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(54) Title: COMPOSITION FOR DYEING KERATIN FIBRES, COMPRISING AT LEAST ONE FREE-RADICAL COMPOUND OF NITROXYL TYPE AND AT LEAST ONE PRIMARY OR SECONDARY ALCOHOL

(57) Abstract: The present invention relates to a dye composition for dyeing keratin fibres, in particular human keratin fibres such as the hair, comprising at least one free-radical compound of the nitroxyl type, at least one primary or secondary alcohol, optionally a nucleophilic agent, and optionally an oxidation catalyst. The invention also relates to the use of this composition for dyeing keratin fibres, and also to the process for dyeing keratin fibres using this composition.



WO 2004/056331 A1

**COMPOSITION FOR DYEING KERATIN FIBRES, COMPRISING AT
LEAST ONE FREE-RADICAL COMPOUND OF NITROXYL TYPE AND AT
LEAST ONE PRIMARY OR SECONDARY ALCOHOL**

The present invention relates to a dye
5 composition for dyeing keratin fibres, in particular
human keratin fibres such as the hair, comprising at
least one free-radical compound of nitroxyl type, at
least one primary or secondary alcohol, optionally a
nucleophilic agent, and optionally an oxidation
10 catalyst.

Two modes of dyeing exist in the field of
dyeing keratin fibres, in particular human keratin
fibres such as the hair, these modes each having their
advantages and drawbacks:

- 15 - *direct dyeing* or *semi-permanent dyeing* consists in
introducing the colour via a coloured molecule, which
is adsorbed onto the surface of the keratin fibres
and/or penetrates by diffusion into the surface layers
of these fibres. One of the advantages of this type of
20 dyeing is that mixing is not necessary at the time of
application. The leave-in times are generally fairly
short and the mild dyeing conditions preserve the
integrity of the keratin fibres, but the colorations
obtained by this mode of dyeing show poor wash fastness
25 and fade out after shampooing only 4 or 5 times.
Furthermore, the ranges of shades obtained are
generally small;

- oxidation dyeing or permanent dyeing uses the oxidative condensation of colourless or weakly coloured molecules, known as oxidation bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols or
5 heterocyclic compounds in the presence of an oxidizing agent. This reaction leads to the formation of insoluble coloured polymer compounds which are trapped in the keratin fibres. The main advantage of oxidation dyeing lies in the longevity of the colorations
10 obtained, in particular in the fastness to washing and to external agents such as light, bad weather, permanent waving, perspiration and rubbing, and also in the production of a wide range of shades. However, this type of dyeing entails mixing the oxidizing agent,
15 generally aqueous hydrogen peroxide, with oxidation bases at the time of use. Furthermore, the chemical dyeing conditions, such as the pH and an oxidizing medium, result in degradation of the keratin fibres. Moreover, this mode of dyeing requires relatively long
20 leave-in times.

To improve the fastness with respect to repeated shampooing and to reduce the sensitization of the hair by the use of an oxidizing agent, it has been proposed to dye the hair without an oxidizing agent, by
25 reacting an aldehyde or a ketone with a nucleophile. In particular, patents FR 2 787 708, FR 2 787 707, FR 2 787 705 and FR 2 787 706 describe the combination

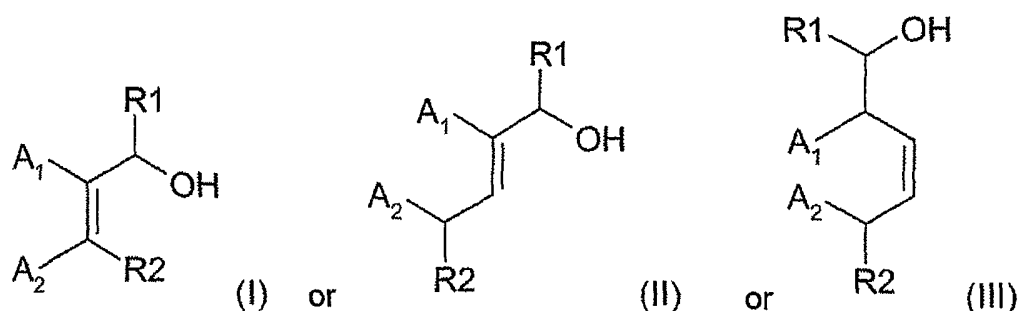
of an aldehyde or a ketone with, respectively, an activated methylene, a cationic derivative, an aliphatic cationic amine and a heterocyclic cationic amine.

5 However, these systems for dyeing via coloured reactions require the mixing, before application, of the aldehyde or the ketone and of the nucleophile, which cannot be stored in the same container without the coloured reaction starting.

10 The aim of the present invention is to provide a novel system for dyeing keratin fibres that does not require the mixing of an aldehyde or a ketone with a nucleophile at the time of application, that has good fastness properties, in particular with respect to
15 repeated washing, and that does not degrade hair fibres.

 This aim is achieved with the present invention, one subject of which is a dye composition for the oxidation dyeing of keratin fibres, comprising,
20 in a medium that is suitable for dyeing:

- at least one free-radical compound of nitroxyl type as oxidation mediator;
- at least one primary or secondary alcohol of formula (I), (II) or (III) and / or one of the addition salts
25 thereof:



in which:

- A_1 and A_2 , which may be identical or different,
 5 represent an aliphatic chain of 2 to 50 carbon
 atoms optionally comprising one or more hetero
 atoms chosen from nitrogen, sulphur, oxygen and
 phosphorus;
- A_1 and A_2 together form:
 - 10 - an unsaturated, aromatic or non-aromatic,
 fused or non-fused monocarbocyclic or
 polycarbocyclic group containing from 6 to 50
 carbon atoms;
 - 15 - an aromatic or non-aromatic, fused or non-
 fused, 5- to 30-membered monoheterocyclic or
 polyheterocyclic group containing one or more
 hetero atoms chosen from nitrogen, sulphur,
 oxygen and phosphorus;
 - 20 - these chains or rings optionally being
 substituted with the following groups: halo; C_1 - C_4
 alkyl optionally substituted with one or more
 hydroxyl, C_1 - C_4 alkoxy, carboxyl, hydrogenocarbonyl
 or C_1 - C_4 alkoxycarbonyl groups; hydroxyl; C_1 - C_4

alkoxy; amino; C₁-C₄ monoalkylamino or
dialkylamino; hydrogenocarbonyl; C₁-C₄
alkylcarbonyl; C₁-C₄ alkoxycarbonyl; nitro;
sulphonato; imidazolio; pyridinio; benzothiazolio;
5 trialkylammonio;
- R₁ represents a hydrogen atom; a C₁-C₄ alkyl
group;
- R₂ represents a hydrogen atom; a halo group; a
C₁-C₄ alkyl group optionally substituted with one
10 or more hydroxyl, C₁-C₄ alkoxy, carboxyl,
hydrogenocarbonyl or C₁-C₄ alkylcarbonyl groups; a
hydroxyl group; a C₁-C₄ alkoxy group; a C₁-C₄
monoalkylamino or dialkylamino group; a C₁-C₄
alkoxycarbonyl group; a C₁-C₄ hydrogenocarbonyl-
15 alkylcarbonyl group; a group of -CHR₃-OH type in
which R₃ may be a hydrogen atom or a C₁-C₄ alkyl
group.

This system makes it possible to generate the
aldehyde or ketone at the time of use of the
20 composition on the hair, in the presence of an
oxidizing agent, which may be atmospheric oxygen. The
aldehyde or ketone thus obtained can then react with a
nucleophile present in the hair or in the composition.

A subject of the present invention is also a
25 process for dyeing keratin fibres, in particular human
keratin fibres such as the hair, using the above

composition, and also a device for performing this process.

A subject of the present invention is also the use of the composition of the invention for the
5 oxidation dyeing of keratin fibres.

In the context of the present invention, the term "alkyl radical" (alk) means a linear or branched radical, for example methyl, ethyl, n-propyl, isopropyl or butyl. An alkoxy radical is a radical alk-O-, an
10 alkylcarbonyl radical is a radical alk-CO-, an alkoxy carbonyl radical is a radical alk-O-CO-, a monoalkylamino or dialkylamino radical is a radical (alk)_nN- with n = 1 or 2, a hydrogenocarbonylalkyl-carbonyl radical is a radical H-CO-alk-CO- with the
15 alkyl radical having the definition given above.

A sulphonato radical is an -SO₃⁻ radical. A trialkylammonio radical is a radical (alk)₃N⁺- with the alkyl radical having the definition given above. The imidazolio, pyridinio and benzothiazolio radicals are
20 the cationic radicals corresponding to the imidazolium, pyridinium and benzothiazolium cations.

A halo group denotes a halogen atom chosen from chlorine, bromine, iodine and fluorine.

A fused or non-fused, aromatic or non-
25 aromatic monocarbocyclic or polycarbocyclic group containing from 6 to 50 carbon atoms may be, for example, a benzene, naphthalene, anthracene or

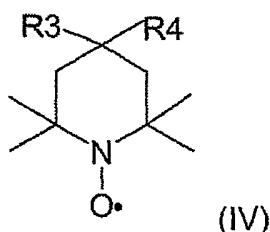
cyclohexane ring system. A 5- to 30-membered aromatic or non-aromatic, fused or non-fused, monoheterocyclic or polyheterocyclic group containing one or more hetero atoms may be, for example, a thiophene, benzofuran, 5 benzothiophene, indole, bipyridine, benzopyran, quinoline, pyrazole, pyridine, pyrrole, furan, imidazole or benzimidazole ring system. The polyheterocycle may be fused or substituted with one or more carbocycles.

10 According to one particular embodiment of the invention, the primary or secondary alcohol is chosen such that the radicals A₁ and A₂ together form a benzene nucleus.

 Preferably, the primary or secondary alcohol 15 is chosen from benzyl alcohol, 2-methylbenzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, 2-hydroxybenzyl alcohol, 1,2-di(hydroxymethyl)benzene, 1,3-di(hydroxymethyl)benzene and 1,4-di(hydroxymethyl)benzene.

20 According to one particular embodiment of the invention, the free-radical compound of nitroxyl type is a 2,2',6,6'-tetramethyl-N-oxylpiperidine derivative of formula (IV) and / or one of the addition salts thereof:

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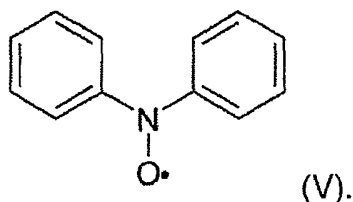
in which R_3 and R_4 , independently of each other, represent a monovalent group chosen from a hydrogen atom; a C_1 - C_4 alkyl group; a hydroxyl group; a C_1 - C_4 alkoxy group; a carboxyl group; a C_1 - C_4 alkoxycarbonyl group; a hydrogenocarbonyl group; an amino group; a C_1 - C_4 acylamino group; a C_1 - C_4 haloacylamino group; an isothiocyanato group; a maleimido group; a phosphonyloxy group; a C_1 - C_4 alkoxyhalophosphonyloxy group; a 4-nitrobenzoyloxy group; or R_3 and R_4 form, with the carbon atom to which they are attached, a carbonyl group.

Examples that may be mentioned include

- 2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-hydroxy-
- 2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-amino-
- 2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-acetamido-
- 2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-(2-bromoacetamido)-
- 2,2',6,6'-tetramethyl-N-oxylpiperidine,
- 4-(2-iodoacetamido)-2,2',6,6'-tetramethyl-N-oxylpiperidine,
- 4-ethoxyfluorophosphonyloxy-2,2',6,6'-tetramethyl-N-oxylpiperidine,
- 4-isothiocyanato-2,2',6,6'-tetramethyl-N-oxylpiperidine,
- 4-maleimido-2,2',6,6'-tetramethyl-N-oxylpiperidine,
- 4-(4-

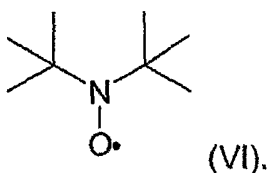
nitrobenzoyloxy)-2,2',6,6'-tetramethyl-N-oxypiperidine, 4-oxo-2,2',6,6'-tetramethyl-N-oxypiperidine and 4-phosphonyloxy-2,2',6,6'-tetramethyl-N-oxypiperidine. 2,2',6,6'-Tetramethyl-N-oxypiperidine, or TEMPO, is particularly preferred.

According to a second particular embodiment of the invention, the free-radical compound of nitroxyl type is N,N-diphenylnitroxyl of formula (V):



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According to a third particular embodiment of the invention, the free-radical compound of nitroxyl type is N,N-di-tert-butyl nitroxyl of formula (VI):

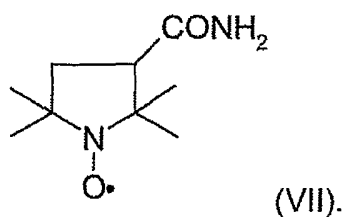


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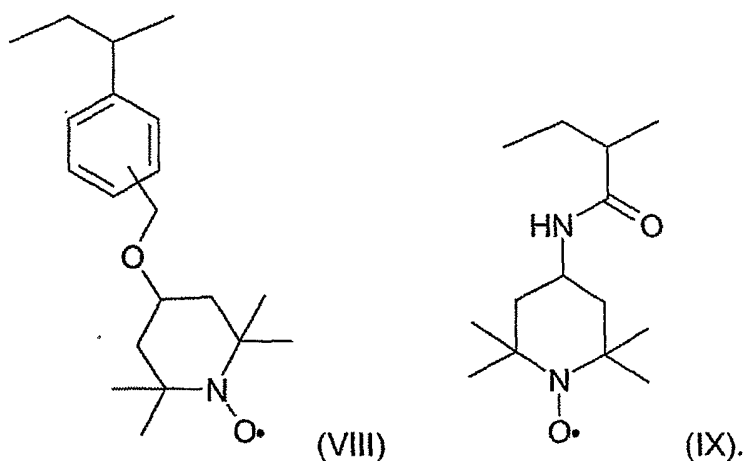
According to a fourth particular embodiment of the invention, the free-radical compound of nitroxyl type is 3-carbamoylproxylene of formula (VII):

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10



According to yet a different embodiment of the invention, the free-radical compound of nitroxyl
 5 type is in the form of a polymer containing at least one of the units of formula (VIII) or (IX) below:



10 In general, the addition salts that may be used in the context of the invention are chosen especially from the addition salts with an acid, such as the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates, tosylates, benzene-
 15 sulphonates, phosphates and acetates, and the addition salts with a base, such as sodium hydroxide, potassium hydroxide, ammonia, amines or alkanolamines.

The concentration of primary or secondary alcohol is generally between 0.01% and 30% by weight and preferably between 0.05% and 20% by weight relative to the total weight of the composition.

5 The concentration of free-radical compound of nitroxyl type is generally between 0.01% and 30% by weight and preferably between 0.05% and 20% by weight relative to the total weight of the composition.

 The dye composition of the invention may also
10 comprise a nucleophilic agent.

 According to one particular embodiment, the nucleophilic agent contains at least one amine, alcohol or activated methylene function. This nucleophilic agent is preferably an aromatic compound substituted
15 with an amine, alcohol or activated methylene function.

 The nucleophilic agent is preferably chosen from para-phenylenediamines, para-aminophenols, ortho-phenylenediamines, ortho-aminophenols, meta-phenylenediamines, meta-aminophenols, aminonaphthalenes,
20 aminohydroxynaphthalenes, triaminobenzenes, tetraamino-
benzenes, diaminophenols, triaminophenols, nitro-para-phenylenediamines, nitro-ortho-phenylenediamines, nitro-meta-phenylenediamines, nitroaminophenols, aminopyridines, aminohydroxypyridines, nitroanilines,
25 diaminodiphenylamines, aminopyrimidines, diamino-
pyrazoles, triaminopyrazoles, aminoindazoles, aminoindoles, aminobenzimidazoles, monohydroxyindoles,

dihydroxyindoles, dihydroxybenzenes, trihydroxybenzenes, hydroxynaphthalenes, monohydroxyindolines, dihydroxyindolines, basic amino acids, oligopeptides, protein hydrolysates, barbituric acids and pyrazolones.

5 When the composition comprises a nucleophilic agent, it is present in an amount generally of between 0.01% and 30% by weight and preferably between 0.05% and 20% by weight relative to the total weight of the composition.

10 The composition of the invention may furthermore contain at least one oxidation catalyst. This catalyst is preferably an oxidase enzyme, preferably a laccase or a peroxidase.

 The oxidase enzymes are obtained by
15 extraction or via biotechnology.

 Among the laccases that may be used according to the invention, mention may be made of laccases that may be obtained from plants: *Anacardiaceae* plants, *Podocarpaceae* plants, *Rosmarinus off.*, *Solanum*
20 *tuberosum*, *Iris sp.*, *Coffea sp.*, *Daucus carota*, *Vinca minor*, *Persea Americana*, *Catharethus roseus*, *Musa sp.*, *Malus pumila*, *Ginkgo biloba*, *Monotropa hypopithys*, *Aesculus sp.*, *Acer pseudoplatanus*, *Prunus persica*, *Pistacia palaestina* and from microorganisms: *Polyporus*
25 *versicolor*, *Rhizoctoniapraticola*, *Rhus vernicifera*, *Scytalidium*, *Polyporus pinsitus*, *Myceliophthora thermophila*, *Rhizoctonia solani*, *Pyricularia orizae*,

Trametes versicolor, *Fomes fomentarius*, *Chaetomium thermophile*, *Neurospora crassa*, *Colorius versicol*, *Botrytis cinerea*, *Rigidoporus lignosus*, *Phellinus noxius*, *Pleurotus ostreatus*, *Aspergillus nidulans*,
5 *Podospora anserina*, *Agaricus bisporus*, *Ganoderma lucidum*, *Glomerella cingulata*, *Lactarius piperatus*, *Russula delica*, *Heterobasidion annosum*, *Thelephora terrestris*, *Cladosporium cladosporioides*, *Cerrena unicolor*, *Coriolus hirsutus*, *Ceriporiopsis*
10 *subvermispora*, *Coprinus cinereus*, *Panaeolus papilionaceus*, *Panaeolus sphinctrinus*, *Schizophyllum commune*, *Dichomitius squalens*, *Acremonium murorum*, and variants thereof.

Among the peroxidases that may be used
15 according to the invention, mention may be made of peroxidases that may be obtained from microorganisms: *Aspergillus oryzae*, *Caldariomyces fumago*, *Inonotus weirii*, *Aspergillus flavus*, *Trametes versicolor*, *Aspergillus ochraceus*, *Phanerochaete chrysosporium*,
20 *Geotrichum candidum*, *Aspergillus parasiticus*, *Cochiliobolus heterostrophus*, *Phellinus pini*, *Phellinus chrysoloma*, *Phellinus weirii*, *Phytophthora palmivora*, *Merulius tremellosus*, *Phanerochaete flavido-alba*, *Phlebia radiata*, *Ceriporiopsis subvermispora*,
25 *Junghuhnia separabilima*, *Phanerochaete sordida*, *Pleurotus eryngii*, *Bjerkandera* sp., *Phlebia ochraceofulva*, *Nematoloma frowardii*, *Dichomitus*

squalens, *Phanerochaete chrysosporium*, *Pycnoporus cinnabarinus*, *Bjerkandera adusta*, *Trametes hirsuta*, *Arthromyces ramosus*, and variants thereof, and from plants: horseradish, *Arachis hypogea* (peanut), *Raphanus*
5 *sativus* (Japanese radish), *Sphagnum magellani*, *Nicotiana tabacum*.

When the composition comprises an oxidation catalyst, it is present in an amount generally of between 0.01% and 30% by weight and preferably between
10 0.05% and 20% by weight relative to the total weight of the composition.

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

The composition of the present invention may also comprise one or more oxidation bases conventionally used in oxidation dyeing. The
20 composition of the present invention may further comprise one or more couplers conventionally used in oxidation dyeing.

The medium that is suitable for dyeing, also known as the dye support, generally consists of water
25 or a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently soluble in water. The alcohols which are

useful in the invention may serve as solvents. The composition may however contain other alcohols as organic solvent. Mention may be made, for example, of C₁-C₄ lower alkanols, such as ethanol and isopropanol; 5 polyols and polyol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, and mixtures thereof.

The solvents are present in proportions 10 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.

The composition in accordance with the 15 invention can also contain various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic 20 polymers or mixtures thereof, inorganic or organic thickeners, and in particular anionic, cationic, nonionic or amphoteric associative polymeric thickeners, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing 25 agents, packaging agents such as, for example, silicones, which may or may not be volatile or modified

or unmodified, film-forming agents, ceramides, preserving agents and opacifiers.

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

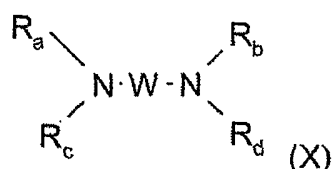
Needless to say, a person skilled in the art will take care to select this or these optional additional compounds such that the advantageous properties intrinsically associated with the oxidation dye composition in accordance with the invention are not, or are not substantially, adversely affected by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

The pH of the dye composition in accordance with the invention is generally between about 3 and 11 and preferably between about 4 and 10. It may be adjusted to the desired value using acidifying or basifying agents usually used in the dyeing of keratin fibres, or alternatively using standard buffer systems.

Among the acidifying agents which may be mentioned, for example, are inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid and lactic acid, and sulphonc acids.

Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and

triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (X) below:



5 in which W is a propylene residue which is optionally substituted with a hydroxyl group or a C₁-C₄ alkyl radical; R_a, R_b, R_c and R_d, which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical, or a C₁-C₄ hydroxyalkyl radical.

10 The dye composition according to the invention may be in various forms, such as in the form of liquids, creams or gels, or in any other form that is suitable for dyeing keratin fibres, and especially human hair.

15 The process for dyeing keratin fibres of the present invention consists in applying to the keratin fibres a composition comprising, in a medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type, at least one primary or secondary
20 alcohol, optionally a nucleophilic agent, and optionally an oxidation catalyst, and in developing the colour using an oxidizing agent.

According to one particular embodiment of the process of the invention, the oxidizing agent is

present in an oxidizing composition that is applied simultaneously or sequentially to the keratin fibres.

According to another particular embodiment of the process of the invention, the oxidizing agent is
5 added to the dye composition just at the time of its application.

According to one variant, the process of the invention consists in applying to the keratin fibres, sequentially and in any order, a first composition
10 comprising, in a medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type and at least one primary or secondary alcohol and a second composition comprising, in a medium that is suitable for dyeing, at least one nucleophilic agent, one of the
15 two compositions or both of them optionally comprising an oxidation catalyst, and then in applying an oxidizing composition comprising, in a medium that is suitable for dyeing, at least one oxidizing agent.

In these various embodiments, the application
20 of each of the compositions may optionally be followed by a rinsing operation.

The action time for each of the compositions is generally between 5 minutes and 1 hour and preferably between 5 minutes and 30 minutes.

25 The application temperature is generally set at between room temperature and 80°C and preferably between room temperature and 60°C.

The oxidizing agents used in the present invention are, for example, hydrogen peroxide, urea peroxide, persalts such as percarbonates, persulphates, perborates, 3-chloroperbenzoates and metal salts such as copper or iron salts, for instance copper II chloride.

If the oxidizing agent is present in an oxidizing composition, this composition may also contain various adjuvants conventionally used in hair dye compositions and as defined above, and its pH may be between 3 and 12 and preferably between 5 and 11. The oxidizing agent concentration is generally such that when the oxidizing composition is mixed with the other compositions, the oxidizing agent concentration in the composition obtained is between 0.01% and 30% by weight and preferably between 0.05% and 20% by weight relative to the total weight of the composition.

The various compositions applied to the keratin fibres may be in various forms, such as in the form of liquids, creams or gels, or in any other form that is suitable for dyeing keratin fibres, and especially human hair.

The oxidizing agent may also be atmospheric oxygen. In this case, the composition is stored in an anaerobic medium and is placed in contact with air at the time of use for dyeing keratin fibres. The invention then has an additional advantage, which is

that of not requiring mixing at the time of application.

A subject of the present invention is also a multi-compartment device for performing the process for
5 dyeing keratin fibres described above.

The multi-compartment device of the invention contains, in a first compartment, a composition comprising, in a medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type, at
10 least one primary or secondary alcohol, optionally a nucleophilic agent and optionally an oxidation catalyst, and, in a second compartment, a composition comprising, in a medium that is suitable for dyeing, at least one oxidizing agent.

15 According to one variant, the device contains, in a first compartment, a composition comprising, in a medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type and at least one primary or secondary alcohol, in a second
20 compartment, a composition comprising, in a medium that is suitable for dyeing, at least one oxidizing agent, and, in a third compartment, a composition comprising, in a medium that is suitable for dyeing, at least one nucleophilic agent.

25 According to one particular embodiment, one of the compositions present in the first and the third compartment or both comprises an oxidation catalyst.

According to one variant, the device contains, in a first compartment, a composition comprising, in a medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type, at
5 least one primary or secondary alcohol and at least one nucleophilic agent, in a second compartment, a composition comprising, in a medium that is suitable for dyeing, at least one oxidizing agent, and, in a third compartment, a composition comprising, in a
10 medium that is suitable for dyeing, at least one oxidation catalyst.

According to another variant, the device contains, in a first compartment, a composition comprising, in a medium that is suitable for dyeing, at
15 least one free-radical compound of nitroxyl type and at least one primary or secondary alcohol, in a second compartment, a composition comprising, in a medium that is suitable for dyeing, at least one oxidizing agent, in a third compartment, a composition comprising, in a
20 medium that is suitable for dyeing, at least one nucleophilic agent, and, in a fourth compartment, a composition comprising, in a medium that is suitable for dyeing, at least one oxidation catalyst.

A subject of the present invention is also an
25 anaerobically packaged aerosol containing a composition comprising, in a medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type, at

least one primary or secondary alcohol, optionally a nucleophilic agent and optionally an oxidation catalyst.

The primary or secondary alcohol does not
5 react with the nucleophilic compound and may be stored in the same container as the said compound.

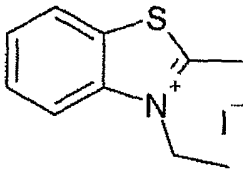
A subject of the present invention is also the use for dyeing keratin fibres of a composition comprising, in a medium that is suitable for dyeing, at
10 least one free-radical compound of nitroxyl type, at least one primary or secondary alcohol, optionally a nucleophilic agent, optionally an oxidation catalyst and optionally an oxidizing agent.

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

EXAMPLES

In the examples that follow, the amounts of the
20 compounds are expressed in grams per 100 g of composition (%) or in moles per 100 g of composition (mol%).

Example 1

Compound	Composition 1	Composition 2
Benzyl alcohol	10^{-2} mol%	10^{-2} mol%
	10^{-2} mol%	10^{-2} mol%
TEMPO	-	10^{-2} mol%
Laccase SP809 (Novo Nordisk)	10%	10%
Titrisol® pH 7 phosphate buffer	qs 100 g	qs 100 g

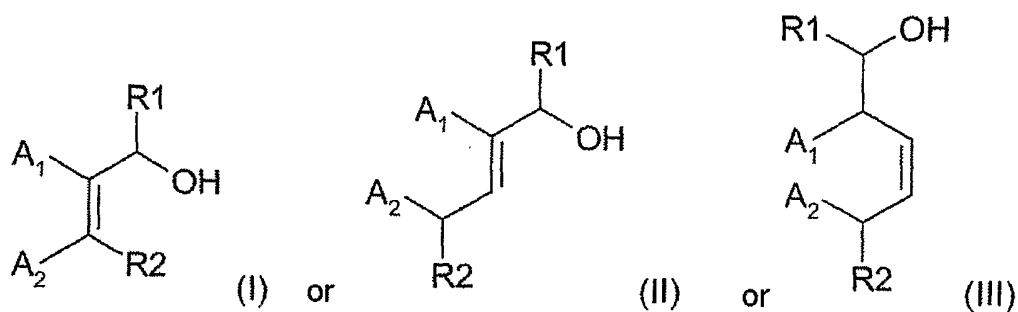
Compositions 1 and 2 are applied to white hair with a leave-in time of 30 minutes, to dewhiten
5 them.

CLAIMS

1. Dye composition for the oxidation dyeing of keratin fibres, comprising, in a medium that is suitable for dyeing:

- 5 - at least one free-radical compound of nitroxyl type as oxidation mediator;
 - at least one primary or secondary alcohol of formula (I), (II) or (III) and / or one of the addition salts thereof:

10



in which:

- A_1 and A_2 , which may be identical or different, represent an aliphatic chain of 2 to 50 carbon atoms optionally comprising one or more hetero atoms chosen from nitrogen, sulphur, oxygen and phosphorus;
- 15 - A_1 and A_2 together form:
- 20 - an unsaturated, aromatic or non-aromatic, fused or non-fused monocarbocyclic or polycarbocyclic group containing from 6 to 50 carbon atoms;

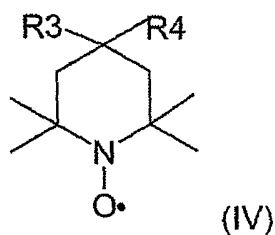
- an aromatic or non-aromatic, fused or non-fused, 5- to 30-membered monoheterocyclic or polyheterocyclic group containing one or more hetero atoms chosen from nitrogen, sulphur, oxygen and phosphorus;
- these chains or rings optionally being substituted with the following groups: halo; C₁-C₄ alkyl optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, hydrogenocarbonyl or C₁-C₄ alkoxycarbonyl groups; hydroxyl; C₁-C₄ alkoxy; amino; C₁-C₄ monoalkylamino or dialkylamino; hydrogenocarbonyl; C₁-C₄ alkylcarbonyl; C₁-C₄ alkoxycarbonyl; nitro; sulphonato; imidazolio; pyridinio; benzothiazolio; and trialkylammonio;
- R₁ represents a hydrogen atom; a C₁-C₄ alkyl group;
- R₂ represents a hydrogen atom; a halo group; a C₁-C₄ alkyl group optionally substituted with one or more hydroxyl, C₁-C₄ alkoxy, carboxyl, hydrogenocarbonyl or C₁-C₄ alkylcarbonyl groups; a hydroxyl group; a C₁-C₄ alkoxy group; a C₁-C₄ monoalkylamino or dialkylamino group; a C₁-C₄ alkoxycarbonyl group; a C₁-C₄ hydrogenocarbonyl-alkylcarbonyl group; a group of -CHR₃-OH type in which R₃ may be a hydrogen atom or a C₁-C₄ alkyl group.

2. Composition according to Claim 1, in which the primary or secondary alcohol is such that A₁ and A₂ together form a benzene nucleus.

3. Composition according to Claim 2, in which the primary or secondary alcohol is chosen from benzyl alcohol, 2-methylbenzyl alcohol, 2-aminobenzyl alcohol, 3-aminobenzyl alcohol, 4-aminobenzyl alcohol, 2-hydroxybenzyl alcohol, 1,2-di(hydroxymethyl)benzene, 1,3-di(hydroxymethyl)benzene and 1,4-di(hydroxymethyl)benzene.

4. Composition according to any one of the preceding claims, in which the free-radical compound of nitroxyl type is chosen from 2,2',6,6'-tetramethyl-N-oxylpiperidine derivatives; N,N-diphenylnitroxyl; N,N-di-*tert*-butylnitroxyl; 3-carbamoylproxylene; polymers containing at least one group derived from 2,2',6,6'-tetramethyl-N-oxylpiperidine.

5. Composition according to Claim 4, in which the free-radical compound of nitroxyl type is a 2,2',6,6'-tetramethyl-N-oxylpiperidine derivative of formula (IV) and / or one of the addition salts thereof:



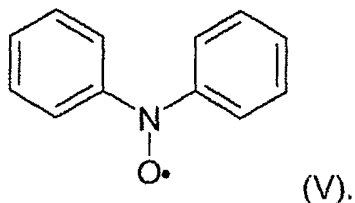
in which R₃ and R₄, independently of each other, represent a monovalent group chosen from a hydrogen atom; a C₁-C₄ alkyl group; a hydroxyl group; a C₁-C₄ alkoxy group; a carboxyl group; a C₁-C₄ alkoxycarbonyl group; a hydrogenocarbonyl group; an amino group; a C₁-C₄ acylamino group; a C₁-C₄ haloacylamino group; an isothiocyanato group; a maleimido group; a phosphonyloxy group; a C₁-C₄ alkoxyhalophosphonyloxy group; a 4-nitrobenzoyloxy group; or R₃ and R₄ form, with the carbon atom to which they are attached, a carbonyl group.

6. Composition according to Claim 5, in which the free-radical compound of nitroxyl type is chosen from 2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-hydroxy-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-amino-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-acetamido-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-(2-bromoacetamido)-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-(2-iodoacetamido)-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-ethoxyfluorophosphonyloxy-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-isothiocyanato-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-maleimido-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-(4-nitrobenzoyloxy)-2,2',6,6'-tetramethyl-N-oxylpiperidine, 4-oxo-2,2',6,6'-tetramethyl-N-

oxylpiperidine and 4-phosphonyloxy-2,2',6,6'-tetramethyl-N-oxylpiperidine.

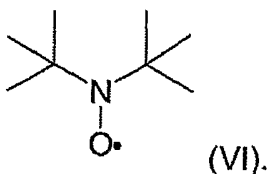
7. Composition according to Claim 6, in which the free-radical compound of nitroxyl type is
5 2,2',6,6'-tetramethyl-N-oxylpiperidine.

8. Composition according to Claim 4, in which the free-radical compound of nitroxyl type is N,N-diphenylnitroxyl of formula (V):



10

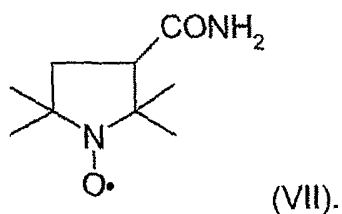
9. Composition according to Claim 4, in which the free-radical compound of nitroxyl type is N,N-di-tert-butyl nitroxyl of formula (VI):



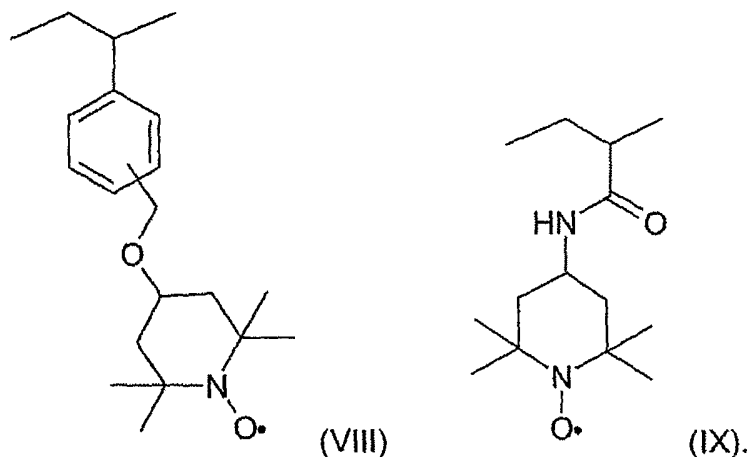
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10. Composition according to Claim 4, in which the free-radical compound of nitroxyl type is 3-carbamoylproxylene of formula (VII):
20

29



11. Composition according to Claim 4, in which the free-radical compound of nitroxyl type is in the form of a polymer containing at least one of the units of formula (VIII) or (IX) below:



12. Composition according to any one of the preceding claims, in which the concentration of primary or secondary alcohol is between 0.01% and 30% by weight relative to the total weight of the composition.

13. Composition according to any one of the preceding claims, in which the concentration of free-radical compound of nitroxyl type is between 0.01% and 30% by weight relative to the total weight of the composition.

14. Composition according to any one of the preceding claims, comprising a nucleophilic agent.

15. Composition according to Claim 14, in which the nucleophilic agent contains at least one
5 amine, alcohol or activated methylene function.

16. Composition according to Claim 15, in which the nucleophilic agent is an aromatic compound.

17. Composition according to Claim 15, in which the nucleophilic agent is chosen from para-
10 phenylenediamines, para-aminophenols, ortho-phenylenediamines, ortho-aminophenols, meta-phenylenediamines, meta-aminophenols, aminonaphthalenes, aminohydroxynaphthalenes, triaminobenzenes, tetraaminobenzenes, diaminophenols, triaminophenols, nitro-para-
15 phenylenediamines, nitro-ortho-phenylenediamines, nitro-meta-phenylenediamines, nitroaminophenols, aminopyridines, aminohydroxypyridines, nitroanilines, diaminodiphenylamines, aminopyrimidines, diamino-pyrazoles, triaminopyrazoles, aminoindazoles,
20 aminoindoles, aminobenzimidazoles, monohydroxyindoles, dihydroxyindoles, dihydroxybenzenes, trihydroxybenzenes, hydroxynaphthalenes, monohydroxyindolines, dihydroxyindolines, basic amino acids, oligopeptides, protein hydrolysates, barbituric acids and pyrazolones.

25 18. Composition according to any one of Claims 14 to 17, in which the concentration of

nucleophilic agent is between 0.01% and 30% by weight relative to the total weight of the composition.

19. Composition according to any one of the preceding claims, comprising an oxidation catalyst.

5 20. Composition according to Claim 19, in which the oxidation catalyst is chosen from oxidase enzymes such as laccase and peroxidase.

21. Composition according to Claim 19 or 20, in which the concentration of oxidation catalyst is
10 between 0.01% and 30% by weight relative to the total weight of the composition.

22. Composition according to any one of the preceding claims, comprising an oxidizing agent.

23. Composition according to Claim 22, in
15 which the oxidizing agent is chosen from hydrogen peroxide, urea peroxide, persalts and metal salts.

24. Composition according to Claim 22 or 23, in which the concentration of oxidizing agent is between 0.01% and 30% by weight relative to the total
20 weight of the composition.

25. Process for dyeing keratin fibres, characterized in that a composition comprising, in a medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type as defined in any one
25 of Claims 1 and 4 to 11 and at least one primary or secondary alcohol as defined in any one of Claims 1 to

3 is applied to the keratin fibres and the colour is developed using an oxidizing agent.

26. Process according to Claim 25, in which the composition also comprises a nucleophilic agent as
5 defined in any one of Claims 14 to 17.

27. Process according to Claim 25 or 26, in which the composition also comprises an oxidation catalyst as defined in Claim 19 or 20.

28. Process according to Claim 25, in which
10 a second composition comprising, in a medium that is suitable for dyeing, at least one nucleophilic agent as defined in any one of Claims 14 to 17 is applied to the keratin fibres.

29. Process according to Claim 28, in which
15 at least one of the compositions applied to the keratin fibres comprises an oxidation catalyst as defined in Claim 19 or 20.

30. Process according to any one of Claims 25 to 29, in which the oxidizing agent is present in an
20 oxidizing composition applied simultaneously or sequentially.

31. Process according to Claim 30, in which the oxidizing agent is chosen from hydrogen peroxide, urea peroxide, persalts and metal salts.

25 32. Process according to Claim 30 or 31, in which the keratin fibres are rinsed between the application of each of the compositions.

33. Process according to any one of Claims 25 to 27, in which the oxidizing agent is added to the dye composition just at the time of application.

34. Process according to Claim 33, in which
5 the oxidizing agent is chosen from atmospheric oxygen, hydrogen peroxide, urea peroxide, persalts and metal salts.

35. Multi-compartment device containing, in a first compartment, a composition comprising, in a
10 medium that is suitable for dyeing, at least one free-radical compound of nitroxyl type as defined in any one of Claims 1 and 4 to 11 and at least one primary or secondary alcohol as defined in any one of Claims 1 to 3, and, in a second compartment, a composition
15 comprising, in a medium that is suitable for dyeing, at least one oxidizing agent.

36. Device according to Claim 35, in which the composition present in the first compartment also comprises a nucleophilic agent as defined in any one of
20 Claims 14 to 17.

37. Device according to Claim 35 or 36, in which the composition present in the first compartment also comprises an oxidation catalyst as defined in Claim 19 or 20.

25 38. Device according to Claim 35, containing, in a third compartment, a composition comprising, in a medium that is suitable for dyeing, at

least one nucleophilic agent as defined in any one of Claims 14 to 17.

39. Device according to Claim 38, in which one of the compositions present in the first and third
5 compartment or both also comprises an oxidation catalyst as defined in Claim 19 or 20.

40. Device according to Claim 36, containing, in a third compartment, a composition comprising, in a medium that is suitable for dyeing, at
10 least one oxidation catalyst as defined in Claim 19 or 20.

41. Device according to Claim 38, in which a fourth compartment contains a composition comprising, in a medium that is suitable for dyeing, at least one
15 oxidation catalyst as defined in Claim 19 or 20.

42. Anaerobically packaged aerosol containing a composition as defined in any one of Claims 1 to 21.

43. Use for dyeing keratin fibres of a
20 composition as defined in any one of Claims 1 to 24.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/15039

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/13

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 378 544 A (OREAL) 7 January 2004 (2004-01-07) paragraphs '0045!', '0105!', '0147!; claim 22 ---	1-43
A,P	WO 03 053375 A (HENKEL KGAA ; NAUMANN FRANK (DE); GABLER MATTHIAS (DE); KAINZ SABIN) 3 July 2003 (2003-07-03) claims 3,10 -----	1-43

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

31 March 2004

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/15039

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1378544	A	07-01-2004	FR 2841901 A1	09-01-2004
			EP 1378544 A2	07-01-2004
			WO 2004005407 A2	15-01-2004
WO 03053375	A	03-07-2003	DE 10163052 A1	17-07-2003
			WO 03053375 A1	03-07-2003