

US 20160136077A1

(19) United States

(12) Patent Application Publication LALLEMAN et al.

(10) **Pub. No.: US 2016/0136077 A1**(43) **Pub. Date:** May 19, 2016

(54) OXIDATION DYEING PROCESS USING A COMPOSITION COMPRISING AN AMINOBENZIMIDAZOLONE OXIDATION BASE AND A METAL CATALYST

(71) Applicant: L'OREAL, Paris (FR)

(72) Inventors: **Boris LALLEMAN**, Paris (FR); **Alain LAGRANGE**, Coupvray (FR); **Marie MIGNON**, Paris (FR)

(21) Appl. No.: 14/899,605

(22) PCT Filed: Jun. 23, 2014

(86) PCT No.: **PCT/EP2014/063181**

§ 371 (c)(1),

(2) Date: Dec. 18, 2015

(30) Foreign Application Priority Data

Jun. 21, 2013	(FR)	1355952
Jun. 21, 2013	(FR)	1355953

Publication Classification

(51)	Int. Cl.	
	A61K 8/49	(2006.01)
	A61Q 5/10	(2006.01)
	A61K 8/31	(2006.01)
	A61K 8/22	(2006.01)
	A61K 8/58	(2006.01)

(52) **U.S. Cl.**

(57) ABSTRACT

The invention relates to a process for dyeing keratin fibres, comprising the use of one or more metal catalysts and of a composition (A) comprising: —one or more oxidizing agents, and —at least one aminobenzimidazole oxidation base of formula (I) in which the radicals R1 to R5 represent, independently of each other, a hydrogen atom; a halogen atom; a C1-C6 alkylradical; a C1-C6 alkoxyradical; a C1-C6 dialkylamino radical; a carboxylic radical (—COOH); a sulfonic radical (—S03H); a phenyl radical; a sat orated or unsaturated 5- to 7-membered heterocyclic radical, comprising one or more heteroatoms chosen from N, O and S.

OXIDATION DYEING PROCESS USING A COMPOSITION COMPRISING AN AMINOBENZIMIDAZOLONE OXIDATION BASE AND A METAL CATALYST

[0001] The present invention relates to a process for dyeing keratin fibres, comprising one or more metal catalysts.

[0002] Many people have sought for a long time to modify the colour of their hair and in particular to mask their grey hair.

[0003] It is known practice to obtain "permanent" or oxidation 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 initially colourless or weakly coloured compounds, which, when combined with oxidizing products, may give rise to coloured compounds via a process of oxidative condensation.

[0004] It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or coloration modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds, such as indole compounds. The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

[0005] The permanent dyeing process thus consists in applying, to the keratin fibres, bases or a mixture of bases and couplers with hydrogen peroxide ($\rm H_2O_2$ or aqueous hydrogen peroxide solution), as oxidizing agent, in leaving to diffuse, and in then rinsing the fibres. The colorations which result therefrom have the advantage of being permanent, strong and resistant to external agents, in particular to light, bad weather, washing operations, perspiration and rubbing actions.

[0006] However, it is still sought to increase the efficiency of the reaction of the oxidation dyes used during this process in order to improve their build-up on keratin fibres. Indeed, such an improvement would make it possible in particular to decrease the contents of the oxidation dyes present in dyeing compositions, to reduce the leave-on time on keratin fibres and/or to use other dye families which have a weak dyeing capacity but which are capable of exhibiting a good toxicological profile, of providing new shades or of producing colorations which are resistant with respect to external agents such as light or shampoos.

[0007] In this regard, it has already been proposed to use cosmetic compositions containing metal catalysts during a dyeing process in order to accelerate the dye oxidation reaction and to improve the intensity of the coloration on the keratin fibres. However, the dyeing power obtained is still not entirely satisfactory and the colorations obtained are generally too selective, i.e. these colorations are not uniform along the keratin fibre.

[0008] There is therefore a real need to provide a process for dyeing keratin fibres which is carried out in the presence of an oxidizing agent and which does not have the drawbacks of the existing processes, i.e. which is capable of resulting in a satisfactory intensity of the oxidation dyes on the keratin fibres while at the same time resulting in relatively non-selective colorations.

[0009] This aim is achieved by the present invention, one subject of which is especially a process for dyeing keratin

fibres, in particular human keratin fibres such as the hair, comprising the use of one or more metal catalysts and of a composition (A) comprising:

[0010] (a) at least one oxidizing agent, and

[0011] (b) at least one oxidation base chosen from:

[0012] i) aminobenzimidazolones of formula (I) below, or an addition salt or solvate thereof

$$\begin{array}{c} R5 \\ R1 \\ R4 \\ R3 \\ R2 \end{array}$$

in which the radicals R1 to R5 represent, independently of each other:

[0013] a hydrogen atom;

[0014] a halogen atom, preferably chosen from F, Cl and Br:

[0015] a linear or branched C1-C6 and preferably C1-C4 alkyl radical, which is optionally substituted, preferably with one or more OH, NH2 or CN groups, preferably OH:

[0016] a linear or branched C1-C6 and preferably C1-C4 alkoxy radical, which is optionally substituted, preferably with one or more OH, NH2 or CN groups;

[0017] a linear or branched C1-C6 and preferably C1-C4 dialkylamino radical, which is optionally substituted, preferably with one or more OH, NH2 or CN groups;

[0018] a carboxylic radical (—COOH);

[0019] a sulfonic radical (—SO3H);

[0020] a phenyl radical, which is optionally substituted, preferably with:

[0021] a halogen atom, preferably a chlorine atom;

[0022] a linear or branched C1-C6 and preferably C1-C4 alkyl group, which is optionally substituted, preferably with one or more halogen atoms, in particular a fluorine atom;

[0023] a linear or branched C1-C6 and preferably C1-C4 alkoxy group, which is optionally substituted, preferably with one or more halogen atoms, in particular a fluorine atom;

[0024] a saturated or unsaturated 5- to 7-membered heterocyclic radical, comprising one or more heteroatoms chosen from N, O and S,

[0025] which is optionally substituted, preferably with:

[0026] a linear or branched, optionally substituted C1-C6 and preferably C1-C4 alkyl group,

[0027] a saturated or unsaturated 5- to 7-membered heterocycle, comprising one or more heteroatoms chosen from N, O and S, preferably O; the said heterocycle possibly being fused with a saturated or unsaturated 5- to 7-membered, preferably 6, ring, optionally comprising one or more heteroatoms,

ii) 2- or 3-aminoindolizines of formula (II)

in which R1 to R7 independently represent a hydrogen atom, a C_1 - C_4 alkyl radical, an optionally substituted phenyl radical, a C_1 - C_4 alkoxy radical, a halogen atom, a carboxylic radical (—COOH or -alkyl-COOH), a carboxamide radical (CONRR'), a nitrile radical (—CN), a sulfone radical (—SO₂R), a sulfoxide radical (—SOR), a sulfonamide radical (—SO₂NRR'), an alkylcarbonyl radical (—CO-alkyl), an alkoxycarbonyl radical (—CO—O-alkyl), a benzoyl radical (—CO-phenyl or -alkyl-CO-phenyl optionally substituted on the phenyl group); R4 to R7 can form, in pairs in an adjacent position, an unsaturated or saturated, optionally substituted, 5- to 6-membered ring which may contain a heteroatom;

with the supplementary condition that R2 or R3 represents an

amino radical (NH₂). and mixture thereof.

[0028] In the context of the invention, the term " C_1 - C_4 alkyl radical" is intended to mean a linear or branched, saturated radical comprising from 1 to 4 carbon atoms, a C_1 - C_4 alkoxy radical is an —O-alkyl radical, a carboxylic radical is a —COOH or -alkyl-COOH radical; a carboxamide radical is a —CONRR' radical in which R and R' may be a hydrogen atom, or an alkyl or phenyl radical; a sulfone radical is an —SO_2RR' radical; a sulfoxide radical is an —SOR radical, a sulfonamide radical is an —SO_NRR' radical, with R and R' as defined above, an alkylcarbonyl radical is a —CO—alkyl radical, an alcoxycarbonyl radical is a —CO—O-alkyl radical, and a benzoyl radical is a —CO-phenyl or -alkyl-CO-phenyl radical with alkyl being as defined above and it being possible for the phenyl groups to be substituted.

[0029] Preferably, in formula (I) above, R2 represents a hydrogen atom, R3 and R5 represent, independently of each other, a hydrogen atom, a halogen atom, in particular Cl or Br; an alkyl radical, preferably methyl; an alkoxy radical, preferably methoxy; or, more preferentially, R1, R2, R3, R4 and R5 represent a hydrogen atom.

[0030] Preferably, in formula (II) above, the R7 radical is a hydrogen atom.

[0031] A subject of the invention is also a hair dye composition comprising one or more oxidation bases of formula (I) and/or (II) and at least 10% and preferably at least 20% of fatty substances, and also the use of this composition for dyeing keratin fibres, especially the hair.

[0032] The dyeing process according to the invention produces a satisfactory colour intensity on keratin fibres while at the same time being sparingly selective, i.e. giving homogeneous colorations along the keratin fibre. Furthermore, the process according to the present invention makes it possible to produce strong and chromatic colorations.

[0033] Moreover, the dyeing process according to the invention makes it possible to improve the intensity of the coloration on the keratin fibres compared with a conventional dyeing process.

[0034] In the process of the invention, the metal catalyst(s) may constitute or form part of a composition (B) which may be mixed with composition (A) before applying the mixture to keratin fibres or applied separately as a pre-treatment or post-treatment with or without intermediate rinsing. It should be noted that composition (B) may consist solely of the metal catalyst(s).

[0035] The present invention also relates to a multi-compartment device comprising a first compartment containing a composition (B) comprising one or more metal catalysts, a second compartment containing a composition (A') comprising one or more oxidation dyes of formula (I) and/or (II), and a third compartment containing a composition (C) comprising one or more oxidizing agents. According to a particular embodiment, one or more fatty substances are present in at least one of the compositions (A') or (C) such that, after mixing together compositions (A') and (C), the content of fatty substances is greater than or equal to 10% by weight relative to the total weight of the mixture of compositions (A') and (C).

[0036] According to a particular embodiment, the device comprises a fourth compartment comprising a composition (D) comprising one or more fatty substances, the said composition (D) being intended to be mixed with compositions (A') and (C), the content of fatty substances preferably being greater than or equal to 10% by weight relative to the total weight of the mixture of compositions (A'), (C) and (D), composition (A') or (C) possibly containing one or more fatty substances.

[0037] Other characteristics and advantages of the invention will emerge more clearly on reading the description and the examples that follow.

[0038] In that which follows and unless otherwise indicated, the limits of a range of values are included in this range.
[0039] The expression "at least one" is equivalent to the expression "one or more".

[0040] The keratin fibres treated via the process according to the invention are preferably the hair.

[0041] The dyeing process according to the present invention uses one or more metal catalysts.

[0042] Metal catalysts are compounds that comprise one or more metals in their structure.

[0043] The metals are chosen from transition metals and rare-earth metals, and alloys thereof.

[0044] In particular, the metals are chosen from transition metals and rare-earth metals.

[0045] Among the transition metals, mention may be made especially of manganese, iron, cobalt, copper, zinc, platinum, nickel, titanium, silver, zirconium, chromium, molybdenum, tungsten, platinum, gold and vanadium, and among these most particularly manganese.

[0046] Among the rare-earth metals, mention may particularly be made of cerium.

[0047] Thus, the metal catalysts are especially catalysts based on transition metals or on rare-earth metals, and more particularly manganese-based, vanadium-based or cerium-based catalysts.

[0048] The metal catalysts used may be chosen from metal salts, metal oxides and metal complexes, and mixtures thereof and solvates thereof, including hydrates.

[0049] For the purposes of the present invention, the term "metal complexes" means systems in which the metal ion, i.e. the central atom, is bonded to one or more electron donors, called ligands, via chemical bonds.

[0050] Preferably, the metal catalysts used in the dyeing process are chosen from metal salts.

[0051] For the purposes of the present invention, the term "metal salts" means the salts derived from the action of an acid on a metal.

[0052] Preferentially, the metal catalysts used in the dyeing process are chosen from transition metal salts, such as manganese salts, and rare-earth metal salts, such as cerium salts, and also mixtures thereof.

[0053] The metal salts may be mineral or organic salts.

[0054] The inorganic metal salts may be chosen from halides, carbonates, sulfates and phosphates, especially hydrated or anhydrous halides.

[0055] According to another preferred variant, the metal salts are in oxidation state II and bear two (poly)hydroxy acid-based ligands.

[0056] The term "(poly)hydroxy acid" means any carboxylic acid which comprises a hydrocarbon-based chain which is linear or branched, and saturated or unsaturated, preferably saturated and/or linear, comprising from 1 to 10 carbon atoms and from 1 to 9 hydroxyl groups, and comprising from 1 to 4 carboxylic groups —C(O)—OH, at least one of the said —C(O)—OH functions of which is in the carboxylate form —C(O)—O— complexed with the metal atom, preferably Mn(II). More particularly, the metal salt is complexed with two carboxylate groups such as that of formula (II):

$$R - C(O) - O - M - O - C(O) - R'$$
 (II)

and also the solvates thereof, such as hydrates, and enantiomers thereof,

[0057] in which formula (II):

[0058] M represents a metal (II) or metal2+ in oxidation state 2.

[0059] R and R', which may be identical or different, represent a (C1-C6)(poly)hydroxyalkyl group.

[0060] The metal catalysts are particularly chosen from organic acid salts of transition metals, especially of manganese, and mineral salts of rare-earth metals, especially of cerium

[0061] According to a particular embodiment of the invention, the manganese is a manganese salt.

[0062] The organic metal salts may be more particularly chosen from organic acid salts such as citrates, lactates, glycolates, gluconates, acetates, propionates, fumarates, oxalates and tartrates, especially gluconates.

[0063] More preferentially, the metal catalysts are chosen from manganese gluconate and cerium chloride heptahydrate, in particular manganese gluconate.

 $\cite{[0064]}$ Preferably, the metal catalyst(s) are chosen from the compounds of formula (II) and more particularly represent manganese gluconate.

[0065] Preferentially, the metal catalysts are chosen from organic acid salts of transition metals, especially of manganese, and mineral salts of rare-earth metals, especially of cerium.

[0066] Composition B may exclusively contain the metal catalyst(s). This composition may also contain other compounds. This composition B may be anhydrous or aqueous.

[0067] The metal catalysts, after mixing with composition (A), may be present in a content ranging from 0.001% to 10% by weight, preferably in a content ranging from 0.001% to 1% by weight, better still ranging from 0.01% to 0.5% by weight relative to the total weight of the final composition after mixing with the oxidizing agent(s).

[0068] As indicated previously, the dyeing process of the invention uses a composition (A) which may comprise one or more fatty substances.

[0069] The term "fatty substance" means an organic compound that is insoluble in water at ordinary room temperature (25° C.) and at atmospheric pressure (760 mmHg) (solubility of less than 5%, preferably less than 1% and even more preferentially less than 0.1%). They have in their structure at least one hydrocarbon-based chain comprising at least 6 carbon atoms or a sequence of at least two siloxane groups. In addition, the fatty substances are generally soluble in organic solvents under the same temperature and pressure conditions, for instance chloroform, ethanol, benzene, liquid petroleum jelly or decamethylcyclopentasiloxane.

[0070] These fatty substances are neither polyoxyethylenated nor polyglycerolated. They are different from fatty acids since salified fatty acids constitute soaps which are generally soluble in aqueous media.

[0071] The fatty substances are in particular chosen from C_6 - C_{16} hydrocarbons or hydrocarbons comprising more than 16 carbon atoms and in particular alkanes, oils of animal origin, oils of plant origin, fluoro oils or glycerides of synthetic origin, fatty alcohols, fatty acid and/or fatty alcohol esters, non-silicone waxes, and silicones.

[0072] It is recalled that, for the purposes of the invention, the fatty alcohols, fatty esters and fatty acids more particularly contain one or more linear or branched, saturated or unsaturated hydrocarbon-based groups comprising 6 to 30 carbon atoms, which are optionally substituted, in particular with one or more (in particular 1 to 4) hydroxyl groups. If they are unsaturated, these compounds may comprise one to three conjugated or non-conjugated carbon-carbon double bonds.

[0073] As regards the C_6 - C_{16} alkanes, they are linear or branched, and possibly cyclic. Examples that may be mentioned include hexane, dodecane, and isoparaffins, for instance isohexadecane and isodecane. The linear or branched hydrocarbons containing more than 16 carbon atoms may be chosen from liquid paraffins, petroleum jelly, liquid petroleum jelly, polydecenes, and hydrogenated polyisobutene such as Parleam®.

[0074] Among the animal oils, mention may be made of perhydrosqualene.

[0075] Among the triglycerides of plant or synthetic origin, mention may be made of liquid fatty acid triglycerides comprising from 6 to 30 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively, for example, sunflower oil, maize oil, soybean oil, marrow oil, grapeseed oil, sesame seed oil, hazelnut oil, apricot oil, macadamia oil, arara oil, castor oil, avocado oil, jojoba oil, shea butter oil, caprylic/capric acid triglycerides, for instance those sold by the company Stéarineries Dubois or those sold under the names Miglyol® 810, 812 and 818 by the company Dynamit Nobel.

[0076] Among the fluoro oils, mention may be made of perfluoromethylcyclopentane and perfluoro-1,3-dimethylcyclohexane, sold under the names Flutec® PC1 and Flutec® PC3 by the company BNFL Fluorochemicals; perfluoro-1,2-dimethylcyclobutane; perfluoroalkanes such as dodecafluoropentane and tetradecafluorohexane, sold under the names PF 5050® and PF 5060® by the company 3M, or bromoperfluorooctyl sold under the name Foralkyl® by the company Atochem; nonafluoromethoxybutane and nonafluoroethoxy-isobutane; perfluoromorpholine derivatives such as 4-(trifluoromethyl)perfluoromorpholine sold under the name PF 5052® by the company 3M.

[0077] The fatty alcohols that may be used in the cosmetic composition (E) are saturated or unsaturated, and linear or branched, and comprise from 6 to 30 carbon atoms and more particularly from 8 to 30 carbon atoms. Examples that may be mentioned include cetyl alcohol, stearyl alcohol and the mixture thereof (cetylstearyl alcohol), octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol, oleyl alcohol and linoleyl alcohol.

[0078] The wax(es) that may be used in composition (A) are chosen especially from carnauba wax, candelilla wax, esparto grass wax, paraffin wax, ozokerite, plant waxes, for instance olive wax, rice wax, hydrogenated jojoba wax or the absolute waxes of flowers such as the essential wax of black-currant blossom sold by the company Bertin (France), animal waxes, for instance beeswaxes, or modified beeswaxes (cerabellina); other waxes or waxy starting materials that may be used according to the invention are especially marine waxes such as the product sold by the company Sophim under the reference M82, and polyethylene waxes or polyolefin waxes in general.

[0079] As regards the fatty acid and/or fatty alcohol esters, which are advantageously different from the triglycerides mentioned above, mention may be made in particular of esters of saturated or unsaturated, linear or branched C_1 - C_{26} aliphatic mono- or polyacids and of saturated or unsaturated, linear or branched C_1 - C_{26} aliphatic mono- or polyalcohols, the total carbon number of the esters more particularly being greater than or equal to 10.

[0080] Among the monoesters, mention may be made of dihydroabietyl behenate; octyldodecyl behenate; isocetyl behenate; cetyl lactate; C₁₂-C₁₅ alkyl lactate; isostearyl lactate; lauryl lactate; linoleyl lactate; oleyl lactate; (iso)stearyl octanoate; isocetyl octanoate; octyl octanoate; cetyl octanoate; decyl oleate; isocetyl isostearate; isocetyl laurate; isocetyl stearate; isodecyl octanoate; isodecyl oleate; isononyl isononanoate; isostearyl palmitate; methylacetyl ricinoleate; myristyl stearate; octyl isononanoate; 2-ethylhexyl isononate; octyl palmitate; octyl pelargonate; octyl stearate; octyldodecyl erucate; oleyl erucate; ethyl and isopropyl palmitates, 2-ethylhexyl palmitate, 2-octyldecyl palmitate, alkyl myristates such as isopropyl, butyl, cetyl, 2-octyldodecyl, myristyl or stearyl myristate, hexyl stearate, butyl stearate, isobutyl stearate; dioctyl malate, hexyl laurate, 2-hexyldecyl laurate.

[0081] Still within the context of this variant, esters of C_4 - C_{22} dicarboxylic or tricarboxylic acids and of C_1 - C_{22} alcohols and esters of mono-, di- or tricarboxylic acids and of C_2 - C_{26} di-, tri-, tetra- or pentahydroxy alcohols may also be used.

[0082] Mention may be made in particular of: diethyl sebacate; diisopropyl sebacate; diisopropyl adipate; di-n-propyl adipate; dioctyl adipate; diisostearyl adipate; dioctyl maleate; glyceryl undecylenate; octyldodecyl stearoyl stearate; pentaerythrityl monoricinoleate; pentaerythrityl tetraisononanoate; pentaerythrityl tetrapelargonate; pentaerythrityl tetraisostearate; pentaerythrityl tetraoctanoate; propylene glycol dicaprylate; propylene glycol dicaprate, tridecyl erucate; triisopropyl citrate; triisostearyl citrate; glyceryl trilactate; glyceryl trioctanoate; trioctyldodecyl citrate; trioleyl citrate, propylene glycol dioctanoate; neopentyl glycol diheptanoate; diethylene glycol diisononanoate; and polyethylene glycol distearates.

[0083] Among the esters mentioned above, it is preferred to use ethyl, isopropyl, myristyl, cetyl or stearyl palmitates,

2-ethylhexyl palmitate, 2-octyldecyl palmitate, alkyl myristates such as isopropyl, butyl, cetyl or 2-octyldodecyl myristate, hexyl stearate, butyl stearate, isobutyl stearate; dioctyl malate, hexyl laurate, 2-hexyldecyl laurate, isononyl isononanoate or cetyl octanoate.

[0084] The composition may also comprise, as fatty ester, sugar esters and diesters of C_6 - C_{30} and preferably C_{12} - C_{22} fatty acids. It is recalled that the term "sugar" means oxygenbearing hydrocarbon-based compounds containing several alcohol functions, with or without aldehyde or ketone functions, and which comprise at least 4 carbon atoms. These sugars may be monosaccharides, oligosaccharides or polysaccharides.

[0085] Examples of suitable sugars that may be mentioned include sucrose (or saccharose), glucose, galactose, ribose, fucose, maltose, fructose, mannose, arabinose, xylose and lactose, and derivatives thereof, in particular alkyl derivatives, such as methyl derivatives, for instance methylglucose.

[0086] The sugar esters of fatty acids may be chosen especially from the group comprising the esters or mixtures of esters of sugars described previously and of linear or branched, saturated or unsaturated C_6 - C_{30} and preferably C_{12} - C_{22} fatty acids. If they are unsaturated, these compounds may comprise one to three conjugated or non-conjugated carbon-carbon double bonds.

[0087] The esters according to this variant may also be chosen from monoesters, diesters, triesters, tetraesters and polyesters, and mixtures thereof.

[0088] These esters may be, for example, oleates, laurates, palmitates, myristates, behenates, cocoates, stearates, linoleates, linolenates, caprates and arachidonates, or mixtures thereof such as, especially, oleopalmitate, oleostearate and palmitostearate mixed esters.

[0089] More particularly, use is made of monoesters and diesters and in particular mono- or di-oleate, -stearate, -behenate, oleate/palmitate, -linoleate, -linolenate or -oleate/stearate of sucrose, glucose or methylglucose.

[0090] An example that may be mentioned is the product sold under the name Glucate® DO by the company Amerchol, which is a methylglucose dioleate.

[0091] Examples of esters or mixtures of esters of sugar of fatty acid that may also be mentioned include:

[0092] the products sold under the names F160, F140, F110, F90, F70 and SL40 by the company Crodesta, respectively denoting sucrose palmitate/stearates formed from 73% monoester and 27% diester and triester, from 61% monoester and 39% diester, triester and tetraester, from 52% monoester and 48% diester, triester and tetraester, from 45% monoester and 55% diester, triester and tetraester, from 39% monoester and 61% diester, triester and tetraester, and sucrose monolaurate;

[0093] the products sold under the name Ryoto Sugar Esters, for example referenced B370 and corresponding to sucrose behenate formed from 20% monoester and 80% diester-triester-polyester;

[0094] the sucrose monopalmitate/stearate-dipalmitate/ stearate sold by the company Goldschmidt under the name Tegosoft® PSE.

[0095] The silicones that may be used in the cosmetic composition of the present invention are volatile or non-volatile, cyclic, linear or branched silicones, which are unmodified or modified by organic groups, having a viscosity from 5×10^{-6} to $2.5~\text{m}^2/\text{s}$ at 25° C., and preferably 1×10^{-5} to $1~\text{m}^2/\text{s}$.

[0096] The silicones that may be used in accordance with the invention may be in the form of oils, waxes, resins or gums.

[0097] Preferably, the silicone is chosen from polydialkylsiloxanes, in particular polydimethylsiloxanes (PDMSs), and organomodified polysiloxanes comprising at least one functional group chosen from poly(oxyalkylene) groups, amino groups and alkoxy groups.

[0098] Organopolysiloxanes are defined in greater detail in Walter Noll's Chemistry and Technology of Silicones (1968), Academic Press. They may be volatile or nonvolatile.

[0099] When they are volatile, the silicones are more particularly chosen from those with a boiling point of between 60° C. and 260° C., and even more particularly from:

[0100] (i) cyclic polydialkylsiloxanes comprising from 3 to 7 and preferably from 4 to 5 silicon atoms. These are, for example, octamethylcyclotetrasiloxane sold in particular under the name Volatile Silicone® 7207 by Union Carbide or Silbione® 70045 V2 by Rhodia, decamethylcyclopentasiloxane sold under the name Volatile Silicone® 7158 by Union Carbide, and Silbione® 70045 V5 by Rhodia, and also mixtures thereof.

[0101] Mention may also be made of cyclocopolymers of the dimethylsiloxane/methylalkylsiloxane type, such as Volatile Silicone® FZ 3109 sold by the company Union Carbide, of formula:

$$\begin{array}{c|c} & & & & & & & \\ & & & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

[0102] Mention may also be made of mixtures of cyclic polydialkylsiloxanes with organosilicon compounds, such as the mixture of octamethylcyclotetrasiloxane and tetra(trimethylsilyl)pentaerythritol (50/50) and the mixture of octamethylcyclotetrasiloxane and oxy-1,1'-bis(2,2,2',2',3,3'-hexatrimethylsilyloxy)neopentane;

[0103] (ii) linear volatile polydialkylsiloxanes containing 2 to 9 silicon atoms and having a viscosity of less than or equal to 5×10^{-6} m²/s at 25° C. An example is decamethyltetrasiloxane sold in particular under the name SH 200 by the company Toray Silicone. Silicones belonging to this category are also described in the article published in Cosmetics and Toiletries, Vol. 91, Jan. 76, pp. 27-32, Todd & Byers, *Volatile Silicone Fluids for Cosmetics*.

[0104] Use is preferably made of non-volatile polydialkylsiloxanes, polydialkylsiloxane gums and resins, polyorganosiloxanes modified with the organofunctional groups above, and also mixtures thereof.

[0105] These silicones are more particularly chosen from polydialkylsiloxanes, among which mention may be made mainly of polydimethylsiloxanes having trimethylsilyl end groups. The viscosity of the silicones is measured at 25° C. according to ASTM Standard 445 Appendix C.

[0106] Among these polydialkylsiloxanes, mention may be made, in a nonlimiting manner, of the following commercial products:

[0107] the Silbione® oils of the 47 and 70 047 series or the Mirasil® oils sold by Rhodia, for instance the oil 70 047 V 500 000;

[0108] the oils of the Mirasil® series sold by the company Rhodia;

[0109] the oils of the 200 series from the company Dow Corning, such as DC200 with a viscosity of 60 000 mm²/s:

[0110] the Viscasil® oils from General Electric and certain oils of the SF series (SF 96, SF 18) from General Electric

[0111] Mention may also be made of polydimethylsiloxanes bearing dimethylsilanol end groups known under the name dimethiconol (CTFA), such as the oils of the 48 series from the company Rhodia.

[0112] In this category of polydialkylsiloxanes, mention may also be made of the products sold under the names Abil Wax® 9800 and 9801 by the company Goldschmidt, which are $poly(C_1-C_{20})$ dialkylsiloxanes.

[0113] The silicone gums that may be used in accordance with the invention are in particular polydialkylsiloxanes and preferably polydimethylsiloxanes with high number-average molecular weights of between 200 000 and 1 000 000, used alone or as a mixture in a solvent. This solvent can be chosen from volatile silicones, polydimethylsiloxane (PDMS) oils, polyphenylmethylsiloxane (PPMS) oils, isoparaffins, polyisobutylenes, methylene chloride, pentane, dodecane and tridecane, or mixtures thereof.

[0114] Products that can be used more particularly in accordance with the invention are mixtures such as:

[0115] mixtures formed from a hydroxy-terminated polydimethylsiloxane or dimethiconol (CTFA), and from a cyclic polydimethylsiloxane, also known as cyclomethicone (CTFA), such as the product Q2 1401 sold by the company Dow Corning;

[0116] mixtures of a polydimethylsiloxane gum and a cyclic silicone, such as the product SF 1214 Silicone Fluid from the company General Electric; this product is an SF 30 gum corresponding to a dimethicone, having a number-average molecular weight of 500 000, dissolved in the oil SF 1202 Silicone Fluid corresponding to decamethylcyclopentasiloxane;

[0117] mixtures of two PDMSs with different viscosities, and more particularly of a PDMS gum and of a PDMS oil, such as the product SF 1236 from the company General Electric. The product SF 1236 is a mixture of a gum SE 30 defined above, with a viscosity of 20 m²/s and of an oil SF 96 with a viscosity of 5×10⁻⁶ m²/s. This product preferably comprises 15% of gum SE 30 and 85% of an oil SF 96.

[0118] The organopolysiloxane resins that may be used in accordance with the invention are crosslinked siloxane systems containing the following units:

[0119] $R_2SiO_{2/2}$, $R_3SiO_{1/2}$, $RSiO_{3/2}$ and $SiO_{4/2}$,

[0120] in which R represents an alkyl containing 1 to 16 carbon atoms. Among these products, the ones that are particularly preferred are those in which R denotes a $\rm C_1$ - $\rm C_4$ lower alkyl group, more particularly methyl.

[0121] Among these resins, mention may be made of the product sold under the name Dow Corning 593 or those sold under the names Silicone Fluid SS 4230 and SS 4267 by the company General Electric, and which are silicones of dimethyl/trimethylsiloxane structure.

[0122] Mention may also be made of the trimethyl siloxy-silicate-type resins sold in particular under the names X22-4914, X21-5034 and X21-5037 by the company Shin-Etsu.

[0123] The organomodified silicones that may be used in accordance with the invention are silicones as defined previously and comprising in their structure one or more organofunctional groups attached via a hydrocarbon-based group.

[0124] Besides the silicones described above, the organomodified silicones may be polydiarylsiloxanes, in particular polydiphenylsiloxanes, and polyalkylarylsiloxanes functionalized by the organofunctional groups mentioned previously.

[0125] The polyalkylarylsiloxanes are particularly chosen from linear and/or branched polydimethyl/methylphenylsiloxanes and polydimethyl/diphenylsiloxanes with a viscosity ranging from 1×10^{-5} to 5×10^{-2} m²/s at 25° C.

[0126] Among these polyalkylarylsiloxanes, examples that may be mentioned include the products sold under the following names:

[0127] the Silbione® oils of the 70 641 series from Rhodia;

[0128] the oils of the Rhodorsil® 70 633 and 763 series from Rhodia:

[0129] the oil Dow Corning 556 Cosmetic Grade Fluid from Dow Corning;

[0130] the silicones of the PK series from Bayer, such as the product PK20;

[0131] the silicones of the PN and PH series from Bayer, such as the products PN1000 and PH1000;

[0132] certain oils of the SF series from General Electric, such as SF 1023, SF 1154, SF 1250 and SF 1265.

[0133] Among the organomodified silicones, mention may be made of polyorganosiloxanes comprising:

[0134] polyethyleneoxy and/or polypropyleneoxy groups optionally comprising C₆-C₂₄ alkyl groups, such as the products known as dimethicone copolyol sold by the company Dow Corning under the name DC 1248 or the oils Silwet® L 722, L 7500, L 77 and L 711 by the company Union Carbide, and the (C₁₂)alkylmethicone copolyol sold by the company Dow Corning under the name Q2 5200;

[0135] substituted or unsubstituted amine groups, such as the products sold under the names GP 4 Silicone Fluid and GP 7100 by the company Genesee or the products sold under the names Q2 8220 and Dow Corning 929 or 939 by the company Dow Corning. The substituted amine groups are, in particular, C₁-C₄ aminoalkyl groups:

[0136] alkoxy groups such as the product sold under the name Silicone Copolymer F-755 by SWS Silicones, and Abil Wax® 2428, 2434 and 2440 by the company Goldschmidt.

[0137] The fatty substances are advantageously chosen from C_6 - C_{16} hydrocarbons or hydrocarbons comprising more than 16 carbon atoms, and in particular alkanes, oils of plant origin, fatty alcohols, fatty acid and/or fatty alcohol esters, and silicones, or mixtures thereof.

[0138] Preferably, the fatty substance is an oil (a compound that is liquid at a temperature of 25° C. and at atmospheric pressure).

[0139] Preferably, the fatty substance is chosen from liquid petroleum jelly, C_6 - C_{16} alkanes, polydecenes, liquid esters of a fatty acid and/or of a fatty alcohol, and liquid fatty alcohols, or mixtures thereof. Better still, the fatty substance is chosen from liquid petroleum jelly, C_6 - C_{16} alkanes and polydecenes.

[0140] Preferably, the fatty substances are present in a content of greater than or equal to 10% by weight relative to the total weight of the cosmetic composition (A).

[0141] Thus, according to a particular embodiment, composition (A) has a content of fatty substances, preferably of oils, preferably ranging from 10% to 70% by weight, even more particularly ranging from 25% to 70% by weight, better still from 25% to 60% by weight and most particularly from 30% to 60% by weight relative to the total weight of composition (A).

[0142] The invention uses an oxidation base of formula (I) and/or (II). Examples of oxidation bases of formula (I) that may be mentioned include the following oxidation bases, salts thereof and solvates thereof:

1.3-dihydro-

5-Amino-6-ethoxybenzimi

dazolone

2H-Benzimidazol-2-one,

5-amino-1,3- dihydro-6-phenyl

5-amino-1,3-dihydro-6-

(4-methyl-1-piperidinyl)

1082387-49-2 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(4-methyl-1-piperazinyl)

t-Bu
$$H_{2N}$$
 NH

926222-67-5 2H-Benzimidazol-2-one, 5-amino-6-[4-(1,1-dimethylethyl) phenyl]-1,3-dihydro

$$\underbrace{ \begin{bmatrix} \\ \\ \\ \end{bmatrix}_{H_2N} }^{H} \underbrace{ \begin{bmatrix} \\ \\ \\ \end{bmatrix}_{NH} }^{H}$$

926224-11-5 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(2-thienyl)-

1082550-34-2 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(4-morpholinyl)

$$H_{2N}$$
 N
 $(CH_{2})_{3}$
 OH

1217244-06-8 6-Amino-5-methoxy-1-(3-hydroxypropyl)-2-benzimidazolone

$$\underbrace{\overset{H}{N}}_{H_2N} \underbrace{\overset{H}{N}}_{N} \underbrace{\overset{O}{N}}_{M}$$

124424-20-0 6-Amino-5-methoxy-1-methyl-2-benzimidazolone

1082551-14-6 2H-Benzimidazol-2-one, 5-amino-6-(4-ethyl-1-piperazinyl)-1,3-dihydro

926250-99-9 2H-Benzimidazol-2-one, 5-amino-6-(3,4-dichlorophenyl) -1,3-dihydro-

$$\begin{array}{c|c} & H \\ \hline \\ H_2N \end{array} \\ \begin{array}{c} H \\ NH \end{array}$$

1082387-50-5 2H-Benzimidazol-2-one, 5-amino-6-(3,4-dihydro-2(1H))isoquinolinyl-1,3-dihydro-

$$F_3C$$

$$NH_2$$

$$NH_2$$

926225-36-7 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-[3-(trifluoromethyl)phenyl]-

926253-29-4 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-[2-(trifluoromethoxy)phenyl]-I

$$H_{2N}$$

1347800-66-1 2H-Benzimidazol-2-one, 6-amino-1,3-dihydro-1-[1-(tetrahydro-2H-pyran-4-yl)-4-piperidinly]-

$$\begin{array}{c} H_2N \\ \\ HO_3S \end{array} \begin{array}{c} H \\ N \\ NH \end{array}$$

330991-27-0 1H-Benzimidazole, 5-sulfonic acid, 6-amino-2,3-dihydro-2-oxo

[0143] Preferably, the oxidation base of formula (I) is 5-amino-2-benzimidazolinone.

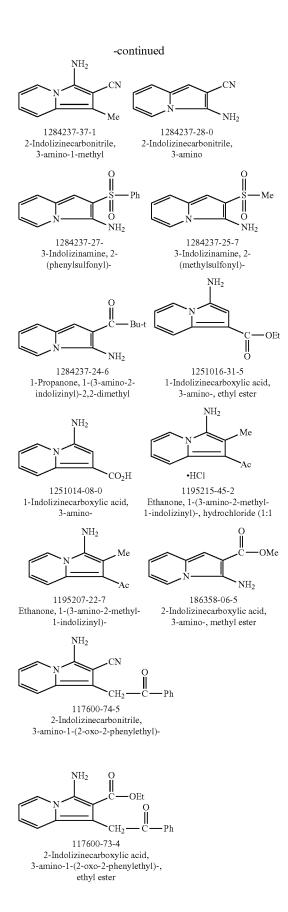
ОМе

 NH_2

[0144] Examples of oxidation bases of formula (II) that may be mentioned include the following 2-aminoindozolines compounds, salts thereof and solvates thereof:

2-amino-7-methyl-, ethyl ester

[0145] Examples of oxidation bases of formula (II) that may be mentioned include the following 3-aminoindozolines compounds, salts thereof and solvates thereof:



1016230-66-2

Pyrrolo[1,2-a]quinoline-

2-carbonitrile, 1-amino

8-carboxylic acid, 1-amino-, methyl ester

[0146] According to one particular embodiment, the oxidation base of formula (II) is preferably chosen from 3-aminoindolizines, preferably with R7 representing a hydrogen atom in formula (II).

[0147] Preferably, the compounds of formula (I) and/or (II) are present in an amount of between 0.0001% and 10% and preferentially between 0.01% and 5% by weight relative to the total weight of composition (A).

[0148] Composition (A) that is useful in the invention comprises an oxidizing agent. Finally, the process is performed with a composition (A) comprising one or more oxidizing agents.

[0149] More particularly, the oxidizing agent(s) are chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts, for instance alkali metal or alkaline-earth metal persulfates, perborates, peracids and precursors thereof, and percarbonates of alkali metals or alkaline-earth metals, and peracids and precursors thereof.

[0150] The oxidizing agent is preferably hydrogen peroxide.

[0151] This oxidizing agent advantageously consists of hydrogen peroxide, the concentration of which may range more particularly from 0.1% to 50% by weight, even more preferentially from 0.5% to 20% by weight and better still from 1% to 15% by weight relative to composition (A).

[0152] The process according to the present invention is performed using a composition (A) comprising one or more oxidation bases of formula (I) and (II) and additional oxidation dyes other than the oxidation bases of formula (I) and (II).

[0153] The additional oxidation dyes are generally chosen from the oxidation bases defined below and couplers.

[0154] By way of example, the additional oxidation bases are chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.

[0155] According to a preferred embodiment, the composition contains an additional oxidation base chosen from heterocyclic bases, in particular pyridine derivatives, pyrimidine derivatives, pyrazolic derivative and mixture thereof, particularly additional oxidation bases of formula (III), their addition salts or solvates:

$$\begin{array}{c} X \\ X \\ Y \\ Y \end{array}$$

[0156] in which:

[0157] X is a —CO— or —CR₁₀— group,

[0158] Y is a nitrogen atom or a —NR₈ group

[0159] Y' is a nitrogen atom or a —NR₉, group

[0160] with R_{10} representing a hydrogen atom, a C_1 - C_4 alkyl radical, which is optionally substituted with one or more hydroxyl or amino groups,

[0161] R₈ represents a C1-C4 alkyl radical substituted with one or more hydroxyl or amino groups;

[0162] R₉ represents a C₁-C₄ alkyl radical, which is optionally substituted with one or more hydroxyl or amino groups, [0163] R₈ and R₉ on the one hand, and R₉ and R₁₀ on the other hand, can form with the atoms that bear them a saturated or unsaturated 5 to 7 membered heterocycle, optionally substituted with one or more halogen atom, one or more hydroxy, amino, or C₁-C₄ alkyl radical, R₇ represents an amino group, a C₁-C₄ alkyl radical group, optionally substituted with one or more hydroxyl or amino groups, a C₁-C₄ alkoxy group optionally substituted with one or more hydroxyl or amino groups.

[0164] the ring containing X, Y and Y' comprising at least a double bond. Oxidation bases of formula (III) or the addition salts may be under the form of solvates, for example hydrates or linear or branched alcohol solvates such as ethanol or isopropanol.

[0165] In a first embodiment, the oxidation bases of formula (III) are chosen from compounds of formula (III'), their addition salts or solvates:

$$N = \begin{pmatrix} NH_2 \\ N \\ R_7 \\ R_8 \end{pmatrix}$$

[0166] R₇ and R₈ having the same meaning as previously defined. R₈ preferably represents a C₁-C₄ alkyl group substituted with at least one hydroxyl group, particularly a hydroxyethyl group, and R₇ represents an amino group. In this embodiment, 2-(4,5-diamino-1H-pyrazol-1-yl)ethanol or an addition salt is preferred.

[0167] In a second embodiment, R_8 and R_9 on the one hand and R_9 and R_{10} on the other hand, form with the atoms that bear them a saturated or unsaturated 5 to 7 membered heterocycle, optionally substituted with one or more halogen atom, one or more hydroxy, amino, or C_1 - C_4 alkyl radical group.

[0168] In this second embodiment, the oxidation bases are preferably chosen from:

a) compounds of formula (III"), theirs addition salts and solvates:

$$(III'')$$

$$N_{N}$$

$$R_{7}$$

 $\rm R_7$ having the same meaning as previously defined, and $\rm R_7$ preferably represents an amino group

[0169] b) compounds of formula (III'"), their addition salts and solvates:

$$(III''')$$

$$NH_2$$

$$R_7$$

[0170] R₇ having the same meaning as previously defined. R₇ preferably represents a C_1 - C_4 alkoxy group optionally substituted with at least one hydroxy group, particularly a hydroxyethoxy group.

[0171] Among the compounds of formula (III"), 2,3-diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-A]pyrazol-1-one or and addition salt is preferred.

[0172] Among the compounds of formula (III'''), 2-[3-aminopyrazolo[1,5-a]pyridin-2-yl]oxy]ethanol or an addition salt are preferred.

[0173] According to another preferred embodiment, the composition contains an additional oxidation base chosen from para phenylene diamine of formula (IV) their addition salts and solvates:

in which:

R'₁, R'₂, R'₃, R'₄ represent independently of each other a hydrogen atom, a linear or branched C1-C6 and preferably C1-C4 alkyl radical, a linear or branched C1-C6 and preferably C1-C4 hydroxy-alkyl radical, a linear or branched C1-C6 and preferably C1-C4 alcoxy-alkyl group.

R'₁ and R'₂ preferably represent independently of each other a linear or branched C1-C4 alkyl radical, a linear or branched C1-C4 hydroxy-alkyl radical or a linear or branched C1-C4 alcoxy-alkyl group, preferably a linear or branched C1-C4 hydroxy-alkyl radical.

R'₃ and R'₄ preferably represent a hydrogen atom.

As example of paraphenylene diamine of formula (IV), mention may be made of N'N-bis(2-hydroxyethyl)-p-phenylene-diamine.

[0174] Composition (A) may also comprise one or more couplers. Among these couplers, mention may be made especially of meta-phenylenediamines, meta-aminophenols, meta-diphenols, monophenols, naphthalene-based couplers and heterocyclic couplers, and also the addition salts thereof.

[0175] In general, the addition salts of the oxidation bases and couplers that may be used in the context of the invention are especially chosen from addition salts with an acid such as hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

[0176] The additional oxidation base(s) each advantageously represent from 0.0001% to 10% by weight relative to the total weight of the composition, and preferably from 0.005% to 5% by weight relative to the total weight of composition (A).

[0177] The content of coupler(s), if they are present, each advantageously represent from 0.0001% to 10% by weight relative to the total weight of the composition, and preferably from 0.005% to 5% by weight relative to the total weight of composition (A).

[0178] According to one embodiment of the invention, the composition comprises at least one oxidation base of formula (I) and/or (II) and at least one coupler, and preferably at least 10% of fatty substance. According to a particular embodiment, the fatty substance is liquid.

[0179] According to a particular embodiment, composition (A) comprises one or more nonionic, preferably oxyalkylenated, surfactants.

[0180] In accordance with a preferred embodiment of the invention, the surfactants are oxyalkylenated nonionic surfactants and are chosen from oxyethylenated C_8 - C_{30} alcohols, and polyoxyethylenated esters of saturated or unsaturated, linear or branched C_8 - C_{30} acids and of sorbitol.

[0181] Preferably, composition (A) comprises one or more nonionic surfactants.

[0182] The surfactant content of composition (A) more particularly represents from 0.1% to 50% by weight and preferably from 0.5% to 30% by weight relative to the weight of the composition under consideration.

[0183] Compositions (A) and/or (B) may also contain various adjuvants conventionally used in hair dye compositions, such as anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof; mineral thickeners, and in particular fillers such as clays or talc; organic thickeners with, in particular, anionic, cationic, nonionic and amphoteric polymeric associative thickeners other than the polymers previously mentioned; antioxidants; penetrants; sequestrants; fragrances; dispersants; film-forming agents; ceramides; preserving agents; opacifiers.

[0184] The above adjuvants are generally present in an amount for each of them of between 0.01% and 20% by weight relative to the weight of the composition under consideration.

[0185] According to one variant, composition (A) may comprise one or more mineral thickeners chosen from organophilic clays.

[0186] The organophilic clay can be chosen from montmorillonite, bentonite, hectorite, attapulgite, sepiolite and mixtures thereof. The clay is preferably a bentonite or a hectorite. [0187] These clays can be modified with a chemical compound chosen from quaternary amines, tertiary amines, amine acetates, imidazolines, amine soaps, fatty sulfates, alkylarylsulfonates and amine oxides, and mixtures thereof. [0188] Mention may be made, as organophilic clays, of quaternium-18 bentonites, such as those sold under the names Bentone 3, Bentone 38 and Bentone 38V by the company Rheox, Tixogel VP by the company United Catalyst and Claytone 34, Claytone 40 and Claytone XL by the company Southern Clay; stearalkonium bentonites, such as those sold under the names Bentone 27 by the company Rheox, Tixogel LG by the company United Catalyst and Claytone AF and Claytone APA by the company Southern Clay; quaternium-18/benzalkonium bentonites, such as those sold under the names Claytone HT and Claytone PS by the company Southern Clay; quaternium-18 hectorites, such as those sold under the names Bentone Gel DOA, Bentone Gel ECO5, Bentone Gel EUG, Bentone Gel IPP, Bentone Gel ISD, Bentone Gel SS71, Bentone Gel VS8 and Bentone Gel VS38 by the company Rheox, and Simagel M and Simagel SI 345 by the company Biophil.

[0189] When it is present, the mineral thickener represents from 1% to 30% by weight relative to the weight of the composition.

[0190] Advantageously, the composition is in the form of a gel or a cream.

[0191] Compositions (A), (A'), (B) or (C) may be anhydrous or aqueous.

[0192] More particularly, for the purposes of the invention, the expression "anhydrous cosmetic composition" means a cosmetic composition with a water content of less than 5% by weight, preferably less than 2% by weight and even more preferably less than 1% by weight relative to the weight of the said composition. It should be noted that the water in question is more particularly bound water, such as the water of crystallization in salts, or traces of water absorbed by the raw materials used in the production of the compositions according to the invention.

[0193] The term "aqueous composition" is intended to mean a composition comprising more than 5% by weight of water, preferably more than 10% by weight of water and even more advantageously more than 20% by weight of water.

[0194] Preferably, composition (A) is an aqueous composition.

[0195] Even more preferentially, the water concentration of composition (A) may range from 10% to 90% and better still from 20% to 80% of the total weight of the composition.

[0196] Compositions (A), (A'), (B) or (C) may optionally comprise one or more organic solvents.

[0197] Examples of organic solvents that may be mentioned include linear or branched C_2 - C_4 alkanols, such as ethanol and isopropanol; glycerol; polyols and polyol ethers, for instance 2-butoxyethanol, propylene glycol, dipropylene glycol, propylene glycol monomethyl ether, diethylene glycol monomethyl ether and monoethyl ether, and also aromatic alcohols, for instance benzyl alcohol or phenoxyethanol, and mixtures thereof.

[0198] The organic solvent(s), if they are present, represent a content usually ranging from 1% to 40% by weight and preferably from 5% to 30% by weight relative to the weight of the composition containing them.

[0199] The pH of compositions (A) and (B), if they are aqueous, ranges from 2 to 13. For composition (A), it preferably ranges from 6.5 to 12 and better still from 8 to 12. The pH

is adapted by using additional acidifying or basifying agents, such as those mentioned below.

[0200] Preferably, composition (A) comprises one or more alkaline agents. By way of example, mention may be made of mineral amines such as aqueous ammonia or organic amines. Organic amines chosen from alkanolamines such as monoal-kanolamines, dialkanolamines or trialkanolamines comprising one to three identical or different C_1 - C_4 hydroxyalkyl radicals, in particular monoethanolamine, are particularly suitable.

[0201] As indicated previously, composition (A) may result from the mixing of a composition (A') comprising one or more oxidation dyes as defined previously and a composition (C) comprising one or more oxidizing agents as defined previously. Compositions (A') and (C) are preferably aqueous. They may especially be in the form of direct or inverse emulsions

[0202] They may also result from the mixing of three compositions, the first two being compositions (A') and (B) above and the third composition being a composition (D) comprising at least one fatty substance as defined previously.

[0203] This composition (D) may be anhydrous or aqueous. It is preferably anhydrous.

[0204] Usually, the pH of the oxidizing composition (C), when it is aqueous, is less than 7.

[0205] In a first variant of the invention, composition (A) and composition (B), which composition (A) may result from the extemporaneous mixing of compositions (A'), (C) and optionally (D), are applied successively to wet or dry keratin fibres, with or without intermediate rinsing.

[0206] Preferably, according to this second variant, there is no intermediate rinsing.

[0207] Preferably, composition (B) is applied before composition (A).

[0208] The leave-on time of composition (B) on the keratin fibres may range from 5 to 15 minutes and is preferably 10 minutes.

[0209] In particular, composition (B) is applied to the keratin fibres and is left on for 10 minutes at room temperature.

[0210] Preferably, composition (B) is sprayed onto the keratin fibres.

[0211] In addition, composition (A) may be left in place on the keratin fibres for a time generally of about from 1 minute to 1 hour, preferably from 5 minutes to 40 minutes and preferably for 35 minutes.

[0212] The temperature during the process is conventionally between room temperature (between 15 and 25° C.) and 80° C. and preferably between room temperature and 60° C.

[0213] According to a preferred embodiment, composition (B) and then composition (A) are applied successively, and without intermediate rinsing, to wet or dry keratin fibres, and the fibres are then dried at a temperature ranging from room temperature to 60° C., preferably at 60° C.

[0214] The drying step may last from 5 to 20 minutes, preferably from 5 to 15 minutes, and in particular lasts 10 minutes

[0215] After the treatment, the human keratin fibres are optionally rinsed with water, optionally washed with a shampoo and then rinsed with water, before being dried or left to dry.

[0216] After the treatment, the keratin fibres are generally dried under a hood at a temperature ranging from 50 to 80° C.

[0217] According to one embodiment, the process for dyeing keratin fibres comprises the use:

[0218] (a) of a composition (B) comprising one or more metal catalysts chosen from transition metal salts, in particular organic acid salts of transition metals, and rare-earth metal salts, in particular mineral salts of rare-earth metals, preferably manganese salts,

[0219] (b) of an anhydrous composition (D) comprising one or more fatty substances chosen from liquid petroleum jelly, C_6 - C_{16} alkanes, polydecenes, liquid esters of fatty acids and/or of fatty alcohols, and liquid fatty alcohols, or mixtures thereof, preferably in an amount of greater than 35%,

[0220] (c) of a cosmetic composition (A') comprising one or more oxidation dyes of formula (I) and/or (II).

[0221] (d) of an oxidizing composition (C) comprising one or more oxidizing agents, and in which composition (B) is applied to the keratin fibres succesively and without intermediate rinsing and the keratin fibres are dried, followed by the application to the said fibres of the composition resulting from the extemporaneous mixing of compositions (A), (C) and (D).

[0222] According to a second embodiment, compositions (A) and (B) are mixed together, and the mixture made is then applied to wet or dry keratin fibres.

[0223] The first variant is preferred.

[0224] Finally, the invention relates to a multi-compartment device comprising a first compartment containing a composition (B) comprising one or more metal catalysts as defined previously, a second compartment containing a composition (A') comprising at least one oxidation base of formula (I) as defined previously, and a third compartment containing a composition (C) comprising one or more oxidizing agents as defined previously, preferably at least one fatty substance as defined previously being present in at least one of the compositions (A') or (C), preferentially such that, after mixing together compositions (A') and (C), the fatty substance content is greater than or equal to 10% by weight relative to the total weight of the mixture of compositions (A') and (C). According to a particular embodiment, the device comprises a fourth compartment comprising a composition (D) comprising one or more fatty substances, the said composition (D) being intended to be mixed with compositions (A') and (C), the content of fatty substances of the mixture (A'), (C) and (D) preferably being greater than or equal to 10% and more preferably greater than or equal to 20% by weight relative to the total weight of the mixture of compositions (A'), (C) and (D), composition (A') or (C) possibly containing one or more fatty substances.

[0225] The device is suitable for implementing the dyeing process according to the present invention.

[0226] The examples that follow serve to illustrate the invention without, however, being limiting in nature.

EXAMPLE 1

[0227] 1. Preparation of the Composition Based on Metal Salts

[0228] Composition (B1) based on metal salts is prepared (the amounts are expressed as weight percentages).

Composition B1	
Laureth-2	2 g
Decyl glucoside	2 g
Liquid petroleum jelly (mineral oil)	78.5 g

-continued

Composition B1	
PEG-150/decyl alcohol/SMDI copolymer (Aculyn 44 sold by Röhm & Haas)	0.5 g
Manganese gluconate (CAS No. 6485-39-8) Water	0.4 g qs 100 g

[0229] 2. Preparation of a Dye Composition A1

[0230] The dye composition is prepared at the time of the use by mixing:

[0231] 6.7 g of composition D1

[0232] 2.7 g of composition A'1 and A'2

[**0233**] 10 g of composition C1

Each of the compositions is described in the following tables, the amounts being expressed as weight percentages, unless otherwise mentioned.

Composition D1

[0234]

Liquid petroleum jelly	64.5
2-Octyldodecanol	11.5
Distearyldimethylammonium-modified hectorite	3
Propylene carbonate	1
Oxyethylenated (4 OE) sorbitan monolaurate	11
Glycol distearate	8
Oxyethylenated (2 OE) lauryl alcohol	1

Composition A'1 and A'2 Containing the Oxidation Base of Formula (I)

[0235]

	A'1	A'2
Oxidation base of formula (I)	20×10^{-3}	20×10^{-3}
5-amino 2-benzimidazolone	mol %	mol %
Coupler		20×10^{-3}
		mol %
Free monoethanolamine	14.37 g	14.37 g
Sodium metabisulfite	0.7 g	0.7 g
L-Ascorbic acid	0.25 g	0.25 g
EDTA	0.287 g	0.287 g
Propylene glycol	6.2 g	6.2 g
Ethanol	15 g	15 g
Hexylene glycol	3 g	3 g
Dipropylene glycol	3 g	3 g
Benzyl alcohol	5 g	5 g
Deionized water	qs 100 g	qs 100 g

Composition C1 (Oxidizing Agent)

[0236]

50% hydrogen peroxide solution	12
Liquid petroleum jelly	20
Cetylstearyl alcohol (30/70 C16/C18)	8
Oxyethylenated cetylstearyl alcohol (33 OE)	3
Tetrasodium pyrophosphate decahydrate	0.03
Sodium hexahydroxystannate	0.04
Diethylenetriaminepentaacetic acid, pentasodium	0.15
salt as a 40% aqueous solution	

-continued

Polydimethyldiallylammonium chloride at 40% in	0.5
water, non-stabilized	
Poly[(dimethyliminio)-1,3-	0.25
propanediyl(dimethyliminio)-1,6-hexanediyl	
dichloride] as an aqueous 60% solution	
Phosphoric acid	qs pH = 2
Oxyethylenated (4 OE) rapeseed acid amides	1.3
Vitamin E	0.1
Glycerol	0.5
Deionized water	qs 100

In composition A'2, the couplers below were used:

Couplers
Resorcinol
Hydroxybenzomorpholine
2-Methyl-5-hydroxyethylaminophenol
2,4-Diaminophenoxyethanol HCl
2-Methylresorcinol
4-Amino-2-hydroxytoluene
2-Amino-3-hydroxypyridine
5-Amino-6-chloro-o-cresol

[0237] I. Procedure

[0238] Composition (B1) based on metal salts is applied to locks of natural hair containing 90% white hairs (NG). The "composition/lock" bath ratio is respectively 1/1 (g/g). The leave-on time is 10 minutes at room temperature.

[0239] The locks of hair are then rinsed and dried manually.

[0240] Dye composition A1 is then applied by brush to each of the locks. The "composition/lock" bath ratio is respectively 1/1 (g/g). It is left to stand for 35 minutes at room temperature.

[0241] After this leave-on time, the locks of hair are washed with iNOA POST shampoo, rinsed and then dried under a hood at a temperature of 60° C.

[0242] II. Results

[0243] The colour of the locks was evaluated in the CIE L*a*b* system, using a Minolta Spectrophotometer CM3600D colorimeter. In this L*a*b* system, L* represents the intensity of the colour, a* indicates the green/red colour axis and b* indicates the blue/yellow colour axis. The lower the value of L*, the darker or more intense the colour.

[0244] a. Calculation of the Colour Power (DE*)

[0245] In the table below, the value of DE* is calculated from the values of L*a*b* according to equation (i) below:

$$DE^* = \sqrt{(L^* - L_o^*)^2 + (a^* - a_o^*)^2 + (b^* - b_o^*)^2}$$
 (i)

[0246] The dyeing power is measured from the values L*, a* and b* measured on locks of natural grey hair after dyeing or, alternatively, on locks of permanent-waved grey hair after dyeing, and L_0 *, a_0 * and b_0 * represent the values measured on natural undyed locks of grey hair or, respectively, on permanent-waved undyed locks of grey hair.

[0247] The greater the value of DE*, the greater the dyeing power. The results in terms of the build-up are collated in the following table.

Oxidation dyes used	Colour	Hair	L*	a*	b*	DE*
u	sing composit	ion A'1				
5-amino 2-benzimidazolone	matt yellow	NG	57.9	3.6	18.4	7.6
u	sing composit	ion A'2				
5-amino 2-benzimidazolone + resorcinol	auburn	NG	37.9	11.2	16.7	29.9
5-amino 2-benzimidazolone + hydroxybenzomorpholine	auburn	NG	43.3	12.5	19.1	25.9
5-amino 2-benzimidazolone + 2-methyl-5-	red	NG	51.8	11.7	19.7	18.6
hydroxyethylaminophenol 5-amino 2-benzimidazolone + 2,4-diaminophenoxyethanol HC1	nacreous brown	NG	22.2	8.57	2.9	45.6
5-amino 2-benzimidazolone + 2- methyl resorcinol	auburn	NG	43.1	11.8	17.2	25.4
5-amino 2-benzimidazolone + 4-amino-2-hydroxytoluene	red	NG	43.9	27.0	26.3	36.3
5-amino 2-benzimidazolone + 2-amino-3-hydroxypyridine	coppery	NG	53.5	15.6	29.6	24.9
5-amino 2-benzimidazolone + 5-amino-6-chloro-o-cresol	red	NG	46.6	19.3	16.5	26.6

[0248] Good dyeing power is obtained;

[0249] When the oxidation base of formula (I) is combined with a coupler, the coloration build-up is further improved, with a diversified range of tints depending on the combined couplers.

EXAMPLE 2

[0250] In this example, a composition as described previously is applied, using as oxidation base 5-amino-2-benzimidazolone combined with the coupler m-aminophenol or 6-hydroxyindole in composition A'2.

[0255] The variation in coloration of the locks between the protected part and the part exposed to light is measured by (ΔE) according to the following equation:

$$\Delta E = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$$

[0256] In this equation, L*, a* and b* represent the values measured after exposure to light and L_0 *, a_0 * and b_0 * represent the values measured without exposure.

[0257] The larger the value of ΔE , the greater the difference in colour of the lock with and without exposure, and, in the present case, the less resistant the coloration to light.

[0258] The results are collated in Table 1 below.

Dyes used	Colour	Hair	L*	a*	b*	DE*	Light- induced loss (% DE*)
5-Amino-2- benzimidazolone + m-aminophenol	Mahogany	NG	28.7	13.8	10.9	39.42	8.5
5-Amino-2- benzimidazolone + 6-hydroxyindole	Mahogany	NG	27.6	11.8	12.5	39.7	9.7

[0251] These compositions are applied after a step of pretreatment with composition B1 described previously and under the conditions of Example 1.

[0252] The locks thus obtained are subjected to a test of exposure to light according to the following protocol.

[0253] The dyed locks are exposed to light from a Xenotest alpha at about $1250 \, \text{W/m}^2$ between 300 and 800 nm. The level of humidity is set at 60%, one $\frac{1}{2}$ of the lock being protected from light using a cover. The test duration is 40 hours.

[0254] After the test, the colour of the protected part and of the part exposed to light of the locks is evaluated in the L*a*b* system, using a Minolta CM3600D® spectrophotometer (illuminant D65). In this L*a*b* system, the three parameters denote, respectively, the intensity luminance (L*), a* 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.

[0259] Good levels of mahogany coloration and also good levels of light fastness were thus obtained, which is confirmed by the colorimetric measurements (high DE values and low losses after exposure to light).

EXAMPLE 3

[0260] 1. Preparation of a Dye Composition A3

[0261] The dye composition is prepared at the time of the use by mixing:

[0262] 6.7 g of composition D1 of example 1 above

[0263] 2.7 g of composition A"2

[0264] 10 g of composition C1 as described in example 1

1

2

3

5

6

[0265] Composition A"2 containing the oxidation base of formula (II):

	A"2	
Oxidation base of formula (II)	20×10^{-3}	mol %
Free monoethanolamine	14.37	g
Sodium metabisulfite	0.7	g
L-Ascorbic acid	0.25	g
EDTA	0.287	g
Propylene glycol	6.2	g
Ethanol	15	g
Hexylene glycol	3	g
Dipropylene glycol	3	
Benzyl alcohol	5	
Deionized water	qs 100	g

[0266] In composition A"2, the oxidation bases below were used:

[0267] I. Procedure

[0268] Composition (B1) based on metal salts as described in example 1 is applied to locks of natural hair containing 90% white hairs (BN) and locks of permanent-waved hair containing 90% white hairs (BP). The "composition/lock" bath ratio is respectively 1/1 (g/g). The leave-on time is 10 minutes at room temperature.

[0269] The locks of hair are then rinsed and dried manually.
[0270] Dye composition A3 is then applied by brush to each of the locks. The "composition/lock" bath ratio is respectively 1/1 (g/g). It is left to stand for 35 minutes at room temperature.
[0271] An other group of locks is treated with composition

A3 only (no pre treatment with composition B1) [0272] After this leave-on time, the locks of hair are washed with iNOA POST shampoo, rinsed and then dried under a hood at a temperature of 60° C.

[0273] II. Results

[0274] The colour power (DE*) is evaluated according to the method of example 1.

Oxidation dyes used	Hair	L*	a*	b*	DE*		
Oxidation base 1							
Without pre-treatment	BN	47.0	1.4	11.8	19.4		
•	BP	44.3	1.2	13.9	24.8		
With pre-treatment (composition B1)	BN	38.5	5.7	11.6	26.0		
	BP	28.4	6.1	9.2	40.2		
Oxidation	base 2						
Without pre-traitement	BN	50.2	1.7	15.2	16.4		
	BP	46.6	1.4	15.2	22.5		
With pre-traitement (composition B1)	BN	28.2	4.5	7.1	36.4		
	BP	25.4	3.6	5.2	43.5		
Oxidation	base 3						
Without pre-traitement	BN	51.8	2.7	16.1	15.1		
Without pre traitement	BP	47.6	1.9	14.9	21.6		
With pre-traitement (composition 1)	BN	28.2	4.5	6.9	36.5		
with pre-distrement (composition 1)	BP	25.1	3.4	5.1	43.8		
Oxidation					,,,,		
Without pre-traitement	BN	51.4	2.0	14.8	15.2		
*****	BP	47.7	1.8	14.5	21.4		
With pre-traitement (composition B1)	BN	33.6	4.7	9.3	30.9		
0.11.1	BP	29.2	3.4	6.7	39.4		
Oxidation	base 5						
Without pre-traitement	BN	51.4	1.5	15.2	15.2		
	BP	50.6	1.0	15.4	18.5		
With pre-traitement (composition B1)	BN	29.7	4.7	7.7	34.9		
1 1 ,	BP	27.2	4.2	6.7	41.5		
Oxidation	base 6						
Without pre-traitement	BN	54.2	2.1	15.2	12.5		
without pre-tranement	BP	50.1	3.2	16.6	19.4		
With pre-traitement (composition B1)	BN	34.4	4.9	8.8	30.2		
with pre-transment (composition B1)	BP	27.3	4.5	6.8	41.3		
	DI	21.3	4.5	0.0	71.5		

The following was observed: without pre-treatment, a matt yellow reflection is obtained; with the pre-treatment with composition B1 followed with composition A3, a nacreous brown is obtained and the coloration build-up is further improved.

EXAMPLE 4

[0275] A dye composition A4 is prepared at the time of the use by mixing:

[0276] 6.7 g of composition D1 of example 1 above

[**0277**] 2.7 g of composition F

[0278] 10 g of composition C1 as described in example 1

A

[0279] Composition F:

	F
Oxidation base of formula (I) compound 1 Heterocyclic oxidation base A	$20 \times 10^{-3} \text{ mol } \%$
Free monoethanolamine Sodium metabisulfite L-Ascorbic acid Propylene glycol Ethanol Hexylene glycol Dipropylene glycol Benzyl alcohol	0.14 g 0.7 g 0.25 g 6.2 g 15.1 g 3 g 3 g 6 g
Deionized water	qs 100 g

In composition F, the following compounds were used:

Compound 1 H_{2N}

 NH_2 N N N

HYDROXYETHOXY AMINOPYRAZOLOPYRIDINE HCL (IMEXINE FAM from CHIMEX)

5-amino-2-benzimidazolone 95-23-3

[0280] I. Procedure

[0281] Composition (B1) based on metal salts as described in example 1 is applied to locks of natural hair containing 90% white hairs (BN) and locks of permanent-waved hair containing 90% white hairs (BP). The "composition/lock" bath ratio is respectively 1/1 (g/g). The leave-on time is 10 minutes at room temperature.

HO

[0282] Composition (B1) based on metal salts as described in example 1 is applied to locks of natural hair containing 90% white hairs (BN) and locks of permanent-waved hair containing 90% white hairs (BP). The "composition/lock" bath ratio is respectively 1/1 (g/g). The leave-on time is 10 minutes at room temperature.

[0283] The locks of hair are then rinsed and dried manually.[0284] Dye composition A3 is then applied by brush to each

[0284] Dye composition A3 is then applied by brush to each of the locks. The "composition/lock" bath ratio is respectively 1/1 (g/g). It is left to stand for 35 minutes at room temperature.

[0285] The locks of hair are then rinsed and dried manually.
[0286] Dye composition A4 is then applied by brush to each of the locks.

[0287] The "composition/lock" bath ratio is respectively 1/1 (g/g). It is left to stand for 35 minutes at room temperature.

[0288] Another group of locks is treated with composition A4 only (no pre treatment with composition B1)

[0289] After this leave-on time, the locks of hair are washed with iNOA POST shampoo, rinsed and then dried under a hood at a temperature of 60° C.

[0290] After that, the locks obtained are subjected to a test of coloration resistance to 10 shampoos according to the following cycle: damping with water, spinning, washing with shampoo, rinsing and drying

[0291] The colour of the hair was determined by using the L*a*b* system, with a MINOLTA CM3600D® spectrophotometer.

 ΔE , which is the color variation between a colored lock and a colored lock after 10 shampoos, is obtained from the following formula:

$$\Delta E = \sqrt{(L^* - L_o^*)^2 + (a^* - a_o^*)^2 + (b^* - b_o^*)^2}$$

wherein L* indicates lightness and a* and b* are the chromaticity coordinates of the colored locks after 10 shampoo whereas L_0^* indicates the lightness and a_0^* et b_0^* are the chromaticity of the colored locks. The lowest is the value of ΔE , the most resistant is the color of the hair.

TABLE 1

		Color	Color loss after 10 shampoos (% DE)					
Without pre treatment								
Compound 1 + base A	BN BP	Black	6.88 3.82					
With pre treatment with B1								
Compound 1 + base A	BN BP	Black	2.20 1.86					

[0292] The color loss is reduced with the pre-treatment with composition B1 containing a metal catalyst.

EXAMPLE 5

[0293] A dye composition A5 is prepared at the time of the use by mixing:

[0294] 6.7 g of composition D1 of example 1 above

[0295] 2.7 g of composition G

[0296] 10 g of composition C1 as described in example 1 [0297] Composition G:

	F
5-amino-2-benzimidazolone N,N-BIS(2-HYDROXYETHYL)-p- PHENYLENEDIAMINE SULFATE	$20 \times 10^{-3} \text{ mol } \%$ $20 \times 10^{-3} \text{ mol } \%$
Free monoethanolamine Sodium metabisulfite L-Ascorbic acid Propylene glycol Ethanol Hexylene glycol Dipropylene glycol	3.5 g 0.7 g 0.25 g 6.2 g 15 g 3 g 3 g
Benzyl alcohol Deionized water	5 g qs 100 g

[0298] Composition (B1) based on metal salts as described in example 1 is applied to locks of natural hair containing 90% white hairs (BN) and locks of permanent-waved hair containing 90% white hairs (BP). The "composition/lock" bath ratio is respectively 1/1 (g/g). The leave-on time is 10 minutes at room temperature.

[0299] The locks of hair are then rinsed and dried manually. [0300] Dye composition A5 is then applied by brush to each of the locks. The "composition/lock" bath ratio is respectively 1/1 (g/g). It is left to stand for 35 minutes at room temperature. [0301] Another group of locks is treated with composition A5 only (no pre treatment with composition B1).

[0302] After this leave-on time, the locks of hair are washed with iNOA POST shampoo, rinsed and then dried under a hood at a temperature of 60° C.

[0303] II. Results

The colour power (dE^*) is evaluated according to the method of example 1.

TABLE 1

		Color	L* (D65)	a* (D65)	b* (D65)	dE*ab (D65)
With pre treatment Without pre- treatment	BN BP BN BP	brown brown	30.66 24.99 32.86 29.77	6.21 8.04 5.47 7.46	6.51 7.98 6.97 7.88	32.32 39.86 29.97 35.11

With the pre-treatment with composition B1 followed with composition A5, the intensity and coloration build-up are improved.

1. Process for dyeing keratin fibres, comprising the use of one or more metal catalysts and of a composition (A) comprising:

one or more oxidizing agents, and

- at least one oxidation base chosen from:
- i) aminobenzimidazolones of formula (I), or an addition salt or solvate thereof

in which the radicals R1 to R5 represent, independently of each other:

- a hydrogen atom;
- a halogen atom, preferably chosen from F, Cl and Br;
- a linear or branched C1-C6 and preferably C1-C4 alkyl radical, which is optionally substituted, preferably with one or more OH, NH2 or CN groups, preferably OH;
- a linear or branched C1-C6 and preferably C1-C4 alkoxy radical, which is optionally substituted, preferably with one or more OH, NH2 or CN groups;
- a linear or branched C1-C6 and preferably C1-C4 dialkylamino radical, which is optionally substituted, preferably with one or more OH, NH2 or CN groups;
- a carboxylic radical (—COOH);
- a sulfonic radical (—SO3H);
- a phenyl radical, which is optionally substituted, preferably with:
 - a halogen atom, preferably a chlorine atom;
 - a linear or branched C1-C6 and preferably C1-C4 alkyl group, which is optionally substituted, preferably with one or more halogen atoms, in particular a fluorine atom;

- a linear or branched C1-C6 and preferably C1-C4 alkoxy group, which is optionally substituted, preferably with one or more halogen atoms, in particular a fluorine atom:
- a saturated or unsaturated 5- to 7-membered heterocyclic radical, comprising one or more heteroatoms chosen from N, O and S, which is optionally substituted, preferably with:
 - a linear or branched, optionally substituted C1-C6 and preferably C1-C4 alkyl group,
 - a saturated or unsaturated 5- to 7-membered heterocycle, comprising one or more heteroatoms chosen from N, O and S, preferably O; the said heterocycle possibly being fused with a saturated or unsaturated 5- to 7-membered, preferably 6, ring, optionally comprising one or more heteroatoms,
- ii) 2- or 3-aminoindolizines of formula (II)

$$R6$$
 $R7$
 $R1$
 $R2$
 $R5$
 $R4$
 $R3$

in which R1 to R7 independently represent a hydrogen atom, a C_1 - C_4 alkyl radical, an optionally substituted phenyl radical, a C_1 - C_4 alkoxy radical, a halogen atom, a carboxylic radical (—COOH or -alkyl-COOH), a carboxamide radical (CONRR'), a nitrile radical (—CN), a sulfone radical (—SO₂R), a sulfoxide radical (—SOR), a sulfonamide radical (—SO₂NRR'), an alkylcarbonyl radical (—CO-alkyl), an alkoxycarbonyl radical (—CO—O-alkyl), a benzoyl radical (—CO-phenyl or -alkyl-CO-phenyl optionally substituted on the phenyl group); R4 to R7 can form, in pairs in an adjacent position, an unsaturated or saturated, optionally substituted, 5- to 6-membered ring which may contain a heteroatom; with the supplementary condition that R2 or R3 represents an amino radical (NH₂).

and mixture thereof.

- 2. Process according to claim 1, characterized in that the metal catalysts are chosen from metal salts, metal oxides and metal complexes, and mixtures thereof.
- 3. Process according to claim 1 or 2, characterized in that the metal catalysts are chosen from transition metal salts and rare-earth metal salts, and also mixtures thereof.
- **4**. Process according to claim **2** or **3**, characterized in that the metal salts are mineral salts chosen from halides, carbonates, sulfates and phosphates, especially hydrated or anhydrous halides.
- 5. Process according to any one of claims 1 to 4, in which the metal catalyst(s) are chosen from metal salts bearing a metal in oxidation state II and two (poly)hydroxy acid-based ligands, particularly the metal salts are complexed with two carboxylate groups such as that of formula (II), and also the solvates thereof such as hydrates, and enantiomers thereof:

$$R - C(O) - O - M - O - C(O) - R'$$
 (II)

in which:

M represents a metal (II) or metal' in oxidation state 2, preferably manganese,

R and R', which may be identical or different, represent a (C1-C6)(poly)hydroxyalkyl group.

- **6.** Process according to claims **1** to **3**, characterized in that the metal salts are organic acid salts chosen from citrates, lactates, glycolates, gluconates, acetates, propionates, fumarates, oxalates and tartrates, especially gluconates.
- 7. Process according to any one of the preceding claims, characterized in that the metal catalysts are chosen from organic acid salts of transition metals, especially of manganese, and mineral salts of rare-earth metals, especially of cerium.
- 8. Process according to any one of the preceding claims, in which the composition comprises (A) at least one fatty substance, the amount of fatty substance preferably being at least 10% by weight relative to the total weight of composition (A).
- **9.** Process according to claim **8**, characterized in that the fatty substances are chosen from C_6 - C_{16} hydrocarbons or hydrocarbons comprising more than 16 carbon atoms, and in particular alkanes, oils of plant origin, fatty alcohols, fatty acid and/or fatty alcohol esters, and silicones, or mixtures thereof.
- 10. Process according to claim 8, characterized in that the fatty substance(s) are chosen from oils that are liquid at room temperature and at atmospheric pressure.
- 11. Process according to claim 8, characterized in that the fatty substances are chosen from liquid petroleum jelly, polydecenes, liquid fatty alcohols and liquid esters of fatty acids or of fatty alcohols, or mixtures thereof.
- 12. Process according to any one of the preceding claims, characterized in that the fatty substances, preferably in the form of oils, are present in a content ranging from 10% to 70% by weight, even more particularly ranging from 25% to 70% by weight, better still from 25% to 60% by weight and most particularly from 30% to 60% by weight relative to the total weight of composition (A).
- 13. Process according to any one of the preceding claims, characterized in that the cosmetic composition (A) also comprises one or more surfactants, which are preferably oxyalky-lenated nonionic surfactants.
- 14. Process according to any one of the preceding claims, characterized in that the oxidation base of formula (I) is chosen from the following compounds, salts thereof or solvates thereof:

$$\begin{array}{c} \text{H}_2\text{N} \\ \text{H}_2\text{N}$$

72735-26-3

2H-Benzimidazol-2-one,

5-amino-4-chloro-1,3-

dihydro

96222-58-1

5-Amino-7-bromo-

2-benzimidazolone

-continued

62419-32-3 5-Amino-6-carboxy-2benzimidazolone

73778-92-4 2(3)-Benzimidazolone 6-amino-1-methyl

52603-44-8 5-Amino-6-ethoxybenzimi dazolone H₂N H NH

926222-51-7 2H-Benzimidazol-2-one, 5-amino-1,3- dihydro-6-phenyl

$$Et_2N$$
 H_2N
 H_2N
 H_3N
 H_4N
 H_4N

1082251-13-5 2H-Benzimidazol-2-one, 5-amino-6-(diethylamino)-1,3- dihydro

$$\begin{array}{c} OMe \\ H\\ N \end{array}$$

101258-00-8 2-Benzimidazolol, 6-amino-4-methoxy

$$\bigcap_{H_2N} \bigvee_{NH} \bigcap_{NH} \bigcap_{NH$$

1082550-33-1 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(1-pyrrolidinyl)

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

1375064-85-9 6-Amino-5-methoxy-1-isopropyl-2-benzimidazolone -continued

$$\begin{array}{c|c} & H \\ \hline \\ N \\ \hline \\ NH_2 \\ \end{array}$$

1159693-98-7 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(1-piperidinyl)

1082508-66-4 2H-Benzimidazol-2-one, 5-amino-6-(hexahydro-1Hazepin-1-yl)-1,3-dihydro

$$\bigcap_{Me} \bigvee_{NH_2} \bigvee_{NH_2} \bigvee_{NH}$$

1082508-65-3 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(4-methyl-1-piperidinyl)

$$\underset{Me}{\overbrace{\hspace{1.5cm}N\hspace{0.5cm}\prod_{NH_2}\hspace{0.5cm}\overset{H}{\underset{NH}}\hspace{0.5cm}}}{\stackrel{H}{\underset{NH}}\hspace{0.5cm}}$$

1082387-49-2 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(4-methyl-1-piperazinyl)

926222-67-5 2H-Benzimidazol-2-one, 5-amino-6-[4-(1,1-dimethylethyl) phenyl]-1,3-dihydro

926224-11-5 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(2-thienyl)-

-continued
$$\stackrel{H}{\underset{NH_2}{\bigvee}}$$

1082550-34-2 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-(4-morpholinyl)

$$\underset{H_2N}{\overset{H}{\bigvee}} \circ \underset{(CH_2)_3 \longrightarrow OH}{\overset{C}{\bigvee}}$$

1217244-06-8 6-Amino-5-methoxy-1-(3-hydroxypropyl)-2-benzimidazolone

124424-20-0 6-Amino-5-methoxy-1-methyl-2-benzimidazolone

1082551-14-6 2H-Benzimidazol-2-one, 5-amino-6-(4-ethyl-1-piperazinyl)-1,3-dihydro

$$CI$$
 H_{2N}
 NH

926250-99-9 2H-Benzimidazol-2-one, 5-amino-6-(3,4-dichlorophenyl) -1,3-dihydro-

1082387-50-5 2H-Benzimidazol-2-one, 5-amino-6-(3,4-dihydro-2(1H))isoquinolinyl-1,3-dihydro-

926225-36-7 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-[3-(trifluoromethyl)phenyl]-

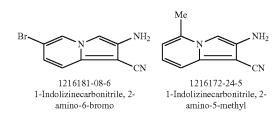
926253-29-4 2H-Benzimidazol-2-one, 5-amino-1,3-dihydro-6-[2-(trifluoromethoxy)phenyl]-I

$$H_{2N}$$

1347800-66-1 2H-Benzimidazol-2-one, 6-amino-1,3-dihydro-1-[1-(tetrahydro-2H-pyran-4-yl)-4-piperidinly]-

330991-27-0 1H-Benzimidazole, 5-sulfonic acid, 6-amino-2,3-dihydro-2-oxo

- **15**. Process according to any one of the preceding claims, characterized in that the compound of formula (I) is 5-amino-2-benzimidazolone, salts thereof or solvates thereof.
- **16.** Process according to any one of the preceding claims, characterized in that the oxidation base of formula (II) is chosen from 2-aminoindolizine.
- 17. Process according to any one of the preceding claims, characterized in that the oxidation base of formula (II) is chosen from the following compounds, salts thereof or solvates thereof:



1179499-93-4 1-Indolizineacetic acid, 2amino-3-(4-methoxybenzoyl)-7-methyl-

1179448-21-5 1-Indolizineacetic acid, 2amino-3-benzoyl-7-methyl

$$\begin{array}{c} \text{HO}_2\text{C} - \text{CH}_2 \\ \text{Me} \\ \text{N} \end{array}$$

1179390-33-0 1-Indolizineacetic acid, 2amino-3-(4-chlorobenzoyl)-7-methyl-

1071698-46-8 2-Indolizinamine, 7-methyl

63014-90-4 2-Indolizinecarbonitrile, 2-amino-7-methyl

$$\begin{array}{c} O \\ \parallel \\ C - OEt \\ N \\ \end{array}$$

63014-83-5 1-Indolizinecarboxylic acid, 3-acetyl-2-amino-7-methyl-, ethyl ester

$$\begin{array}{c} \text{CN} \\ \text{NH}_2 \\ \text{N} \\ \text{O} \end{array}$$

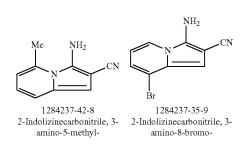
63014-78-8 1-Indolizinecarbonitrile, 2-amino-3-benzoyl-7-methyl

1-Indolizineacetic acid, 2amino-3-(4-chlorobenzoyl)-7-methyl

$$\begin{array}{c} CN \\ NH_2 \\ C \\ Ph \\ O \end{array}$$

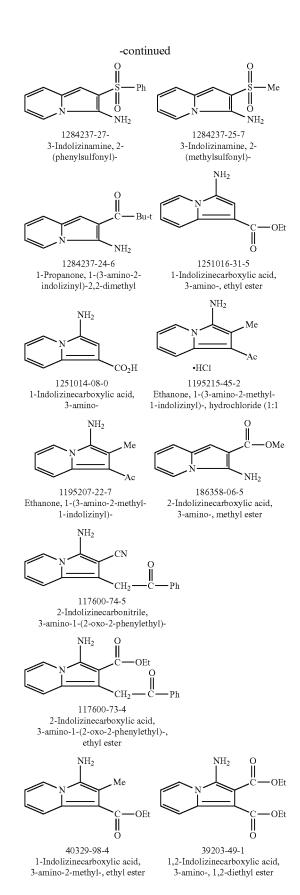
63014-78-8 1-Indolizinecarbonitrile, 2amino-3-benzoyl-7-methyl

- 18. Process according to any one claims 1 to 15, characterized in that the oxidation base of formula (II) is chosen from 3-aminoindolizine.
- 19. Process according to any one of claims 1 to 15, characterized in that the oxidation base of formula (II) is chosen from the following compounds, salts thereof or solvates thereof:



3-amino-1-methyl

3-amino



1284237-36-0

Pyrrolo[2,1-a]isoquinoline-2-carbonitrile, 3-amino

-continued
$$\mathbb{N}$$
 \mathbb{N} $\mathbb{N$

1284237-40-6 Pyrrolo[1,2-a][1,8]naphthyridine-8-carbonitrile, 9-amino-

186358-10-1 Pyrrolo[1,2-a]quinoline-8-carboxylic acid, 1-amino-, methyl ester

- 20. Process according to any one of the preceding claims, characterized in that the oxidizing agent is hydrogen peroxide
- 21. Process according to any one of the preceding claims, characterized in that a composition (B) comprising the said metal catalyst(s) and composition (A) are mixed together, and the mixture made is then applied to wet or dry keratin fibres.
- 22. Process according to any one of the preceding claims, characterized in that a composition (B) comprising the said metal catalyst(s) and composition (A) are successively applied to wet or dry keratin fibres, with or without intermediate rinsing, preferably without intermediate rinsing, and preferably composition (B) is applied before composition (A).
- 23. Process according to any one of the preceding claims, characterized in that composition (A) results from the mixing of two or three compositions including at least one composition (A') comprising one or more oxidation dyes and a composition (C) comprising one or more oxidizing agents and optionally a composition (D) comprising one or more fatty substances.
- **24**. Dye composition comprising at least one oxidation base of formula (I) and/or (II) as defined in any one of the preceding claims, at least 10% of fatty substance and an oxidizing agent.
- 25. Dye composition according to the preceding claim, characterized in that it comprises one or more fatty substances, preferably oils, in a concentration ranging from 10% to 70% by weight, even more particularly ranging from 25% to 70% by weight, better still from 25% to 60% by weight and most particularly from 30% to 60% by weight, relative to the total weight of the composition.

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