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(54) Title: METHOD FOR STRIPPING THE ARTIFICIAL COLOUR FROM KERATIN FIBRES WITH DIHYDROXYISOQUINOLINIUM SALTS

(57) Abstract: The present invention relates to a method for stripping the artificial colour from keratin fibres such as the hair with dihydroxyisoquinolinium salts, and also to the use of dihydroxyisoquinolinium salts for stripping the artificial colour from human keratin fibres such as the hair.



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Description

Title of the invention: METHOD FOR STRIPPING THE ARTIFICIAL COLOUR FROM KERATIN FIBRES WITH DIHYDROXYISOQUINOLINIUM SALTS

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The present invention relates to a method for stripping the artificial colour from human keratin fibres such as the hair, using a composition comprising one or more dihydroxyisoquinolinium salts, and also to the use of a composition comprising one or more dihydroxyisoquinolinium salts for stripping the artificial colour from human keratin fibres such as the hair.

10

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

It is known practice to dye keratin fibres, in particular human keratin fibres such as the hair, to obtain "permanent" colourings with dyeing compositions containing oxidation dye precursors, which are generally known as oxidation bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols, or heterocyclic compounds such as pyrazoles, pyrazolinones or pyrazolo-pyridines. These oxidation bases are colourless or weakly coloured compounds which, when combined with oxidizing products, may give rise to coloured compounds via a process of oxidative condensation.

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

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The second type of dyeing is "semi-permanent" dyeing or direct dyeing, which consists in applying, to the keratin fibres, direct dyes, which are coloured and colouring molecules that have affinity for said fibres, in leaving them on for a time, and then in rinsing them off.

30

In order to perform these dyeing operations, the direct dyes generally used are chosen from nitrobenzene, anthraquinone, nitropyridine, azo, xanthene, acridine, azine and triarylmethane direct dyes, and natural dyes.

To vary the shades obtained in oxidation dyeing, or to enrich them with tints, oxidation dyes may be used in combination with direct dyes.

The term "direct dye" means natural and/or synthetic dyes, other than oxidation dyes. They are dyes that will superficially diffuse on the fibre and dye the fibres by themselves.

The direct dye(s) may be natural or synthetic, cationic, anionic or non-ionic direct dyes.

The term "natural dyes" or "dyes of natural origin" is intended to mean dyes derived from natural materials (plant, mineral or animal origin), for instance extracts, ground material and decoctions, which have a greater or smaller concentration of dyes.

Among the natural dyes are included compounds that may be present in nature and that are reproduced by chemical (semi)synthesis.

The natural dyes may be chosen especially from spinulosin, orceins, polyphenols or ortho-diphenols (also known as ODPs in the rest of the description) and all extracts rich in ODPs, curcumin, indole derivatives such as isatin or indole-2,3-dione, indigoids including indigo, phthalocyanines and porphyrins in particular complexed to a metal, glycosyl or non-glycosyl iridoids, chromene dyes, anthraquinone and naphthoquinone dyes such as lawsone or henna, juglone, spinulosin, chromene or chroman dyes, such as neoflavanols and neoflavanones, flavanols; and anthocyanidols. Use may also be made of extracts or decoctions containing these natural dyes and especially plant extracts or poultices containing said dyes.

For various reasons, such as the wish to partially or totally modify the shade thus given to the head of hair by oxidation dyeing or direct dyeing, or the wish to remove this colouration, the user may be led to partially or totally destroy the dyes thus formed or introduced into or onto the hair. Stripping of the artificial colour of the keratin fibres is then performed.

The term “artificial colour” is intended to mean a colour obtained by means of the two types of dyeing described above.

This stripping is generally performed via methods using oxidizing or reducing systems.

5 However, the prior art stripping techniques, which use peroxygenated reagents such as persulfates, perborates or percarbonates of ammonium or of alkali metals, that are combined at the time of use with an aqueous composition of hydrogen peroxide, are often very aggressive and modify the chemical structure of keratin.

10 This results in poor cosmetic properties of the hair, such as difficulty in disentangling, an unpleasant feel or rough and dull hair, but especially a degradation of the keratin fibres.

This fibre degradation is particularly undesirable since it irreversibly deteriorates the physicochemical properties of the hair. Said hair becomes more porous and
15 consequently more difficult to dry, it exhibits a greater sensitivity to various other hair treatments such as dyeing or permanent-waving, and it experiences an unfavourable modification of its mechanical properties and its surface properties, which results for example in a decrease in the tensile breaking strength or an increase in the coefficient of friction.

20 There is thus a real need to provide a method which makes it possible to overcome these drawbacks.

The applicant has thus discovered, surprisingly, that the use of dihydroxyisoquinolinium salts for stripping the artificial colour from human keratin fibres, preferably the hair, makes it possible to overcome the drawbacks
25 described above.

A subject of the invention is thus a method for stripping the artificial colour from human keratin fibres such as the hair, which comprises applying to said artificially dyed fibres, a composition comprising one or more dihydroxyisoquinolinium salts as defined below by formulae (I) and (II).

30 Another subject of the invention is a method implementing:

- a step of dyeing human keratin fibres such as the hair using a dye composition comprising one or more dyes chosen from oxidation dyes and/or direct dyes,
- a step of stripping the artificial colour from said fibres using a composition comprising one or more dihydroxyisoquinolinium salts as defined below.

5 Finally, a subject of the invention is the use of a composition comprising one or more dihydroxyisoquinolinium salts as defined below, for stripping the artificial colour from human keratin fibres such as the hair.

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

In the text hereinbelow, unless otherwise indicated, the limits of a range of values are included in that range, notably in the expressions "*between*" and "*ranging from ... to ...*".

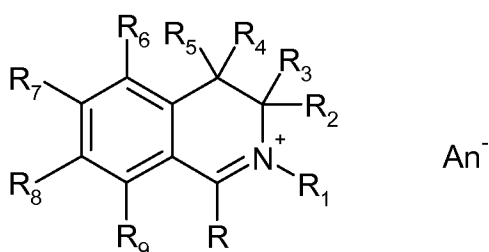
15 The expression "*at least one*" used in the present description is equivalent to the expression "*one or more*".

For the purposes of the present invention, the expression "stripping the artificial colour from human keratin fibres such as the hair" is intended to mean removing the artificial colour from human keratin fibres such as the hair, previously dyed using an oxidation dyeing and/or direct dyeing composition.

20 The stripping method differs from a method for bleaching or lightening keratin fibres such as the hair which aims to degrade the melanin pigments of the hair.

In the context of the invention, use is made of one or more compounds of formula (I) or (II) and also the addition salts thereof and the solvates thereof, for stripping the artificial colour from human keratin fibres such as the hair:

25 formula (I)



in which:

- R represents:

- a hydrogen atom,
- a linear or branched C₁-C₁₂ alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, C₁-C₆ alkoxy, cyano and amino –NR₁₀R₁₁ groups,

- R₁ represents:

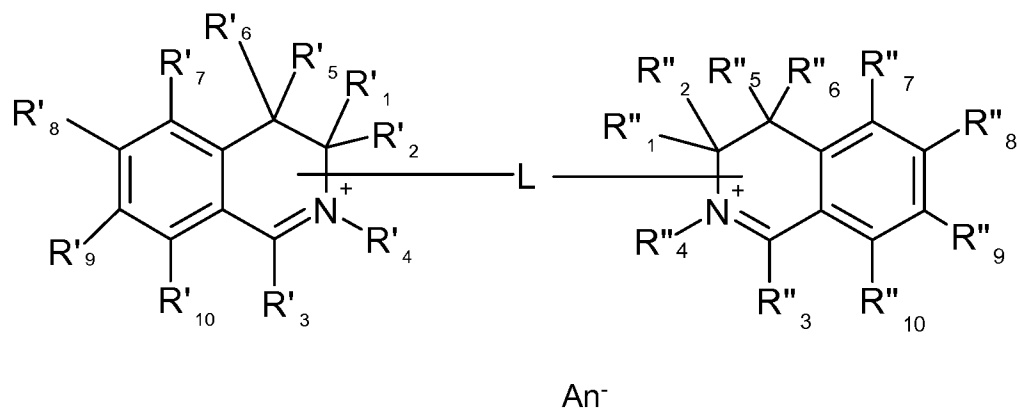
- a linear or branched, unsubstituted C₁-C₁₂ alkyl radical,
- a linear or branched C₁-C₂₀ alkyl radical, substituted with a group chosen from:

- a hydroxyl group,
- a C₁-C₆ alkoxy group,
- an amino group –NR₁₀R₁₁,
- an amino group – NR₁₂R₁₃,
- a carboxyl group –COOH,
- a cyano group,
- a halogen atom,
- an aminocarbonyl group –CONH₂,
- a (C₁-C₆)alkoxycarbonyl group,
- a saturated or unsaturated, optionally aromatic, 5- or 6-membered heterocycle, optionally substituted with one or more radicals, which may be identical or different, chosen from:
 - a linear or branched C₁-C₆ alkyl radical,
 - a linear or branched C₁-C₆ hydroxyalkyl radical,
 - a C₁-C₆ alkoxy radical,
 - a hydroxyl radical,

- an amino radical $\text{--NR}_{10}\text{R}_{11}$,
 - a pyrrolidine, piperidine or morpholine radical,
 - an ammonium radical $\text{N}^+\text{R}_a\text{R}_b\text{R}_c$ in which R_a , R_b and R_c denote, independently of one another, a linear or branched $\text{C}_1\text{--C}_6$ alkyl radical or a $\text{C}_1\text{--C}_6$ hydroxyalkyl radical,
- a saturated or unsaturated, optionally aromatic, 5- or 6-membered cationic heterocycle optionally substituted with one or more radicals, which may be identical or different, chosen from a linear or branched $\text{C}_1\text{--C}_6$ alkyl radical, a $\text{C}_1\text{--C}_6$ hydroxyalkyl radical, a $\text{C}_1\text{--C}_6$ alkoxy radical, a hydroxyl radical and an amino radical $\text{--NR}_{10}\text{R}_{11}$,
 - an ammonium radical $\text{N}^+\text{R}_a\text{R}_b\text{R}_c$ in which R_a , R_b and R_c denote, independently of one another, a linear or branched $\text{C}_1\text{--C}_6$ alkyl radical or a $\text{C}_1\text{--C}_6$ hydroxyalkyl radical,
 - it being understood that when R_1 represents an alkyl radical substituted with a cationic group, then the electrical neutrality of the compounds of formula (I) is ensured by the presence of one or more anions X^- , X^- adding to the anion An^- ,
- R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 represent, independently of one another, a radical chosen from:
 - a hydrogen atom,
 - a halogen atom,
 - a linear or branched $\text{C}_1\text{--C}_6$ alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, $\text{C}_1\text{--C}_6$ alkoxy and amino $\text{--NR}_{10}\text{R}_{11}$ groups,
 - a $\text{C}_1\text{--C}_6$ alkoxy radical,
 - a hydroxyl radical,
 - an amino radical $\text{--NR}_{10}\text{R}_{11}$,
 - an aminocarbonyl radical --CONH_2 ,
 - a carboxyl radical --COOH ,

- R_{10} and R_{11} , which may be identical or different, denote a hydrogen atom or a linear or branched C_1 - C_6 alkyl radical,
- R_{12} and R_{13} , which may be identical or different, denote a linear or branched C_1 - C_6 alkyl radical, substituted with a hydroxyl group;

5 formula (II)



in which:

- $R'_1, R'_2, R'_3, R'_5, R'_6, R'_7, R'_8, R'_9, R'_{10}, R''_1, R''_2, R''_3, R''_5, R''_6, R''_7, R''_8, R''_9$ and R''_{10} represent, independently of one another, a radical chosen from:
 - a hydrogen atom,
 - a halogen atom,
 - a C_1 - C_6 alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, C_1 - C_6 alkoxy, cyano and amino $-NR'_aR'_b$ groups,
 - a C_1 - C_6 alkoxy radical,
 - a hydroxyl radical,
 - an amino radical $-NR'_aR'_b$,
 - an aminocarbonyl radical $-CONH_2$,
 - a carboxyl radical $-CO_2H$,
- R'_4 and R''_4 represent, independently of one another:

- a C₁-C₆ alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, amino -NR'_aR'_b, C₁-C₆ alkoxy, cyano, aminocarbonyl -CONH₂ and carboxyl -CO₂H groups,

• it being understood that a radical chosen from the R'_i radicals and a radical chosen from the R''_j radicals together form:

- a divalent radical L representing a linear or branched, saturated or unsaturated C₁-C₁₅ alkylene radical, optionally substituted with one or more hydroxyl groups and/or interrupted with one or more non-adjacent heteroatoms chosen from oxygen, nitrogen and sulfur atoms, or

- a covalent single bond,

• R'_i represents one of the radicals R'₁ to R'₁₀ and R''_j represents one of the radicals R''₁ to R''₁₀; i and j denoting an integer ranging from 1 to 10,

• R'_a and R'_b represent, independently of one another, a hydrogen atom or a linear or branched, saturated or unsaturated C₁-C₆ alkyl radical,

• An⁻ denotes an anion or a mixture of anions ensuring the electrical neutrality of the compounds of formula (I) or (II).

The term "anion or a mixture of anions ensuring the electrical neutrality of the compounds of formula (I) or (II)" is intended to mean more particularly an anion or an anionic group chosen from: i) a halide such as a chloride or a bromide; ii) a nitrate; iii) a sulfonate including C₁-C₆ alkylsulfonates: Alk-S(O)₂O⁻ such as methylsulfonate or mesylate and ethylsulfonate; iv) an arylsulfonate: Ar-S(O)₂O⁻ such as benzenesulfonate and toluenesulfonate or tosylate; v) citrate; vi) succinate; vii) tartrate; viii) lactate; ix) an alkyl sulfate: Alk-O-S(O)O⁻ such as methyl sulfate or ethyl sulfate; x) an aryl sulfate: Ar-O-S(O)O⁻ such as benzene sulfate or toluene sulfate; xi) an alkoxy sulfate: Alk-O-S(O)₂O⁻ such as methoxy sulfate or ethoxy sulfate; xii) an aryloxy sulfate: Ar-O-S(O)₂O⁻, xiii) a phosphate O=P(OH)₂-O⁻, O=P(O⁻)₂-OH, O=P(O⁻)₃, HO-[P(O)(O⁻)]_w-P(O)(O⁻)₂ with w being an integer between 1 and 15; xiv) acetate; xv) triflate; and xvi) a borate such as tetrafluoroborate, xvii) a disulfate (O=)₂S(O⁻)₂ or SO₄²⁻ and the monosulfate HSO₄⁻; xviii) the carbonate CO₃²⁻ or the hydrogen carbonate HCO₃⁻.

The term "addition salts of the compounds of formulae (I) and (II) according to the invention" thus means addition salts with an organic or mineral acid, and addition salts with an organic or mineral base.

The addition salts of the compounds of formulae (I) and (II) according to the invention are in particular chosen from addition salts with an acid, such as hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, methanesulfonates, phosphates and acetates, and the addition salts with a base such as sodium hydroxide, potassium hydroxide, ammonia, amines or alkanolamines.

Moreover, the solvates of the compounds of formulae (I) and (II) according to the invention more particularly represent the hydrates of said compounds and/or the combination of said compounds with a linear or branched C₁ to C₄ alcohol such as methanol, ethanol, isopropanol or n-propanol. Preferably, the solvates are hydrates.

The compound(s) of formula (I) or (II) defined in this way thus correspond to substituted or unsubstituted dihydroisoquinolinium salts or to double dihydroisoquinolinium salts which are symmetrical.

Preferably, the invention uses a composition comprising one or more compounds of formula (I) for stripping the artificial colour from human keratin fibres such as the hair.

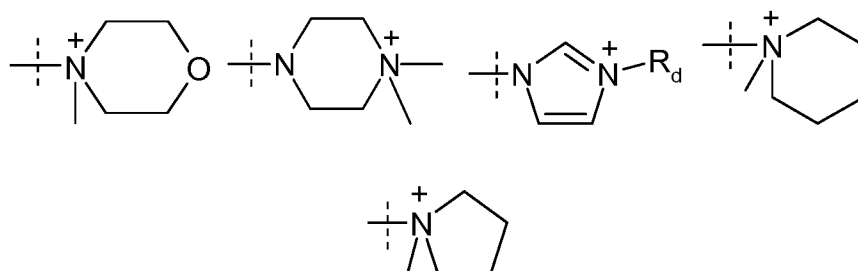
In one embodiment, R represents in formula (I):

- a hydrogen atom, or
- a linear C₁-C₄ alkyl radical optionally substituted with a cyano group.

According to one embodiment, R₁ represents in formula (I):

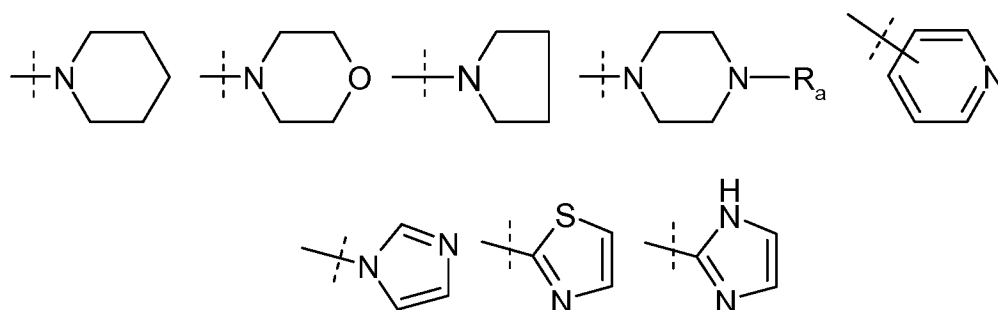
- an unsubstituted linear C₁-C₆ alkyl radical, or
- a linear C₁-C₆ alkyl radical substituted with:
 - a group -NR₁₀R₁₁ in which R₁₀ and R₁₁, which may be identical or different, represent a C₁-C₃ alkyl radical,
 - a cyano group,

- a halogen atom,
- a (C₂-C₆)alkoxycarbonyl group,
- a saturated or unsaturated, optionally aromatic, 5- or 6-membered cationic heterocycle chosen from the following formulae:



R_d corresponding to a linear C₁-C₄ and preferably C₁ alkyl radical,

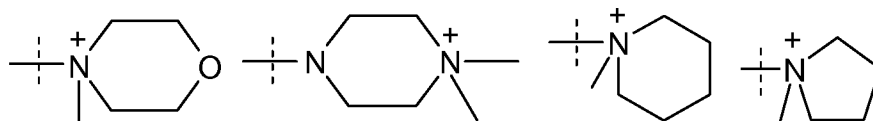
- an ammonium radical N⁺R_aR_bR_c in which R_a, R_b and R_c denote, independently of one another, a C₁-C₃ and preferably C₁ alkyl radical,
- a saturated or unsaturated, optionally aromatic, 5- or 6-membered heterocycle, chosen from:



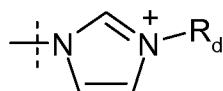
in which R_a corresponds to a C₁-C₃ and preferably C₁ alkyl radical,

- said heterocycle being optionally substituted with an amino radical -NR₁₀R₁₁ in which R₁₀ and R₁₁ are as defined above, or with an ammonium radical N⁺R_aR_bR_c in which R_a, R_b and R_c are as defined above.

According to one embodiment, the cationic heterocycle is chosen from:

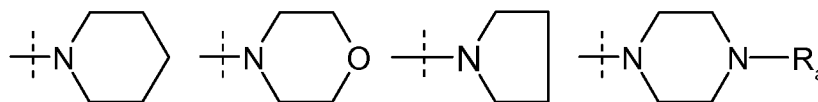


According to another embodiment, the cationic heterocycle is aromatic and especially corresponds to:

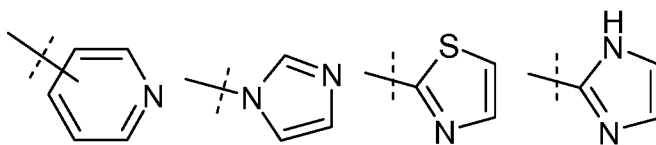


- 5 in which R_d corresponds to a linear C_1 - C_4 and preferably C_1 alkyl radical.

According to one embodiment, the heterocycle is chosen from:



According to one embodiment, the heterocycle is aromatic and is chosen from:



- 10 The R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 groups preferably represent, independently of one another, a hydrogen atom, or a linear C_1 - C_4 alkyl radical, optionally substituted with a C_1 - C_4 alkoxy group.

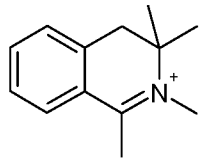
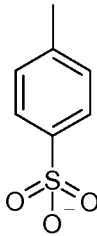
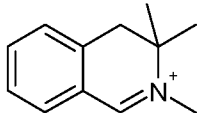
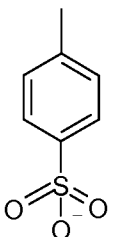
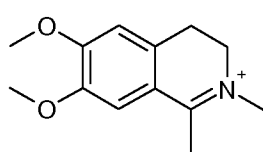
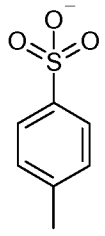
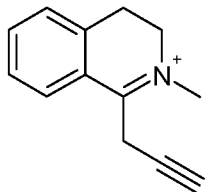
- 15 Preferably, An^- and X^- represent, independently of one another, an anion chosen from halides, in particular chloride and bromide; (C_1-C_6) alkylsulfonates chosen from methylsulfonate or mesylate and ethylsulfonate; arylsulfonates chosen from benzenesulfonate and toluenesulfonate or tosylate; tartrate; citrate; lactate; succinate; (C_1-C_6) alkyl sulfates chosen from methyl sulfate and ethyl sulfate; aryl sulfates chosen from benzene sulfate and toluene sulfate; alkoxy sulfates chosen from methoxy sulfate and ethoxy sulfate; the phosphates as defined previously;
- 20 acetate, disulfate and carbonate.

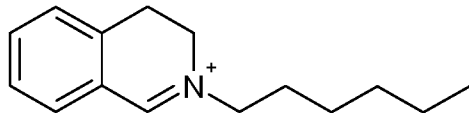
Even better still, An^- is an anion chosen from halides, in particular chloride and bromide, and para-toluenesulfonate.

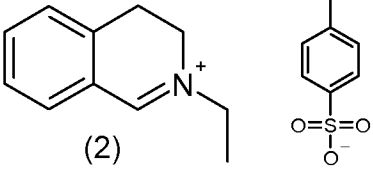
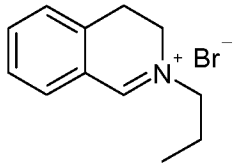
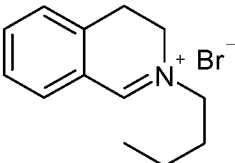
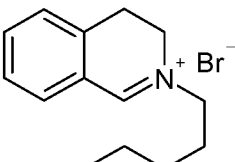
According to one embodiment in which X^- is present, An^- is more particularly an anion chosen from halides, in particular chloride and bromide, and X^- corresponds to para-toluenesulfonate.

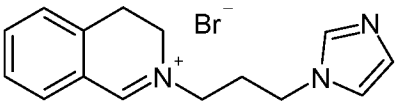
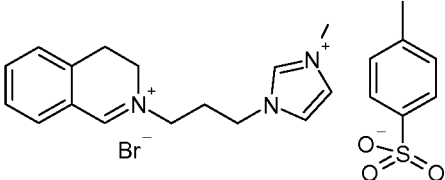
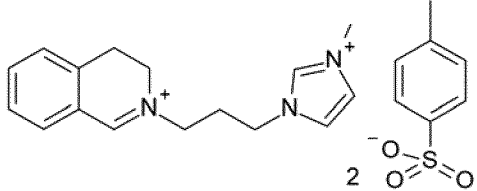
In one particular embodiment of the invention, the compounds of formula (I) or (II) are chosen from the following compounds:

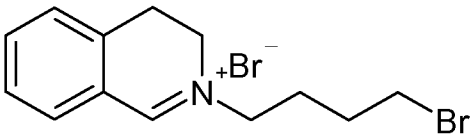
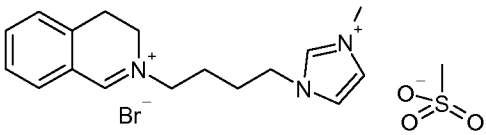
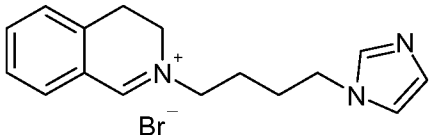
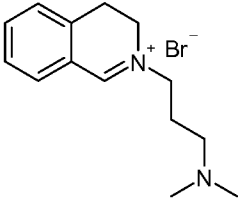
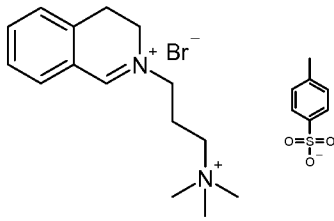
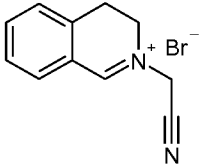
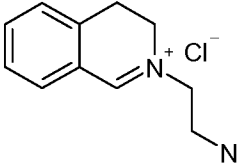
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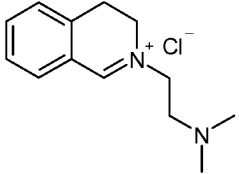
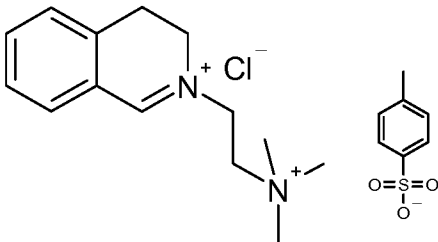
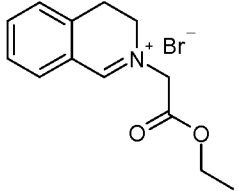
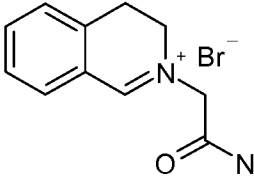
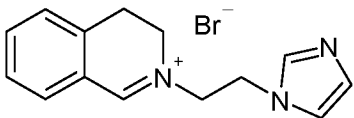
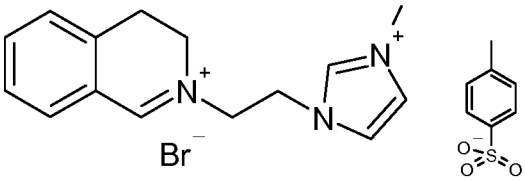
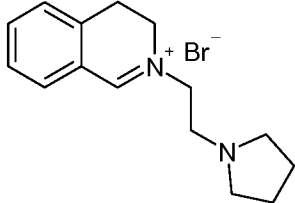
 	1,2,3,3-tetramethyl-3,4-dihydroisoquinolinium toluenesulfonate Compound 1
 	2,3,3-trimethyl-3,4-dihydroisoquinolinium toluene-4-sulfonate Compound 2
 	6,7-dimethoxy-1,2-dimethyl-3,4-dihydroisoquinolinium toluene-4-sulfonate Compound 3
 BF_4^-	1-(cyanomethyl)-2-methyl-3,4-dihydroisoquinolinium tetrafluoroborate Compound 4

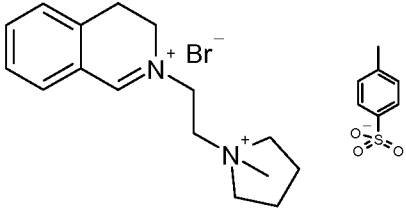
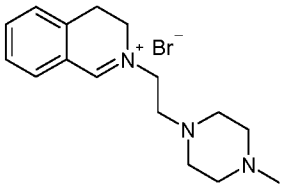
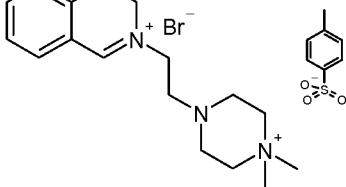
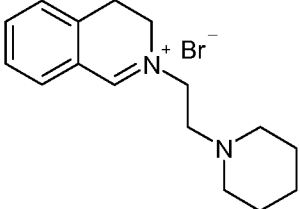
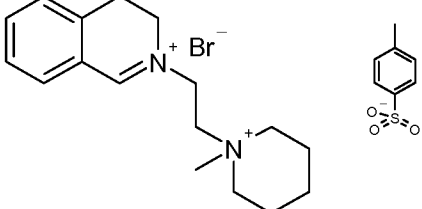
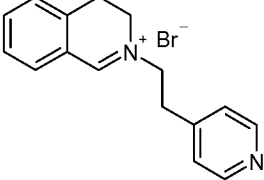
 Br^-	2-hexyl-3,4-dihydroisoquinolinium bromide Compound 5
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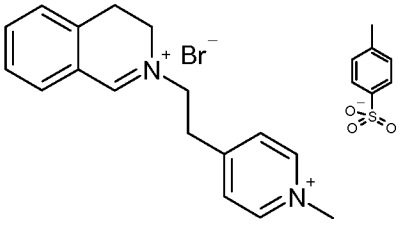
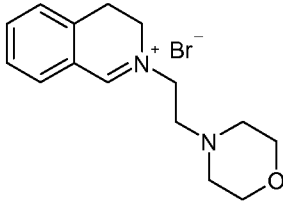
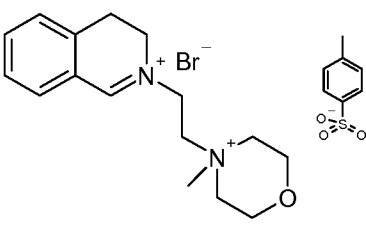
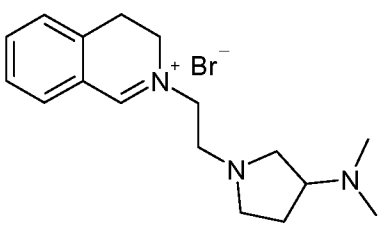
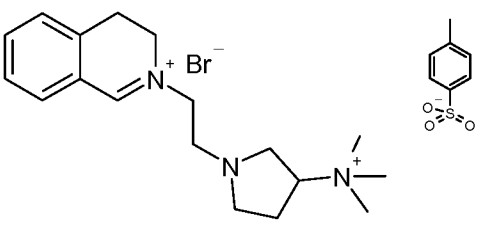
 (2)	2-ethyl-3,4-dihydroisoquinolinium toluene-4-sulfonate Compound 6
	2-propyl-3,4- dihydroisoquinolinium bromide Compound 7
	2-butyl-3,4-dihydroisoquinolinium bromide Compound 8
	2-pentyl-3,4- dihydroisoquinolinium bromide Compound 9

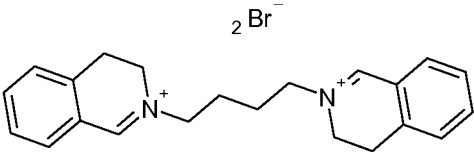
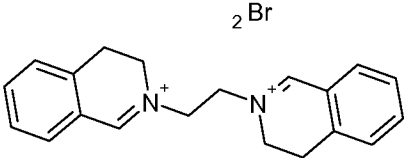
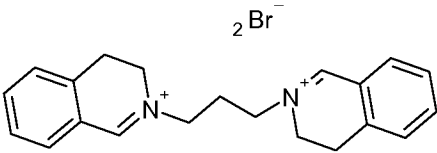
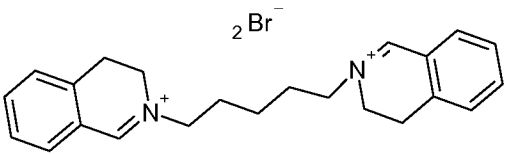
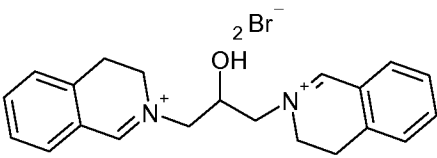
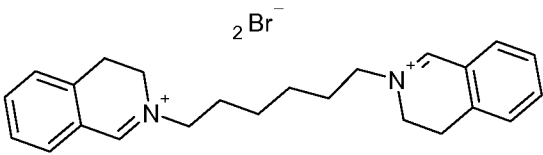
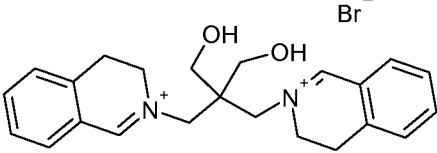
	2-(3-imidazol-1-ylpropyl)-3,4- dihydroisoquinolinium bromide Compound 10
	2-[3-(3-methyl-1H-imidazol-3- ium-1-yl)propyl]-3,4- dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 11
	2-[3-(3-methyl-1H-imidazol-3- ium-1-yl)propyl]-3,4- dihydroisoquinolinium bis(4- methylbenzenesulfonate) Compound 12

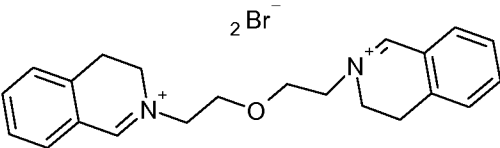
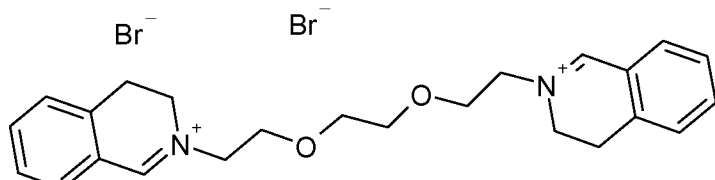
	2-(4-bromobutyl)-3,4-dihydroisoquinolinium bromide Compound 13
	2-[4-(3-methyl-1H-imidazol-3-ium-1-yl)butyl]-3,4-dihydroisoquinolinium bromide methanesulfonate Compound 14
	2-(4-imidazol-1-ylbutyl)-3,4-dihydroisoquinolinium bromide Compound 15
	2-(3-dimethylaminopropyl)-3,4-dihydroisoquinolinium bromide Compound 16
	2-[3-(trimethylammonio)propyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 17
	2-cyanomethyl-3,4-dihydroisoquinolinium bromide Compound 18
	2-(2-aminoethyl)-3,4-dihydroisoquinolinium chloride Compound 19

	2-(2-dimethylaminoethyl)-3,4-dihydroisoquinolinium chloride Compound 20
	2-[2-(trimethylammonio)ethyl]-3,4-dihydroisoquinolinium chloride 4-methylbenzenesulfonate Compound 21
	2-ethoxycarbonylmethyl-3,4-dihydroisoquinolinium bromide Compound 22
	2-carbamoylmethyl-3,4-dihydroisoquinolinium bromide Compound 23
	2-(2-imidazol-1-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 24
	2-[3-(3-methyl-1H-imidazol-3-ium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 25
	2-(2-pyrrolidin-1-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 26

	2-[2-(1-methylpyrrolidinium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 27
	[2-(4-methylpiperazin-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide Compound 28
	2-[2-(4,4-dimethylpiperazin-4-ium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 29
	2-(2-piperidin-1-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 30
	2-[2-(1-methylpiperidinium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 31
	2-(2-pyridin-4-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 32

	2-[2-(1-methylpyridinium-4-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 33
	2-(2-morpholin-4-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 34
	2-[2-(4-methylmorpholin-4-ium-4-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 35
	2-[2-(3-dimethylaminopyrrolidin-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide Compound 36
	2-[2-[3-(trimethylammonio)pyrrolidin-1-yl]ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 37

	2,2'-butane-1,4-diylbis(3,4-dihydroisoquinolinium dibromide Compound 38
	2,2'-ethane-1,4-diylbis(3,4-dihydroisoquinolinium dibromide Compound 39
	2,2'-propane-1,4-diylbis(3,4-dihydroisoquinolinium dibromide Compound 40
	2,2'-pentane-1,4-diylbis(3,4-dihydroisoquinolinium dibromide Compound 41
	2,2'-(2-hydroxypropane-1,3-diyl)bis(3,4-dihydroisoquinolinium dibromide Compound 42
	2,2'-hexane-1,4-diylbis(3,4-dihydroisoquinolinium dibromide Compound 43
	2,2'-[2,2-bis(hydroxymethyl)propane-1,3-diyl]bis(3,4-dihydroisoquinolinium

	dibromide Compound 44
	2,2'-(oxydiethane-2,1-diyl)di-3,4-dihydroisoquinolinium dibromide Compound 45
	2,2'-[ethane-1,2-diylbis(oxyethane-2,1-diyl)]di-3,4-dihydroisoquinolinium dibromide Compound 46

and also mixtures thereof.

Even more preferentially, the compounds of formula (I) are chosen from the compounds (1) to (37), better still from the compounds (1) to (3) and (10) to (37), and even better still from the compounds (1), (11) and (12) and also mixtures thereof.

Preferably, the compound(s) (I) and (II) and/or the addition salt(s) thereof and/or the solvate(s) thereof is (are) used in a proportion ranging from 0.1% to 100% by weight, more preferentially from 1% to 50% by weight, better still from 2% to 20% by weight, even better still from 5% to 15% by weight, relative to the total weight of the composition.

The pH of the composition used in the invention ranges generally from 1 to 7, preferably from 1 to 6, better from 2 to 5 and better still from 2 to 4.

The method according to the invention may also use one or more chemical oxidizing agents.

Among the chemical oxidizing agents used conventionally, mention may be made of hydrogen peroxide, compounds that can produce hydrogen peroxide by hydrolysis, such as urea peroxide or persalts such as perborates, percarbonates and persulfates, hydrogen peroxide being particularly preferred.

- 5 Preferably, the chemical oxidizing agent(s) is (are) used in a proportion ranging from 2% to 20% by weight, even better still from 7% to 12% by weight, relative to the total weight of the composition.

In one preferred embodiment, the method uses one or more chemical oxidizing agents, preferably hydrogen peroxide. According to this embodiment, the method
10 preferably uses a composition C) comprising one or more compounds of formula (I) or of formula (II) and/or the addition salts thereof and/or the solvates thereof, and one or more chemical oxidizing agents, preferably hydrogen peroxide. The composition C) can be obtained by mixing, at the time of use (extemporaneous mixing), a composition C1) comprising one or more compounds of formula (I) or
15 of formula (II) and/or the addition salts thereof and/or the solvates thereof, and a composition C2) comprising one or more chemical oxidizing agents, preferably hydrogen peroxide.

According to the invention, the term "ready-to-use composition" is used to refer to the composition applied to the keratin fibres, such as the hair. The ready-to-use
20 composition can result from the mixing of the compositions C1) and C2) as previously described, and corresponding to the composition C).

The ready-to-use composition used in the method of the invention preferably comprises the compound(s) of formula (I) or (II) and/or the addition salts thereof and/or the solvates thereof in a total content ranging from 0.1% to 100% by
25 weight, more preferentially from 1% to 50% by weight, better still from 2% to 20% by weight, even better still from 5% to 15% by weight, relative to the total weight of the ready-to-use composition.

The ready-to-use composition may also comprise one or more fatty substances, which are preferably liquid(s) (or oil(s)).

30 The term "fatty substance" is intended to mean an organic compound that is insoluble in water at ordinary 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
5 in organic solvents under the same temperature and pressure conditions, for instance chloroform, ethanol, benzene, liquid petroleum jelly or decamethylcyclopentasiloxane.

The term "*oil*" is intended to mean a "fatty substance" that is liquid at ambient temperature (25°C) and at atmospheric pressure (760 mmHg or 1.013×10^5 Pa).

10 The term "non-silicone oil" is intended to mean an oil not containing any silicon atoms (Si) and the term "silicone oil" is intended to mean an oil containing at least one silicon atom.

More particularly, the fatty substances are chosen from C₆-C₁₆ hydrocarbons, non-silicone (hydrocarbon-based) oils comprising more than 16 carbon atoms, of
15 plant, animal, mineral or synthetic origin, triglycerides of plant or synthetic origin, fluoro oils, fatty alcohols, non-salified fatty acids, esters of fatty acid and/or of fatty alcohol other than triglycerides, non-silicone waxes other than solid fatty alcohols and than solid synthetic esters, and silicones, and mixtures thereof.

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

25 As C₆-C₁₆ hydrocarbons, mention may in particular be made of C₆-C₁₆ alkanes, the latter being linear, branched, or optionally cyclic.

Examples that may be mentioned include hexane, dodecane and isoparaffins such as isohexadecane and isodecane.

Mention may also be made of the following compounds:

30 - a mixture of C₁₅-C₁₆ branched alkanes, for example that which is sold by the company SEPPIC under the name Emogreen L15;

- a mixture of C₁₃-C₁₅ linear and/or branched alkanes, for example that which is sold by the company SEPPIC under the name Emosmart L15.

The hydrocarbon-based oils comprising more than 16 carbon atoms may be linear or branched. They may be chosen from liquid paraffins, petroleum jelly, liquid petroleum jelly, polydecenes, and hydrogenated polyisobutene such as Parleam®, squalane, squalene, and mixtures thereof.

Among the hydrocarbon-based oils of plant origin, mention may be made of the refined plant perhydrosqualene sold under the name Fitoderm by the company Cognis; the plant squalane sold, for example, under the name Squalive by the company Biosynthis.

A hydrocarbon-based oil of animal origin that may be mentioned is perhydrosqualene.

The triglycerides of plant or synthetic origin are preferably chosen from liquid fatty acid triglycerides containing from 6 to 30 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively, more particularly from those present in plant oils, for instance sunflower oil, corn 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 or synthetic 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, and mixtures thereof.

The fluoro oils may be chosen from 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 alternatively bromoperfluorooctyl sold under the name Foralkyl® by the company Atochem; nonafluoromethoxybutane and nonafluoroethoxyisobutane; perfluoromorpholine derivatives such as 4-trifluoromethyl perfluoromorpholine sold under the name PF 5052® by the company 3M.

The fatty alcohols that are suitable for use in the invention are more particularly chosen from linear or branched, saturated or unsaturated alcohols comprising from 8 to 30 carbon atoms. Examples that may be mentioned include cetyl alcohol, stearyl alcohol and a mixture thereof (cetylstearyl alcohol),
5 octyldodecanol, 2-butyloctanol, 2-hexyldecanol, 2-undecylpentadecanol, oleyl alcohol, linolenyl alcohol, ricinoleyl alcohol, undecylenyl alcohol and linoleyl alcohol, and mixtures thereof.

The fatty acids that may be used in the context of the invention are more particularly chosen from saturated or unsaturated carboxylic acids containing
10 from 6 to 30 carbon atoms and in particular from 9 to 30 carbon atoms. They are advantageously chosen from myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid and isostearic acid. These fatty acids are, in the composition of the invention, not salified with organic or mineral bases, so as not to give rise to soaps.

15 As regards the esters of fatty acids and/or of fatty alcohols other than the triglycerides mentioned above and plant waxes, mention may be made in particular of esters of saturated or unsaturated, linear C₁-C₂₆ or branched C₃-C₂₆ aliphatic monoacids or polyacids and of saturated or unsaturated, linear C₁-C₂₆ or branched C₃-C₂₆ aliphatic monoalcohols or polyalcohols, the total carbon number
20 of the esters being greater than or equal to 6 and more advantageously greater than or equal to 10.

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
25 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 isononanoate; octyl palmitate; octyl pelargonate; octyl stearate; octyldodecyl erucate; oleyl erucate;
30 ethyl and isopropyl palmitates, 2-ethylhexyl palmitate, 2-octyldodecyl 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 and mixtures thereof.

Still within the context of this variant, esters of C₄-C₂₂ dicarboxylic or tricarboxylic acids and of C₁-C₂₂ alcohols and esters of mono-, di- or tricarboxylic acids and of C₂-C₂₆ di-, tri-, tetra- or pentahydroxy alcohols may also be used.

Mention may especially be made of: diethyl sebacate; diisopropyl sebacate; diisopropyl adipate; di-n-propyl adipate; dioctyl adipate; diisostearyl adipate; dioctyl maleate; glyceryl undecylenate; octyldodecyl stearyl stearate; pentaerythrityl monoricinoleate; pentaerythrityl tetraisononanoate; pentaerythrityl tetrapelargonate; pentaerythrityl tetraisostearate; pentaerythrityl tetraoctanoate; propylene glycol dicaprylate; propylene glycol dicaprinate; 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, and mixtures thereof.

Among the esters mentioned above, it is preferred to use ethyl, isopropyl, myristyl, cetyl or stearyl palmitate, 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, and mixtures thereof.

The composition may also comprise, as fatty ester, sugar esters and diesters of C₆-C₃₀ and preferably C₁₂-C₂₂ fatty acids. It is recalled that the term "sugar" is intended to mean oxygen-bearing hydrocarbon-based compounds bearing 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.

Examples of suitable sugars that may be mentioned include sucrose, glucose, galactose, ribose, fucose, maltose, fructose, mannose, arabinose, xylose and lactose, and derivatives thereof, especially alkyl derivatives, such as methyl derivatives, for instance methylglucose.

The esters of sugars and of fatty acids may especially be chosen from the group comprising the esters or mixtures of esters of sugars described previously and of linear or branched, saturated or unsaturated C₆-C₃₀, preferably C₁₂-C₂₂, fatty acids. If they are unsaturated, these compounds may comprise one to three
5 conjugated or unconjugated carbon-carbon double bonds.

The esters according to this variant may also be chosen from mono-, di-, tri- and tetraesters, polyesters, and mixtures thereof.

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

More particularly, use is made of monoesters and diesters and especially sucrose, glucose or methylglucose monooleate or dioleate, stearate, behenate, oleopalmitate, linoleate, linolenate or oleostearate.

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

Examples of esters or mixtures of esters of sugar and of fatty acid that may also be mentioned include:

- the products sold under the names F160, F140, F110, F90, F70 and SL40 by
20 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
25 sucrose monolaurate;

- 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;

- the sucrose mono-dipalmito-stearate sold by the company Goldschmidt under
30 the name Tegosoft® PSE.

The non-silicone wax(es) other than solid fatty alcohols and solid synthetic esters are chosen especially from carnauba wax, candelilla wax, esparto wax, paraffin wax, ozokerite, plant waxes, such as olive tree wax, rice wax, hydrogenated jojoba wax or absolute flower waxes, such as the blackcurrant blossom essential wax sold by the company Bertin (France), or animal waxes, such as beeswaxes or modified beeswaxes (cerabellina); other waxes or waxy raw materials that may be used according to the invention are especially marine waxes, such as the wax sold by the company Sophim under the reference M82, polyethylene waxes or polyolefin waxes in general.

The fatty substance(s) do not comprise any C₂-C₃ oxyalkylene units. Preferably, they do not contain any glycerol units. More particularly, the fatty substances are other than fatty acids.

More particularly, the fatty substances are chosen from compounds that are liquid or pasty at ambient temperature and at atmospheric pressure.

Preferably, the fatty substance is a compound that is liquid at a temperature of 25°C and at atmospheric pressure, or oil.

According to one preferred variant, the fatty substances are not silicone-based.

The fatty substances are preferably chosen from C₆-C₁₆ hydrocarbons, hydrocarbon-based oils comprising more than 16 carbon atoms, of plant, animal, mineral or synthetic origin, triglycerides of plant or synthetic origin, fatty alcohols, fatty acid and/or fatty alcohol esters, or mixtures thereof.

Preferably, the fatty substance is chosen from linear or branched hydrocarbon-based oils, of mineral or synthetic origin, comprising more than 16 carbon atoms, or mixtures thereof, for instance liquid petroleum jelly.

When the ready-to-use composition used in the method of the invention comprises one or more fatty substances, which are preferably liquid, the total content thereof preferably ranges from 1% to 90% by weight, more preferentially from 10% to 80% by weight, better still from 20% to 70%, even more preferentially from 25% to 60%, even better still from 35% to 65% by weight, relative to the total weight of the ready-to-use composition.

The ready-to-use composition may also comprise one or more surfactants, preferably one or more non-ionic surfactants. Preferably, the non-ionic surfactant(s) are chosen from oxyalkylenated (OA), preferably oxyethylenated, non-ionic surfactants.

- 5 According to one particular embodiment, the ready-to-use composition comprises at least one oxyalkylenated (OA) non-ionic surfactant comprising a number of OA units ranging from 1 to 9 and at least one oxyalkylenated (OA) non-ionic surfactant comprising at least 10 OA units.

10 The weight ratio, in the composition of the invention, of the amount of oxyalkylenated non-ionic surfactant(s) comprising a number of OA units ranging from 1 to 9 to the amount of oxyalkylenated non-ionic surfactant(s) comprising at least 10 OA units is greater than 1, preferably greater than or equal to 1.2, better still greater than or equal to 1.5 and even better still greater than or equal to 2.

15 Preferably, the oxyalkylenated non-ionic surfactants according to the invention are chosen from oxyethylenated non-ionic surfactants.

Preferably, according to this embodiment, the ready-to-use composition according to the invention comprises at least one oxyethylenated (OE) non-ionic surfactant comprising a number of OE units ranging from 1 to 9 and at least one oxyethylenated (OE) non-ionic surfactant comprising at least 10 OE units.

20 The weight ratio, in the ready-to-use composition of the invention, of the amount of oxyethylenated non-ionic surfactant(s) comprising a number of OE units ranging from 1 to 9 to the amount of oxyethylenated non-ionic surfactant(s) comprising at least 10 OE units is greater than 1, preferably greater than or equal to 1.2, better still greater than or equal to 1.5 and even better still greater than or
25 equal to 2.

This weight ratio may range, for example, from 1.2 to 15, better still from 1.5 to 10 and even better still from 2 to 5.

The oxyethylenated non-ionic surfactants comprising a number of OE units ranging from 1 to 9 and the oxyethylenated (OE) non-ionic surfactants comprising
30 at least 10 OE units can be chosen from the following categories:

- oxyethylenated (C₈-C₂₄)alkylphenols,
- saturated or unsaturated, linear or branched, oxyethylenated, C₈-C₃₀ and preferably C₁₂-C₂₂ fatty alcohols,
- saturated or unsaturated, linear or branched, oxyethylenated C₈-C₃₀ amides,
- 5 •esters of saturated or unsaturated, linear or branched, C₈-C₃₀ acids and of polyethylene glycols,
- polyoxyethylenated esters of saturated or unsaturated, linear or branched, C₈-C₃₀ acids and of sorbitol,
- saturated or unsaturated, oxyethylenated plant oils,
- 10 and mixtures thereof.

Preferably, the oxyethylenated non-ionic surfactant comprising at least 10 OE units and the oxyethylenated non-ionic surfactant comprising from 1 to 9 OE units are chosen from oxyethylenated, saturated or unsaturated, linear or branched, preferably linear, C₈-C₃₀, preferably C₁₂-C₂₂ and better still C₁₄-C₂₀, fatty alcohols, 15 for instance cetyl alcohol, oleyl alcohol, oleocetyl alcohol, behenyl alcohol, cetearyl alcohol and stearyl alcohol, and mixtures thereof, and more preferably stearyl alcohol.

Use is preferably made, as oxyethylenated non-ionic surfactant comprising from 1 to 9 OE units, of oxyethylenated non-ionic surfactants comprising from 2 to 8 20 and preferably from 2 to 4 OE units, for instance the products of addition of ethylene oxide and stearyl alcohol such as stearyl alcohol 2 OE (CTFA name: Steareth-2).

The oxyethylenated non-ionic surfactants comprising at least 10 OE units used in the invention may in particular contain a number of oxyethylene groups, ranging 25 from 10 to 50, preferably from 15 to 30 and better still from 15 to 25, for instance the products of addition of ethylene oxide and stearyl alcohol such as stearyl alcohol 20 OE (CTFA name: Steareth-20).

The content of oxyalkylenated, preferably oxyethylenated, non-ionic surfactant(s) comprising from 1 to 9 oxyalkylene units, preferably oxyethylene units, in the 30 ready-to-use composition according to the invention may range from 0.5% to

15% by weight, preferably from 1% to 10% by weight and better still from 2% to 6% by weight relative to the total weight of the composition.

The content of oxyalkylenated, preferably oxyethylenated, non-ionic surfactants comprising at least 10 oxyalkylene groups, preferably oxyethylene groups, in the ready-to-use composition according to the invention may range from 0.1% to 15% by weight, preferably from 0.5% to 10% by weight and better still from 1% to 5% by weight relative to the total weight of the composition.

The total amount of oxyalkylenated, preferably oxyethylenated, non-ionic surfactants in the ready-to-use composition may range from 1% to 25% by weight, preferably from 2% to 15% by weight and better still from 3% to 7% by weight relative to the total weight of the composition.

The ready-to-use composition used in the method of the invention generally comprises water. When the composition is aqueous, the water content can range from 10% to 95% by weight, preferably from 20% to 70%, better still from 20% to 50% by weight, relative to the ready-to-use composition.

The composition comprising one or more compounds of formulae (I) and (II) and/or the addition salts thereof and/or the solvates thereof may comprise one or more additional ingredients chosen from ionic liquids, organic solvents, anionic surfactants, cationic surfactants or non-ionic surfactants, other than those listed above, and amphoteric surfactants, cationic, anionic, non-ionic or amphoteric polymers or mixtures thereof, antidandruff agents, anti-seborrhoea agents, agents for preventing hair loss and/or for promoting hair regrowth, vitamins and provitamins including panthenol, sunscreens, mineral or organic pigments, sequestrants, plasticizers, solubilizers, acidifying agents, mineral or organic thickeners, especially polymeric thickeners, opacifiers or nacreous agents, antioxidants, hydroxy acids, fragrances, preservatives, pigments and ceramides.

Another subject of the invention is a method for stripping the artificial colour from human keratin fibres, such as the hair, which comprises the steps consisting:

- in mixing, immediately before use, one or more compounds of formula (I) or (II) defined above, and/or the addition salts thereof and/or the solvates thereof, with

a composition comprising one or more chemical oxidizing agents, preferably hydrogen peroxide,

- in applying the mixture obtained to the human keratin fibres to be stripped,
- in leaving on the mixture for a sufficient time, for example between 1 minute and 1 hour, preferably between 5 and 50 minutes, more preferentially between 15 and 45 minutes, in order to obtain the desired stripping, and
- in removing the stripping mixture by rinsing with water, optionally followed by washing with a shampoo, then optionally by drying.

Another subject of the invention is a method implementing:

- a step of dyeing human keratin fibres such as the hair using a dye composition comprising one or more dyes chosen from oxidation dyes and/or direct dyes,
- a step of stripping the artificial colour from said fibres using a composition comprising one or more compounds of formulae (I) and (II) and/or the addition salts thereof and/or the solvates thereof as previously described, preferably in the presence of one or more chemical oxidizing agents, preferably hydrogen peroxide.

According to this embodiment, the method preferably uses a composition C) as defined above.

Finally, a subject of the invention is the use of a composition comprising one or more compounds of formula (I) or of formula (II) and/or the addition salts thereof and/or the solvates thereof as previously described, for stripping the artificial colour from human keratin fibres such as the hair.

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

EXAMPLES

Example 1

The following oxidizing composition A was prepared from the following ingredients in the following proportions indicated as % by weight of product relative to the total weight of the composition in Table 1:

Table 1

Oxidizing composition A	% by weight
White mineral oil	50
Oxyethylenated stearyl alcohol (2 units of ethylene oxide (or 2 EO))	3.5
Oxyethylenated stearyl alcohol (20 OE)	1.5
Vitamin E	0.2
Tetrasodium pyrophosphate decahydrate	0.04
Etidronic acid, tetrasodium salt, as an aqueous solution at 30% by weight	0.2
Sodium salicylate	0.035
Hydrogen peroxide as a 50% solution (200 vol. aqueous hydrogen peroxide solution)	18
Water	qs 100

A 1 g lock of natural hair containing 90% grey hairs was dyed beforehand with a Movida chestnut brown dye under the following conditions: 5 g of dye mixture, obtained by mixing the dye support and the oxidizing agent that are sold by L'Oreal, in the proportions 1 + 2, were applied to the lock for a leave-on time of 15 minutes.

The lock was then rinsed, washed with a shampoo, and then dried.

10 g of 2-[3-(3-methyl-1H-imidazol-3-ium-1-yl)propyl]-3,4-dihydroisoquinolinium bis(4-methylbenzenesulfonate) (compound 12 according to the invention) were

mixed with 90 g of oxidizing composition A. The pH was 2.5 ± 0.5 . This mixture was then applied to the lock for 30 minutes, at 33°C in a proportion of 10 g of mixture per 1 g of hair. The lock was then rinsed, then shampooed and dried.

5 Example 2 (comparative example)

The following oxidizing composition B was prepared from the following ingredients in the following proportions indicated as % by weight of product relative to the total weight of the composition in Table 2:

Table 2

Oxidizing composition B	% by weight
Sodium persulfate	33
Potassium persulfate	20
Ethylenediaminetetraacetic acid	1
Sodium carboxymethylcellulose	4
Sodium lauryl sulfate powder	14
Ultramarine blue (CI 77007)	0.5
Strontium peroxide	11.5
Anhydrous sodium metasilicate	9
Ammonium chloride	5
Mixture of di(2-ethylhexyl) sulfosuccinate, monosodium salt/sodium benzoate	2

Another lock dyed beforehand with Movida chestnut brown dye in the same way as that indicated in Example 1 was subjected to stripping using the oxidizing composition B mixed with hot water in a 1:2 weight ratio for 30 minutes at 33°C. 10 g of mixture were applied to 1 g of lock of hair. The lock was then rinsed, then shampooed and dried.

Example 3 (Estimation of lightening)

In order to demonstrate the impact of each of the methods on the melanin pigments of the hair, undyed natural chestnut brown locks (Tone depth 4, TD4) were treated either with the method of Example 1 using compound 12 according to the invention, or with the method of Example 2 using the oxidizing composition B. This estimation was carried out on locks which had not been artificially dyed so that the effect was not masked by the dyeing.

The colour of the locks treated in Examples 1, 2 and 3 was then evaluated with an SF600X Datacolor spectrophotometer (illuminant D65, angle 10°, specular component included), in the CIELab system.

In this $L^* a^* b^*$ system, the three parameters denote, respectively, the colour intensity (L^*), the green/red colour axis (a^*) and the blue/yellow colour axis (b^*).

The higher the value of L^* , the lighter the colour.

In the case of the stripping of the previously dyed locks of Examples 1 and 2, the colour variation between the coloured locks of hair and the locks of hair after stripping is defined by the parameter ΔE_{ab}^* and is calculated according to the following Equation 1:

Equation 1

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

In this Equation 1, the parameters L^* , a^* and b^* represent the values measured on the locks of hair after stripping with:

- compound 12 of the invention combined with the oxidizing compound A or
- the oxidizing composition B mixed with water,

and the parameters L_0^* , a_0^* and b_0^* represent the values measured on the locks of hair dyed with Movida dye.

The higher the ΔE_{ab}^* value, the better the stripping of the keratin fibres.

In the case of the treatment of the natural chestnut brown locks of Example 3, the colour variation between the natural locks of hair and the locks of hair after treatment is defined by the parameter $\Delta E'$ and is calculated according to the following Equation 2:

5 Equation 2

$$\Delta E' = \sqrt{(L'^* - L'_0)^2 + (a'^* - a'_0)^2 + (b'^* - b'_0)^2}$$

In this Equation 2, the parameters L'^* , a'^* and b'^* represent the values measured on the locks of hair after treatment with:

- compound 12 of the invention combined with the oxidizing compound A or
- 10 - the oxidizing composition B mixed with water,

and the parameters L'_0 , a'_0 and b'_0 represent the values measured on the natural chestnut brown locks.

The lower the $\Delta E'$ value, the less the lock is lightened, which corresponds to less degradation of the melanin pigments.

15 The results are collated in Table 3 below.

Table 3

	ΔE_{ab}^* (relative to the Movida-dyed lock)	$\Delta E'$ (relative to the TD4 lock)
Compound 12 + Composition A	25.6	7.7
Composition B + water	19.1	11.3

The method using compound 12 according to the invention results in a higher ΔE_{ab}^* value, and thus in better stripping compared with the comparative method,
20 on previously dyed locks.

Moreover, the treatment carried out with compound 12 on natural locks results in a lower $\Delta E'$ value, and thus in less degradation of the melanin pigments of the hair compared with the comparative treatment.

5 Example 4

A lock was dyed with a Movida chestnut brown dye in the same way as that indicated in Example 1, with the exception that the leave-on time was 10 minutes.

10 g of 1,2,3,3-tetramethyl-3,4-dihydroisoquinolinium toluenesulfonate
(compound 1 according to the invention) were mixed with 90 g of oxidizing
10 composition A of example 1. This mixture was then applied to the lock for 30
minutes at 33°C, in a proportion of 10 g of mixture per 1 g of hair.

The lock was then rinsed, then shampooed and dried.

Further the same procedure was used for 2-[3-(3-methyl-1H-imidazol-3-ium-1-
yl)propyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate
15 (compound 11 according to the invention).

Other locks were prepared according to Examples 2 and 3.

The colour of the locks treated in Examples 4, 2 and 3 was then evaluated with
the same procedure as described above, with a Konica-Minolta CM 3600A
spectrocolorimeter (illuminant D65, angle 10°, specular component included), in
20 the CIELab system .

The results are collated in the Table 4 below.

Table 4

	ΔE_{ab}^* (relative to the Movida-dyed lock)	$\Delta E'$ (relative to the TD4 lock)
Compound 1 + Composition A	13.59	6.23
Compound 11 + Composition A	18.33	6.1
Composition B + water	11.48	10.44

The method using compound 1 or 11 according to the invention results in a higher ΔE_{ab}^* value, and thus in better stripping compared with the comparative method, on previously dyed locks.

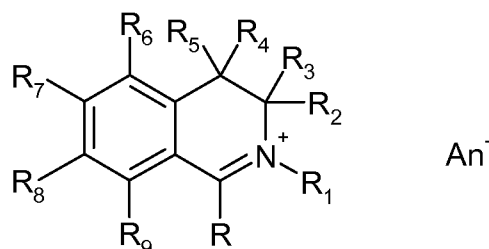
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Moreover, the treatment carried out with compound 1 or 11 on natural locks results in a lower $\Delta E'$ value, and thus in less degradation of the melanin pigments of the hair compared with the comparative treatment.

Claims

1. Method for stripping the artificial colour from human keratin fibres such as the hair, which comprises applying to said artificially dyed fibres a composition comprising one or more compounds of formula (I) or (II) and/or the addition salts thereof and/or the solvates thereof:

formula (I)



in which:

- R represents:

- a hydrogen atom,
- a linear or branched C₁-C₁₂ alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, C₁-C₆ alkoxy, cyano and amino -NR₁₀R₁₁ groups,

- R₁ represents:

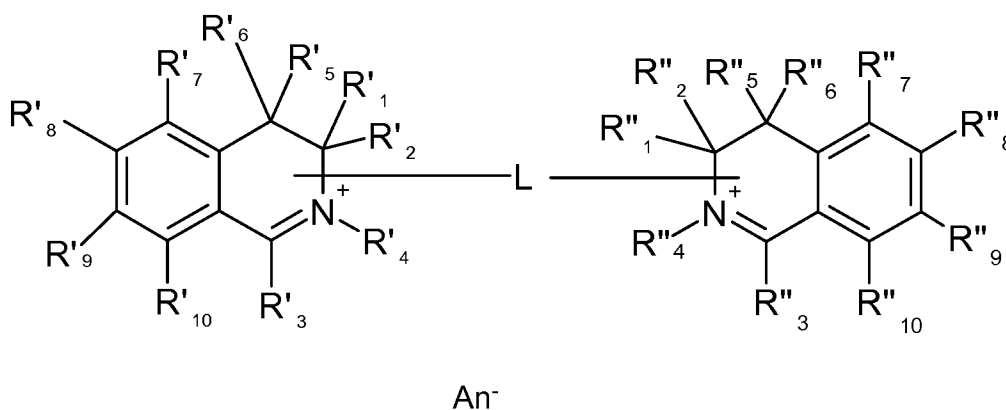
- a linear or branched, unsubstituted C₁-C₁₂ alkyl radical,
- a linear or branched C₁-C₂₀ alkyl radical, substituted with a group chosen from:
 - a hydroxyl group,
 - a C₁-C₆ alkoxy group,
 - an amino group -NR₁₀R₁₁,
 - an amino group -NR₁₂R₁₃,
 - a carboxyl group -COOH,
 - a cyano group,
 - a halogen atom,

- an aminocarbonyl group $-\text{CONH}_2$,
 - a $(\text{C}_1\text{-C}_6)$ alkoxycarbonyl group,
 - a saturated or unsaturated, optionally aromatic, 5- or 6-membered heterocycle, optionally substituted with one or more radicals, which may be identical or different, chosen from:
 - a linear or branched $\text{C}_1\text{-C}_6$ alkyl radical,
 - a linear or branched $\text{C}_1\text{-C}_6$ hydroxyalkyl radical,
 - a $\text{C}_1\text{-C}_6$ alkoxy radical,
 - a hydroxyl radical,
 - an amino radical $-\text{NR}_{10}\text{R}_{11}$,
 - a pyrrolidine, piperidine or morpholine radical,
 - an ammonium radical $\text{N}^+\text{R}_a\text{R}_b\text{R}_c$ in which R_a , R_b and R_c denote, independently of one another, a linear or branched $\text{C}_1\text{-C}_6$ alkyl radical or a $\text{C}_1\text{-C}_6$ hydroxyalkyl radical,
 - a saturated or unsaturated, optionally aromatic, 5- or 6-membered cationic heterocycle optionally substituted with one or more radicals, which may be identical or different, chosen from a linear or branched $\text{C}_1\text{-C}_6$ alkyl radical, a $\text{C}_1\text{-C}_6$ hydroxyalkyl radical, a $\text{C}_1\text{-C}_6$ alkoxy radical, a hydroxyl radical and an amino radical $-\text{NR}_{10}\text{R}_{11}$,
 - an ammonium radical $\text{N}^+\text{R}_a\text{R}_b\text{R}_c$ in which R_a , R_b and R_c denote, independently of one another, a linear or branched $\text{C}_1\text{-C}_6$ alkyl radical or a $\text{C}_1\text{-C}_6$ hydroxyalkyl radical,
 - it being understood that when R_1 represents an alkyl radical substituted with a cationic group, then the electrical neutrality of the compounds of formula (I) is ensured by the presence of one or more anions X^- , X^- adding to the anion An^- ,
- R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 represent, independently of one another, a radical chosen from:

- a hydrogen atom,
- a halogen atom,
- a linear or branched C₁-C₆ alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, C₁-C₆ alkoxy and amino -NR₁₀R₁₁ groups,
- a C₁-C₆ alkoxy radical,
- a hydroxyl radical,
- an amino radical -NR₁₀R₁₁,
- an aminocarbonyl radical -CONH₂,
- a carboxyl radical -COOH,

- R₁₀ and R₁₁, which may be identical or different, denote a hydrogen atom or a linear or branched C₁-C₆ alkyl radical,
- R₁₂ and R₁₃, which may be identical or different, denote a linear or branched C₁-C₆ alkyl radical, substituted with a hydroxyl group,

formula (II)



in which:

- R'₁, R'₂, R'₃, R'₅, R'₆, R'₇, R'₈, R'₉, R'₁₀, R''₁, R''₂, R''₃, R''₅, R''₆, R''₇, R''₈, R''₉ and R''₁₀ represent, independently of one another, a radical chosen from:
 - a hydrogen atom,
 - a halogen atom,

- a C₁-C₆ alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, C₁-C₆ alkoxy, cyano and amino -NR'_aR'_b groups,
- a C₁-C₆ alkoxy radical,
- 5 - a hydroxyl radical,
- an amino radical -NR'_aR'_b,
- an aminocarbonyl radical -CONH₂,
- a carboxyl radical -CO₂H,

- R'₄ and R''₄ represent, independently of one another:

10 - a C₁-C₆ alkyl radical optionally substituted with one or more groups, which may be identical or different, chosen from hydroxyl, amino -NR'_aR'_b, C₁-C₆ alkoxy, cyano, aminocarbonyl -CONH₂ and carboxyl -CO₂H groups,

- it being understood that a radical chosen from the R'_i radicals and a radical chosen from the R''_j radicals together form:

- 15 - a divalent radical L representing a linear or branched, saturated or unsaturated C₁-C₁₅ alkylene radical, optionally substituted with one or more hydroxyl groups and/or interrupted with one or more non-adjacent heteroatoms chosen from oxygen, nitrogen and sulfur atoms, or
- a covalent single bond,

20 • R'_i represents one of the radicals R'₁ to R'₁₀ and R''_j represents one of the radicals R''₁ to R''₁₀; i and j denoting an integer ranging from 1 to 10,

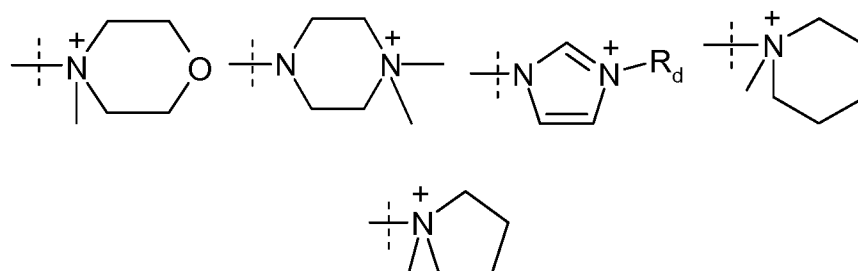
- R'_a and R'_b represent, independently of one another, a hydrogen atom or a linear or branched, saturated or unsaturated C₁-C₆ alkyl radical,

25 • An⁻ denotes an anion or a mixture of anions ensuring the electrical neutrality of the compounds of formula (I) or (II).

2. Method according to Claim 1, characterized in that R represents in formula (I), a hydrogen atom or a linear C₁-C₄ alkyl radical, optionally substituted with a cyano group.

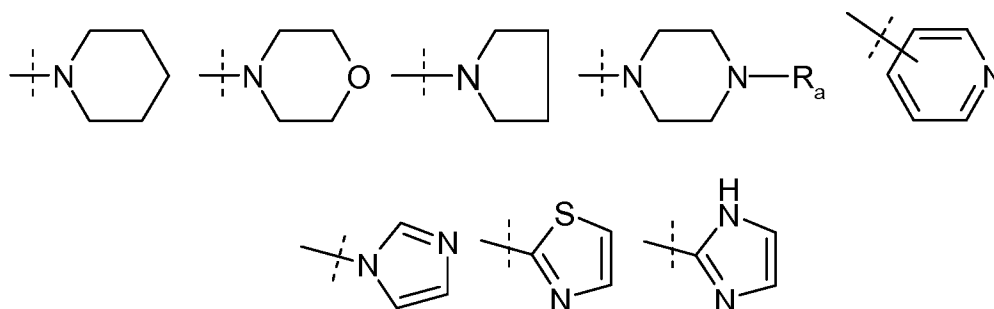
3. Method according to Claim 1 or 2, characterized in that R_1 represents in formula (I):

- an unsubstituted linear C_1 - C_6 alkyl radical, or
- a linear C_1 - C_6 alkyl radical substituted with:
 - a group $-NR_{10}R_{11}$ in which R_{10} and R_{11} , which may be identical or different, represent a C_1 - C_3 alkyl radical,
 - a cyano group,
 - a halogen atom,
 - a $(C_2$ - $C_6)$ alkoxycarbonyl group,
 - a saturated or unsaturated, optionally aromatic, 5- or 6-membered cationic heterocycle chosen from the following formulae:



R_d corresponding to a linear C_1 - C_4 and preferably C_1 alkyl radical,

- an ammonium radical $N^+R_aR_bR_c$ in which R_a , R_b and R_c denote, independently of one another, a C_1 - C_3 and preferably C_1 alkyl radical,
- a saturated or unsaturated, optionally aromatic, 5- or 6-membered heterocycle, chosen from:



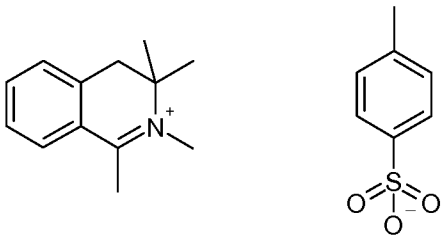
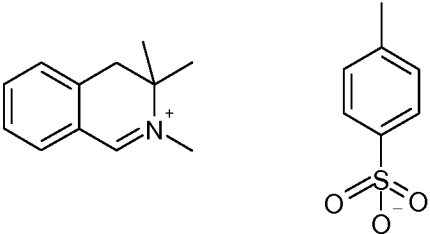
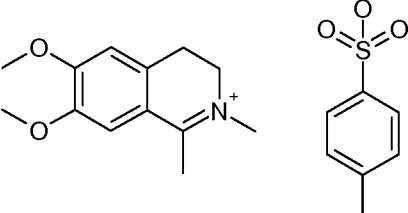
in which R_a corresponds to a C_1 - C_3 and preferably C_1 alkyl radical,

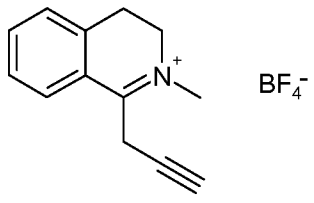
said heterocycle being optionally substituted with an amino radical $-NR_{10}R_{11}$ in which R_{10} and R_{11} are as defined in claim 1, or with an ammonium radical $N^+R_aR_bR_c$ in which R_a , R_b and R_c are as defined in claim 1.

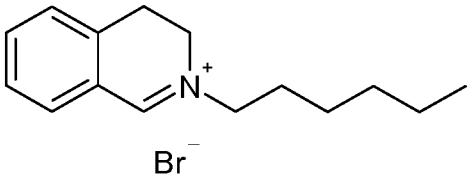
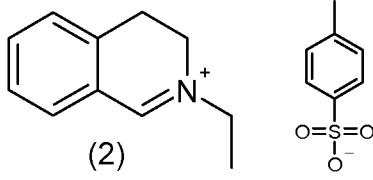
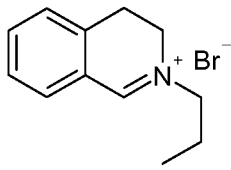
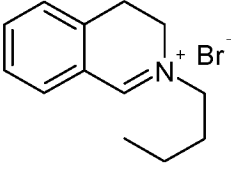
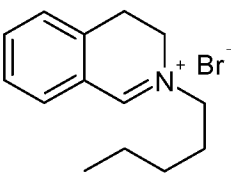
4. Method according to any one of the preceding claims, characterized in that R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 represent, independently of one another, a hydrogen atom, or a linear C_1 - C_4 alkyl radical, optionally substituted with a C_1 - C_4 alkoxy group.

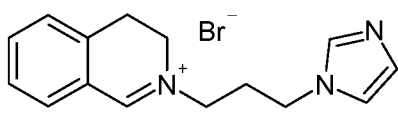
5. Method according to any one of the preceding claims, characterized in that An^- is an anion chosen from halides, in particular chloride and bromide, and para-toluenesulfonate.

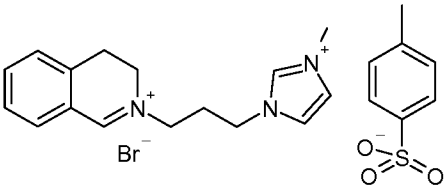
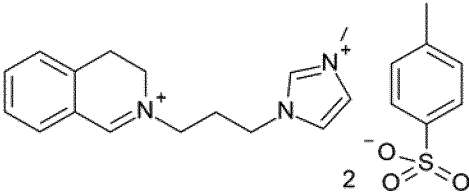
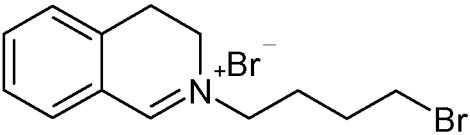
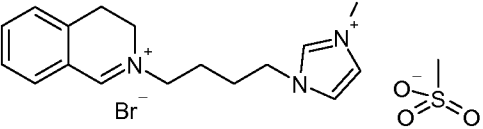
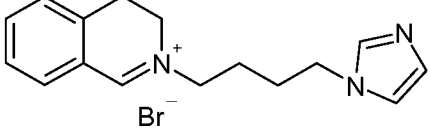
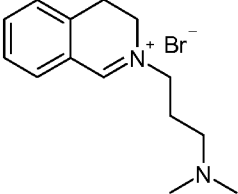
6. Method according to any one of the preceding claims, characterized in that the compounds of formula (I) or (II) are chosen from the following compounds:

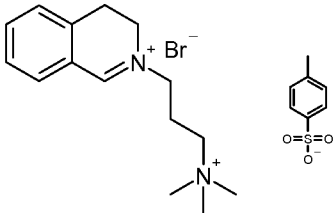
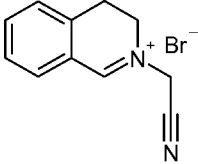
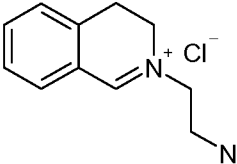
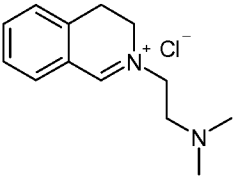
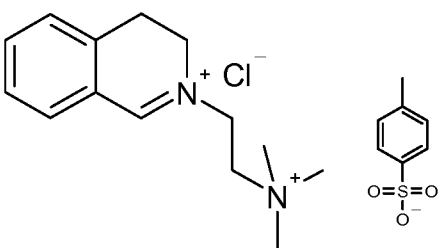
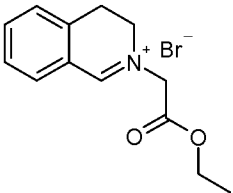
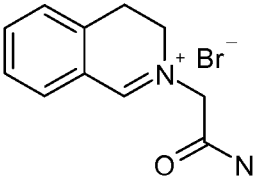
	1,2,3,3-tetramethyl-3,4-dihydroisoquinolinium toluenesulfonate Compound 1
	2,3,3-trimethyl-3,4-dihydroisoquinolinium toluene-4-sulfonate Compound 2
	6,7-dimethoxy-1,2-dimethyl-3,4-dihydroisoquinolinium toluene-4-sulfonate Compound 3

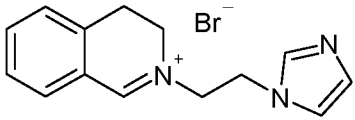
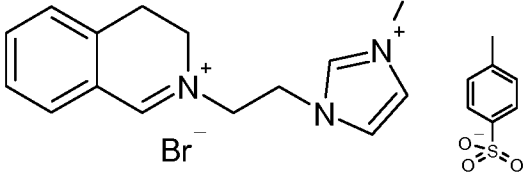
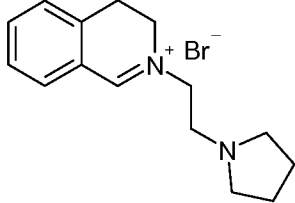
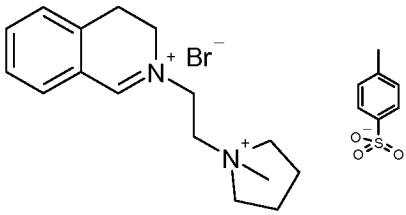
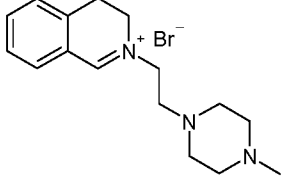
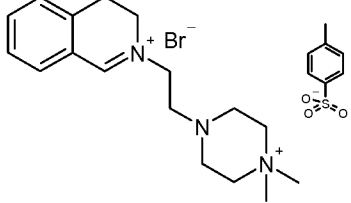
	1-(cyanomethyl)-2-methyl- 3,4-dihydroisoquinolinium tetrafluoroborate Compound 4
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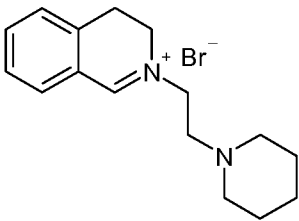
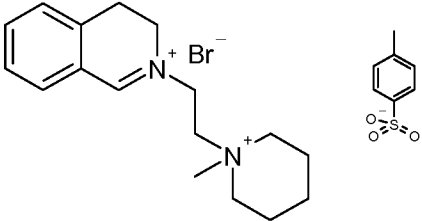
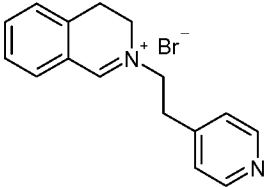
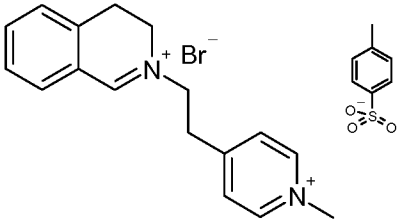
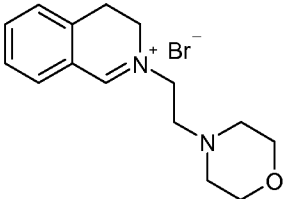
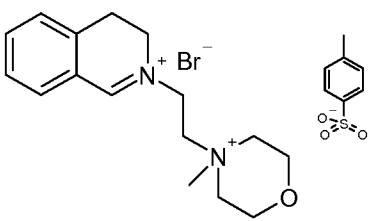
	2-hexyl-3,4- dihydroisoquinolinium bromide Compound 5
 (2)	2-ethyl-3,4-dihydroisoquinolinium toluene-4-sulfonate Compound 6
	2-propyl-3,4- dihydroisoquinolinium bromide Compound 7
	2-butyl-3,4-dihydroisoquinolinium bromide Compound 8
	2-pentyl-3,4- dihydroisoquinolinium bromide Compound 9

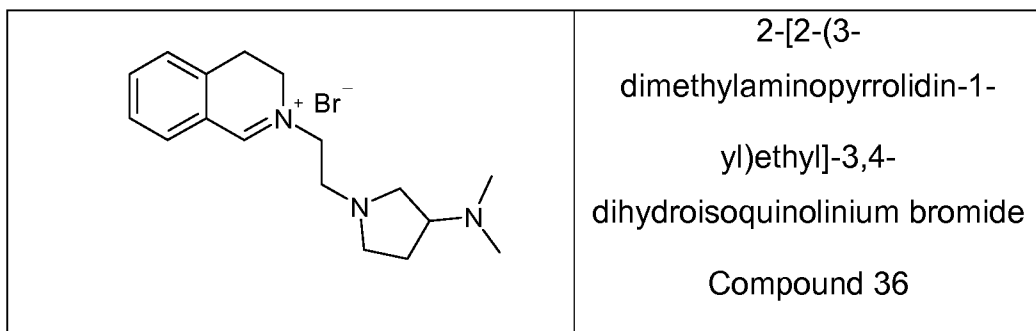
	2-(3-imidazol-1-ylpropyl)-3,4- dihydroisoquinolinium bromide Compound 10
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	2-[3-(3-methyl-1H-imidazol-3-ium-1-yl)propyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 11
	2-[3-(3-methyl-1H-imidazol-3-ium-1-yl)propyl]-3,4-dihydroisoquinolinium bis(4-methylbenzenesulfonate) Compound 12
	2-(4-bromobutyl)-3,4-dihydroisoquinolinium bromide Compound 13
	2-[4-(3-methyl-1H-imidazol-3-ium-1-yl)butyl]-3,4-dihydroisoquinolinium bromide methanesulfonate Compound 14
	2-(4-imidazol-1-ylbutyl)-3,4-dihydroisoquinolinium bromide Compound 15
	2-(3-dimethylaminopropyl)-3,4-dihydroisoquinolinium bromide Compound 16

	2-[3-(trimethylammonio)propyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 17
	2-cyanomethyl-3,4-dihydroisoquinolinium bromide Compound 18
	2-(2-aminoethyl)-3,4-dihydroisoquinolinium chloride Compound 19
	2-(2-dimethylaminoethyl)-3,4-dihydroisoquinolinium chloride Compound 20
	2-[2-(trimethylammonio)ethyl]-3,4-dihydroisoquinolinium chloride 4-methylbenzenesulfonate Compound 21
	2-ethoxycarbonylmethyl-3,4-dihydroisoquinolinium bromide Compound 22
	2-carbamoylmethyl-3,4-dihydroisoquinolinium bromide Compound 23

	2-(2-imidazol-1-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 24
	2-[3-(3-methyl-1H-imidazol-3-ium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 25
	2-(2-pyrrolidin-1-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 26
	2-[2-(1-methylpyrrolidinium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 27
	[2-(4-methylpiperazin-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide Compound 28
	2-[2-(4,4-dimethylpiperazin-4-ium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 29

	2-(2-piperidin-1-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 30
	2-[2-(1-methylpiperidinium-1-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 31
	2-(2-pyridin-4-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 32
	2-[2-(1-methylpyridinium-4-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 33
	2-(2-morpholin-4-ylethyl)-3,4-dihydroisoquinolinium bromide Compound 34
	2-[2-(4-methylmorpholin-4-ium-4-yl)ethyl]-3,4-dihydroisoquinolinium bromide 4-methylbenzenesulfonate Compound 35



7. Method according to any one of the preceding claims, characterized in that the pH of the composition ranges from 1 to 7, preferably from 1 to 6, better from 2 to 5.

5 8. Method according to any one of the preceding claims, using one or more chemical oxidizing agents.

9. Method according to Claim 8, characterized in that the chemical oxidizing agent is hydrogen peroxide.

10 10. Method for stripping the artificial colour from human keratin fibres such as the hair, using a composition comprising one or more compounds of formula (I) or (II) as defined in any one of Claims 1 to 6, and/or the addition salts thereof and/or the solvates thereof, and one or more chemical oxidizing agents, preferably hydrogen peroxide.

15 11. Stripping method according to Claim 10, characterized in that it comprises the steps consisting:

- in mixing, immediately before use, one or more compounds of formula (I) or (II), and/or the addition salts thereof and/or the solvates thereof, with a composition comprising one or more chemical oxidizing agents, preferably hydrogen peroxide,

20 - in applying the mixture obtained to the human keratin fibres to be stripped,

- in leaving on the mixture for a time sufficient to obtain the desired stripping, and

- in removing the stripping mixture by rinsing with water, followed by washing with a shampoo, then by drying.

12. Method for treating human keratin fibres such as the hair, implementing:

5 - a step of dyeing human keratin fibres such as the hair using a dye composition comprising one or more dyes chosen from oxidation dyes and/or direct dyes,

10 - a step of stripping the artificial colour from said fibres using a composition comprising one or more compounds of formulae (I) and (II) as defined in any one of Claims 1 to 6 and/or the addition salts thereof and/or the solvates thereof, preferably in the presence of one or more chemical oxidizing agents, preferably hydrogen peroxide.

15 13. Use of a composition comprising one or more compounds of formulae (I) and (II) as defined in any one of Claims 1 to 6 and/or the addition salts thereof and/or the solvates thereof, for stripping the artificial colour from human keratin fibres such as the hair.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/067493

A. CLASSIFICATION OF SUBJECT MATTER

INV. A61K8/49 A61Q5/10 A61Q5/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61K A61Q

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

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

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/109183 A1 (OREAL [FR]) 29 June 2017 (2017-06-29)	1-11
Y	page 31 - page 40 page 46 - page 50; claim 7 -----	1-13
X	WO 2017/109184 A1 (OREAL [FR]) 29 June 2017 (2017-06-29)	1-11
Y	page 22 - page 25 -----	1-13
Y	Wilfried Umbach: "9.5 Haarfarbänderungsmittel - 9.5.1.3 Anwendung" In: "Kosmetik und Hygiene", 30 June 2004 (2004-06-30), Wiley-VCH, Weinheim, XP055563746, ISBN: 978-3-527-30996-2 page 299, page 299 ----- -/-	1-13



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

5 August 2019

Date of mailing of the international search report

13/08/2019

Name and mailing address of the ISA/

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Bader, Karl Günther

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/067493

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2007 047688 A1 (HENKEL AG & CO KGAA [DE]) 9 April 2009 (2009-04-09)	1-11
Y	page 50; claim 5 -----	1-13
X	FR 3 046 167 A1 (OREAL [FR]) 30 June 2017 (2017-06-30)	1-11
Y	page 30; claim 6 -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/067493

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 2017109184 A1	29-06-2017	BR 112018012110 A2 CN 108430988 A EP 3394043 A1 FR 3046170 A1 KR 20180081613 A US 2018369105 A1 WO 2017109184 A1	04-12-2018 21-08-2018 31-10-2018 30-06-2017 16-07-2018 27-12-2018 29-06-2017
DE 102007047688 A1	09-04-2009	DE 102007047688 A1 EP 2192957 A1 WO 2009043613 A1	09-04-2009 09-06-2010 09-04-2009
FR 3046167 A1	30-06-2017	NONE	