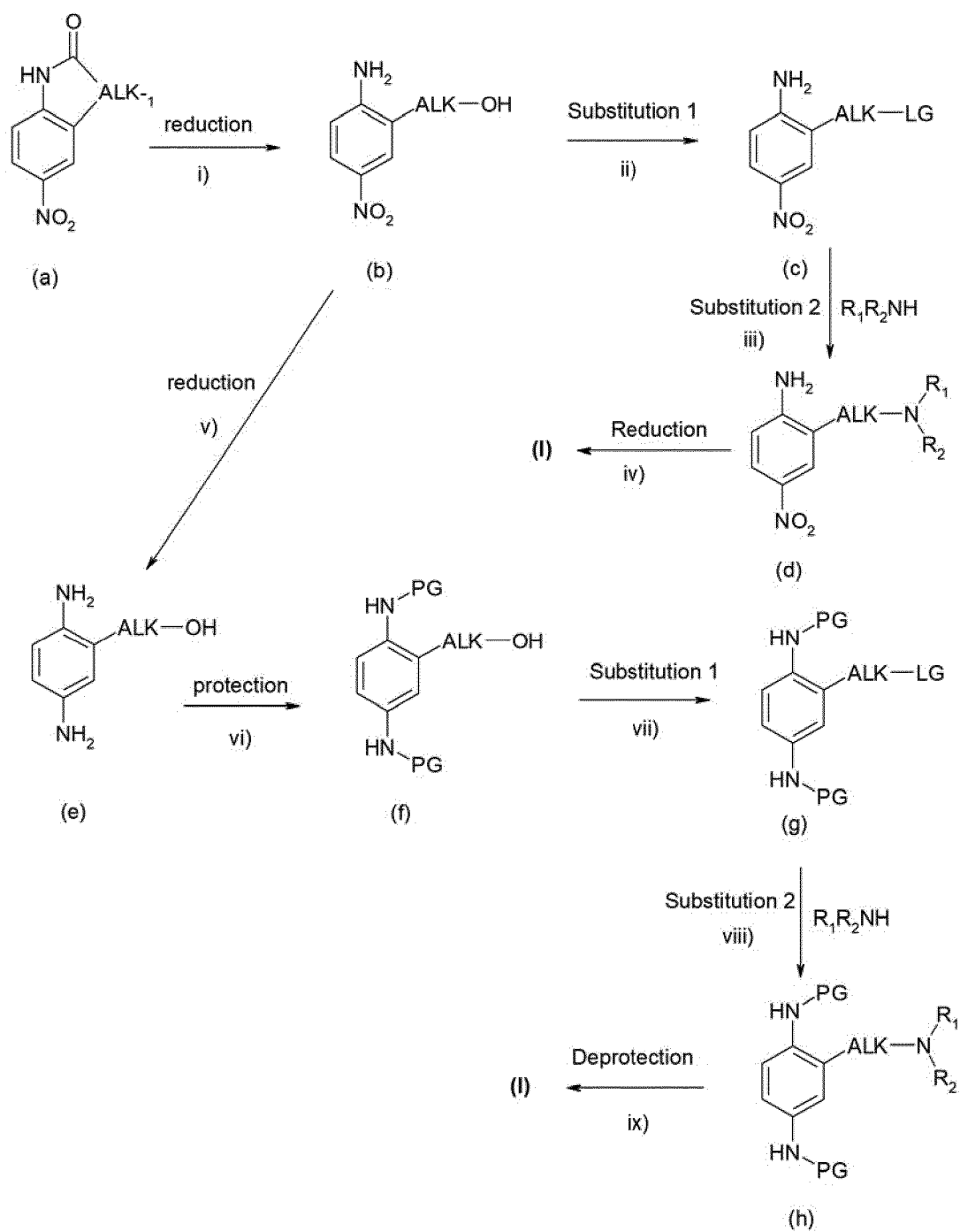
- 5
- a composition (A) as defined according to either of Claims 1 and 9; and
 - a different composition (B) comprising one or more chemical oxidizing agents as defined according to Claim 10.

14. Process for dyeing keratin fibres according to Claim 12, characterized in that it comprises:

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- at least one step (i) of applying to said keratin fibres a composition (A) as defined according to either of Claims 1 and 9;
 - at least one step (ii) of applying to said keratin fibres a different composition (B) comprising one or more chemical oxidizing agents as defined according to Claim 10;
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- it being understood that steps (i) and (ii) of application to said keratin fibres are performed simultaneously or sequentially;
- preferably, step(s) (i) are performed before step(s) (ii).

15. Process for preparing the compounds of formula (I) as defined according to any one of Claims 1 to 8, according to the following chemical synthetic scheme:

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in which scheme:

- R_1 and R_2 are as defined according to any one of Claims 1 and 3 to 7,
- ALK is as defined according to either of Claims 1 and 2,
- ALK_{-1} represents a linear or branched alkylene chain including from 2 to 7 carbon atoms, optionally substituted with one or more identical or

different halogen atoms, and/or with one or more identical or different radicals chosen from among the radicals: i) hydroxyl, ii) C₁-C₆ alkoxy,

- LG represents a nucleofugal group such as halogen, tosyl or triflate,
- PG representing a protecting group which withstands the reaction conditions of the entire synthesis up to the deprotection step;

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the process consisting:

* either, in a first step i), in reducing the bicyclic amido derivative (a) to give the 4-nitroaniline compound substituted in alpha to the amino with a hydroxy-ALK group (b); preferably, this step is performed in a polar protic or aprotic organic solvent such as a (C₁-C₆)alkanol, in particular methanol or tetrahydrofuran (THF), in the presence of a reducing agent chosen in particular from borohydrides of an alkaline agent such as NaBH₄; and then, in a second step ii), in transforming the hydroxyl group of compound (b) into a nucleofugal leaving group LG such as halogen, triflate, tosylate, mesylate, for example *via* a (C₁-C₆)alkylsulfonyl halide such as methanesulfonyl chloride, step ii) performed in particular in a polar or non-polar protic solvent such as THF, preferably in the presence of an alkaline agent such as *N,N*-diisopropylethylamine (DIPEA); and then, in a third step iii), in substituting the nucleofugal group LG with an amine N(H)R₁R₂ with R₁ and R₂ as defined previously, preferably in alkaline medium; and then, in a fourth step iv), in reducing the nitro compound (d) in particular by catalytic hydrogenation preferably with palladium, nickel, zinc, iron or tin preferably on graphite, such as Pd(II)/C, to give the compound of formula (I) as defined according to any one of Claims 1 to 8;

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* or, after the first step i), in a second step v), in reducing the 4-nitroaniline derivative substituted in alpha to the amino with a hydroxy-ALK group (b), preferably by catalytic hydrogenation to give the 1,4-phenylenediamine compound substituted in alpha to the amino with a hydroxy-ALK group (e), and then, in a third step vi), in protecting the amino groups with a protecting group in particular via a reagent such as R-C(Y_a)-Y_a-C(Y_a)-R' with R and R', which may be identical or different, representing a (C₁-C₆)alkyl group, and Y_a, which may be identical or different, representing an oxygen or sulfur atom; preferably, said reagent is acetic anhydride; followed by steps vii) and viii) of substitutions 1 and 2 under the same conditions as during steps ii) and iii) to give compounds (c) and (d), respectively, and compound (h) is then deprotected, in particular in a preferably polar protic organic solvent, more preferentially in the presence of one or more mineral or organic acids, more preferentially mineral acids

such as hydrochloric acid, to give the compound of formula (I) as defined according to any one of Claims 1 to 8.

- 5 16. Multi-compartment dyeing device or "kit" comprising:
- a first compartment containing a composition as defined according to either of Claims 1 to 9; and
 - a second compartment containing one or more chemical oxidizing agents as defined in Claim 10.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/062831

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K8/41 C07C211/51 A61Q5/10 C07D211/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C A61K A61Q C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/012316 A1 (NISSAN CHEMICAL IND LTD [JP]) 29 January 2015 (2015-01-29) page 7; compounds A-2, A-5 examples 1, 7 -----	1,2,6
X	US 2012/088040 A1 (MATSUMORI MASAKI [JP] ET AL) 12 April 2012 (2012-04-12)	1-9
Y	page 7; compounds B14-, B16, B-17 page 16 - page 19; tables 4A, 5A, 6A page 5; compounds A-1, A-5, A-6 -----	15
X	FR 3 044 899 A1 (HENKEL AG & CO KGAA [DE]) 16 June 2017 (2017-06-16)	1-14,16
Y	page 9 - page 29 page 42 - page 47; examples -----	15



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 July 2019

Date of mailing of the international search report

25/07/2019

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Patteux, Claudine

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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