Title: PROCESS FOR DYEING KERATIN FIBRES USING HYDROXYBENZALDEHYDE DERIVATIVES, OXIDIZING AGENTS AND ALKalinizing AGENTS IN THE PRESENCE OF HEAT

Abstract: One subject of the invention is a process for dyeing keratin fibres, especially the hair, using i) at least one hydroxy benzaldehyde derivative, ii) at least one oxidizing agent, and iii) at least one alkalinizing agent in the presence of heat. Another subject of the invention is a cosmetic composition for dyeing keratin fibres comprising the ingredients i) to iii) as defined previously. Another subject of the invention is a multicompartiment device comprising the ingredients i), ii) and iii). This dyeing process makes it possible to obtain better colorations that are chromatic, intense and long-lasting without the use of oxidation bases such as paraphenylenediamines and para-aminophenols.
PROCESS FOR DYEING KERATIN FIBRES USING HYDROXYBENZALDEHYDE DERIVATIVES, OXIDIZING AGENTS AND ALKALINIZING AGENTS IN THE PRESENCE OF HEAT

One subject of the invention is a process for dyeing keratin fibres, especially the hair, using \( i \) at least one hydroxybenzaldehyde derivative, \( ii \) at least one oxidizing agent, and \( Hi \) at least one alkalinizing agent in the presence of heat. This dyeing process makes it possible to obtain colorations that are chromatic, intense, deep and long-lasting even in the absence of oxidation bases such as para-phenylenediamines and para-aminophenols, or of active CH compounds.

It is known practice to obtain "permanent" colorations 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 colourless or weakly coloured compounds, which, when combined with oxidizing products, give rise to coloured compounds via 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 having light stability and stability to shampooing.

This oxidation dyeing process consists in applying to the keratin fibres bases or a mixture of bases and couplers with hydrogen peroxide (\( \text{H}_2\text{O}_2 \) or aqueous hydrogen peroxide solution), as oxidizing agent, in leaving it to diffuse, and then in rinsing the fibres. The colorations resulting therefrom are permanent, strong and resistant to external agents, especially to light, adverse weather conditions, washing, perspiration and rubbing.

Derivatives of 5,6-dihydroxyindoles are also capable of generating deep shades by "autoxidation", but the resulting colorations are not always satisfactory, especially in terms of chromaticity, strength, remanence or change in colour after shampooing and exposure to light.

To attain deep shades, the presence of para-phenylenediamine oxidation bases is virtually indispensable.

It is also known to dye keratin fibres with dye compositions containing direct dyes. The conventional dyes that are used are, in particular, dyes of the nitrobenzene, anthraquinone, nitropyridine, azo, cationic azo, xanthene, acridine, azine or triarylmethane nitrobenzene type or natural dyes. These dyes, which are coloured and colouring molecules that have an affinity for the fibres, are applied to the keratin fibres for a time necessary for obtaining the desired coloration, then rinsed. The colorations resulting therefrom are chromatic colorations that are, however, only temporary or semi-permanent since the nature of the interactions that bind the direct dyes to the keratin fibre and their desorption from the surface and/or the core of the fibre are responsible for their weak dyeing power and their poor fastness with respect to washing or perspiration. One known variant is to apply to keratin fibres, instead of direct
dyes, dye precursors that form the colour in situ via a chemical reaction. For example, in patents US 6,790,239 and US 6,770,102, and international patent applications WO 2006/131 163 and WO 2006/002710 aromatic aldehyde/ketone precursors have been described that condense with active CH precursors to form, in situ, the direct dye after release of water. These direct dyes are also light-sensitive due to the low resistance of the chromophore to photochemical attack, and lead to fading of the coloration of the hair over time. These dyes do not make it possible to obtain satisfactory colorations, especially in terms of remanence.

Other documents mention the use of 2-hydroxy- or 4-hydroxy-3-methoxybenzaldehyde for colouring the hair in the presence of oxidation bases of 2-aminophenol type and 2,5-diaminotoluene type (FR 2 462 907 and of DE 28 30 497 - Schwarzkopf).

There is thus a real need to find new means of dyeing keratin fibres that make it possible to obtain uniform, strong and/or chromatic colorations with deep shades, ideally without conventional aromatic amines such as para-phenylenediamines and para-aminophenols, which would be light-fast, resistant to adverse weather conditions, persistent with regard to washing operations and perspiration, which do not stain and are sufficiently stable in the presence of oxidizing agents such as an aqueous hydrogen peroxide solution in order to be able to obtain a simultaneous lightening of the fibre with the aforementioned advantages.

This objective is achieved by the present invention, one subject of which is a process for dyeing keratin fibres, comprising:
a) the application to the keratin fibres of:

![Chemical structure](image)

(1)

in which formula (1):

R₁, R₂, R³, R⁴ and R⁵, which may be identical or different, represent a hydrogen or halogen atom, or a group chosen from:
- a hydroxy;
- a linear or branched (C₁-C₆)alkyl which is optionally substituted, especially
by at least one hydroxyl group;
- a linear or branched \((C_1-C_9)\)alkoxy;
- a carboxyl \(-C(0)\text{-OH}\) or carboxylate \(-C(0)\text{-0}^+\), \(M^+\); with \(M^+\) representing a cationic counterion such as an alkali metal or alkaline-earth metal, or an ammonium;
- a carbamoyl \(-O-C(0)\text{-NR}_aR_b\) with \(R_a\) and \(R_b\), which may be identical or different, representing a hydrogen atom or a linear or branched \((CrC_5)\)alkyl group; particularly \(-O-C(0)\text{-NH}_2\);
- an amido \(-C(0)\text{-NR}_6^7\) or \(-NR_6^7-C(0)\text{-R}^7\) with \(R_6^7\) and \(R_7\), which may be identical or different, representing a hydrogen atom or a \((CrC_5)\)alkyl group, particularly \(-C(0)\text{-NH}_2\);
- an ester \(-C(0)\text{-0-R}^8\) or \(-O-C(0)\text{-R}^8\), with \(R_8\) representing a \((C_1-C_9)\)alkyl group, particularly \(-C(0)\text{-0-R}^8\);
- a \((CrC_5)\)alkylcarbonyl;
- a carboxaldehyde \(-C(0)\text{H}\); and
- an amino \(NR_aR_b\) with \(R_a\) and \(R_b\), as defined previously;
- or else \(R^1\) and \(R^2\), or \(R^2\) and \(R^3\), or \(R^3\) and \(R^4\) form, together with the carbon atoms to which they are attached, a 6-membered (hetero)aryl group such as phenyl;

on condition that at least one of the two radicals \(R^1\) or \(R^3\) represents a hydroxyl group; with, when \(R^1\) represents a hydroxyl group, then \(R^2\) or \(R^3\) or \(R^4\) or \(R^5\) represents a hydrogen atom; and when \(R^3\) represents a hydroxyl group then \(R^1\) or \(R^2\) or \(R^4\) or \(R^5\) represents a hydrogen atom;

- \(\text{ii)}\) at least one chemical oxidizing agent; and
- \(\text{iii)}\) at least one alkanizing agent;

b) then a heat treatment of the keratin fibres at a temperature above 30°C, preferably between 30°C and 80°C;

it being understood that the total concentration of hydroxybenzaldehyde derivatives of formula (I) is greater than 1% relative to the total weight of ingredients \(\text{i)}\), \(\text{ii)}\) and \(\text{iii)}\), or of the total weight of the composition(s) used in the process.

Another subject of the invention is a cosmetic composition for dyeing keratin fibres, comprising:
- \(\text{i)}\) at least one derivative of formula (I), as defined previously;
- \(\text{ii)}\) at least one chemical oxidizing agent; and
- \(\text{iii)}\) at least one alkanizing agent;

it being understood that:
- the pH of the composition is above 7 and preferably between 7.5 and 12;
- the compound(s) of formula (I) comprise at least one of the two radicals $R^1$ or $R^3$
  which represents a hydroxyl group; with, when $R^1$ represents a hydroxyl group,
  then $R^2$ or $R^3$ or $R^4$ or $R^5$ represents a hydrogen atom; and when $R^3$
  represents a hydroxyl radical then $R^1$ or $R^2$ or $R^4$ or $R^5$ represents a hydrogen atom;

- the total concentration of hydroxybenzaldehyde derivatives of formula (I) is greater
  than 1% relative to the total weight of the ingredients ii) and Hi), and

- when the hydroxybenzaldehyde derivative of formula (I) represents a compound
  chosen from 3,4-dihydroxybenzaldehyde; 4-hydroxy-2-methoxybenzaldehyde;
  3,5-dimethoxybenzaldehyde; 4-hydroxy-1-naphthaldehyde; 3,5-dimethyl-4-
  hydroxybenzaldehyde, then the alkanilizing agent Hi) is other than
  monoethanolamine; and

- when the hydroxybenzaldehyde derivative of formula (I) represents a compound
  chosen from 4-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-3-
  methoxybenzaldehyde, which is in the presence of 2-aminophenol, 2,5-
  diaminotoluene sulphate; then the alkanilizing agent Hi) is other than ammonium
  hydroxide.

Another subject of the invention relates to a multicompartment device comprising the
ingredients i) to Hi) as defined previously.

The composition and dyeing process of the invention have the advantage of dyeing
human keratin fibres, with strong, chromatic dyeing results that are resistant to washing,
perspiration, sebum and light, and that are moreover long-lasting, without impairing said
fibres. Furthermore, the colorations obtained using the process give uniform colours from the
root to the end of a fibre (little coloration selectivity). The shades obtained after dyeing with
the composition or the process of the invention are very intense, in particular at a temperature
above room temperature, preferably at a temperature between 45°C and 80°C.

Moreover, the colorations obtained with the composition or the process of the invention
are compatible with conventional oxidation conditions for lightening hair. The colorations are
particularly persistent with regard to shampooing operations.

Unless otherwise indicated in the present invention it is understood that:
- the "aryl" radical represents a fused or nonfused monocyclic or polycyclic carbon-based
group containing from 6 to 22 carbon atoms, and in which at least one ring is aromatic;
  preferably, the aryl radical is a phenyl, biphenyl, naphthyl, indenyl, anthracenyl or
tetrahydronaphthyl; preferably, the aryl radical is a phenyl;

- a "heteroaryr" radical represents a fused or nonfused, optionally cationic, 5- to 22-
  membered monocyclic or polycyclic group, comprising from 1 to 6 heteroatoms chosen
from nitrogen, oxygen, sulphur and selenium atoms, and at least one ring of which is aromatic; preferentially, a heteroaryl radical is chosen from acridinyl, benzimidazolyl, benzobistriazolyl, benzopyrazolyl, benzopyridazinyl, benzoquinolyl, benzothiazolyl, benzotriazolyl, benzoazolyl, pyridyl, tetrazolyl, dihydrothiazolyl, imidazopyridyl, imidazolyl, indolyl, isoquinolyl, naphthoimidazolyl, naphthooxazolyl, pyridopyrazolyl, oxadiazolyl, oxazolyl, oxazolopyridyl, phenazinyl, phenoxyazolyl, pyrazinyl, pyrazolyl, pyrillyl, pyrazolyltriazyl, pyridyl, pyrimidyl, pyrindinoimidazolyl, pyrrolyl, quinolyl, tetrazolyl, thiadiazolyl, thiazolyl, thiazolopyridyl, thiazoylimidazolyl, thiopyryl, triazolyl, xanthyl and the ammonium salts thereof;

- a "cationic heteroaryl radicar" is a heteroaryl group as defined previously, which comprises an endocyclic or exocyclic cationic group,
  - when the charge is endocyclic, it is included in the electron derealization via the mesomeric effect, for example it is a pyridinium, imidazolium or indolinium group:

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N
R
```

```
N
R
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with R and R' being a heteroaryl substituent as defined previously and particularly a (hydroxy)(CrC₈)alkyl group such as methyl;
  - when the charge is exocyclic, it is not included in the electron derealization via the mesomeric effect, for example it is an ammonium or phosphonium substituent R⁺ such as trimethylammonium, which is outside the heteroaryl such as pyridyl, indolyl or imidazolyl in question:

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R'
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R'
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with R a heteroaryl substituent as defined previously and R⁺ an ammonium RₐRₐRₐRₐN⁺⁻, phosphonium RₐRₐRₐP⁻⁺ or ammonium RaRₐRcN⁺⁻(CrC₈)alkylamino group with Rₐ, Rₐ and Rₐ, which may be identical or different, representing a hydrogen atom or a (C₇-C₈)alkyl group such as methyl;

- the "aryP" or "heteroaryP" radical or the aryl or heteroaryl part of a radical may be substituted with at least one substituent borne by a carbon atom, chosen from:
  - a C₆-C₁₆ and preferably C₁-C₈ alkyl radical optionally substituted with one or more radicals chosen from hydroxyl, C₁-C₂ alkoxy, (poly)hydroxyl(C₂-C₄)alkoxy, acylamino, amino substituted with two, identical or different, C₁-C₄ alkyl radicals, optionally bearing at least one hydroxyl group, or the two radicals possibly forming, with the
nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered and preferably 5- or 6-membered heterocycle optionally comprising another heteroatom that is identical to or different from nitrogen;

- a halogen atom such as chlorine, fluorine or bromine;
- a hydroxyl group;
- a (CrC₂)alkoxy radical;
- a (CrC₂)alkylthio radical;
- a (poly)hydroxy(C₂-C₄)alkoxy radical;
- an amino radical;
- a 5- or 6-membered heterocycloalkyl radical such as cyclohexyl;
- an optionally cationic 5- or 6-membered heteroaryl radical, preferentially imidazolium, optionally substituted with a (C₁-C₄)alkyl radical, preferentially methyl;
- an amino radical substituted with one or two identical or different (C₁-C₈)alkyl radicals, optionally substituted with at least:

1) one hydroxyl group;
2) one amino group optionally substituted with one or two optionally substituted C₁-C₃ alkyl radicals, said alkyl radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other heteroatom identical to or different from nitrogen;

- N(R)-C(0)-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 (CrC₂)alkyl radical;
- R₂N-C(0)- in which the radicals R, which may be identical or different, represent a hydrogen atom or a (C₁-C₄)alkyl radical optionally bearing at least one hydroxyl group;
- R'-S(O)₂-N(R)- in which the radical R represents a hydrogen atom or a C₁-C₄ alkyl radical optionally bearing at least one hydroxyl group and the radical R' represents a (Ci-C₄)alkyl radical, or a phenyl radical;
- R₂N-S(O)₂- in which the radicals R, which may be identical or different, represent a hydrogen atom or a (C₁-C₄)alkyl radical optionally bearing at least one hydroxyl group;
- a carboxylic radical in acid or salified (preferably with an alkali metal or a substituted or unsubstituted ammonium) form;
- a cyano group;
- a polyhaloalkyi group containing from 1 to 6 carbon atoms and comprising from 1 to 6 identical or different halogen atoms, the polyhaloalkyi group is, for example, trifluoromethyl;

- an "alkyl" radical is a saturated, linear or branched C₁-C₁₆, preferably C₁-C₈ hydrocarbon-based radical such as methyl or ethyl;
the expression "optionally substituted" attributed to the alkyl radical implies that said alkyl radical may be substituted with one or more radicals chosen from the following groups: i) hydroxyl, ii) (C_{1-6})alkoxy, iii) acylamino, iv) amino optionally substituted with one or two identical or different (C_{1-6})alkyl radicals, said alkyl radicals possibly forming, with the nitrogen atom that bears them, a 5- to 7-membered heterocycle optionally comprising another heteroatom identical to or different from nitrogen; v) or a quaternary ammonium group -N^{+}R'R''R''', An' for which R', R'' and R''', which may be identical or different, represent a hydrogen atom or a (CrC_{6})alkyl group, or alternatively -N^{+}R'R''R''' forms a heteroaryl such as imidazolium optionally substituted with a (C_{1-6})alkyl group, and An' represents the counterion of the organic or mineral acid or of the corresponding halide; preferably when the alkyl radical is optionally substituted, it is substituted with at least one hydroxyl, especially hydroxymethyl, group;

- an "alkoxy" radical is an alkyl-oxy or alkyl-O- radical for which the alkyl radical is a linear or branched C_{1-16} and preferentially C_{1-8} hydrocarbon-based radical;

- an "alkylthio" radical is an alkyl-S- radical for which the alkyl radical is a linear or branched C_{1-16} and preferentially C_{1-8} hydrocarbon-based radical;

- an "active CH" or "active methylene" compound is a reactive compound that contains a "CH" or "methylene" group which may readily lose or release a proton from said CH or methylene group, i.e. for which the carbon atom that bears the proton of the CH or methylene is directly bonded to an electron-deficient cationic heteroaryl group:

\[
\text{(active CH)}
\]

with
- R representing a hydrogen atom, a (C_{1-6}) alkyl group, or aryl group or electron-withdrawing group, in particular those that are electron-withdrawing via an \(-M\) mesomeric effect such as cyano \(-CN\) or \(-C(0)OR'\) with R' representing a C_{1-6} alkyl group or a hydrogen atom;
- Het^{+} representing a cationic heteroaryl group with an endocyclic cationic charge, i.e. the charge of which is included in the aromaticity of said heteroaryl and which is stabilized via a mesomeric effect;

the active methylene compound is in particular of formula \((\text{II2})\) below:

\[
\text{(II2)}
\]
in which formula (II):

- R' represents an optionally substituted (C₆₋₃₋₆)alkyl group;

\[
\begin{array}{c}
\text{R} \text{C}_{2} \text{H}_2 \text{N}^+ \\
\end{array}
\]

represents a heteroaryl group with an endocyclic cationic charge

5 comprising from 5 to 13 ring members, which may possibly also comprise the
cationic nitrogen atom, and comprising from 1 to 3 heteroatoms chosen from
nitrogen, oxygen and sulphur, and which bears, on a carbon atom of the heteroaryl,
a group R-CH₂⁻⁻⁻ with R representing a hydrogen atom or a (CrC₆₋₃₋₆)alkyl or aryl group;
such as imidazolium, oxazolium, thiazolium, pyridinium, pyrimidinium such as 2-
oxopyrimidinium, quinolinium, the group R-CH₂⁻⁻⁻ being at position 2 or 4 of the
pyridinium or quinolinium or at position 2, 4 or 5 of the imidazolium, oxazolium or
thiazolium group, or at position 4 and 6 of the pyrimidinium such as 2-
oxopyrimidinium;

- the limit values delimiting the extent of a range of values are included in this range of
values; and

- the expression "at least" is understood to mean "one or more".

\textit{j) hydroxybenzaldehyde derivative of formula (I)}

20 One particular embodiment of the invention relates to hydroxybenzaldehyde derivatives
or mixtures thereof of formula (I) in which at least one of the two radicals R¹ and/or R₅
represent(s) a hydroxyl group and in which R¹, R², R₃, R₄ and R₅ represent, independently of
one another, a hydrogen or halogen atom, preferably a chlorine atom or a group chosen
from:

- a hydroxyl;
- a linear or branched C₁₋₃₋₆ alkyl;
- a linear or branched C₁₋₃₋₆ alkoxy, preferably a methoxy radical;
- a carboxyl -C(0)-OH;
- a carboxaldehyde -C(0)H; and
- a di(C₁₋₃₋₆)alkylamino; or else
- R¹ and R², or R² and R₃, or R₃ and R⁴ form, together with the carbon atoms to which
they are attached, an aromatic ring containing 6 carbon atoms;
on the condition that when R¹ represents a hydroxyl group, then R² or R₃ or R₄ or R₅
represents a hydrogen atom; and when R₃ represents a hydroxyl group then R¹ or R² or
R⁴ or R₅ represents a hydrogen atom.

The advantageous compounds of (I) of the invention are those from the table below:
<table>
<thead>
<tr>
<th>Names</th>
<th>Structure</th>
<th>Names</th>
<th>Structure</th>
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<tbody>
<tr>
<td>3,4-Dihydroxybenzaldehyde (protocatechualdehyde)</td>
<td><img src="image1" alt="Structure 1" /></td>
<td>4-Hydroxy-3-methoxybenzaldehyde (vanillin)</td>
<td><img src="image2" alt="Structure 2" /></td>
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<tr>
<td>4-Hydroxybenzene-1,3-dicarbaldehyde</td>
<td><img src="image3" alt="Structure 3" /></td>
<td>2,4-Dihydroxybenzaldehyde</td>
<td><img src="image4" alt="Structure 4" /></td>
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<tr>
<td>3,4,5-Trihydroxybenzaldehyde</td>
<td><img src="image5" alt="Structure 5" /></td>
<td>3,5-Dimethyl-4-hydroxybenzaldehyde</td>
<td><img src="image6" alt="Structure 6" /></td>
</tr>
<tr>
<td>3,4-Dihydroxy-5-methoxybenzaldehyde</td>
<td><img src="image7" alt="Structure 7" /></td>
<td>2,3,4-Trihydroxybenzaldehyde</td>
<td><img src="image8" alt="Structure 8" /></td>
</tr>
<tr>
<td>2,4,6-Trihydroxybenzaldehyde</td>
<td><img src="image9" alt="Structure 9" /></td>
<td>3,5-Dichloro-2-hydroxybenzaldehyde</td>
<td><img src="image10" alt="Structure 10" /></td>
</tr>
<tr>
<td>2,4-Dihydroxybenzaldehyde</td>
<td><img src="image11" alt="Structure 11" /></td>
<td>4-Hydroxybenzaldehyde</td>
<td><img src="image12" alt="Structure 12" /></td>
</tr>
<tr>
<td>3,4,5-Trihydroxybenzaldehyde</td>
<td><img src="image13" alt="Structure 13" /></td>
<td>4-Hydroxy-2-methylbenzaldehyde</td>
<td><img src="image14" alt="Structure 14" /></td>
</tr>
<tr>
<td>3,4-Dihydroxy-5-methoxybenzaldehyde</td>
<td><img src="image15" alt="Structure 15" /></td>
<td>4-Hydroxy-3-methoxybenzaldehyde</td>
<td><img src="image16" alt="Structure 16" /></td>
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<tr>
<td>3,5-Dichloro-2-hydroxybenzaldehyde</td>
<td><img src="image17" alt="Structure 17" /></td>
<td>2,4,5-Trihydroxybenzaldehyde</td>
<td><img src="image18" alt="Structure 18" /></td>
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<tr>
<td></td>
<td>2-Hydroxy-3-methylbenzaldehyde</td>
<td>4-Hydroxy-3-chloro-benzaldehyde</td>
<td>3,4-Dihydroxybenzaldehyde</td>
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Preferably, the derivatives of formula (I) are chosen from compounds 1 to 10 as defined in the preceding table.

According to one particular embodiment of the invention that makes it possible to obtain intense, deep colorations, the hydroxybenzaldehyde derivatives or mixtures thereof are chosen from those of formula (II):

\[
\begin{array}{c}
\text{R'}_1 \text{ represents a hydrogen atom or a hydroxyl group;}
\text{R'}_2 \text{ represents a hydrogen atom, or a group chosen from a hydroxyl, a carboxaldehyde, a linear or branched C}_{1-4} \text{ alkyl and a linear or branched C}_{1-4} \text{ alkoxy;}
\text{R'}_4 \text{ represents a hydrogen atom or a group chosen from a hydroxyl, a linear or branched C}_{1-4} \text{ alkyl and a linear or branched C}_{1-4} \text{ alkoxy;}
\text{R'}_5 \text{ represents a hydrogen atom or a hydroxyl group;}
\end{array}
\]

with, more particularly:

- \( R'_{1} = \text{OH} \) and \( R'_{5} = \text{OH} \) or a linear or branched C\(_{1-5}\) alkoxy; and/or
- \( R'_{2} = \text{OH or C(0)H and } R'_{4} = \text{OH or a linear or branched } C_{1-5} \text{ alkoxy}; \)
- and \( R'_{1} \) or \( R'_{2} \) or \( R'_{4} \) or \( R'_{5} \) denotes a hydrogen atom.

The preferred compounds (II) are the following:

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<td>7</td>
<td>9</td>
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</tr>
</tbody>
</table>

and/or the organic or mineral base salts thereof and/or solvates thereof.

According to the invention, the hydroxybenzaldehyde derivative(s) of formula (I) are synthetic, natural, or are found in natural extracts. For example, mention may be made of hydroxybenzaldehydes such as vanillin (4-hydroxy-3-methoxybenzaldehyde), isovanillin (3-hydroxy-4-methoxybenzaldehyde) or ethyl vanillin (4-hydroxy-3-ethoxybenzaldehyde) derived from extract of vanilla or Vanilla planifolia or Vanilla tahitensis, protocatechualdehyde derived from extract of Cassia garrettiana, gallaldehyde derived from extract of Boletus scaber.

According to one embodiment, the derivative(s) of formula (I) are present in the composition or in the process without the presence of oxidizing agent or coupler.

According to another embodiment, oxidation dyes are present optionally with couplers.

The coloration observed is compatible with conventional oxidation conditions for lightening hair. The coloration is persistent with regard to shampooing operations.

In the latter variant, the derivative(s) of formula (I) are at a total concentration that is at least 10 times higher than the concentration of other oxidation dyeing precursors, for instance the bases and couplers optionally present in the mixture.

Preferably, the hydroxybenzaldehyde derivative(s) or mixtures thereof of formula (I) exist in the composition or in the process according to the invention at a concentration of greater than 1 g per 100 g (%) relative to the total weight of the composition containing the hydroxybenzaldehyde derivative(s) or the extract(s) comprising them, particularly between
between 1 g % and 10 g % and preferably between 1 g % and 5 g %.

**ii) chemical oxidizing agent**

According to the dyeing process of the invention, said process uses a chemical oxidizing agent. The expression "chemical oxidizing agent" is understood to mean an oxidizing agent other than the oxygen from the air.

*The expression "chemical oxidizing agent" is understood more particularly to mean:*

10 a) ozone;

b) alkali metal or quaternary ammonium persalts such as perborates, persulphates, percarbonates, peroxodiphosphates or Oxone®; the oxidizing agent is particularly chosen from sodium perborate, sodium persulphate, potassium persulphate, ammonium persulphate, sodium percarbonate and potassium percarbonate;

c) aliphatic C<sub>1</sub>-C<sub>6</sub> and aromatic C<sub>6</sub>-C<sub>20</sub> organic peracids, and the percarboxylate forms thereof, such as performic acid, peracetic acid, perbenzoic acid derivatives, trifluoroacetic acid, peroxyphthalic acid, peroxymaleic acid, peroxypropionic acid; the oxidizing agent is particularly peracetic acid;

d) organic peroxides such as dioxirane, C<sub>1</sub>-C<sub>6</sub> alkyl peroxides, benzoyl peroxide, peroxo(CrC<sub>2</sub>)[alkyl carboxylates, bis(tri)(CrC<sub>2</sub>)[alkylsilyl] peroxides such as bis(trimethylsilyl) peroxide, C<sub>1</sub>-C<sub>6</sub> alkyl peroxydicarbonates, and sodium nonanoyloxybenzene sulphonate as described in patents WO 1995/000625 and US 4 412 934;

e) oxidizing anions such as nitrites, nitrates, hypochlorites, hypobromites, hypiodites, chlorites, bromites, iodites, chlorates, bromates, iodates and periodates; the oxidizing agent is particularly chosen from an alkali metal hypochlorite or periodate such as sodium hypochlorite or sodium periodate;

f) stable N-oxy (NO) radicals such as the 2,2,6,6-tetra(CrC<sub>2</sub>)[alkylpiperidino]oxy or 2,2,6,6-tetra(Ci-C<sub>2</sub>)[alkylmorpholinooxy] radical, nitrosodisulphonate Fremy salts and morpholine N-oxide; the oxidizing agent is particularly chosen from the 2,2,6,6-tetramethylpiperidylxyloxy radical.

g) multivalent iodine derivatives such as iodosetriacetate, iodosobenzene, iodobenzenetriacetate, iodoperbenzoic acid derivatives, periodinanes, alkyls and benzyl hypiodites;

35 more preferentially, the oxidizing agent is chosen from iodosetriacetate, iodosobenzene, iodobenzenetriacetate, iodoperbenzoic acid and Dess-Martin periodinane;

h) the following organic compounds: N-halosuccinimides, trichloroisocyanuric acid, N-hydroxyphthalimide, alkyl nitrites;

40 the optional supports for these oxidizing agents a) to h) may be chosen from silica, alumina, charcoal and charged or neutral polymers;
i) hydrogen peroxides or system(s) that generate hydrogen peroxide such as:
   i-1) urea peroxide;
   i-2) polymeric complexes that can release hydrogen peroxide, such as polyvinylpyrrolidone/H₂O₂ in particular in the form of powders, and the other polymeric complexes described in US 5 008 093; US 3 376 110; US 5 183 901;
   i-3) oxidases that produce hydrogen peroxide in the presence of a suitable substrate (for example glucose in the case of glucose oxidase or uric acid with uricase);
   i-4) metal peroxides that generate hydrogen peroxide in water, for instance calcium peroxide or magnesium peroxide;
   i-5) perborates; or
   i-6) percarbonates.

More particularly the chemical oxidizing agent(s) is (are) chosen from i) hydrogen peroxide or systems that generate hydrogen peroxide. More particularly H₂O₂.

According to one preferred embodiment of the invention, the process uses one or more system(s) that generate hydrogen peroxide, chosen from i) urea peroxide, i-2) polymeric complexes that can release hydrogen peroxide, chosen from polyvinylpyrrolidone/H₂O₂; i-3) oxidases; i-5) perborates and i-6) percarbonates.

More preferably, the composition according to the invention comprises hydrogen peroxide.

Moreover, the composition(s) comprising the hydrogen peroxide or the generator(s) of hydrogen peroxide may also contain various adjuvants conventionally used in hair dye compositions and as defined hereinbelow under the heading "cosmetic composition".

According to one particular embodiment of the invention, the hydrogen peroxide or the system(s) that generate hydrogen peroxide that is (are) used preferably represent from 0.001 % to 12% by weight expressed as hydrogen peroxide relative to the total weight of the composition(s) containing it or them. More particularly, the process of the invention or the composition of the invention contains hydrogen peroxide or an aqueous hydrogen peroxide solution at the 20-volume concentration of between 1 g and 70 g per 100 g (%) of the composition containing said peroxide; preferably between 3 g % and 50 g % and especially between 3 g % and 50 g %.

**Hi) alkanizing agent**

The alkanizing agent present in the composition according to the invention or used in the dyeing process according to the invention as a fourth ingredient **Hi)** is an agent for increasing the pH of the composition(s) in which it is present. The alkanizing agent is a Bronsted, Lowry or Lewis base. It may be mineral or organic.
Particularly, said agent is chosen from i) (bi)carbonates, ii) aqueous ammonia, iii) alkanolamines such as monoethanolamine, diethanolamine, triethanolamine and derivatives thereof, iv) oxyethylenated and/or oxypropylenated ethylenediamines, v) mineral or organic hydroxides, vi) alkali metal silicates such as sodium metasilicates, vii), amino acids, preferably basic amino acids such as arginine, lysine, ornithine, citrulline and histidine, and viii) the compounds of formula (III) below:

\[
\begin{array}{c}
\text{R}_a \\
\text{R}_b \\
\text{R}_c \\
\text{R}_d (\text{III})
\end{array}
\]

in which formula (III) \(W\) is a divalent \((C_1-C_5)\text{alkylene group} \) optionally interrupted by at least one heteroatom such as \(O, S, NR_e\), and/or said alkylene group is optionally substituted with at least one hydroxyl group or a \((C_1-C_4)\text{alkyl radical} \); \(R_a, R_b, R_c, R_d\) and \(R_e\), which may be identical or different, represent a hydrogen atom, \((C_1-C_4)\text{alkyl or C}_1-C_4 \text{hydroxyalkyl} \), preferably a propylene group.

The mineral or organic hydroxides are preferably chosen from a) hydroxides of an alkali metal, b) hydroxides of an alkaline-earth metal, for instance sodium hydroxide or potassium hydroxide, c) hydroxides of a transition metal, such as hydroxides of metals from groups III, IV, V and VI, d) hydroxides of lanthanides or actinides, quaternary ammonium hydroxides and guanidinium hydroxide.

The hydroxide may be formed in situ, for instance guanidine hydroxide, by reacting calcium hydroxide and guanidine carbonate.

The term "(bi)carbonates i)" means:

a) carbonates of alkali metals \((\text{Met}^{2+}, \text{CO}_3^{2-})\), of alkaline-earth metals \((\text{Met'}^{2+}, \text{CO}_3^{2-})\) of ammonium \(((\text{R}''_4 \text{N})^+_2, \text{CO}_3^{2-})\) or of phosphonium \(((\text{R}''_4 \text{P})^-_2, \text{CO}_3^{2-})\) with \(\text{Met}^+\) representing an alkaline-earth metal and \(\text{Met}^+\) representing an alkali metal, and \(\text{R}''\), which may be identical or different, represent a hydrogen atom, an optionally substituted \((\text{CrC}_6)\text{alkyl group such as a hydroxyethyl group} \), and

b) bicarbonates, also known as hydrogen carbonates, of the following formulae:

\[ \text{R}^{+}, \text{HC}_2 \text{O}_3^{-}\] with \(\text{R}^+\) representing a hydrogen atom, an alkali metal, an ammonium group \(\text{R}''_4 \text{N}^-\) or a phosphonium group \(\text{R}''_4 \text{P}^-\) where \(\text{R}''\), which may be identical or different, represent a hydrogen atom, an optionally substituted \((\text{CrC}_6)\text{alkyl group such as a hydroxyethyl group and, when \(\text{R}''\) represents a hydrogen atom, the hydrogen carbonate is then known as a dihydrogen carbonate \((\text{CO}_2, \text{H}_2\text{O})\); and

\[ \text{Met}^{2+} (\text{HC}_2 \text{O}_3)^2\] with \(\text{Met}^+\) representing an alkaline-earth metal.

More particularly, the alkanilizing agent is chosen from alkali metal or alkaline-earth metal (bi)carbonates; preferentially alkali metal (bi)carbonates.
Mention may be made of Na, K, Mg and Ca carbonates or hydrogen carbonates and mixtures thereof, and in particular sodium hydrogen carbonate. These hydrogen carbonates may originate from a natural water, for example spring water from the Vichy basin or from La Roche Posay or Badoit water (cf. for example, patent document FR 2 814 943). In particular, mention may be made of sodium carbonate [497-19-8] = Na₂CO₃, sodium hydrogen carbonate or sodium bicarbonate [144-55-8] = NaHCO₃, and sodium dihydrogen carbonate = Na(HCO₃)₂.

According to one particularly advantageous embodiment, the alkanalizing agent(s) HI are chosen from i) bicarbonates, particularly alkali metal or ammonium bicarbonates, ii) aqueous ammonia, iii) alkanolamines such as ethanolamine or 2-amino-2-methyl-1-propanol, more preferably aqueous ammonia.

The alkanalizing agent(s) as defined previously preferably represent(s) from 10⁻³ to 2.5x10⁻¹ mol per 100 g (%) of the composition containing said alkanalizing agents. Particularly from 0.05 to 0.5 mol% preferably from 0.1 to 0.25 g % by weight of the composition.

iv) optionally sulphate salt:

The process or the composition according to the invention may contain at least one (di)sulphate. The term "sulphates" is understood to mean the salts derived from sulphuric acid H₂SO₄, the sulphate ion of which is SO₄²⁻ (See "Sulfites, Thiosulfates, and Dithionites" in Ullmann's Encyclopedia of Industrial Chemistry; 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim - http://onlinelibrary.wiley.com/doi/10.1002/14356007.a25_477/pdf). The pH of the sulphates according to the invention is neutral or even slightly acid (pH between 7 and 6.6).

According to another preferred embodiment of the invention, the sulphates are sulphates of formula M₂SO₃ or M'SO₃ or a hydrogen sulphate of formula MHSO₃ with M representing an alkali metal such as Na or K or (di)(Cr₆)(alkyl)ammonium or tri(C₆H₅)alkylammonium such as NH₄⁺, or else disulphates of formula M'S₂O₅ with M' representing an alkali-earth metal.

The sulphates of the invention are in particular salts of alkali metals or alkaline-earth metals or ammonium, (di)(Cr₆)alkylammonium or tri(C₆H₅)alkylammonium; preferably the cationic counterion of the sulphate is chosen from sodium and potassium, and ammonium.

Preferably, the sulphate salts according to the invention are chosen from:

a) ammonium sulphate [10196-04-0]: (NH₄)₂SO₃;
b) sodium sulphate [7757-83-7]: Na₂SO₃; and
c) sodium hydrogen sulphate [7631-90-5]: NaHSO₃.

According to one preferred embodiment of the invention, the sulphate salt(s) used in the composition or in the process of the invention represent from 0.001% to 10% by weight
approximately, of the total weight of the composition(s) containing this or these sulphate salts, and more preferably still from 0.05% to 0.1% by weight approximately.

v) optionally one or more mordants

The composition according to the invention may contain at least one mordant or the process of the invention may involve a supplementary step with at least one mordant. The term "mordant" is understood to mean a mordanting agent conventionally used in the textile industry and which is cosmetically acceptable, preferably in the form of metal salts such as iron, aluminium, titanium, calcium, manganese, copper, zinc and strontium salts. By way of example, the mordant may be iron sulphate, manganese gluconate, copper sulphate, zinc gluconate, calcium chloride, magnesium chloride, potassium titanyl oxalate or strontium acetate. Preferably, the mordant used is iron sulphate.

The mordants are particularly found in the composition in proportions between 0.001% and 10% relative to the total weight of the composition containing them.

According to another particular embodiment of the invention, neither the dyeing process nor the composition of the invention use or contain a mordanting agent.

water:

According to one embodiment of the invention, water is preferably included in the process of the invention. It may originate from the moistening of the keratin fibres and/or from the composition(s) comprising compounds \( f \) to \( H_l \) as defined previously or from one or more other compositions. Preferably, the water comes from at least one composition comprising at least one compound chosen from \( f \) to \( H_l \) as defined previously.

cosmetic compositions:

The cosmetic compositions according to the invention are cosmetically acceptable, i.e. they comprise a dye support that generally contains water or a mixture of water and of one or more organic solvents or a mixture of organic solvents.

The term "organic solvent" means an organic substance that is capable of dissolving or dispersing another substance without chemically modifying it.

Organic solvents:

Examples of organic solvents that may be mentioned include \( C_1-C_4 \) lower alkanols, such as ethanol and isopropanol; polyols and polyol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, hexylene glycol, and also aromatic alcohols, for instance benzyl alcohol or phenoxyethanol.

The organic solvents are present in proportions preferably of between 1% and 40% by
weight approximately and even more preferentially between 5% and 30% by weight approximately relative to the total weight of the dye composition.

Adjuvants:

The composition(s) of the dyeing process 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, penetrants, sequestrants, fragrances, buffers, dispersants, conditioning agents, for instance volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents and opacifiers.

Said adjuvants are preferably chosen from surfactants such as anionic or nonionic surfactants or mixtures thereof and mineral or organic thickeners.

The above adjuvants are generally present in an amount for each of them of between 0.01% and 40% by weight relative to the weight of the composition, and preferably between 0.1% 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 additional compound(s) such that the advantageous properties intrinsically associated with the composition(s) that is (are) useful in the dyeing process in accordance with the invention are not, or are not substantially, adversely affected by the envisioned addition(s).

Additional dyes:

The process using ingredients \( i \) to \( Hi \) as defined previously or the cosmetic composition according to the invention comprising ingredients \( i \) to \( Hi \) as defined previously may also use or comprise one or more additional direct dyes. These direct dyes are chosen, for example, from those conventionally used in direct dyeing, and among which mention may be made of any commonly used aromatic and/or non-aromatic dye such as neutral, acidic or cationic nitrobenzene direct dyes, neutral, acidic or cationic azo direct dyes, natural direct dyes other than \( ortho \)-diphenols, neutral, acidic or cationic quinone and in particular anthraquinone direct dyes, azine, triarylmethane, indoamine, methine, styryl, porphyrin, metalloporphyrin, phthalocyanine and methine cyanine direct dyes, and fluorescent dyes. All these additional dyes are other than the \( ortho \)-diphenol derivatives according to the invention.

Among the natural direct dyes, mention may be made of lawsone, juglone, indigo, isatin, curcumin, spinulosin, apigeninid and orceins. Extracts or decoctions containing these natural dyes and in particular henna-based poultices or extracts, may also be used.

The additional direct dye(s) used in the composition(s) preferably represent from 0.001% to 10% by weight approximately, of to the total weight of the composition(s) containing them, and even more preferentially from 0.05% to 5% by weight approximately.

The compositions of the process using ingredients \( i \) to \( Hi \) as defined previously or the
cosmetic composition according to the invention comprising ingredients i) to Hi) as defined previously may also use or comprise one or more oxidation bases and/or one or more couplers conventionally used for the dyeing of keratin fibres.

Among the oxidation bases, mention may be made of para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, bis-para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.

Among these couplers, mention may be made especially of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers, and the addition salts thereof. According to one particular embodiment of the invention, neither the process of the invention, nor the composition of the invention contain a coupler, especially meta-aminophenols.

More particularly, the process or the composition of the invention use or contain at least one oxidation dye, and bases and couplers, chosen from:

- 2,3-diamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one and also salts thereof such as 2,3-diamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one dimethanesulphonate;
- diaminoo-N,N-dihydropyrazolone derivatives of formula (IV) or an addition salt thereof:

\[
\begin{align*}
R_1 & \quad \text{in which formula (IV):} \\
R_i, R_2, R_3 \text{ and } R_4, & \text{ which may be identical or different, represent:} \\
& \text{a linear or branched } C_{1-6} \text{ alkyl radical which is optionally substituted with one or more radicals selected from the group consisting of a radical } OR_5, \text{ a radical } NR_6R_7, \text{ a} \\
& \text{carboxyl radical, a sulphonyl radical, a carboxamido radical } CON R_8R_9, \text{ a} \\
& \text{sulphonamido radical } SO_2NR_6R_7, \text{ a heteroaryl, an aryl optionally substituted with a} \\
& \text{(CrC _2)} \text{alkyl group, a hydroxyl, a } C_{1-2} \text{ alkoxy, an amino or a (di)alkyl(CrC _2)} \text{amino;} \\
& \text{an aryl radical optionally substituted with one or more of a } (C_1-C_4) \text{alkyl, a hydroxyl, a} \\
& \text{C_{1-2} alkoxy, an amino or a (di)(CrC _2)} \text{alkylamino;} \\
& \text{a 5- or 6-membered heteroaryl radical which is optionally substituted with one or more} \\
& \text{radicals selected from a } (C_1-C_4) \text{alkyl and a } (C_1-C_2) \text{alkoxy;} \\
R_3 \text{ and } R_4 & \text{ may also represent a hydrogen atom;} \\
R_5, R_6 \text{ and } R_7, & \text{which may be identical or different, represent a hydrogen atom; a linear} \\
& \text{or branched } C_{1-4} \text{ alkyl radical which is optionally substituted with one or more radicals} \\
& \text{selected from the group consisting of a hydroxyl, a } C_{1-2} \text{ alkoxy, a carboxamido} \\
CON R_8R_9, \text{ a sulphonyl } SO_2R_8, \text{ an aryl optionally substituted with a } (C_1-C_4) \text{alkyl, a} \\
& \text{hydroxyl, a } C_{1-2} \text{ alkoxy, an amino, a (di)alkyl(CrC _2)} \text{amino; an aryl optionally} \\
& \text{substituted with a } (C_1-C_4) \text{alkyl, a hydroxyl, a } C_{1-2} \text{ alkoxy, an amino or a (di)alkyl(d-} \end{align*}
\]
C2)amino;
R6 and R7, which may be identical or different, may also represent a carboxamido radical CONR8Rg or a sulphonyl S02R8;
R8 and R9, which may be identical or different, represent a hydrogen atom; a linear or branched C1-C4 alkyl radical which is optionally substituted with one or more of a hydroxyl or a C1-C2 alkoxy;
R1 and R2, on the one hand, and R3 and R4, on the other hand, may form, with the nitrogen atoms to which they are attached, a saturated or unsaturated 5- or 7-membered heterocycle which is optionally substituted with one or more radicals selected from the group consisting of halogen atoms, amino, (di)(C1-C4)alkylamino, hydroxyl, carboxyl, carboxamido and (C1-C2)alkoxy radicals, C1-C4 alkyl radicals optionally substituted with one or more hydroxyl, amino, (di)alkylamino, alkoxy, carboxyl or sulphonyl radicals;
R3 and R4 may also form, together with the nitrogen atom to which they are attached, a 5- or 7-membered heterocycle, the carbon atoms of which can be replaced with an optionally substituted oxygen or nitrogen atom;
More particularly the derivatives of formula (IV) or the addition salts thereof are chosen from:

- 4,5-diamino-1,2-dimethyl-1,2-dihydropyrazol-3-one;
- 4-amino-5-methylamino-1,2-dimethyl-1,2-dihydropyrazol-3-one;
- 4-amino-5-dimethylamino-1,2-dimethyl-1,2-dihydropyrazol-3-one;
- 4-amino-5-(2-hydroxyethyl)amino-1,2-dimethyl-1,2-dihydropyrazol-3-one;
- 4-amino-5-(pyrrolidin-1-yl)-1,2-dimethyl-1,2-dihydropyrazol-3-one;
- 4-amino-5-(piperidin-1-yl)-1,2-dimethyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-1,2-bis(2-hydroxyethyl)-1,2-dihydropyrazol-3-one;
- 4-amino-5-methylamino-1,2-bis(2-hydroxyethyl)-1,2-dihydropyrazol-3-one;
- 4-amino-5-dimethylamino-1,2-bis(2-hydroxyethyl)-1,2-dihydropyrazol-3-one;
- 4-amino-5-(2-hydroxyethyl)amino-1,2-bis(2-hydroxyethyl)-1,2-dihydropyrazol-3-one;
- 4-amino-5-(pyrrolidin-1-yl)-1,2-bis(2-hydroxyethyl)-1,2-dihydropyrazol-3-one;
- 4-amino-5-(piperidin-1-yl)-1,2-bis(2-hydroxyethyl)-1,2-dihydropyrazol-3-one;
- 4,5-diamino-1,2-diethyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-1-ethyl-2-methyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-2-ethyl-1-methyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-1-phenyl-2-methyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-2-ethyl-1-methyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-1-phenyl-2-methyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-1-(2-hydroxyethyl)-2-methyl-1,2-dihydropyrazol-3-one;
- 4,5-diamino-2-(2-hydroxyethyl)-1-methyl-1,2-dihydropyrazol-3-one;
- 2,3-diamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
- 2-amino-3-methylamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
- 2-amino-3-dimethylamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
- 2-amino-3-ethylamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2-amino-3-isopropylamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2-amino-3-(2-hydroxyethyl)amino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2-amino-3-(2-hydroxypropyl)amino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2-amino-3-bis(2-hydroxyethyl)amino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2-amino-3-(pyrrolidin-1-yl)-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2-amino-3-(3-hydroxypyrrolidin-1-yl)-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2-amino-3-(piperidin-1-yl)-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2,3-diamino-6-hydroxy-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2,3-diamino-6-methyl-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2,3-diamino-6-dimethyl-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one;
2,3-diamino-5,6,7,8-tetrahydro-1 H,6H-pyridazino[1,2-a]pyrazol-1-one;
2,3-diamino-5,6,7,8-tetrahydro-1 H,6H-pyridazino[1,2-a]pyrazol-1-one;

- salts of 4-(3-aminopyrazolo[1,5-a]pyridin-2-yl)-1,1-dimethylpiperazin-1-ium, especially the halides such as 4-(3-aminopyrazolo[1,5-a]pyridin-2-yl)-1,1-dimethylpiperazin-1-ium hydrochloride chloride; and

- 3-aminopyrazolo[1,5-a]pyridine derivatives of formula (V) below and also the salts and solvates thereof:

\[ \text{NH}_2 \quad \text{(V)} \]

in which formula (V):

- \( \text{Z}_1 \) and \( \text{Z}_2 \) independently represent: i) a single covalent bond, ii) a divalent radical chosen from an oxygen atom and a radical \(-\text{NR}_6(\text{R}_7)_P\),
  - with \( p = 0 \) or \( 1 \) with, when \( p \) is equal to 0 then \( \text{R}_6 \) represents a hydrogen atom or a \( \text{C}_1-\text{C}_6 \) alkyl radical, or \( \text{R}_6 \), with \( \text{R}_1 \), respectively \( \text{R}_2 \), form, together with the nitrogen atom to which they are attached, a substituted or unsubstituted, saturated or unsaturated, aromatic or nonaromatic, 5- to 8-membered heterocycle, optionally containing one or more heteroatoms or groups selected from \( \text{N, O, S, SO}_2 \) and \(-\text{CO}-\), it being possible for the heterocycle to be cationic and/or substituted with a cationic or noncationic radical,
  - when \( p \) is equal to 1 then \(-\text{NR}_6\text{R}_7\) is a cationic radical in which \( \text{R}_6 \) and \( \text{R}_7 \) independently represent an alkyl radical,

- \( \text{Z}_1 \) may also represent a divalent radical \(-\text{S}_-\), \(-\text{SO}_-\) or \(-\text{SO}_2\) when \( \text{R}_1 \) is a methyl radical;

- it being understood that at least one of \( \text{Z}_1 \) and \( \text{Z}_2 \) is other than a single covalent bond,

- \( \text{R}_1 \) and \( \text{R}_2 \) independently represent a hydrogen or halogen atom, or a group chosen
from:
- a C1-C10 alkyl radical which is optionally substituted and optionally interrupted by
  a heteroatom or a group selected from O, N, Si, S, SO and SO₂;
- a C1-C10 alkyl radical which is substituted and/or interrupted by a cationic radical,
- an SO₃H radical,
- a 5- to 8-membered ring which is substituted or unsubstituted, saturated, unsaturated or aromatic and optionally comprises one or more heteroatoms or groups selected from N, O, S, SO₂ and -CO₂-, it being possible for the ring to be cationic and/or substituted with a cationic radical,

when Z₁, respectively Z₂, represents a covalent bond, then R₁, respectively R₂, may also represent:
- an optionally substituted C₁-C₆ alkylcarbonyl radical;
- a radical -O-CO-R, -CO-O-R, NR-CO-R' or -CO-NRR' in which R and R' independently represent a hydrogen atom or an optionally substituted C₁-C₆ alkyl radical;
- R₃, R₄ and R₅, which may be identical or different, represent:
  - a hydrogen atom;
  - a hydroxyl radical;
  - a C₆ alkylthio radical;
- a C₆ alkylamino radical;
- a C₆ dialkylamino radical in which the alkyl radicals may form, with the nitrogen atom to which they are attached, a saturated or unsaturated, aromatic or nonaromatic, 5- to 8-membered heterocycle, which may contain one or more heteroatoms or groups selected from N, O, S, SO₂ and CO₂, it being possible for the heterocycle to be cationic and/or substituted with a cationic radical;
- an optionally substituted C₁-C₆ alkylcarbonyl radical;
- a radical -O-CO-R, -CO-O-R, NR-CO-R' or -CO-NRR' with R and R' as defined previously;
- a halogen;
- a radical -NHSO₃H;
- an optionally substituted C₄ alkyl radical;
- an optionally substituted, saturated or unsaturated or aromatic carbon-based ring;
- R₃, R₄ and R₅, may form, in pairs, a saturated or unsaturated ring;

X represents an anionic counterion or group of anions making it possible to ensure the electronegativity of the derivative of formula (V), with the condition that at least one of the groups Z₁, R₁, Z₂, and R₂ represents a cationic radical.
More particularly the derivatives of formula (V) or the addition salts thereof are chosen from:

1. 

\[
\text{[2-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)ethyl]trimethylammonium}
\]

2. 

\[
3-(3-Aminopyrazolo[1,5-a]pyridin-2-yl)-1-methyl-3H-imidazol-1-ium
\]

3. 

\[
[2-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)ethyl]-ethyldimethylammonium
\]

4. 

\[
[2-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)ethyl](2-hydroxyethyl)dimethylammonium
\]

5. 

\[
[3-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)propyl]trimethylammonium
\]

6. 

\[
3-[3-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)propyl]-1-methyl-3H-imidazol-1-ium
\]
3-[3-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium

N-{2-[(3-aminopyrazolo[1,5-a]pyridin-2-yl)oxy]ethyl}-N-isopropyl-N-methylpropan-2-aminium

3-[2-(3-Aminopyrazolo[1,5-a]pyridin-2-yloxy)ethyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium

2-[[3-aminopyrazolo[1,5-a]pyridin-2-yl]oxy]-N,N,N-trimethylethanaminium

1-[2-[[3-aminopyrazolo[1,5-a]pyridin-2-yl]oxy]ethyl]-1-methylpyrrolidinium

1-[2-[[3-aminopyrazolo[1,5-a]pyridin-2-yl]oxy]ethyl]-1-methylpiperidinium

4-[[2-[(3-aminopyrazolo[1,5-a]pyridin-2-yl)oxy]ethyl]-4-methylmorpholin-4-ium

3-[3-(3-Aminopyrazolo[1,5-a]pyridin-2-yloxy)propyl]-1-methyl-3H-imidazol-1-ium

[1-(3-Aminopyrazolo[1,5-a]pyridin-2-yl)prrrolidin-3-y]trimethylammonium

4-(3-Aminopyrazolo[1,5-a]pyridin-2-yl)-1,1-dimethylpiperazin-1-ium

4-[2-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)ethyl]-1,1-dimethylpiperazin-1-ium

4-[2-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)ethyl]-1-methyl-1-propylpiperazin-1-ium

4-(3-Aminopyrazolo[1,5-a]pyridin-2-yl)-1-(2-hydroxyethyl)piperazin-1-ium

[4-(3-Aminopyrazolo[1,5-a]pyridin-2-ylamino)phenyl]trimethylammonium
4-[(3-Aminopyrazolo[1,5-a]pyridin-2-yl)-1,1-dimethyl[1,4]diazepan-1-iurri

[2-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-ylamino)ethyl]trimethylammonium

4-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)l-1 ,1-dimethylpiperazin-1-ium

4-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)-1-(2-hydroxyethyl)-l-methylpiperazin-1-ium

[1-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)pyrrolidin-3-yl]trimethylammonium

{1-[2-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yloxy)ethyl]pyrrolidir 1,3-yl]-trimethylammonium
1-{2-[{(3-amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)oxy}ethyl]-1-methylpyrrolidinium

1-{2-[{(3-amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)oxy}ethyl]-1-methylpiperidinium

4-{2-[{(3-amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)oxy}ethyl]-4-methylmorpholinium

2-{[(3-amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)oxy]-N,N,N-trimethylethanaminium

N-{2-[{(3-amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)oxy}ethyl]-N-isopropyl-N-methylpropan-2-aminium

[3-{(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)oxy}propyl]trimethyl-ammonium
4-{2-[(3-amino-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-2-yl)amino]ethyl}-
4-methylmorpholin-4-ium

N-{2-[(3-amino-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-2-yl)amino]ethyl}-
N-isopropyl-N-methylpropan-2-aminium

[1-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)pyrrolidin-3-yl](2-hydroxyethyl)-
dimethylammonium

{1-[2-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yl)oxy]ethyl]pyrrolidin-3-yl}-
trimethylammonium

[3-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-ylamino)propyl]-
trimethylammonium

[3-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yloxy)propyl]-
trimethylammonium
[3-(3-Amino-4-dimethylaminopyrazolo[1,5-a]pyridin-2-ylamino)propyl]trimethylammonium

[2-(3-Amino-4-dimethylaminopyrazolo[1,5-a]pyridin-2-ylamino)ethyl]trimethylammonium

4-(3-Amino-4-dimethylaminopyrazolo[1,5-a]pyridin-2-yl)-1-methylpiperazin-1-ium

[1-(3-Amino-4-dimethylaminopyrazolo[1,5-a]pyridin-2-yl)pyrrolidin-3-yl]-trimethylammonium

3-[2-(3-Amino-4-dimethylaminopyrazolo[1,5-a]pyridin-2-yloxy)ethyl]-1-methyl-3H-imidazol-1-ium

[2-(3-Amino-4-dimethylaminopyrazolo[1,5-a]pyridin-2-yloxy)ethyl]-trimethylammonium
(1-[2-(3-Amino-4-dimethylaminopyrazolo[1,5-a]pyridin-2-yloxy)ethyl]pyrrolidin-3-yl)-trimethylammonium

(3-Amino-2-methanesulphonylpyrazolo[1,5-a]pyridin-4-yl)trimethylammonium

(3-Amino-2-methoxypyrazolo[1,5-a]pyridin-4-yl)trimethylammonium

- salts of 2-[(3-aminopyrazolo[1,5-a]pyridin-2-yl)oxy]ethanol, especially 2-[(3-aminopyrazolo[1,5-a]pyridin-2-yl)oxy]ethanol hydrochloride; and
- derivatives of a 3-aminopyrazolo[1,5-a]pyridine derivative of formula (VI) and also the salts and solvates thereof:

\[
\text{(VI)}
\]

in which formula (VI):

- \( Z_1 \) represents an oxygen atom or a group NR\(_6\), when \( Z_1 \) represents NR\(_6\) then \( R_1 \) and \( R_6 \) may form, together with the nitrogen atom to which they are attached, an optionally substituted, saturated or unsaturated or aromatic 5- to 8-membered heterocycle;
  - \( Z_1 \) may also represent a divalent radical S, SO or SO\(_2\) when \( R_1 \) represents CH\(_3\);

- \( R_1 \) and \( R_6 \) independently represent:
  - a hydrogen atom;
  - an optionally substituted C1-C10 alkyl radical, it being possible for the substituent to be an optionally substituted, saturated or unsaturated or aromatic 5- to 8-membered (hetero)cycle;
  - an optionally substituted, saturated or unsaturated or aromatic 5- to 8-membered
(hetero)cycle;

- \( R_2, R_3, R_4 \) and \( R_5 \) independently represent:
  - a hydrogen atom;
  - an optionally substituted \( C_1-C_4 \) alkyl radical;
  - a group chosen from \( \text{NH}_2, NHR_{10}, \text{NR}_{12}R_{12}, \text{OH} \) or \( \text{OR}_{9} \), with \( R_9 \) and \( R_{10} \) representing an optionally substituted, linear or branched \( C_1-C_6 \) alkyl, \( R_{11} \) and \( R_{12} \), which may be identical or different, representing an optionally substituted, linear or branched \( C_1-C_6 \) alkyl, it being possible for \( R_{11} \) and \( R_{12} \) to form, together with the nitrogen atom to which they are attached, a saturated or unsaturated or aromatic 5- to 8-membered heterocycle optionally containing one or more other heteroatoms or groups chosen from \( N, O, S, S0_2 \) and \( \text{CO} \), the heterocycle being optionally substituted;

- \( R_2, R_3, R_4, R_5 \) may form, in pairs, with the adjacent radicals, an optionally substituted, saturated or unsaturated (hetero)cycle;

More particularly the derivatives of formula (VI) or the addition salts thereof are chosen from:

\[
\text{N-2-Methylpyrazolo[1,5-a]pyridine-2,3-diamine}
\]

\[
\text{N-2-Ethylpyrazolo[1,5-a]pyridine-2,3-diamine}
\]

\[
(3\text{-Aminopyrazolo[1,5-a]pyridin-2-ylamino)}\text{methanol}
\]

\[
1-(3\text{-Aminopyrazolo[1,5-a]pyridin-2-ylamino)}\text{propan-2-ol}
\]
2-[(3-Aminopyrazolo[1,2-\text{a}]pyridin-2-yl)(2-hydroxyethyl)amino]ethanol

2-pyrrolidin-1-ylpyrazolo[1,5-a]pyridin-3-ylamine

1-(3-Aminopyrazolo[1,2-\text{a}]pyridin-2-yl)pyrrolidin-3-ol

2-(3-Dimethylaminopyrrolidin-1-yl)pyrazolo[1,5-a]pyridin-3-ylamine

2-[1,4]Diazepan-1-ylpyrazolo[1,5-a]pyridin-3-ylamine

2-(4-Methyl[1,4]diazepam-1-yl)pyrazolo[1,5-a]pyridin-3-ylamine

1-[4-(3-Aminopyrazolo[1,5-a]pyridin-2-yl)][1,4]diazepam-1-yiethanone

N2-(2-piperazin-1-ylethyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

2-(4-Methylpiperazin-1-yl)pyrazolo[1,5-a]pyridin-3-ylamine
N-2-[2-(4-Methylpiperazin-1-yl)ethyl]pyrazolo[1,5-a]pyridine-2,3-diamine

N-2-[2-(4-Propylpiperazin-1-yl)ethyl]pyrazolo[1,5-a]pyridine-2,3-diamine

2-[4-(3-Aminopyrazolo[1,5-a]pyridin-2-yl)piperazin-1-yl]ethanol

N-2-(3-Imidazol-1-yl-propyl)pyrazolo[1,5-a]pyridine-2,3-diamine

2-(3-Imidazol-1-yl-propoxy)pyrazolo[1,5-a]pyridin-3-ylamine

2-(2-Dimethylaminoethoxy)pyrazolo[1,5-a]pyridin-3-ylamine

2-(3-Dimethylaminopropoxy)pyrazolo[1,5-a]pyridin-3-ylamine

2-Methanesulphonylpyrazolo[1,5-a]pyridin-3-ylamine
2-(2-imidazol-1-yl-ethoxy)-6,7-dimethylpyrazolo[1,5-a]pyridin-3-ylamine

2-(2-Dimethylaminoethoxy)-6,7-dimethylpyrazolo[1,5-a]pyridin-3-ylamine

2-[2-(3-Dimethylaminopyrrolidin-1-yl)ethoxy]-6,7-dimethylpyrazolo[1,5-a]pyridin-3-ylamine

2-Methoxy-6,7-dimethylpyrazolo[1,5-a]pyridin-3-ylamine

2-Ethoxy-6,7-dimethylpyrazolo[1,5-a]pyridin-3-ylamine

2-Isopropoxy-6,7-dimethylpyrazolo[1,5-a]pyridin-3-ylamine
2-(3-Amino-6,7-dimethylpyrazolo[1,5-a]pyridin-2-yloxy)ethanol

6,7-Dimethyl-2-methylsulphanylpyrazolo[1,5-a]pyridine-3-ylamine

N-2-(3-Dimethylaminopropyl)-N-5,N-5-dimethylpyrazolo[1,5-a]-pyridine-2,3,5-triamine

N-2-(2-Dimethylaminoethyl)-N-5,N-5-dimethylpyrazolo[1,5-a]pyridine-2,3,5-triamine

N-5,N-5-Dimethyl-2-(4-methylpiperazin-1-yl)pyrazolo[1,5-a]pyridine-3,5-diamine

2-(3-Dimethylaminopyrrolidin-1-yl)-N-5,N-5-dimethylpyrazolo[1,5-a]-pyridine-3,5-diamine
2-Methoxy-N-5,N-5-dimethylpyrazolo[1,5-a]pyridine-3,5-diamine

2-Ethoxy-N-5,N-5-dimethylpyrazolo[1,5-a]pyridine-3,5-diamine

2-Isopropoxy-N-5,N-5-dimethylpyrazolo[1,5-a]pyridine-3,5-diamine

2-(3-Amino-5-dimethylaminopyrazolo[1,5-a]pyridin-2-yloxy)ethanol

N-5,N-5-Dimethyl-2-methylsulphonylpyrazolo[1,5-a]pyridine-3,5-diamine

N2-(2-Dimethylaminoethyl)-4-ethyl-7-methylpyrazolo[1,5-a]pyridine-2,3-diamine

4-Ethyl-7-methyl-2-(4-methylpiperazin-1-yl)pyrazolo[1,5-a]pyridin-3-ylamine
2-[4-(3-Amino-4-ethyl-7-methylpyrazolo[1,5-a]pyridin-2-yl)piperazin-1-yl]ethanol

2-(3-Dimethylaminopyrrolidin-1-yl)-4-ethyl-7-methylpyrazolo[1,5-a]pyridin-3-ylamine

N2-(3-Dimethylaminopropyl)-4-ethyl-7-methylpyrazolo[1,5-a]pyridine-2,3-diamine

4-Ethyl-2-(2-imidazol-1-ylethoxy)-7-methylpyrazolo[1,5-a]pyridin-3-ylamine

2-(2-Dimethylaminoethoxy)-4-ethyl-7-methylpyrazolo[1,5-a]pyridin-3-ylamine

2-[2-(3-Dimethylaminopyrrolidin-1-yl)ethoxy]-4-ethyl-7-methylpyrazolo[1,5-a]pyridin-3-ylamine
4-Ethyl-2-methoxy-7-methylpyrazolo[1,5-a]pyridin-3-ylamine

2-Ethoxy-4-ethyl-7-methylpyrazolo[1,5-a]pyridin-3-ylamine

4-Ethyl-2-isopropoxy-7-methylpyrazolo[1,5-a]pyridin-3-ylamine

2-(3-Amino-4-ethyl-7-methylpyrazolo[1,5-a]pyridin-2-yloxy)ethanol

4-Ethyl-2-methanesulphonyl-7-methylpyrazolo[1,5-a]pyridin-3-ylamine

4-Ethyl-2-methylsulphanylpyrazolo[1,5-a]pyridin-3-ylamine

2-(methylsulphanyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-3-amine
1-(3-amino-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-2-yl)piperidin-3-ol

2-piperazin-1-yl-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-3-amine

2-(4-methylpiperazin-1-yl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-3-amine

2-[4-(3-amino-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-2-yl)piperazin-1-yl]ethanol

N2-[2-(dimethylamino)ethyl]-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-[3-(dimethylamino)propyl]-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-[2-(1H-imidazol-1-yl)ethyl]-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine
N2-[3-(1H-imidazol-1-yl)propyl]-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-(2-pyridin-2-ylethyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-(2-pyridin-3-ylethyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-(2-pyridin-4-ylethyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-(2-piperidin-1-ylethyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-(2-morpholin-4-ylethyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine

N2-(2-pyrrolidin-1-ylethyl)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridine-2,3-diamine
2-(2-pyridin-4-ylethoxy)-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-3-amine

2-methoxy-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-3-amine

2-ethoxy-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-3-amine

2-isopropoxy-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-3-amine

2-[(3-amino-7,8-dihydro-6H-cyclopenta[e]pyrazolo[1,5-a]pyridin-2-yl)oxy]ethanol

- 5-[(2-hydroxyethyl)amino]-2-methylphenol;
- 3,4-dihydro-2H-1,4-benzoxazin-6-ol;
- 3-amino-2-chloro-6-methylphenol;
- 2-aminopyridin-3-ol;
- 2-methylbenzene-1,3-diol;
- 2-(2,4-diaminophenoxy)ethanol hydrochloride; and
cationic aminopyridine derivatives of general formula (VII), addition salts thereof with an acid and solvates thereof:

\[
\begin{align*}
\text{(VII)} \\
\end{align*}
\]

in which formula (VII) the group \( Z; R \) bears the cationic charge,

- \( Z \) is an oxygen atom or a group \( NR_2 \).
R2 is a hydrogen atom or a linear or branched C1-C4 alkyl radical, a benzyl radical or an acetyl radical;

R1 is a saturated, linear or branched C1-C10 alkyl radical, which is substituted with or interrupted by a cationic radical, optionally interrupted by one or more oxygen atoms and/or by one or more groups NR2, optionally substituted with one or more radicals chosen from hydroxyl, alkoxy and C1-C4 hydroxyalkyl radicals, or R1 is a saturated or unsaturated or aromatic cationic 5- to 8-membered heterocycle optionally substituted with one or more radicals chosen from C1-C4 alkyl, hydroxyl, C1-C4 alkoxy, amino, (C1-C4)alkylamino, di(C1-C4)alkylamino, thio, (C1-C4)alkythio, carboxyl, (C1-C4)alkylcarbonyl, sulphonyl, amido and C1-C4 hydroxyalkyl radicals;

when Z1 represents NR2 then

- R1 and R2 may form, together with the nitrogen atom to which they are attached, a saturated or unsaturated cationic 5- to 8-membered heterocycle optionally substituted with one or more radicals chosen from C1-C10 alkyl radicals and hydroxyl, C1-C4 alkoxy, amino, (C1-C4)alkylamino, di(C1-C4)alkylamino, thio, (C1-C4)alkythio, carboxyl, (C1-C4)alkylcarbonyl, sulphonyl, amido and C1-C4 hydroxyalkyl radicals, it being possible for this heterocycle to contain one or more heteroatoms chosen from N or O, preferably N, or

- Ri and R2 may form, together with the nitrogen atom to which they are attached, a saturated or unsaturated noncaticonic 5- to 8-membered heterocycle substituted with a cationic radical and optionally substituted with one or more radicals chosen from C1-C10 alkyl radicals and hydroxyl, C1-C4 alkoxy, amino, (C1-C4)alkylamino, di(C1-C4)alkylamino, thio, (C1-C4)alkythio, carboxyl, (C1-C4)alkylcarbonyl, sulphonyl, amido and C1-C4 hydroxyalkyl radicals;

R is chosen from a hydrogen atom, halogens selected from fluorine, chlorine and bromine, linear or branched C1-C4 alkyl radicals and carboxyl (-COOH) and (C1-C4)alkoxycarbonyl radicals;

An- represents an anionic counterion or group of anions.

More particularly the derivatives of formula (VII) or the addition salts thereof are chosen from:

2-[(3,5-diaminopyridin-2-yl)amino]-N,N,N-trimethylthanolammonium,
2-[(3,5-diaminopyridin-2-yl)(methyl)amino]-N,N,N-trimethylthanolammonium,
1-[(3,5-diaminopyridin-2-yl)amino]ethyl]-1-methylpyrrolineum,
1-[(3,5-diaminopyridin-2-yl)-N,N,N-trimethylpyrroldin-3-ammonium,
1-[(3,5-diaminopyridin-2-yl)amino]propyl]-3-(2-hydroxyethyl)-1 H-imidazol-3-ium,
1-[(3,5-diaminopyridin-2-yl)amino]propyl]-1 -methylpyrrolineum,
1-[(3,5-diaminopyridin-2-yl)amino]propyl]-1 -methylpyrroldinum,
1-[(3,5-diaminopyridin-2-yl)amino]ethyl]-3-methyl-1 H-imidazol-3-ium,
4-{3-[(3,5-diaminopyridin-2-yl)amino]propyl}-4-methylmorpholin-4-ium,
4-{2-[3-(3,5-diaminopyridin-2-yl)amino]ethyl}-4-methylmorpholin-4-ium,
1-[2-([2-(3,5-diaminopyridin-2-yl)amino]ethyl)amino]ethyl-1-methylpiperidinium,
1-[2-([3,5-diaminopyridin-2-yl)amino]ethyl)amino]ethyl-1-methylpyrroloidinium,
1-(2-([3,5-diaminopyridin-2-yl)amino]ethyl)amino)ethyl)-3-methyl-1-H-imidazol-3-ium,
4-([2-(3,5-diaminopyridin-2-yl)amino]ethyl)amino)ethyl]-4-methylmorpholinium,
2-([2-(3,5-diaminopyridin-2-yl)amino]ethyl)amino)-N,N,N-trimethylpropan-1-amine,
3-([2-(3,5-diaminopyridin-2-yl)amino]ethyl)amino)-N,N,N-trimethylpropan-1-amine,
1-([3,5-diaminopyridin-2-yl)amino]propyl)-3-methyl-1-H-imidazol-3-ium,
1-([3-(3,5-diaminopyridin-2-yl)amino]ethyl)amino)propyl]-3-methyl-1-H-imidazol-3-ium,
4-([2-(3,5-diaminopyridin-2-yl)amino]ethyl)amino)propyl]-1,1-dimethylpiperazin-1-ium,
1-([3,5-diaminopyridin-2-yl)amino]ethoxy)propyl]-1-methylpiperidinium,
4-([2-(3,5-diaminopyridin-2-yl)amino]ethyl)amino)propyl]-4-methylmorpholin-4-ium,
3-([2-(3,5-diaminopyridin-2-yl)amino]ethyl)amino)-N-ethyl-N-methyl-N-propylpropan-1-amine,
3-[3,5-diaminopyridin-2-yl)amino]-N,N,N-trimethylpropan-1-amine,
3-[3,5-diaminopyridin-2-yl)amino]-N,N,N-trimethylpropan-1-amine,
1-([3,5-diaminopyridin-2-yl)amino]ethyl)-3-(2-hydroxyethyl)-1-H-imidazol-3-ium,
4-(3,5-diaminopyridin-2-yl)-1-(2-hydroxyethyl)-1-methylpiperazin-1-ium,
4-(3,5-diaminopyridin-2-yl)-1,1-bis(2-hydroxyethyl)piperazin-1-ium,
4-(3,5-diaminopyridin-2-yl)1-(2-trimethylethan)-morpholin-ammonium,
4-(3,5-diaminopyridin-2-yl)-(2-methyldiethylethan)-morpholin-ammonium,
4-(3,5-diaminopyridin-2-yl)morpholin2-1,1-dimethylpyrroloidinium,
(3,5-diaminopyridin-2-yl)3-trimethyl piperidin-ammonium,
(3,5-diaminopyridin-2-yl)-4-trimethyl piperidin-ammonium, and
4-(3,5-diaminopyridin-2-yl)-1,1-dimethylpiperazin-1-ium.

The oxidation base(s) present in the composition(s) are each generally present in an amount of between 0.001% and 10% by weight, of the total weight of the corresponding composition(s).
When the oxidation bases, in particular aromatic amines such as \textit{para}-phenylenediamines and/or \textit{para}-aminophenols are present in the composition of the invention or are used in the process of the invention, they are in amounts such that the ratio of the amount of hydroxybenzaldehyde derivatives of formula (I) as defined previously/the amount of oxidation base is at least greater than 5; preferably greater than 20.

According to one preferred embodiment of the invention, the dyeing process and the composition according to the invention do not comprise oxidation bases, in particular \textit{para}-phenylenediamines and/or \textit{para}-aminophenols.

The cosmetic composition(s) of the invention may be in various galenic forms, such as a powder, a lotion, a foam, a cream or a gel, or in any other form that is suitable for dyeing keratin fibres. They may also be packaged in a propellant-free pump-action bottle or under pressure in an aerosol container in the presence of a propellant and form a foam.

\textit{pH of the composition(s)}

The pH of the composition(s) containing \textit{Hi} the alkalinizing agent(s) is above 7 and preferably between 8 and 12. It is particularly between 8 and 10.

If the composition(s) contain(s) no alkalinizing agent, the pH of the composition(s) containing the oxidizing agent, such as hydrogen peroxide or the system that generates hydrogen peroxide, is preferably below 7, more particularly between 1 and 5.

Preferably, the composition(s) that contain(s) the hydroxybenzaldehyde derivative(s) of formula (I) as defined previously and that contain(s) no alkalinizing agent are at a pH of below 7 and preferably of between 3 and 6.5.

According to one particular embodiment of the invention, the compositions containing the sulphate salt(s) that contain or do not contain alkalinizing agent are at a pH of above 7 and preferably of between 8 and 12.

The pH of these compositions may be adjusted to the desired value by means of acidifying or alkalinizing agents usually used in the dyeing of keratin fibres as defined in "\textit{Hi} alkalinizing agent" above, or alternatively using standard buffer systems.

Among the acidifying agents of the compositions, mention may particularly be made of those chosen from a salt derived from \textit{i}) hydrochloric acid HCl, \textit{ii}) hydrobromic acid HBr, \textit{iii}) sulphuric acid H$_2$SO$_4$; \textit{iv}) alkylsulphonic acids: Alk-S(0)_2OH such as methylsulphonic acid and ethylsulphonic acid; \textit{v}) arylsulphonic acids: Ar-S(0)$_2$OH such as benzenesulphonic acid and toluenesulphonic acid; \textit{vi}) citric acid; \textit{vii}) succinic acid; \textit{viii}) tartaric acid; \textit{ix}) lactic acid; \textit{x}) phosphoric acid H$_3$PO$_4$; \textit{xi}) acetic acid CH$_3$C(0)OH; \textit{xii}) triflic acid CF$_3$SO$_3$H; and \textit{xiii}) tetrafluoroboric acid HBF$_4$.

\textit{Dyeing process according to steps a) and b)}

Preferably, the process of the invention does not use an active CH compound, and the
composition according to the invention does not contain an active CH compound.

According to one particular embodiment of the invention, the dyeing process is carried out:

a) by applying to the keratin fibres, in one or more steps, one or more cosmetic compositions containing the following ingredients, taken together or separately in said composition(s):
   i) at least one hydroxybenzaldehyde derivative of formula (I) as defined previously;
   ii) at least one oxidizing agent, preferably a chemical oxidizing agent; and
   iii) at least one alkalinizing agent;

   it being understood that:
   - the pH of the composition comprising the ingredient(s) iii) is basic i.e. above 7; preferably between 7.5 and 12; and
   - the total concentration of hydroxybenzaldehyde derivatives of formula (I) is greater than 1% relative to the total weight of the composition(s) comprising the ingredients i), ii) and iii); and

b) by heat treatment of the keratin fibres at a temperature above 30°C.

The waiting time between the steps of applying the compositions comprising the ingredient(s) i), ii) and/or iii) is set at between 3 and 120 minutes, preferentially between 10 and 60 minutes and more particularly between 15 and 45 minutes.

The keratin fibres may or may not be moistened beforehand.

More particularly, in the process of the invention, the chemical oxidizing agent(s) such as hydrogen peroxide ii) are either in a mixture with the ingredients i), or are applied in a composition without the other ingredients ii) and iii).

One particular embodiment of the invention relates to dyeing processes with step a) that is carried out in one or two application steps.

According to one particular embodiment of the invention, step a) of the process for dyeing keratin fibres is carried out by applying to the keratin fibres the preferably aqueous, cosmetic composition according to the invention comprising:

i) at least one derivative of formula (I), as defined previously;
ii) at least one oxidizing agent, preferably a chemical oxidizing agent; and
iii) at least one alkalinizing agent;

it being understood that:
- the composition preferably does not contain an active CH compound;
- the pH of the composition is basic i.e. above 7; preferably between 7.5 and 12;
- the compound(s) of formula (I) comprise at least one of the two radicals R¹ or R³ which represents a hydroxyl group; with, when R¹ represents a hydroxyl radical, then R² or R³ or R⁴ or R⁵ represents a hydrogen atom; and when R³ represents a hydroxyl radical then R¹ or R² or R⁴ or R⁵ represents a hydrogen atom;
- the total concentration of hydroxybenzaldehyde derivatives of formula (I) is greater than 1% relative to the total weight of the composition comprising the ingredients i)
to \(H_i\).

The waiting time after application is generally set at between 5 minutes and 24 hours, particularly between 10 and 120 minutes and more particularly between 15 and 60 minutes, especially between 15 and 45 minutes.

According to another particular embodiment of the invention, step a) of the process for dyeing keratin fibres is performed in two steps.

In a first variant, step a) involves applying to said fibres a cosmetic composition comprising the ingredients \(i\), \(ii\) as defined previously, and then, in a second step, a cosmetic composition comprising the ingredient \(Hi\) as defined previously is applied to said fibres, it being understood that at least one of the two cosmetic compositions is aqueous.

In a second variant of the process for dyeing keratin fibres, step a) firstly comprises applying to said fibres a composition comprising the ingredients \(i\) and \(Hi\) as defined previously, and then, in a second step, a second cosmetic composition comprising the ingredient(s) \(ii\) as defined previously is applied to said fibres, it being understood that preferably at least one of the two compositions is aqueous.

According to one preferred dyeing process of the invention, said step a) ends with the treatment of the keratin fibres with the ingredient \(Hi\).

The application temperature of step a) of the process of the invention is generally between room temperature \((15^\circ C \text{ to } 25^\circ C)\) and \(150^\circ C\) and particularly between \(15^\circ C\) and \(85^\circ C\), and preferably between \(20^\circ C\) and \(60^\circ C\). If the application is carried out at a temperature above the temperature of \(30^\circ C\), then it is possible to do away with step b) of the process of the invention. According to one preferred embodiment of the invention, the application of the composition(s) according to step a) of the process is carried out at room temperature, i.e. at \(25^\circ C\).

In step b) of the process of the invention, after application of the composition(s) according to step a) of the process of the invention, the hair is subjected to a heat treatment by heating at a temperature above room temperature, i.e. above \(30^\circ C\), particularly at a temperature between \(35^\circ C\) and \(80^\circ C\). More particularly between \(40^\circ C\) and \(50^\circ C\), such as \(45^\circ C\).

In practice, the heat treatment operation of step b) of the process of the invention may be performed using a a hairstyling hood, a hairdryer or an infrared ray emitter or other standard heating appliances.

It is possible to use, both as heating means and as hair straightening means, a heating iron at a temperature of between \(60^\circ C\) and \(220^\circ C\) and preferably between \(120^\circ C\) and \(200^\circ C\).

One advantageous aspect relates to the dyeing process as described previously, preceded by one or more mordanting steps by pretreating the keratin fibres with at least one mordant as defined previously (see "\(w) \text{ optionally one or more mordant(s)}\)"). The mordant(s) are especially in a cosmetic composition and are applied at least 5 minutes before the implementation of the dyeing process comprising the ingredients \(i\) to \(Hi\) as defined
previously. The mordant used is particularly iron sulphate.

Another advantageous aspect relates to the dyeing process as described previously, followed by post-treatment steps such as shampooing using a standard shampoo, rinsing, for example with water, and/or drying the keratin fibres by heat treatment as defined below.

Preferably, the dyeing process according to the invention is carried out in one step by applying to the keratin fibres the composition according to the invention comprising the ingredients \(i\) to \(H_i\) as defined previously, followed by post-treatment steps of rinsing, for example with water, of shampooing with a standard shampoo, and/or drying the keratin fibres.

In all the particular embodiments and variants of the processes described previously, the compositions mentioned are ready-to-use compositions that may result from the extemporaneous mixing of two or more compositions and especially of compositions present in dyeing kits.

**Dyeing device or "kit":**

Another subject of the invention is a multicompartment dyeing device or "kit". Advantageously, this kit comprises from 2 to 5 compartments containing from 2 to 5 compositions in which the ingredients \(i\) at least one hydroxybenzaldehyde derivative of formula \((I)\), as defined previously, \(ii\) at least one chemical oxidizing agent such as hydrogen peroxide and \(Hi\) at least one alkalinizing agent as defined previously are distributed.

According to a first variant, the kit comprises three compartments, the first two compartments comprising, respectively, the powdered ingredients \(i\) and \(Hi\) as defined previously and the third compartment containing an aqueous composition such as water. In this case, the compound(s) \(ii\) are hydrogen peroxide precursors.

Or else the kit comprises four compartments, the first three compartments comprising, respectively, the powdered ingredients \(i)\), \(ii\) and \(Hi\) as defined previously and the fourth compartment containing an aqueous composition such as water.

Another variant concerns a kit comprising three compartments, one of which contains at least one aqueous composition, and comprising an ingredient \(i\) to \(Hi\) as defined previously.

Another preferred embodiment concerns a device comprising three compartments:

(a) a first compartment contains a composition containing:
\(i\) at least one hydroxybenzaldehyde derivative of formula \((I)\) as defined previously; and (b) a second compartment contains a composition containing:
\(ii\) at least one chemical oxidizing agent such as hydrogen peroxide;
(c) a third compartment contains \(Hi\) at least one alkalinizing agent as defined previously.

In this other embodiment, at least one of the three compositions is preferably aqueous and the hydroxybenzaldehyde derivative(s) of formula \((I)\) may be in powder form.
Among the two-compartment kits, it is also possible to have kits that contain, in a first compartment, a composition comprising compounds i) and iii) as defined previously and, in a second compartment, a composition comprising compound ii) at least one chemical oxidizing agent such as hydrogen peroxide as defined previously.

According to one variant, the device according to the invention also comprises an additional composition (c) comprising one or more treating or mordanting agents.

The compositions of the device according to the invention are packaged in separate compartments, optionally accompanied by suitable application means, which may be identical or different, such as fine brushes, coarse brushes or sponges.

The device mentioned above may also be equipped with a means for dispensing the desired mixture on the hair, for instance the devices described in patent FR 2 586 913.

EXAMPLES OF DYEING

EXAMPLE A:

The following composition was prepared:

Composition for 100 g:
3 g of hydroxybenzaldehyde compound j) according to the invention;
5 g of 20% aqueous ammonia;
30 g of 20-volume aqueous hydrogen peroxide solution;
62 g of water.

The above composition is applied with a bath ratio of 1 g of hair per 5 g of composition. The locks of hair are grey containing 90% natural white (90% NW) hairs. The composition is left on the lock for 15 or 30 minutes at 45°C. The locks are then rinsed, shampooed and dried with a hairdryer.

Colorimetric results:

The coloration of the hair is evaluated visually and read on a Minolta spectrocolorimeter (CM3600d, illuminant D65, angle 10°, SCI values) for the L*, a*, b* colorimetric measurements.

In this L*, a*, b* system, L* represents the intensity of the colour, a* indicates the green/red colour axis and b* the blue/yellow colour axis. The lower the value of L, the darker or more intense the colour. The higher the value of a*, the redder the shade, and the higher the value of b*, the yellower the shade.

The variation in coloration between the dyed locks of natural white hair that are untreated (control) and after treatment are defined by (ΔΕ*) according to the following equation:
\[ \Delta E^* = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2} \]

In this equation, \( L^* \), \( a^* \) and \( b^* \) represent the values measured after dyeing natural hair containing 90% white hairs, and \( L_0^* \), \( a_0^* \) and \( b_0^* \) represent the values measured for natural hair containing 90% untreated hairs.

The higher the value of \( \Delta E \), the greater the difference in colour between the control locks and the dyed locks.

The coloration is very persistent with regard to washing operations and light.

<table>
<thead>
<tr>
<th>Hydroxybenzaldehyde compound ( i )</th>
<th>Structures</th>
<th>( L^* )</th>
<th>( \Delta E ) rise</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>37.5</td>
<td>20.7</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>28.1</td>
<td>30.0</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>25.7</td>
<td>33.1</td>
</tr>
<tr>
<td>9</td>
<td><img src="image9.png" alt="Structure 9" /></td>
<td>36.3</td>
<td>27.5</td>
</tr>
</tbody>
</table>

**EXAMPLE B:**

The following composition was prepared:

Composition for 100 g:
- 1.5 g of hydroxybenzaldehyde compound \( i \) according to the invention;
- 1 g of alkaline agent (ethanolamine, or sodium hydoxide, or arginine, or sodium bicarbonate, or ammonium bicarbonate or 2-amino-2-methyl-1-propanol);
- 30 g of 20-volume aqueous hydrogen peroxide solution; and
- 67.5 g of water.

The above composition is applied with a bath ratio of 1 g of hair per 5 g of composition. The locks of hair are grey containing 90% natural white (90% NW) hairs. The composition is left on the lock for 30 minutes at 45°C. The locks are then rinsed, shampoed and dried with a
The following composition was prepared:

<table>
<thead>
<tr>
<th>Composition for 100g:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 1 g of hydroxybenzaldehyde compound i) according to the invention;</td>
</tr>
<tr>
<td>- 2 g of 20% aqueous ammonia;</td>
</tr>
<tr>
<td>- 12 g of 20-volume aqueous hydrogen peroxide solution; and</td>
</tr>
<tr>
<td>- 85 g of water.</td>
</tr>
</tbody>
</table>

The above composition is applied with a bath ratio of 1 g of hair per 5 g of composition. The locks of hair are grey containing 90% natural white (90% NW) hairs. The composition is left on the lock for 30 minutes at 45°C. The locks are then rinsed, shampooed and dried with a hairdryer.

### Hydroxybenzaldehyde compound i)

<table>
<thead>
<tr>
<th>Structures</th>
<th>Visual results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dark orange</td>
</tr>
<tr>
<td>4</td>
<td>Dark orange</td>
</tr>
<tr>
<td>7</td>
<td>Mahogany</td>
</tr>
<tr>
<td>9</td>
<td>Dark orange</td>
</tr>
</tbody>
</table>

### EXAMPLE C:

5

The following composition was prepared:

<table>
<thead>
<tr>
<th>Composition for 100g:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 1 g of hydroxybenzaldehyde compound i) according to the invention;</td>
</tr>
<tr>
<td>- 2 g of 20% aqueous ammonia;</td>
</tr>
<tr>
<td>- 12 g of 20-volume aqueous hydrogen peroxide solution; and</td>
</tr>
<tr>
<td>- 85 g of water.</td>
</tr>
</tbody>
</table>

The above composition is applied with a bath ratio of 1 g of hair per 5 g of composition. The locks of hair are grey containing 90% natural white (90% NW) hairs. The composition is left on the lock for 30 minutes at 45°C. The locks are then rinsed, shampooed and dried with a hairdryer.
<table>
<thead>
<tr>
<th></th>
<th><img src="image" alt="Structural Formula" /></th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td><img src="image" alt="Structural Formula" /></td>
<td>Dark brown</td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Structural Formula" /></td>
<td>Dark pink</td>
</tr>
<tr>
<td>8</td>
<td><img src="image" alt="Structural Formula" /></td>
<td>Brown</td>
</tr>
<tr>
<td>9</td>
<td><img src="image" alt="Structural Formula" /></td>
<td>Brown</td>
</tr>
</tbody>
</table>
CLAIMS

1. Process for dyeing keratin fibres, comprising:
   a) the application to the keratin fibres of:
      i) at least one hydroxybenzaldehyde derivative of formula (I) and also the organic or mineral acid or base salts thereof, and solvates thereof such as hydrates:

   \[
   \begin{align*}
   &R^1, R^2, R^3, R^4 \text{ and } R^5, \text{ which may be identical or different, represent a hydrogen or halogen atom, or a group chosen from:} \\
   &\begin{align*}
   &\text{a hydroxyl;} \\
   &\text{an optionally substituted linear or branched } (C_1-C_2) \text{alkyl;} \\
   &\text{a linear or branched } (CrC_5) \text{alkoxy;} \\
   &\text{a carboxyl } -C(0)-OH \text{ or carboxylate } -C(0)-O^{-} \text{ with } M^+ \text{ representing a cationic counterion such as an alkali metal or alkaline-earth metal, or an ammonium;} \\
   &\text{a carboxamoyl } -O-C(0)-NR^6R^7 \text{ with } R^6 \text{ and } R^7, \text{ which may be identical or different, representing a hydrogen atom or a linear or branched } (CrC_5) \text{alkyl group; particularly } -O-C(0)-NH_2; \\
   &\text{an amidino } -C(0)-N-R^6 \text{ or } -NR^6C(0)-R^7 \text{ with } R^6 \text{ and } R^7, \text{ which may be identical or different, representing a hydrogen atom or a } (CrC_5) \text{alkyl group, particularly } -C(0)-NH_2; \\
   &\text{an ester } -C(0)-0-R^8 \text{ or } -0-C(0)-R^8 \text{ with } R^8 \text{ representing a } (C_1-C_9) \text{alkyl group, particularly } -C(0)-0-R^8; \\
   &\text{a } (CrC_5) \text{alkylcarbonyl;} \\
   &\text{a carboxaldehyde } -C(0)H; \text{ and} \\
   &\text{an amino } NR^6R^7 \text{ with } R^6 \text{ and } R^7, \text{ as defined previously;} \\
   &\text{or else } R^1 \text{ and } R^2; \text{ or } R^2 \text{ and } R^3; \text{ or } R^3 \text{ and } R^4 \text{ form, together with the carbon atoms to which they are attached, a 6-membered (hetero)aryl group such as phenyl;}
   \end{align*}
   \\
   \text{on condition that at least one of the two radicals } R^1 \text{ or } R^3 \text{ represents a hydroxyl group; with, when } R^1 \text{ represents a hydroxyl group, then } R^2 \text{ or } R^3 \text{ or } R^4 \text{ or } R^5 \text{ represents a hydrogen atom; and when } R^3 \text{ represents a hydroxyl group then } R^1 \text{ or } R^2 \text{ or } R^4 \text{ or } R^5 \text{ represents a hydrogen atom;}
   \\
   \text{ii) at least one chemical oxidizing agent; and}
   \end{align*}
   \]
Hi) at least one alkalinizing agent;
b) then a heat treatment of the keratin fibres at a temperature above 30°C;
it being understood that the total concentration of hydroxybenzaldehyde derivatives of
formula (I) is greater than 1% relative to the total weight of ingredients i), ii) and Hi), or of the
total weight of the composition(s) used in the process.

2. Dyeing process according to the preceding claim, in which the
hydroxybenzaldehyde derivative(s) of formula (I) contain at least one of the two radicals R¹
and/or R³ which represent(s) a hydroxyl group and R², R³, R⁴ and R⁵ represent,

independently of one another, a hydrogen or halogen atom, or a group chosen from:
- a hydroxyl;
- a linear or branched C₁-C₄ alkyl;
- a linear or branched C₁-C₄ alkoxy;
- a carboxaldehyde -C(0)-OH;
- a carboxaldehyde -C(0)H; and
- a di(Ci-C₄)alkylamino; or else
- R¹ and R², or R² and R³, or R³ and R⁴ form, together with the carbon atoms to which
they are attached, an aromatic ring containing 6 carbon atoms;
on the condition that when R¹ represents a hydroxyl group then R² or R³ or R⁴ or R⁵
represents a hydrogen atom; and when R³ represents a hydroxyl group then R¹ or R² or
R⁴ or R⁵ represents a hydrogen atom.

3. Dyeing process according to either one of the preceding claims, in which the
hydroxybenzaldehyde derivative(s) of formula (I) or mixtures thereof are chosen from those
of formula (II):

\[
\begin{align*}
R_1' & \quad R_2' \\
\text{O} & \quad \text{H} \\
\text{R}_3' & \quad \text{R}_4' \\
\text{HO} & \quad \text{R}_5'
\end{align*}
\]

(II)
in which formula (II):

> R¹' represents a hydrogen atom or a hydroxyl group;
> R²' represents a hydrogen atom, or a group chosen from a hydroxyl, a
carboxaldehyde, a linear or branched C₁-C₄ alkyl and a linear or branched C₁-C₄
alkoxy;
> R³' represents a hydrogen atom or a group chosen from a hydroxyl, a linear or
branched C₁-C₄ alkyl and a linear or branched C₁-C₄ alkoxy;
> R⁴' represents a hydrogen atom or a hydroxyl group;

4. Dyeing process according to Claim 1 or 2, in which the hydroxybenzaldehyde
derivative(s) of formula (I) or mixtures thereof are chosen from those of formula (II):

\[
\begin{align*}
\text{(II)}
\end{align*}
\]

- \( R'_1 = \text{OH} \) and \( R'_5 = \text{OH} \) or a linear or branched \( \text{C}_1\text{C}_5 \) alkoxy; and/or
- \( R'_2 = \text{OH} \) or \( \text{C}(0)\text{H} \) and \( R'_4 = \text{OH} \) or a linear or branched \( \text{C}_1\text{C}_5 \) alkoxy;
- and \( R'i \) or \( R'_2 \) or \( R'_4 \) or \( R'_5 \) denotes a hydrogen atom.

5. Dyeing process according to any one of the preceding claims, in which the hydroxybenzaldehyde derivative(s) of formula (I) or mixtures thereof are chosen from those from the table below:

<table>
<thead>
<tr>
<th>Names</th>
<th>Structure</th>
<th>Names</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3,4-Dihydroxybenzaldehyde (protocatechualdehyde)</td>
<td>2</td>
<td>4-Hydroxy-3-methoxy benzaldehyde (vanillin)</td>
</tr>
<tr>
<td>3</td>
<td>4-Hydroxybenzene-1,3-dicarbaldehyde</td>
<td>4</td>
<td>2,4-Dihydroxybenzaldehyde</td>
</tr>
<tr>
<td>5</td>
<td>3,4,5-Trihydroxybenzaldehyde</td>
<td>6</td>
<td>3,5-Dimethyl-4-hydroxybenzaldehyde</td>
</tr>
<tr>
<td>7</td>
<td>3,4-Dihydroxy-5-methoxybenzaldehyde</td>
<td>8</td>
<td>2,3,4-Trihydroxybenzaldehyde</td>
</tr>
<tr>
<td>9</td>
<td>2,4,6-Trihydroxybenzaldehyde</td>
<td>10</td>
<td>3,5-Dichloro-2-hydroxybenzaldehyde</td>
</tr>
<tr>
<td>11</td>
<td>2,4-Dihydroxybenzaldehyde</td>
<td>12</td>
<td>4-Hydroxybenzaldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>13</td>
<td>3,4,5-Trihydroxy-benzaldehyde</td>
<td>14</td>
<td>4-Hydroxy-2-methyl-benzaldehyde</td>
</tr>
<tr>
<td>15</td>
<td>3,4-Dihydroxy-5-methoxy-benzaldehyde</td>
<td>16</td>
<td>4-Hydroxy-3-methoxy-benzaldehyde</td>
</tr>
<tr>
<td>17</td>
<td>3,5-Dichloro-2-hydroxy-benzaldehyde</td>
<td>18</td>
<td>2,4,5-Trihydroxy-benzaldehyde</td>
</tr>
<tr>
<td>19</td>
<td>2-Hydroxy-3-methyl-benzaldehyde</td>
<td>20</td>
<td>4-Hydroxy-3-chloro-benzaldehyde</td>
</tr>
<tr>
<td>21</td>
<td>3,4-Dihydroxy-benzaldehyde</td>
<td>22</td>
<td>5-Formyl-2-hydroxy-benzoic acid</td>
</tr>
<tr>
<td>23</td>
<td>3,5-Di-tert-butyl-2-hydroxy-benzaldehyde</td>
<td>24</td>
<td>4-Hydroxy-2,6-dimethoxy-benzaldehyde</td>
</tr>
<tr>
<td>25</td>
<td>2-hydroxy-benzaldehyde</td>
<td>26</td>
<td>4-Hydroxy-3,5-dimethoxy-benzaldehyde</td>
</tr>
<tr>
<td>27</td>
<td>3,5-Di-tert-butyl-4-hydroxy-benzaldehyde</td>
<td>28</td>
<td>4-Hydroxy-naphthalene-1-carbaldehyde</td>
</tr>
</tbody>
</table>
6. Dyeing process according to the preceding claim, in which the hydroxybenzaldehyde derivative(s) of formula (I) or mixtures thereof are chosen from compounds 1 to 10 and particularly 1, 3, 4, 7 and 9.

7. Dyeing process according to any one of the preceding claims, in which ii) the
chemical oxidizing agent(s) are chosen from:

- **a)** ozone;
- **b)** alkali metal or quaternary ammonium persalts, persulphates, percarbonates, peroxodiphosphates or Oxone®;
- **c)** aliphatic C₆-C₁₀ and aromatic C₆-C₂₀ organic peracids, and the percarboxylate forms thereof;
- **d)** organic peroxides;
- **e)** oxidizing anions;
- **f)** stable N-oxy (NO) radicals;
- **g)** multivalent iodine derivatives;
- **h)** the following organic compounds: N-halosuccinimides, trichloroisocyanuric acid, N-hydroxyphthalimide, alkyl nitrites;
- **i)** the optional supports for these oxidizing agents **a)** to **h)** may be chosen from silica, alumina, charcoal and charged or neutral polymers;
- **j)** hydrogen peroxide or system(s) that generate hydrogen peroxide such as:
  - **i)** urea peroxide;
  - **i-2)** polymeric complexes that can release hydrogen peroxide;
  - **i-3)** oxidases that produce hydrogen peroxide in the presence of a suitable substrate;
  - **i-4)** metal peroxides that generate hydrogen peroxide in water, for instance calcium peroxide or magnesium peroxide;
  - **i-5)** perborates; or
  - **i-6)** percarbonates.

8. Dyeing process according to any one of the preceding claims, in which **ii)** the chemical oxidizing agent(s) is (are) chosen from hydrogen peroxide.

9. Dyeing process according to the preceding claim, in which the hydrogen peroxide is at a 20-volume concentration of between 1 g and 70 g per 100 g (%) of the composition containing said peroxide; preferably between 3 g % and 50 g % and especially between 3 g % and 50 g %.

10. Dyeing process according to any one of the preceding claims, in which **Hi)** the alkanolamines such as monoethanolamine, diethanolamine, triethanolamine and derivatives thereof, d) oxyethylenated and/or oxypropylenated ethylenediamines, e) mineral or organic hydroxides, f) alkali metal silicates such as sodium metasilicates, g) amino acids, preferably basic amino acids such as arginine, lysine, ornithine, citrulline and histidine, and h) the compounds of formula (III) below:
in which \( W \) is a divalent \((C_1-C_6)\)alkylene group optionally interrupted by at least one heteroatom such as \( O, S, NR_e \), and/or said alkylene group is optionally substituted with at least one hydroxyl group or a \((C_1-C_4)\)alkyl radical; \( R_a, R_b, R_d \), and \( R_e \), which may be identical or different, represent a hydrogen atom, \((C_1-C_4)\)alkyl or \( C_1-C_4 \) hydroxalkyl.

11. Dyeing process according to any one of the preceding claims, in which \( H1 \) the alkanizing agent is aqueous ammonia.

12. Dyeing process according to any one of the preceding claims, which does not use \( \text{para-phenylenediamines} \text{ or \text{para-aminophenols}} \).

13. Dyeing process according to any one of the preceding claims, which uses at least one oxidation dye, base and/or coupler, chosen from:
- 2,3-diamino-6,7-dihydro-1 H,5H-pyrazolo[1,2-a]pyrazol-1-one and also the salts thereof such as dimethanesulphonate;
- diamino-N,N-dihydropyrazolone derivatives of formula (IV) or an addition salt thereof:

\[
\begin{align*}
&\text{O} \\
&\text{N} \\
&\text{N} \\
&\text{R}_1 \text{N} \text{R}_3 \text{R}_4 \\
&\text{R}_2
\end{align*}
\]

(IV)

in which formula (IV): \( R_1, R_2, R_3 \) and \( R_4 \), which may be identical or different, represent:
- a linear or branched \( C_1-C_6 \) alkyl radical which is optionally substituted with one or more radicals selected from the group consisting of a radical \( \text{OR}_6 \), a radical \( \text{NR}_6 \text{R}_7 \), a carboxyl radical, a sulphonyl radical, a carboxamido radical \( \text{CONR}_6 \text{R}_7 \); a sulphonamido radical \( \text{SO}_2 \text{NR}_6 \text{R}_7 \); a heteroaryl, an aryl optionally substituted with a \((C_1-C_4)\)alkyl group, a hydroxyl, a \( C_1-C_2 \) alkoxy, an amino or a \((C_1-C_2)\)alkylamino;
- an aryl radical optionally substituted with one or more of a \((C_1-C_4)\)alkyl, a hydroxyl, a \( C_1-C_2 \) alkoxy, an amino or a \((C_1-C_2)\)alkylamino;
- a 5- or 6-membered heteroaryl radical which is optionally substituted with one or more radicals selected from a \((C_1-C_4)\)alkyl and a \((C_1-C_2)\)alkoxy; \( R_3 \) and \( R_4 \) may also represent a hydrogen atom;
- \( R_5, R_6, R_7 \), which may be identical or different, represent a hydrogen atom; a linear or branched \( C_1-C_4 \) alkyl radical which is optionally substituted with one or more radicals selected from the group consisting of a hydroxyl, a \( C_1-C_2 \) alkoxy, a carboxamido.
CONR₈R₉, a sulphonyl S₀₂R₈, an aryl optionally substituted with a (C₁-C₄)alkyl, a hydroxyl, a C₁-C₂ alkoxy, an amino, a (di)alkyl(C₆H₅)amino; an aryl optionally substituted with a (C₁-C₄)alkyl, a hydroxyl, a C₁-C₂ alkoxy, an amino or a (di)alkyl(d-C₂)amino;

R₆ and R₇, which may be identical or different, may also represent a carboxamido radical CONR₈R₉; or a sulphonyl S₀₂R₈;

R₈ and R₉, which may be identical or different, represent a hydrogen atom; a linear or branched C₁-C₄ alkyl radical which is optionally substituted with one or more of a hydroxyl or a C₁-C₂ alkoxy;

R₁ and R₂, on the one hand, and R₃ and R₄, on the other hand, may form, with the nitrogen atoms to which they are attached, a saturated or unsaturated 5- or 7-membered heterocycle which is optionally substituted with one or more radicals selected from the group consisting of halogen atoms, amino, (di)(C₁-C₄)alkylamino, hydroxyl, carboxyl, carboxamido and (C₁-C₂)alkoxy radicals, C₁-C₄ alkyl radicals optionally substituted with one or more hydroxyl, amino, (di)alkylamino, alkoxy, carboxyl or sulphonyl radicals;

R₃ and R₄ may also form, together with the nitrogen atom to which they are attached, a 5- or 7-membered heterocycle, the carbon atoms of which can be replaced with an optionally substituted oxygen or nitrogen atom;

- salts of 4-(3-aminopyrazolo[1,5-a]pyridin-2-yl)-1,1-dimethylpiperazin-1-ium, especially the halides such as hydrochloride chloride;

- 3-aminopyrazolo[1,5-a]pyridine derivatives of formula (V) below and also the salts and solvates thereof:

![Diagram](image)

in which formula (V):

- Z₁ and Z₂ independently represent: i) a single covalent bond; ii) a divalent radical chosen from an oxygen atom and a radical -NR₆(R₇)ₓ⁻,
  - with p = 0 or 1 with, when p is equal to 0 then R₆ represents a hydrogen atom or a C₁-C₆ alkyl radical, or R₆, with R₁, respectively R₂, form, together with the nitrogen atom to which they are attached, a substituted or unsubstituted, saturated or unsaturated, aromatic or nonaromatic, 5-to 8-membered heterocycle, optionally containing one or more heteroatoms or groups selected from N, O, S, S₀₂ and -CO₂⁻, it being possible for the heterocycle to be cationic and/or substituted with a cationic or noncationic radical,
- when \( p \) is equal to 1 then \(-NR_6R_7\) is a cationic radical in which \( R_6 \) and \( R_7 \)
independently represent an alkyl radical,

\[ o \] \( Z_1 \) may also represent a divalent radical \(-S-, \ -SO- \) or \(-SO_2-\) when \( R_1 \) is a methyl radical;

\[ o \] it being understood that at least one of \( Z_1 \) and \( Z_2 \) is other than a single covalent bond,

\[ o \] \( R_3 \) and \( R_4 \) independently represent a hydrogen or halogen atom, or a group chosen from:

- a \( C_1-C_6 \) alkyl radical which is optionally substituted and optionally interrupted by a
  heteroatom or a group selected from \( O, N, Si, S, SO \) and \( SO_2 \),
- a \( C_1-C_6 \) alkyl radical which is substituted and/or interrupted by a cationic radical,
- an \( SO_3H \) radical,
- a 5- to 8-membered ring which is substituted or unsubstituted, saturated or unsaturated or aromatic and optionally contains one or more heteroatoms or groups selected from \( N, O, S, SO_2 \) and \(-CO-\), it being possible for the ring to be
cationic and/or to be substituted with a cationic radical,

when \( Z_1 \), respectively \( Z_2 \), represents a covalent bond, then \( R_1 \), respectively \( R_2 \), may also represent:

- an optionally substituted \( C_1-C_6 \) alkylcarbonyl radical;
- a radical \(-O-CO-R, \ -CO-O-R, \ NR-CO-R' \) or \(-CO-NRR'\) in which \( R \) and \( R' \)
independently represent a hydrogen atom or an optionally substituted \( C_1-C_6 \) alkyl radical;

\[ o \] \( R_3, R_4 \) and \( R_5 \), which may be identical or different, represent:

- a hydrogen atom;
- a hydroxyl radical;
- a \( C_1-C_6 \) alkoxy radical;
- a \( C_1-C_6 \) alkylthio radical;
- an amino radical;
- a monoalkylamino radical;

- a \( C_1-C_6 \) dialkylamino radical in which the alkyl radicals may form, with the nitrogen
to which they are attached, a saturated or unsaturated, aromatic or nonaromatic, 5- to 8-membered heterocycle, which may contain one or more heteroatoms or groups selected from \( N, O, S, SO_2 \) and \( CO \), it being possible for the heterocycle to be
cationic and/or substituted with a cationic radical;

- an optionally substituted \( C_1-C_6 \) alkylcarbonyl radical;
- a radical \(-O-CO-R, \ -CO-O-R, \ NR-CO-R' \) or \(-CO-NRR'\) with \( R \) and \( R' \) as defined
  previously;
- a halogen;
- a radical \(-NHSO_3H\);

- an optionally substituted \( C_1-C_4 \) alkyl radical;

- an optionally substituted, saturated or unsaturated or aromatic carbon-based ring;
- $R_3$, $R_4$ and $R_5$, may form, in pairs, a saturated or unsaturated ring;
  - $X$ represents an anionic counterion or group of anions making it possible to ensure the electronegativity of the derivative of formula (V), with the condition that at least one of the groups $Z_1$, $R_1$, $Z_2$, and $R_2$ represents a cationic radical:
- salts of 2-[(3-aminopyrazolo[1,5-a]pyridin-2-yl)oxy]ethanol, especially hydrochloride;
- derivatives of a 3-aminopyrazolo[1,5-a]pyridine derivative of formula (VI) and also the salts and solvates thereof

![Diagram](attachment:image.png)

in which formula (VI):
  - $Z_1$ represents an oxygen atom or a group NR$_6$, when $Z_1$ represents NR$_6$ then $R_1$ and R$_6$ may form, together with the nitrogen atom to which they are attached, an optionally substituted, saturated or unsaturated or aromatic 5- to 8-membered heterocycle;
  - $Z_1$ may also represent a divalent radical S, SO or SO$_2$ when $R_1$ represents CH$_3$;
  - $R_1$ and $R_6$ independently represent:
    - a hydrogen atom;
    - an optionally substituted C$_1$-C$_{10}$ alkyl radical, it being possible for the substituent to be an optionally substituted, saturated or unsaturated or aromatic 5- to 8-membered (hetero)cycle;
    - an optionally substituted, saturated or unsaturated or aromatic 5- to 8-membered (hetero)cycle;
  - $R_2$, $R_3$, $R_4$ and $R_5$ independently represent:
    - a hydrogen atom;
    - an optionally substituted C$_1$-C$_4$ alkyl radical;
    - a group chosen from NH$_2$, NHR$_{10}$, NR$_{11}$R$_{12}$, OH or OR$_9$, with $R_9$ and $R_{10}$ representing an optionally substituted, linear or branched C$_1$-C$_6$ alkyl, R$_{11}$ and R$_{12}$, which may be identical or different, representing an optionally substituted, linear or branched C$_1$-C$_6$ alkyl, it being possible for R$_{11}$ and R$_{12}$ to form, together with the nitrogen atom to which they are attached, a saturated or unsaturated or aromatic 5- to 8-membered heterocycle optionally containing one or more other heteroatoms or groups chosen from N, O, S, SO$_2$ and CO, the heterocycle being optionally substituted;
  - $R_2$, $R_3$, $R_4$, $R_5$, may form, in pairs, with the adjacent radicals, an optionally substituted, saturated or unsaturated (hetero)cycle;
• 5-[(2-hydroxyethyl)amino]-2-methylphenol;
• 3,4-dihydro-2H-1,4-benzoxazin-6-ol;
• 3-amino-2-chloro-6-methylphenol;
• 2-aminopyridin-3-ol;
• 2-methylbenzene-1,3-diol;
• 2-(2,4-diaminophenoxy)ethanol hydrochloride; and
• cationic aminopyridine derivatives of general formula (VII), addition salts thereof with an acid and solvates thereof:

\[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{H} \\
\text{N} \\
\text{Z}_1 \text{R}_1 \\
\text{An-}
\end{array}
\]

(VII)

in which formula (VII) the group $Z_1R_1$ bears the cationic charge,

- $Z_1$ is an oxygen atom or a group $NR_2^-$;
- $R_2$ is a hydrogen atom or a linear or branched $C_1$-$C_4$ alkyl radical, a benzyl radical or an acetyl radical;
- $R_1$ is a saturated, linear or branched $C_1$-$C_{10}$ alkyl radical, which is substituted with or interrupted by a cationic radical, optionally interrupted by one or more oxygen atoms and/or by one or more groups $NR_2^-$, optionally substituted with one or more radicals chosen from hydroxyl, alkoxy and $C_1$-$C_4$ hydroxyalkyl radicals, or $R_1$ is a saturated or unsaturated or aromatic cationic 5- to 8-membered heterocycle optionally substituted with one or more radicals chosen from $C_1$-$C_4$ alkyl, hydroxyl, $Cl$-$C_4$ alkoxy, amino, $(C_1$-$C_4)$alkylamino, di$(C_1$-$C_4)$alkylamino, thio, $(C_1$-$C_4)$alkylthio, carboxyl, $(C_1$-$C_4)$alkylcarbonyl, sulphonyl, amido and $C_1$-$C_4$ hydroxyalkyl radicals; when $Z_1$ represents $NR_2^-$ then

- $R_1$ and $R_2$ may form, together with the nitrogen atom to which they are attached, a saturated or unsaturated cationic 5- to 8-membered heterocycle optionally substituted with one or more radicals chosen from $C_1$-$C_{10}$ alkyl radicals and hydroxyl, $C_1$-$C_4$ alkoxy, amino, $(C_1$-$C_4)$alkylamino, di$(C_1$-$C_4)$alkylamino, thio, $(C_1$-$C_4)$alkylthio, carboxyl, $(C_1$-$C_4)$alkylcarbonyl, sulphonyl, amido and $C_1$-$C_4$ hydroxyalkyl radicals, it being possible for this heterocycle to contain one or more heteroatoms chosen from N or O, preferably N, or

- $RI$ and $R_2$ may form, together with the nitrogen atom to which they are attached, a saturated or unsaturated noncationic 5- to 8-membered heterocycle substituted with a cationic radical and optionally substituted with one or more radicals chosen from $C_1$-$C_{10}$ alkyl radicals and hydroxyl, $C_1$-$C_4$ alkoxy, amino, $(C_1$-$C_4)$alkylamino, di$(Cl$-$C_4)$alkylamino, thio, $(C_1$-$C_4)$alkylthio, carboxyl, $(C_1$-$C_4)$alkylcarbonyl,
sulphonyl, amido and C₁-C₄ hydroxyalkyl radicals;

- R is chosen from a hydrogen atom, halogens selected from fluorine, chlorine and bromine, linear or branched C₁-C₄ alkyl radicals and carboxyl (-COOH) and (Cl-C₄)alkoxycarbonyl radicals; and

- An represents an anionic counterion or group of anions.

14. Dyeing process according to any one of the preceding claims, which does not use an activated-CH compound.

15. Cosmetic composition comprising:

- at least one derivative of formula (I), as defined in any one of Claims 1 to 6;
- at least one chemical oxidizing agent as defined in any one of Claims 1 and 7 to 9; and
- at least one alkalinizing agent as defined in any one of Claims 1, 10 and 11;

it being understood that:

- the pH of the composition is above 7;
- the compound(s) of formula (I) comprise at least one of the two radicals R¹ or R³ which represents a hydroxyl group; with, when R¹ represents a hydroxyl group, then R² or R³ or R⁴ or R⁵ represents a hydrogen atom; and when R³ represents a hydroxyl radical then R¹ or R² or R⁴ or R⁵ represents a hydrogen atom;
- the total concentration of hydroxybenzaldehyde derivatives of formula (I) is greater than 1% relative to the total weight of the ingredients ii) and Hi) and
- when the hydroxybenzaldehyde derivative of formula (I) represents a compound chosen from 3,4-dihydroxybenzaldehyde; 4-hydroxy-2-methoxybenzaldehyde; 3,5-dimethoxybenzaldehyde; 4-hydroxy-1-naphthaldehyde; 3,5-dimethyl-4-hydroxybenzaldehyde, then the alkalinizing agent Hi) is other than monoethanolamine; and
- when the hydroxybenzaldehyde derivative of formula (I) represents a compound chosen from 4-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-3-methoxybenzaldehyde, which is in the presence of 2-aminophenol, 2,5-diaminotoluene sulphonate; then the alkalinizing agent Hi) is other than ammonium hydroxide.

16. Multicompartment device comprising from 2 to 4 compartments containing from 2 to 4 compositions in which the ingredients i), ii), Hi) as defined in any one of Claims 1 to 14 are distributed, said compositions being aqueous or pulverulent, with at least one of these compositions being aqueous.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. A61Q5/10 A61K8/31 A61K8/368 A61K8/34

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

A61Q A61K

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 practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>EP 2 014 275 A2 (HENKEL AG &amp; CO KGAA [DE]) 14 January 2009 (2009-01-14) page 3, paragraph 16 - page 4, paragraph 18 page 5, paragraph 42 - page 6, paragraph 44 examples -----</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

- Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier document but published on or after the international filing date
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  - "O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search 26 March 2012

Date of mailing of the international search report 04/04/2012

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentplein 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Ruckebusch, Virgine

Form PCT/ISA/210 (second sheet) (April 2005)
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