OXIDIZING COMPOSITION AND USES FOR DYEING, FOR PERMANENTLY RESHAPING OR FOR BLEACHING KERATIN FIBRES

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Appl. No.: 10/832,390

Filed: Apr. 27, 2004

Related U.S. Application Data

Continuation of application No. 09/877,031, filed on Jun. 11, 2001, now abandoned, which is a division of application No. 09/319,208, filed on Jun. 2, 1999, now Pat. No. 6,273,920, filed as 371 of international application No. PCT/FR98/02022, filed on Sep. 22, 1998.

Foreign Application Priority Data

Oct. 3, 1997 (FR) ........................................ 97/12361

Publication Classification

Int. Cl7 ............................................ A61K 7/13
U.S. Cl. ................................................. 8/405

ABSTRACT

The present application relates to a cosmetic composition intended for treating keratin fibres, comprising, in a support which is suitable for keratin substances:

(a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said substances;

(b) at least one nonionic amphiphilic polymer containing at least one fatty chain and at least one hydrophilic unit;

as well as to processes for treating keratin fibres, in particular processes for dyeing, permanently reshaping or bleaching the hair, using this composition.
OXIDIZING COMPOSITION AND USES FOR
DYING, FOR PERMANENTLY RESHAPING OR
FOR BLEACHING KERATIN FIBRES

[0001] The present invention relates to an oxidizing com-
position intended for treating keratin fibres, comprising at
least one enzyme of 2-electron oxidoreductase type in the
presence of at least one donor for the said enzyme and at
least one nonionic amphiphilic polymer containing at least
one fatty chain and at least one hydrophilic unit, as well as
to its uses for dyeing, for permanently reshaping or for
bleaching keratin fibres, in particular human hair.

[0002] It is known to dye keratin fibres, and in particular
human hair, with dye compositions containing oxidation dye
precursors, in particular para-phenylenediamines, ortho-
or para-aminophenols and heterocyclic bases which are gen-
erally referred to as oxidation bases. Oxidation dye precursors,
or oxidation bases, are colourless or weakly coloured com-
ounds which, when combined with oxidizing products, can
give rise to coloured compounds and dyes by a process of
oxidative condensation.

[0003] It is also known that the shades obtained with these
oxidation bases can be varied by combining them with couplers or colour modifiers, the latter being chosen in parti-
cular from aromatic meta-diamines, meta-aminophen-
ols, meta-diphenols and certain heterocyclic compounds.

[0004] The variety of compounds used as regards the
oxidation bases and the couplers allows a wide range of
colours to be obtained.

[0005] The so-called “permanent” coloration obtained by
means of these oxidation dyes must moreover satisfy a
certain number of requirements. Thus it must have no
toxicological drawbacks, it must be able to give shades of
the desired intensity and it must be able to withstand external
agents (light, bad weather, washing, permanent-waving,
perspiration, rubbing).

[0006] The dyes must also be able to cover white hair and,
lastly, they must be as unselective as possible, i.e. they must
give the smallest possible colour differences along the same
length of keratin fibre, which may in fact be differently
sensitized (i.e. damaged) between its tip and its root.

[0007] The oxidation dyeing of keratin fibres is generally
carried out in alkaline medium, in the presence of hydrogen
peroxide. However, the use of alkaline media in the presence
of hydrogen peroxide has the drawback of causing appreci-
able degradation of the fibres, as well as considerable
bleaching of the keratin fibres, which is not always desir-
able.

[0008] The oxidation dyeing of keratin fibres can also be
carried out using oxidizing systems other than hydrogen
peroxide, such as enzymatic systems. Thus, it has already
been proposed to dye keratin fibres, in particular in patent
application EP-A-0,310,675, with compositions comprising
an oxidation dye precursor in combination with enzymes
such as pyranose oxidase, glucose oxidase or uricase, in the
presence of a donor for the said enzymes. Although being
used under conditions which do not result in degradation of
the keratin fibres which is comparable to that caused by the
dyes used in the presence of hydrogen peroxide, these dye
formulations nevertheless lead to colorations which are still
insufficient, both as regards the homogeneity of the colour
distributed along the fibre (“unison”) and as regards the
chromaticity (luminosity) and the dyeing power.

[0009] It is known that the most common technique for
obtaining a permanent reshaping of the hair consists, in a
first stage, in opening the keratin —S—S-disulphide (cyste-
tine) bonds using a composition containing a suitable
reducing agent (reduction step) followed, after having rinsed
the hair thus treated, by reconstituting, in a second stage, the
said disulphide bonds by applying to the hair, which has
been placed under tension beforehand (curlers and the like),
an oxidizing composition (oxidation step, also known as the
fixing step) so as finally to give to the hair the desired shape.
This technique thus makes it equally possible either to make
the hair wavy or to straighten it or to remove its curliness.
The new shape given to the hair by a chemical treatment
such as above is remarkably long-lasting and in particular
resists the action of washing with water or shampoos, as
opposed to simple standard techniques for temporary
reshaping, such as hairsetting.

[0010] The reducing compositions which may be used in
order to carry out the first step of a permanent-waving
operation generally contain, as reducing agents, sulphis-
bisulphites, alkylphosphines or, preferably, thioles. Among
the thioles, those commonly used are cysteine and the various
derivatives thereof, cysteamine and the derivatives thereof,
thiolic acid or thioglycolic acid, the salts thereof and the
esters thereof, in particular glyceryl thioglycolate.

[0011] As regards the oxidizing compositions needed to
carry out the fixing step, use is usually made in practice of
compositions based on aqueous hydrogen peroxide, sodium
bromate or persalts such as sodium perborate, which have
the drawback of being liable to damage the hair.

[0012] The problem of the technique of the permanent-
wavering operations known to date is that their application to
the hair induces long-term adverse changes in the quality of
the hair. The essential causes of these adverse changes in the
quality of the hair are a reduction in its cosmetic properties,
such as its sheen and its feel, and degradation of its mechani-
cal properties, more particularly degradation of its mecha-
nical strength due to swelling of the keratin fibres during the
rinsing between the reduction step and the oxidation step,
which can also be reflected by an increase in its porosity. The
hair is weakened and can become brittle during subsequent
treatments such as blow-drying.

[0013] The same problem of adverse changes in keratin
fibres is encountered during processes for bleaching the hair.

[0014] It is known that the permanent reshaping or bleach-
ing of keratin fibres can also be carried out under milder
conditions using oxidizing systems other than hydrogen
peroxide, such as enzymatic systems. Thus, processes for the
permanent reshaping or bleaching of keratin fibres have
already been proposed, in particular in patent application
EP-A-0,310,675, with compositions comprising an enzyme
such as pyranose oxidase, glucose oxidase or uricase, in the
presence of a donor for the said enzyme. Although being
used under conditions which do not result in degradation of
the keratin fibres which is comparable to that caused by
conventional permanent-waving or bleaching processes,
these oxidizing formulations nevertheless lead to results
which are still insufficient, as regards the curl hold over time,
as regards the compatibility of permanent-waved or
bleached hair with subsequent treatments, as regards the degradation of the mechanical properties of the permanent waved hair, in particular the reduction of the porosity of the hair, and as regards the reduction of the cosmetic properties such as the feel, or alternatively as regards the uniformity of the bleaching along the keratin fibres.

[0015] The aim of the present invention is to solve the problems mentioned above.

[0016] The Applicant has discovered, surprisingly, novel compositions containing, as oxidizing system, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one nonionic amphiphilic polymer containing at least one fatty chain and at least one hydrophilic unit which will be defined in more detail below, which can constitute, in the presence of oxidation dye precursors (oxidation bases) and optionally couplers, ready-to-use dye formulations which lead to more homogeneous, more intense and more chromatic colorations without giving rise to any significant degradation, or bleaching, of the keratin fibres, these colorations being relatively unselective and showing good resistance to the various aggressive factors to which the hair may be subjected.

[0017] The Applicant has also discovered, unexpectedly, that the use, in a process for the permanent reshaping of keratin fibres, of an oxidizing composition containing, as oxidizing system, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one nonionic amphiphilic polymer containing at least one fatty chain and at least one hydrophilic unit, makes it possible to solve the technical problems mentioned above. In particular, this type of oxidizing composition improves the curl hold obtained over time, substantially reduces the porosity of permanent-waved hair and improves the compatibility of permanent-waved hair with respect to subsequent treatments.

[0018] The Applicant has also discovered, surprisingly, that the use, in a process for bleaching keratin fibres, of an oxidizing composition containing, as oxidizing system, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one nonionic amphiphilic polymer containing at least one fatty chain and at least one hydrophilic unit, makes it possible to solve the technical problems mentioned above, in particular to improve the compatibility of bleached hair with respect to subsequent treatments. This type of oxidizing composition gives a more uniform bleaching effect on the hair and improves the cosmetic properties, such as the feel.

[0019] These discoveries form the basis of the present invention.

[0020] The subject of the present invention is thus, firstly, a cosmetic and/or dermatological composition intended for treating keratin fibres, in particular human keratin fibres and more particularly human hair, comprising, in a support which is suitable for keratin fibres:

[0021] (a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme,

[0022] (b) at least one nonionic amphiphilic polymer containing at least one fatty chain and at least one hydrophilic unit.

[0023] The 2-electron oxidoreductase(s) used in the oxidizing compositions in accordance with the invention can be chosen in particular from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

[0024] According to the invention, the 2-electron oxidoreductase is preferably chosen from uricases of animal, microbiological or biotechnological origin.

[0025] By way of example, mention may be made in particular of uricase extracted from boar liver, uricase from Arthrobacter globiformis, as well as uricase from Aspergillus flavus.

[0026] The 2-electron oxidoreductase(s) can be used in pure crystalline form or in a form diluted in a diluent which is inert with respect to the said 2-electron oxidoreductase.

[0027] The 2-electron oxidoreductase(s) in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the composition, and even more preferably from 0.1 to 5% by weight approximately relative to this weight.

[0028] According to the invention, the term donor is understood to refer to the various substrates also necessary for the functioning of the said 2-electron oxidoreductase(s).

[0029] The nature of the donor (or substrate) for the said enzyme varies depending on the nature of the 2-electron oxidoreductase used. For example, as donors for the pyranose oxidases, mention may be made of D-glucose, L-sorbitose and D-xylose; as a donor for the glucose oxidases, mention may be made of D-glucose; as donors for the glycerol oxidases, mention may be made of glycerol and dihydroxyacetone; as donors for the lactate oxidases, mention may be made of lactic acid and its salts; as donors for the pyruvate oxidases, mention may be made of pyruvic acid and its salts; and lastly, as donors for the uricases, mention may be made of uric acid and its salts.

[0030] The donor(s) (or substrate(s)) used in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the composition in accordance with the invention, and even more preferably from 0.1 to 5% approximately relative to this weight.

[0031] The nonionic amphiphilic polymers containing at least one fatty chain and at least one hydrophilic unit, used according to the invention, are preferably chosen from:

[0032] (1) celluloses modified with groups containing at least one fatty chain;

[0033] as examples, mention may be made of:

[0034] hydroxyethylcelluloses modified with groups containing at least one fatty chain, such as alkyl, aryalkyl or alkylaryl groups or mixtures thereof, and in which the alkyl groups are preferably C₆H₄(C₂₃ alkyl)s sold by the company Aqualon, or the product Bermocoll EHM 100 sold by the company Berol Nobel,

[0035] those modified with polyalkylene glycol alkylphenyl ether groups, such as the product Amercell
Polymer HM-1500 (polyethylene glycol (15) ether of nonylphenol) sold by the company Americhol.

(0036) (2) hydroxypropylguars modified with groups containing at least one fatty chain, such as the product Esator HM 22 (C12 alkyl chain) sold by the company Lamberti, or the products Miracare XC95-3 (C14 alkyl chain) and RE205-1 (C20 alkyl chain) sold by the company Rhône-Poulenc.

(0037) (3) polyurethane ethers containing at least one fatty chain such as C6-C30 alkyl or alkaryl groups, for instance the products Dapral T 210 and Dapral T 212 sold by the company Akzo.

(0038) (4) copolymers of vinyl pyrrolidone and of hydrophobic monomers containing a fatty chain;

(0039) as examples, mention may be made of:

(0040) the products Antaron V216 or Ganex V216 (vinylpyrrolidone/hexadecene copolymer) sold by the company I.S.P.,

(0041) the products Antaron V220 or Ganex V220 (vinylpyrrolidone/cicosene copolymer) sold by the company I.S.P.

(0042) (5) copolymers of C6-C8 alkyl methacrylates or acrylates and of amphiphilic monomers containing at least one fatty chain, such as, for example, the oxyethylated methyl methacrylate/stearyl acrylate copolymer sold by the company Goldschmidt under the name Antil 208.

(0043) (6) copolymers of hydrophilic methacrylates or acrylates and of hydrophobic monomers containing at least one fatty chain, such as, for example, polyethylene glycol methacrylate/lauryl methacrylate copolymer.

(0044) The nonionic amphiphilic polymers containing at least one fatty chain and at least one hydrophilic unit, according to the invention, are preferably used in an amount which can range from about 0.05 to 10% by weight relative to the total weight of the dye composition applied to the fibres. More preferably, this amount ranges from about 0.2 to 5% by weight.

(0045) A subject of the present invention is also a ready-to-use composition for the oxidation dying of keratin fibres, and in particular human keratin fibres such as the hair, of the type comprising, in a medium which is suitable for dying, at least one oxidation base and, where appropriate, one or more couplers, which is characterized in that it contains:

(0046) (a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme,

(0047) (b) at least one nonionic amphiphilic polymer containing at least one fatty chain and at least one hydrophilic unit.

(0048) The nature of the oxidation base(s) used in the ready-to-use dye composition is not a critical factor. They can be chosen, in particular, from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

(0049) Among the para-phenylenediamines which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (I) below, and the addition salts thereof with an acid:

\[
\text{I}
\]

(0050) in which:

(0051) R1 represents a hydrogen atom, a C1-C4 alkyl radical, a C7-C9 monohydroxyalkyl radical, a C2-C6 polyhydroxyalkyl radical, a (C1-C4)alkoxy(C6-C9)alkyl radical, a C2-C6 alkyl radical substituted with a nitrogenous group, a phenyl radical or a 4'-aminophenyl radical;

(0052) R2 represents a hydrogen atom, a C1-C4 alkyl radical, a C7-C9 monohydroxyalkyl radical, a C2-C6 polyhydroxyalkyl radical, a (C1-C4)alkoxy(C6-C9)alkyl radical or a C2-C6 alkyl radical substituted with a nitrogenous group;

(0053) R3 represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C1-C4 alkyl radical, a C1-C4 monohydroxyalkyl radical, a C2-C6 hydroxyalkoxy radical, an acetylaminoglycol radical, a C2-C6 mesyloxalkoxy radical or a carbamoylaminoglycol radical;

(0054) R4 represents a hydrogen or halogen atom or a C2-C4 alkyl radical.

(0055) Among the nitrogenous groups of formula (I) above, mention may be made in particular of amino, mono(C1-C4)alkylamino, di(C1-C4)alkylamino, tri(C1-C4)alkylamino, monohydroxy(C1-C4)amino, imidazolinium and ammonium radicals.


Among the para-phenylenediamines of formula (I) above, para-toluylenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethoxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2-β-acetylaminoethoxy-para-phenylenediamine and the addition salts thereof with an acid are most particularly preferred.

According to the invention, the term double bases is understood to refer to the compounds containing at least two aromatic rings bearing amino and/or hydroxyl groups.

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

\[
\begin{align*}
Z_1 & \quad Z_2 \\
R_1 & \quad R_2 \\
R_3 & \quad R_4 \\
R_5 & \quad R_6 \\
R_7 & \quad R_8 \\
\end{align*}
\]

in which:

- \(Z_1\) and \(Z_2\), which may be identical or different, represent a hydroxyl or \(-\text{NH}_2\) radical which may be substituted with a \(C_1-C_4\) alkyl radical or with a linker arm \(Y\);
- \(Z_1\) and \(Z_2\), which may be identical or different, represent a hydroxyl or \(-\text{NH}_2\) radical which may be substituted with a \(C_1-C_4\) alkyl radical or with a linker arm \(Y\);
- the linker arm \(Y\) represents a linear or branched alkylene chain containing from 1 to 14 carbon atoms, which may be interrupted by or terminated with one or more nitrogenous groups and/or one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or \(C_1-C_4\) alkyl radicals;
- \(R_1\) and \(R_2\) represent a hydrogen or halogen atom, a \(C_1-C_4\) alkyl radical, a \(C_1-C_4\) monohydroxyalkyl radical, a \(C_1-C_4\) polyhydroxyalkyl radical, a \(C_1-C_4\) aminoalkyl radical or a linker arm \(Y\);
- \(R_3\) and \(R_4\) represent a hydrogen or halogen atom, a \(C_1-C_4\) alkyl radical, a \(C_1-C_4\) monohydroxyalkyl radical, a \(C_1-C_4\) polyhydroxyalkyl radical, a \(C_1-C_4\) aminoalkyl radical or a linker arm \(Y\);
- \(R_5\) and \(R_6\), \(R_7\) and \(R_8\), \(R_9\) and \(R_{10}\), \(R_{11}\) and \(R_{12}\) which may be identical or different, represent a hydrogen atom, a linker arm \(Y\) or a \(C_1-C_4\) alkyl radical;
- it being understood that the compounds of formula (II) contain only one linker arm \(Y\) per molecule.

Among the nitrogenous groups of formula (II) above, mention may be made in particular of amino, mono(\(C_1-C_4\))alkylamino, di(\(C_1-C_4\))alkylamino, tri(\(C_1-C_4\))alkylamino, monohydroxy(\(C_1-C_4\))alkylamino, imidazolium and ammonium radicals.

Among the double bases of formula (II) above, mention may be made more particularly of \(N,N'-\text{bis}(\beta\text{-hydroxyethyl})-N,N'-\text{bis}(4'-aminophenyl)-1,3-diaminopropanol}, \(N,N'-\text{bis}(\beta\text{-hydroxyethyl})-N,N'-\text{bis}(4'-aminophenyl)-ethylenediamine}, \(N,N'-\text{bis}(4\text{-aminophenyl})\text{-tetramethylenediamine}, \(N,N'-\text{bis}(\beta\text{-hydroxyethyl})-N,N'-\text{bis}(4\text{-aminophenyl})\text{-tetramethylenediamine}, \(N,N'-\text{bis}(4\text{-methylaminophenyl})\text{-tetramethylenediamine}, \(N,N'-\text{bis}(\beta\text{-hydroxyethyl})-N,N'-\text{bis}(4'-\text{amino-3'-methylphenyl})\text{-ethylenediamine} and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxoacetae, and the addition salts thereof with an acid.

Among these double bases of formula (II), \(N,N'-\text{bis}(\beta\text{-hydroxyethyl})-N,N'-\text{bis}(4'-aminophenyl)-1,3-diaminopropanol and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxoacetae, or one of the addition salts thereof with an acid, are particularly preferred.

Among the para-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to formula (III) below, and the addition salts thereof with an acid:

\[
\begin{align*}
R & \quad R_1 \\
R_2 & \quad R_3 \\
R_4 & \quad R_5 \\
\end{align*}
\]

in which:

- \(R_1\), \(R_2\) represent a hydrogen or halogen atom or a \(C_1-C_4\) alkyl, \(C_1-C_4\) monohydroxyalkyl, \(C_1-C_4\) polyhydroxyalkyl, \(C_1-C_4\) aminoalkyl or hydroxy(\(C_1-C_4\))alkyl radical;
- \(R_1\), \(R_2\) represent a hydrogen or halogen atom or a \(C_1-C_4\) alkyl, \(C_1-C_4\) monohydroxyalkyl, \(C_1-C_4\) polyhydroxyalkyl, \(C_1-C_4\) aminoalkyl or hydroxy(\(C_1-C_4\))alkyl radical;
- it being understood that at least one of the radicals \(R_{13}\) or \(R_{14}\) represents a hydrogen atom.

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

Among the ortho-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of 2-aminophenol, 2-amino-5-methyl phenol, 2-amino-6-
methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

Among the heterocyclic bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of pyridine derivatives, pyrimidine derivatives, pyrazole derivatives and pyrazolopyrimidine derivatives, and the addition salts thereof with an acid.

Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB 1,026,978 and GB 1,153,196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxyppyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxyppyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

Among the pyrimidine derivatives, mention may be made more particularly of the compounds described, for example, in German patent DE 2,359,399 or Japanese patent JP 88-169,571 or patent application WO 96/15765, such as 2,4,5,6-tetraminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, and the addition salts thereof with an acid.

Among the pyrazole derivatives, mention may be made more particularly of the compounds described in patents DE 3,843,892, DE 4,133,957 and patent applications DE 94/08969, DE 94/08970, DE 94/233,749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tet-butyl-1-methylpyrazole, 4,5-diamino-3-tet-butyl-3-methylpyrazole, 4,5-diamino-1-(3-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxyethylpyrazole, 4,5-diamino-3-hydroxyethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5(2-aminomethyl)-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4(β-hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives, mention may be made more particularly of the pyrazolopyrimidines of formula (IV) below, and the addition salts thereof with an acid or with a base and the tautomeric forms thereof, when a tautomeric equilibrium exists:

[0081] in which:

\[ R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8; \]

which may be identical or different, denote a hydrogen atom, a C\(_1\)-C\(_4\) alkyl radical, an aryl radical, a C\(_1\)-C\(_4\) hydroxalkyl radical, a C\(_1\)-C\(_4\) polyhydroxalkyl radical, a C\(_1\)-C\(_4\) alkoxy(C\(_1\)-C\(_4\))alkyl radical, a C\(_1\)-C\(_4\) aminooalkyl radical (it being possible for the amine to be protected with an acetyl, ureido or sulphonyl radical), a (C\(_1\)-C\(_4\))alkylamino(C\(_1\)-C\(_4\))alkyl radical, a di(C\(_1\)-C\(_4\))alkylamino(C\(_1\)-C\(_4\))alkyl radical (it being possible for the dialkyl radicals to form a 5- or 6-membered carbon-based ring or a heterocycle), a hydroxy(C\(_1\)-C\(_4\))alkyl- or di[hydroxy(C\(_1\)-C\(_4\))alkyl]amino(C\(_1\)-C\(_4\))alkyl radical;

[0083] the radicals X, which may be identical or different, denote a hydrogen atom, a C\(_1\)-C\(_4\) alkyl radical, an aryl radical, a C\(_1\)-C\(_4\) hydroxalkyl radical, a C\(_1\)-C\(_4\) polyhydroxalkyl radical, a C\(_1\)-C\(_4\) aminooalkyl radical, a (C\(_1\)-C\(_4\))alkylamino(C\(_1\)-C\(_4\))alkyl radical, a di(C\(_1\)-C\(_4\))alkylamino(C\(_1\)-C\(_4\))alkyl radical (it being possible for the dialkyls to form a 5- or 6-membered carbon-based ring or a heterocycle), a hydroxy(C\(_1\)-C\(_4\))alkyl- or di[hydroxy(C\(_1\)-C\(_4\))alkyl]amino(C\(_1\)-C\(_4\))alkyl radical, an amino radical, a (C\(_1\)-C\(_4\))alkyl- or di(C\(_1\)-C\(_4\))alkyl amino radical; a halogen atom, a carboxylic acid group or a sulphonic acid group;

[0084] i is equal to 0, 1, 2 or 3;

[0085] p is equal to 0 or 1;

[0086] q is equal to 0 or 1;

[0087] n is equal to 0 or 1;

[0088] with the proviso that:

[0089] the sum p+q is other than 0;

[0090] when p+q is equal to 2, then n is equal to 0 and the groups NR\(_1\)R\(_{16}\) and NR\(_2\)R\(_{18}\) occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions;

[0091] when p+q is equal to 1, then n is equal to 1 and the group NR\(_1\)R\(_{16}\) (or NR\(_2\)R\(_{18}\)) and the OH group occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions.

[0092] When the pyrazolo[1,5-a]pyrimidines of formula (IV) above are such that they contain a hydroxyl group on one of the positions 2, 5 or 7 α to a nitrogen atom, a tautomeric equilibrium exists represented, for example, by the following scheme:

[0093] Among the pyrazolo[1,5-a]pyrimidines of formula (IV) above, mention may be made in particular of:

[0094] pyrazolo[1,5-a]pyrimidine-3,7-diamine;

[0095] 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
[0096] pyrazolo[1,5-a]pyrimidine-3,5-diamine;
[0097] 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;
[0098] 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
[0099] 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
[0100] 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)ethanol;
[0101] 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)ethanol;
[0102] 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxy-ethyl)amino)ethanol;
[0103] 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxy-ethyl)amino)ethanol;
[0104] 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
[0105] 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
[0106] 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
[0107] and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.
[0108] The pyrazolo[1,5-a]pyrimidines of formula (IV) above can be prepared by cyclization starting with an aminopyrazole, according to the syntheses described in the following references:
[0115] The pyrazolo[1,5-a]pyrimidines of formula (IV) above can also be prepared by cyclization starting from hydrazine, according to the syntheses described in the following references:
[0119] The oxidation base(s) in accordance with the invention preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.
[0120] The couplers which can be used are those used conventionally in oxidation dye compositions, i.e. meta-phenyleneamines, meta-aminophenols and meta-diphenols, mono- or polyhydroxylated naphthalene derivatives, sesamol and its derivatives and heterocyclic compounds such as, for example, indole derivatives, indoline derivatives, benzimidazole derivatives, benzophenone derivatives, resorcinol derivatives, pyrazoloazole derivatives, pyrroloazole derivatives, imidazolozole derivatives, pyrazolopyrimidine derivatives, pyrazoline-3,5-dione derivatives, pyrrol[3,2-d]oxazole derivatives, pyrazolo[3,4-d]thiazole derivatives, thiazoloazole 5-oxide derivatives and thiazolozole 8-dioxide derivatives, and the addition salts thereof with an acid.
[0121] These couplers can be chosen in particular from 2-methyl-5-aminophenol, 2-N-(β-hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β-hydroxyethoxy)benzene, 2-amino-4-(β-hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, sesamol, 4-naphthol, 6-hydroxynaphthole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindole, 2,6-dihydroxy-4-methylpyridine, 1H-3-methylpyrazol-5-one and 1-phenyl-3-methylpyrazol-5-one, and the addition salts thereof with an acid.
[0122] When they are present, these couplers preferably represent from 0.0001 to 10% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.
[0123] In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.
[0124] The dye composition of the invention can also contain, in addition to the oxidation dye precursors defined above and the optional combined couplers, direct dyes to enrich the shades with glints. These direct dyes can then be chosen in particular from nitro dyes, azo dyes or anthraquinone dyes.
[0125] The subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.
[0126] According to this process, at least one ready-to-use dye composition as defined above is applied to the fibres, for a period which is sufficient to develop the desired coloration, after which the fibres are rinsed, optionally washed with shampoo rinsed again and dried.
[0127] The time required to develop the coloration on the keratin fibres is generally between 3 and 60 minutes and even more precisely between 5 and 40 minutes.
[0128] According to a specific embodiment of the invention, the process includes a first step which consists in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at
least one oxidation base and optionally at least one coupler as defined above, and, on the other hand, a composition (B) containing, in a medium which is suitable for dyeing, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme and at least one nonionic amphiphilic polymer containing at least one hydrophilic unit and at least one fatty chain, and then in mixing them together at the time of use, before applying this mixture to the keratin fibres.

[0129] According to another specific embodiment of the invention, the nonionic amphiphilic polymer can be incorporated into composition (A).

[0130] Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices can be equipped with means for applying the desired mixture to the hair, such as the devices described in patent FR-2,586,913 in the name of the Applicant.

[0131] A subject of the present invention is also a novel process for treating keratin substances, in particular the hair, in order to obtain a permanent reshaping of this hair, in particular in the form of permanent-waved hair, this process comprising the following steps: (i) a reducing composition is applied to the keratin substance to be treated, the keratin substance being placed under mechanical tension before, during or after the said application, (ii) the keratin substance is optionally rinsed, (iii) an oxidizing composition as defined above is applied to the optionally rinsed keratin substance, (iv) the keratin substance is optionally rinsed again.

[0132] The first step (i) of this process consists in applying a reducing composition to the hair. This application is carried out lock by lock or all at once.

[0133] The reducing composition comprises, for example, at least one reducing agent, which can be chosen in particular from thioglycolic acid, cysteine, cysteamine, glycercyl thioglycolate, thiolic acid or thiolic acid or thioglycolic acid salts.

[0134] The usual step for placing the hair under tension in a shape corresponding to the desired final shape for this hair (for example curls) can be carried out by any suitable means, in particular mechanical means, which are suitable and known per se for maintaining the hair under tension, such as, for example, rollers, curlers and the like.

[0135] The hair can also be shaped without the aid of external means, simply with the fingers.

[0136] Before carrying out the following optional rinsing step (ii), the hair onto which the reducing composition has been applied should, conventionally, be left to stand for a few minutes, generally between 5 minutes and one hour, preferably between 10 and 30 minutes, so as to give the reducing agent enough time to act correctly on the hair. This waiting phase preferably takes place at a temperature ranging from 35°C to 45°C, while preferably also protecting the hair with a hood.

[0137] In the optional second step of the process (step (ii)), the hair impregnated with the reducing composition is then rinsed thoroughly with an aqueous composition.

[0138] Next, in a third step (step (iii)), the oxidizing composition of the invention is applied to the hair thus rinsed, with the aim of fixing the new shape given to the hair.

[0139] As in the case of the application of the reducing composition, the hair onto which the oxidizing composition has been applied is then, conventionally, left for a standing or waiting phase lasting a few minutes, generally between 3 and 30 minutes, preferably between 5 and 15 minutes.

[0140] If the hair was maintained under tension by external means, these means (rollers, curlers or the like) can be removed from the hair before or after the fixing step.

[0141] Lastly, in the final step of the process according to the invention (step (iv)), which is also optional, the hair impregnated with the oxidizing composition is rinsed thoroughly, generally with water.

[0142] Hair which is soft and easy to disentangle is finally obtained. The hair is wavy.

[0143] The oxidizing composition according to the invention can also be used in a process for bleaching keratin fibres, and in particular the hair.

[0144] The bleaching process according to the invention comprises a step of applying an oxidizing composition according to the invention to the keratin fibres in the presence or absence of an auxiliary oxidizing agent. Conventionally, a second step of the bleaching process according to the invention is a step of rinsing the keratin fibres.

[0145] The medium which is suitable for the keratin fibres (or the support) for the ready-to-use dye compositions and for the oxidizing compositions used for the permanent reshaping or bleaching of keratin fibres in accordance with the invention generally consists of water or a mixture of water and at least one organic solvent in order to dissolve the compounds which would not be sufficiently soluble in water. By way of organic solvent, mention may be made, for example, of C₂-C₄ alkanols such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxycethanol, propylene glycol, propylene glycol monomethyl ether, diethylen glycol monoethyl ether and monomethyl ether, and aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

[0146] The solvents can be present in proportions preferably of between 1 and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

[0147] The pH of the ready-to-use dye compositions and of the oxidizing compositions used for the permanent reshaping or bleaching of the keratin fibres in accordance with the invention is chosen such that the enzymatic activity of the 2-electron oxidoreductase is not adversely affected. It is generally between 5 and 11 approximately, and preferably between 6.5 and 10 approximately. It can be adjusted to the desired value using acidifying or basifying agents usually used for dyeing keratin fibres.

[0148] Among the acidifying agents, mention may be made, by way of example, of inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid or lactic acid, and sulphonic acids.
Among the basifying agents, mention may be made, by way of example, of aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamines, 2-methyl-2-aminopropanol and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (V) below:

\[
\begin{align*}
R_{13} & \quad W \quad R_{15} \\
S_{14} & \quad N \quad S_{16}
\end{align*}
\]

in which W is a propylene residue optionally substituted with a hydroxyl group or a C1-C4 alkyl radical; R13, R14, R15 and R16 which may be identical or different, represent a hydrogen atom or a C1-C4 alkyl or C1-C4 hydroxyalkyl radical.

The ready-to-use dye compositions and the oxidizing compositions for the permanent reshaping or bleaching of keratin fibres in accordance with the invention can also contain various adjuvants used conventionally in compositions for dyeing, permanently reshaping or bleaching the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic (other than those of the invention), amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic thickeners, antioxidants, enzymes other than the 2-electron oxidoreductases used in accordance with the invention, such as, for example, peroxidases, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners, such as, for example, silicones, film-forming agents, preserving agents and opacifiers.

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

The ready-to-use dye compositions and the oxidizing compositions used for the permanent reshaping or bleaching of keratin fibres in accordance with the invention can be in various forms, such as in the form of liquids, creams or gels, which are optionally pressurized, or in any other form which is suitable for dyeing, permanently reshaping or bleaching keratin fibres, and in particular human hair.

In the case of a ready-to-use dye composition, the oxidation dye(s) and the 2-electron oxidoreductase(s) are present in the said composition, which must be free of oxygen gas, so as to avoid any premature oxidation of the oxidation dye(s).

Concrete examples illustrating the invention will now be given.

In the text hereinafore and hereinafter, except where otherwise mentioned, the percentages are expressed on a weight basis.

The examples which follow illustrate the invention without being limiting in nature.

EXAMPLE 1

Dye Composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uracase from Arthrobacter globiformis at a concentration of 20 International Units (I.U.)/mg, sold by the company Sigma</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Uric acid</td>
<td>1.65 g</td>
</tr>
<tr>
<td>Ethanol</td>
<td>20.0 g</td>
</tr>
<tr>
<td>(C2-C16)alkyl polyglucoside as an aqueous solution containing 80% active material (A.M.), sold under the name Oranim CG110 by the company SEPPIC</td>
<td>8.0 g</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>0.32 g</td>
</tr>
<tr>
<td>Polyurethane ether (diurethane of oxy-ethylene and oxypropylene (C5-C16) alcohols, sold under the name Durol T212 by the company Akzo</td>
<td>1.0 g</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>0.32 g</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>0.32 g</td>
</tr>
</tbody>
</table>

This ready-to-use dye composition was applied to locks of natural grey hair containing 90% white hairs for 30 minutes. The hair was then rinsed, washed with a standard shampoo and then dried.

Locks of hair dyed a matt dark-blonde colour were obtained.

EXAMPLE 2

Oxidizing Composition for Permanent-Waving or Bleaching

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uracase from Arthrobacter globiformis at a concentration of 20 International Units (I.U.)/mg, sold by the company Sigma</td>
<td>1.8 g</td>
</tr>
<tr>
<td>Uric acid</td>
<td>1.65 g</td>
</tr>
<tr>
<td>Ethanol</td>
<td>20.0 g</td>
</tr>
<tr>
<td>(C2-C16)alkyl polyglucoside as an aqueous solution containing 80% active material (A.M.), sold under the name Oranim CG110 by the company SEPPIC</td>
<td>8.0 g</td>
</tr>
<tr>
<td>PEARLS Plus Grade 330 GS by the company Aquaon</td>
<td>0.25 g</td>
</tr>
<tr>
<td>2-methyl-2-amino-1-propanol</td>
<td>qs</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>qs</td>
</tr>
</tbody>
</table>

1. Cosmetic and/or dermatological composition intended for treating keratin fibres, in particular human keratin fibres and more particularly human hair, comprising, in a support which is suitable for keratin fibres:

(a) at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme,

(b) at least one nonionic amphiphilic polymer containing at least one hydrophilic unit and at least one fatty chain.

2-32. (canceled)