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(54) **Title:** PROCESS FOR TREATING KERATIN FIBERS

(57) **Abstract:** The present invention relates to a process for treating keratin fibers, in particular hair, comprising the steps of: applying onto the keratin fibers a composition comprising at least 0.001% by weight, relative to the total weight of the composition, of one or more oxidative dyes; placing the keratin fibers in an occlusive space; and heating the keratin fibers to from 50 to 250 °C. The present invention can provide a new coloring process for keratin fibers, such as hair, based on oxidative coloring(s) which can provide the keratin fibers with more intense color, better level of color coverage, and resistance to external factors or agents such as a shampoo.

## DESCRIPTION

## PROCESS FOR TREATING KERATIN FIBERS

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## TECHNICAL FIELD

The present invention relates to a process for treating keratin fibers such as hair.

## BACKGROUND ART

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It is known to dye keratin fibers and in particular human hair with dyeing compositions containing oxidative dyes precursors, generally called oxidative bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidative bases are generally combined with couplers. These bases and these couplers are colorless or weakly colored compounds which, combined with oxidizing products, can give rise to colored compounds through an oxidative condensation process.

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This type of dyeing by oxidation makes it possible to get colors with very high visibility, coverage of white hair and in a wide variety of shades. However, there are real needs to develop hair dyeing methods, using composition(s) containing oxidative dye(s), leading to more intense color, allowing better level of color coverage of keratin fibers particularly Asian (Chinese, Japanese, and the like) hair, i.e., low selectivity, and resistance to external factors or agents (light, weather, shampooing).

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## DISCLOSURE OF INVENTION

Thus, an objective of the present invention is to provide a dyeing process which is based on oxidative dye(s) having both better level of color coverage of keratin fibers – but also offering more intense coloring – and resistance to external factors or agents.

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The above objective of the present invention can be achieved by a process for treating keratin fibers, in particular hair, comprising the steps of:  
applying onto the keratin fibers a composition comprising at least 0.001% by weight, relative to the total weight of the composition, of one or more oxidative dyes;  
placing the keratin fibers in an occlusive space; and  
heating the keratin fibers to from 50 to 250 °C.

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The process may further comprise the step of rinsing the keratin fibers after the step of applying the composition onto the keratin fibers and/or after the step of heating the keratin fibers.

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The process may further comprise providing the keratin fibers with mechanical tension.

The occlusive space may be formed by at least one coating means. The coating means may be rigid or flexible. The coating means may comprise at least one member selected from the group consisting of a film and a sheet.

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According to the present invention, the keratin fibers may be heated at 60 °C to 150 °C during the step of heating the keratin fibers. The keratin fibers may be heated by at least one heater providing at least one selected from the group consisting of hot air, hot steam, high frequency induction heating, microwave heating, infrared ray irradiation, laser, and flash lamp irradiation. The above coating means may comprise the heater.

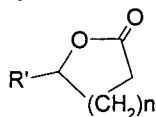
The oxidative dye may be selected from oxidation bases and couplers.

It is preferable that the oxidation bases be selected from ortho- and para-phenylenediamines, double bases, ortho- and para-aminophenols, heterocyclic bases and acid addition salts thereof.

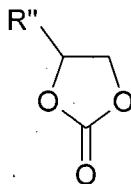
It is preferable that the couplers be selected from meta-aminophenols, meta-phenylenediamines, meta-diphenols, naphthols, heterocyclic couplers and acid addition salts thereof.

The composition may comprise the oxidative dye in an amount of 0.001 to 30% by weight, relative to the total weight of the composition.

It is preferable that the composition comprise at least one organic compound which is liquid at 25 °C and atmospheric pressure (760 mmHg) with a value of Hansen solubility parameter ( $\delta H$ ) of less than 16 MPa<sup>1/2</sup> at 25 °C. This organic compound may be chosen among C<sub>5</sub>-C<sub>30</sub> alkanols; alcohol ethers, particularly C<sub>1</sub>-C<sub>4</sub> ether of C<sub>5</sub>-C<sub>30</sub> alcohols, preferably saturated, optionally interrupted by one or more non vicinal ether groups; aliphatic esters of C<sub>1</sub>-C<sub>4</sub> carboxylic acids and C<sub>3</sub>-C<sub>10</sub> monoalcohols or C<sub>3</sub>-C<sub>10</sub> polyols, optionally interrupted by one or more non vicinal ether groups; aromatic ethers, particularly C<sub>6</sub>-C<sub>10</sub>, of C<sub>1</sub>-C<sub>6</sub> alkyl, optionally bearing a hydroxyl group; alkanol with aryl or oxyaryl substituting group, particularly wherein the aryl part is a C<sub>6</sub>-C<sub>10</sub> aryl, preferably C<sub>6</sub>, and the alkanol is a C<sub>1</sub>-C<sub>4</sub> alkyl; lactones particularly of formula (I)



wherein R' represents a hydrogen, a (C<sub>1</sub>-C<sub>8</sub>) alkyl group, a (C<sub>1</sub>-C<sub>4</sub>) hydroxyalkyl group, n means 1, 2 or 3; alkylene carbonate of formula (II) :



wherein R'' represents a hydrogen atom, a (C<sub>1</sub>-C<sub>8</sub>) alkyl group, a (C<sub>1</sub>-C<sub>4</sub>) hydroxyalkyl group.

The composition may comprise at least one oxidizing agent.

The composition may comprise at least one synthetic direct dye and/or at least one natural direct dye.

Another aspect of the present invention is use of a composition for treating keratin fibers at a

temperature from 50 to 250 °C in an occlusive space, comprising at least one oxidative dye as mentioned above in an amount of 0.001% by weight or more, relative to the total weight of the composition. The composition may comprise at least one oxidizing agent.

- 5 The present invention also relates to a kit for treating keratin fibers, comprising:  
a device comprising  
at least one coating means to form an occlusive space, and  
at least one heater to heat the keratin fibers to from 50 to 250 °C in the occlusive space;  
and  
10 a composition comprising at least 0.001% by weight, relative to the total weight of the  
composition, of one or more oxidative dyes, as previously defined, and optionally comprising at  
least one oxidizing agent.

### BEST MODE FOR CARRYING OUT THE INVENTION

15 After diligent research, the inventors have discovered that it is possible to achieve a dyeing  
process for keratin fibers, such as hair, based on oxidative dye(s) which can provide the keratin  
fibers with intense color, better level of color coverage, and resistance to external factors or agents  
such as a shampoo.

20 According to the present invention, the above coloring process involves in heating keratin fibers in  
a closed or occlusive environment, which limits the evaporation of water or moisture from the  
keratin fibers and maintains the keratin fibers at a higher temperature in the wet state.

25 Thus, the present invention is a process for treating keratin fibers comprising the steps of:  
applying onto the keratin fibers a composition comprising at least 0.001% by weight, relative to  
the total weight of the composition, of one or more oxidative dyes;  
placing the keratin fibers in an occlusive space; and  
heating the keratin fibers to from 50 to 250 °C.

30 Accordingly, the present invention can provide keratin fibers with more intense color, lower  
selectivity (better level of color coverage along with the keratin fibers from root to tip), and  
resistance to external factors or agents such as a shampoo.

35 (Composition)

The composition used for the present invention contains at least one oxidative dye. Two or more  
types of the oxidative dye may be used in combination.

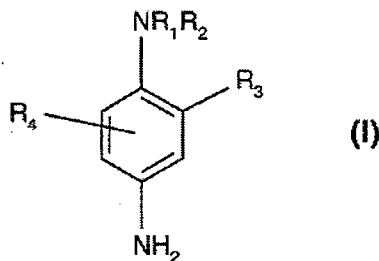
40 The oxidative dye can be selected from oxidation bases and couplers.

The oxidation base can be selected from those conventionally known in oxidation dyeing,  
preferably from the group consisting of ortho- and para-phenylenediamines, double bases, ortho-  
and para-aminophenols, heterocyclic bases and the acid addition salts thereof.

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There may be mentioned in particular:

- (I) the para-phenylenediamines of the following formula (I) and their addition salts with an acid:



in which:

- 5 R<sub>1</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a monohydroxy(C<sub>1</sub>-C<sub>4</sub> alkyl) radical, a polyhydroxy-(C<sub>2</sub>-C<sub>4</sub> alkyl) radical, a (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical, a C<sub>1</sub>-C<sub>4</sub> alkyl radical substituted with a nitrogen-containing group, a phenyl radical or a 4'-aminophenyl radical; R<sub>2</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a monohydroxy(C<sub>1</sub>-C<sub>4</sub> alkyl) radical, a polyhydroxy(C<sub>2</sub>-C<sub>4</sub> alkyl) radical, a (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical or a C<sub>1</sub>-C<sub>4</sub> alkyl radical substituted with a nitrogen-containing group;
- 10 R<sub>1</sub> and R<sub>2</sub> may also form with the nitrogen atom carrying them a 5- or 6-membered nitrogen-containing heterocycle optionally substituted with one or more alkyl, hydroxyl or ureido groups;
- 15 R<sub>3</sub> represents a hydrogen atom, a halogen atom such as a chlorine atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, a sulpho radical, a carboxyl radical, a monohydroxy(C<sub>1</sub>-C<sub>4</sub> alkyl) radical, a hydroxy(C<sub>1</sub>-C<sub>4</sub> alkoxy) radical, an acetylamino(C<sub>1</sub>-C<sub>4</sub> alkoxy) radical, a mesylamino(C<sub>1</sub>-C<sub>4</sub> alkoxy) radical or a carbamoylamino(C<sub>1</sub>-C<sub>4</sub> alkoxy) radical; and
- R<sub>4</sub> represents a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical.
- 20 Among the nitrogen-containing groups of formula (I) above, there may be mentioned in particular the amino, mono(C<sub>1</sub>-C<sub>4</sub>)alkylamino, (C<sub>1</sub>-C<sub>4</sub>)dialkylamino, (C<sub>1</sub>-C<sub>4</sub>)trialkylamino, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino, di(monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl)amino, imidazolium and ammonium radicals.
- 25 Among the para-phenylenediamines of formula (I) above, there may be mentioned more particularly para-phenylenediamine, para-tolylenediamine, 2-chloro-paraphenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethylpara-phenylenediamine, N,N-diethyl-para-phenylenediamine,
- 30 N,N-dipropyl-paraphenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-paraphenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-paraphenylenediamine, 2-isopropyl-para-phenylenediamine,
- 35 N-(β-hydroxypropyl)-paraphenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methylpara-phenylenediamine, N,N-(ethyl-β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine,

2- $\beta$ -acetylamino-ethyloxy-para-phenylenediamine, N-( $\beta$ -methoxyethyl)-para-phenylenediamine, 2-methyl-1-N- $\beta$ -hydroxyethyl-para-phenylenediamine, N-(4-aminophenyl)-3-hydroxy-pyrrolidine, 2-[[2-[(4-Aminophenyl)amino]ethyl](2-hydroxyethyl)amino]-ethanol, and their addition salts with an acid.

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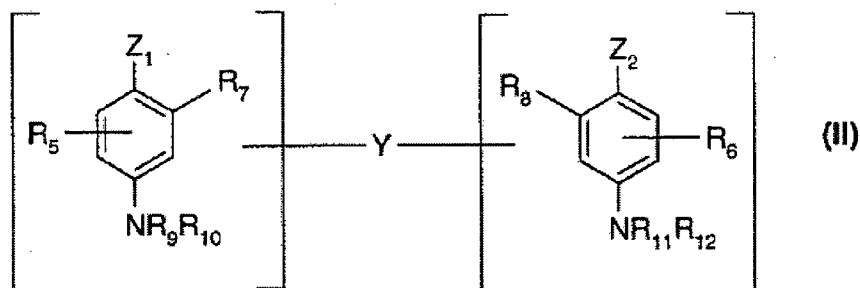
Among the para-phenylenediamines of formula (I) above, there are most particularly preferred para-phenylenediamine, para-tolylenediamine, 2-isopropyl-paraphenylenediamine, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine, and their addition salts with an acid.

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- (II) According to the invention, "double bases" is understood to mean compounds containing at least two aromatic rings on which amino and/or hydroxyl groups are carried.

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Among the double bases which can be used as oxidation bases in the dyeing compositions in accordance with the invention, there may be mentioned in particular compounds corresponding to the following formula (II), and their addition salts with an acid:



20 in which:

- $Z_1$  and  $Z_2$ , which are identical or different, represent a hydroxyl or  $-NH_2$  radical which may be substituted with a  $C_1$ - $C_4$  alkyl radical or with a linking arm Y;
- the linking arm Y represents a linear or branched alkylene chain comprising from 1 to 14 carbon atoms, which may be interrupted by or which may end with one or more nitrogen-containing groups and/or one or more heteroatoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or  $C_1$ - $C_6$  alkoxy radicals;
- $R_5$  and  $R_6$  represent a hydrogen or halogen atom, a  $C_1$ - $C_4$  alkyl radical, a monohydroxy( $C_1$ - $C_4$  alkyl) radical, a polyhydroxy( $C_2$ - $C_4$  alkyl) radical, an amino( $C_1$ - $C_4$  alkyl) radical or a linking arm Y;
- $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$  and  $R_{12}$ , which are identical or different, represent a hydrogen atom, a linking arm Y or a  $C_1$ - $C_4$  alkyl radical; it being understood that the compounds of formula (II) contain only one linking arm Y per molecule.

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Among the nitrogen-containing groups of formula (II) above, there may be mentioned in particular the amino, mono( $C_1$ - $C_4$ )alkylamino, ( $C_1$ - $C_4$ )dialkylamino, ( $C_1$ - $C_4$ )trialkylamino, monohydroxy( $C_1$ - $C_4$ )alkylamino, imidazolium and ammonium radicals.

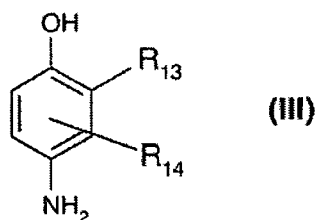
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Among the double bases of formulae (II) above, there may be mentioned more particularly

N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol,  
 N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine,  
 N,N'-bis(4-aminophenyl)-tetramethylenediamine,  
 N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine,  
 5 N,N'-bis(4-methylaminophenyl)tetramethylenediamine,  
 N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylene-diamine,  
 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and their addition salts with an acid.

Among these double bases of formula (II),  
 10 N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol,  
 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane or one of their addition salts with an acid are  
 particularly preferred.

- (III) The para-aminophenols corresponding to the following formula (III), and their addition  
 15 salts with an acid:



in which:

- R<sub>13</sub> represents a hydrogen atom, or a halogen atom such as fluorine, a C<sub>1</sub>-C<sub>4</sub> alkyl,  
 monohydroxy(C<sub>1</sub>-C<sub>4</sub> alkyl), (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)-alkyl, amino(C<sub>1</sub>-C<sub>4</sub> alkyl) or  
 20 hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino-(C<sub>1</sub>-C<sub>4</sub> alkyl) radical,  
 - R<sub>14</sub> represents a hydrogen atom, or a halogen atom such as fluorine, a C<sub>1</sub>-C<sub>4</sub> alkyl,  
 monohydroxy(C<sub>1</sub>-C<sub>4</sub> alkyl), polyhydroxy(C<sub>2</sub>-C<sub>4</sub> alkyl), amino(C<sub>1</sub>-C<sub>4</sub> alkyl), cyano(C<sub>1</sub>-C<sub>4</sub> alkyl) or  
 (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical.

25 Among the para-aminophenols of formula (III) above, there may be mentioned more particularly  
 para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol,  
 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol,  
 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol,  
 4-amino-2-( $\beta$ -hydroxyethylaminomethyl)phenol, and their addition salts with an acid.

30 - (IV) The ortho-aminophenols which can be used as oxidation bases in the context of the present  
 invention are chosen in particular from 2-aminophenol, 2-amino-1-hydroxy-5-methylbenzene,  
 2-amino-1-hydroxy-6-methylbenzene, 5-acetamido-2-aminophenol, and their addition salts with  
 acid.

35 - (V) Among the heterocyclic bases which can be used as oxidation bases in the dyeing  
 compositions in accordance with the invention, there may be mentioned more particularly  
 pyridine derivatives, pyrimidine derivatives, pyrazole derivatives, and their addition salts with an  
 acid.

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Among the pyridine derivatives, there may be mentioned more particularly the compounds described for example in Patents GB 1,026,978 and GB 1,153,196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-( $\beta$ -methoxyethyl)amino-3-amino-6-methoxypyridine, 3,4-diaminopyridine, and their addition salts with an acid.

Among the pyrimidine derivatives, there may be mentioned more particularly the compounds described, for example, in Patents DE 2 359 399; JP 88-169571; JP 91-10659 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triamino-pyrimidine, and the pyrazolopyrimidine derivatives such as those mentioned in patent application FR-A-2 750 048 and among which there may be mentioned pyrazolo[1,5-a]-pyrimidine-3,7-diamine; 2,5-dimethyl-pyrazolo[1,5-a]-pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidin-7-ol; 3-amino-pyrazolo[1,5-a]pyrimidin-5-ol; 2-(3-amino-pyrazolo-[1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-amino-pyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxy-ethyl)amino]-ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol, 5,6-dimethylpyrazolo-[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo-[1,5-a]pyrimidine-3,7-diamine, 2,5,N7,N7-tetramethyl-pyrazolo[1,5-a]pyrimidine-3,7-diamine, 3-amino-5-methyl-7-imidazolylpropyl-aminopyrazolo[1,5-a]-pyrimidine, their addition salts and their tautomeric forms, when a tautomeric equilibrium exists and their addition salts with an acid.

Among the pyrazole derivatives, there may be mentioned more particularly the compounds described in Patents DE 3 843 892, DE 4 133 957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988 such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)-pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazino-pyrazole, 1-benzyl-4,5-diamino-3-methyl-pyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tertbutyl-3-methylpyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)pyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxy-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropyl-pyrazole, 4,5-diamino-3-methyl-1-isopropyl-pyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triamino-pyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole, 3,5-diamino-4-( $\beta$ -hydroxy-ethyl)amino-1-methylpyrazole, and their addition salts with an acid.

Among the heterocyclic bases which can be used as oxidation bases, there may be mentioned more particularly diaminopyrazolopyrazolones and especially 2,3-diamino-6,7-dihydro-1H5H-[pyrazolo1,2,a]pyrazol-1-one and the addition salts of these diaminopyrazolopyrazolones with an acid.



The couplers may be an oxidation coupler which can be selected from those conventionally known in oxidation dyeing, preferably from the group consisting of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthols, heterocyclic couplers and the acid addition salts thereof.

The heterocyclic couplers may be selected from the group consisting of indole derivatives, indoline derivatives, sesamol and its derivatives, pyridine derivatives, pyrazolotriazole derivatives, pyrazolones, indazoles, benzimidazoles, benzothiazoles, benzoxazoles, 1,3-benzodioxoles, quinolines and their addition salts with an acid.

These couplers are more particularly chosen from 2,4-diamino-1-( $\beta$ -hydroxyethoxy)benzene, 2-methyl-5-aminophenol, 5-N-( $\beta$ -hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 2-chloro-3-amino-6-methylphenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2-amino-4-( $\beta$ -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 2-methyl-5-hydroxyethylaminophenol, 4-amino-2-hydroxytoluene, 1,3-bis(2,4-diaminophenoxy)-propane, sesamol, 1-amino-2-methoxy-4,5-methylene-dioxybenzene,  $\alpha$ -naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxy-indoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one, 2-amino-3-hydroxypyridine, 3,6-dimethyl-pyrazolo[3,2-c]-1,2,4-triazole, 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole and their addition salts with an acid.

In general, the addition acid salts of the oxidation bases and couplers are chosen in particular from hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

The composition used for the present invention contains an oxidative dye or dyes (oxidation base(s) and/or coupler(s)) in an amount of 0.001% by weight or more, and may contain, for example, 0.001 to 30% by weight, preferably 0.01 to 20% by weight, and more preferably 0.1 to 10% by weight, relative to the total weight of the composition.

The compositions used for the present invention may also contain at least one additional dye which can be chosen among the direct dyes, more particularly the synthetic direct dyes and the natural direct dyes.

Non-limiting examples of appropriate synthetic direct dyes include neutral, anionic(acidic), and cationic dyes azo, methine, carbonyl, azine, nitro(hetero)aryl types or tri(hetero)arylmethane direct dyes, porphyrins and phthalocyanines, fluorescent dyes, alone or as mixtures.

More particularly, the azo dyes comprise an  $-N=N-$  functional group, the two nitrogen atoms of which are not simultaneously involved in a ring. However, it is not ruled out for one of the two nitrogen atoms of the  $-N=N-$  sequence to be involved in a ring.

The dyes of the family of the methines are more particularly compounds comprising at least one

sequence chosen from  $>C=C<$  and  $-N=C<$ , the two atoms of which are not simultaneously involved in a ring. However, it is specified that one of the nitrogen or carbon atoms of the sequences can be involved in a ring. More particularly, the dyes of this family result from compounds of the following types: true methine (comprising one or more abovementioned  $-C=C-$  sequences); azomethine (comprising at least one or more  $-C=N-$  sequences) with, for example, the azacarbocyanines and their isomers, the diazacarbocyanines and their isomers, the tetraazacarbocyanines; mono- and diarylmethane; indoamines (or diphenylamines); indophenols; indoanilines.

10 As regards the dyes of the family of the carbonyls, mention may be made, for example, of nonnatural dyes chosen from acridone, benzoquinone, anthraquinone, naphthoquinone, benzanthrone, anthranthrone, pyranthrone, pyrazolanthrone, pyrimidinoanthrone, flavanthrone, indanthrone, flavone, (iso)violanthrone, isoindolinone, benzimidazolone, isoquinolinone, anthrapyridone, pyrazoloquinazolone, perinone, quinacridone, quinophthalone, naphthalimide, 15 anthrapyrimidine, diketopyrrolopyrrole or coumarin dyes.

As regards the dyes of the family of the cyclic azines, mention may in particular be made of azine, xanthene, thioxanthene, fluorindine, acridine, (di)oxazine, (di)thiazine or pyronine dyes.

20 The nitro(hetero)aromatic dyes are more particularly nitrobenzene or nitropyridine direct dyes.

As regards the dyes of porphyrin or phthalocyanine type, use may be made of cationic or noncationic compounds optionally comprising one or more metals or metal ions, such as, for example, alkali and alkaline earth metals, zinc and silicon.

25 As used herein, the term "fluorescent dyes" is understood to mean fluorescent compounds and optical brighteners. In at least one embodiment, the fluorescent dye is soluble in the medium of the composition.

30 Fluorescent dyes are fluorescent compounds which absorb visible radiation, for example, wavelengths ranging from 400 to 800 nm, and which are capable of re-emitting light in the visible region at a higher wavelength. According to one embodiment, the fluorescent dyes useful for the present invention re-emit orange-colored fluorescent light. They exhibit, for instance, a maximum re-emission wavelength ranging from 500 to 700 nm.

35 Non-limiting examples of fluorescent dyes include compounds known in the art, for example, those described in Ullmann's Encyclopedia of Industrial Chemistry, Release 2004, 7th edition, "Fluorescent Dyes" chapter.

40 The optical brighteners, are colorless transparent compounds as they do not absorb in visible light but only in ultraviolet light (wavelengths ranging from 200 to 400 nanometers) and convert the energy absorbed into fluorescent light of higher wavelength emitted in the visible part of the spectrum, generally in the blue and/or green, that is to say in wavelengths ranging from 400 to 550 nanometers.

45 Optical brighteners are known in the art, for example, they are described in Ullmann's

Encyclopedia of Industrial Chemistry (2002), "Optical Brighteners" and Kirk-Othmer Encyclopedia of Chemical Technology (1995): "Fluorescent Whitening Agents".

The fluorescent dyes which can be used in the composition of the present disclosure include compounds known from the art, for example, those described in French Patent No. 2 830 189.

5

Mention may be made, as examples of synthetic direct dyes which are particularly suitable, of nitrobenzene dyes, azo, azomethine or methine direct dyes, azacarbocyanines, such as tetraazacarbocyanines (tetraazapentamethines), quinone and in particular anthraquinone, naphthoquinone or benzoquinone direct dyes, or azine, xanthene, triarylmethane, indoamine, phthalocyanine and porphyrin direct dyes, alone or as mixtures. More preferably still, these additional synthetic direct dyes are chosen from nitrobenzene dyes, azo, azomethine or methine direct dyes and tetraazacarbocyanines (tetraazapentamethines); alone or as mixtures.

As natural direct dye, mention may be made of quinone dyes (such as lawsone and juglone), alizarin, purpurin, laccic acid, carminic acid, kermesic acid, purpurogallin, protocatechaldehyde, indigo, sorghum, isatin, betanin, curcuminoids (such as curcumin), spinulosin, various types of chlorophyll and chlorophyllin, hematoxylin, hematein, brazilein, brazilin, safflower dyes (such as carthamin), flavonoids (such as rutin, quercetin, catechin, epicatechin, morin, apigenidin, and sandalwood), anthocyanins (such as apigeninidin and apigenidin), carotenoids, tannins, orceins, santalins and cochineal carmine.

The composition used for the present invention may contain at least one additional direct dye, natural or synthetic, in an amount of 0.01 to 30% by weight, preferably 1 to 20% by weight, and more preferably 2 to 10% by weight, relative to the total weight of the composition.

25

The composition used for the present invention may contain at least one oxidizing agent. Two or more types of the oxidizing agent may be used in combination.

The oxidizing agent may be chosen from hydrogen peroxide, peroxygenated salts, and compounds capable of producing hydrogen peroxide by hydrolysis. For example, the oxidizing agent can be chosen from aqueous hydrogen peroxide solution, urea peroxide, alkali metal bromates and ferricyanides and persalts such as perborates and persulfates. At least one oxidase enzyme chosen, for example, from laccases, peroxidases and 2-electron oxidoreductases such as uricase may also be used as the oxidizing agent, where appropriate in the presence of the respective donor or co-factor thereof.

35

In one embodiment, the oxidizing agent is hydrogen peroxide, such as an aqueous hydrogen peroxide solution.

The hydrogen peroxide concentration may range from 0.15 to 12% by weight such as from 0.6 to 9% by weight relative to the total weight of the oxidizing agent. The concentration of compounds capable of forming hydrogen peroxide by hydrolysis may range from 0.1 to 25% by weight relative to the total weight of the oxidizing agent.

In one embodiment, when the oxidizing agent is an aqueous hydrogen peroxide solution, the

45

oxidizing agent may contain at least one hydrogen peroxide stabilizer, which may be chosen, for example, from alkali metal and alkaline-earth metal pyrophosphates, alkali metal and alkaline-earth metal stannates, phenacetin and salts of acids and of oxyquinoline, for example, oxyquinoline sulphate. In another embodiment, at least one stannate optionally in combination with at least one pyrophosphate is used.

It is also possible to use salicylic acid and its salts, pyridinedicarboxylic acid and its salts, paracetamol.

In the oxidizing agent, the concentration of the hydrogen peroxide stabilizer(s) may range from 0.0001 to 5% by weight such as from 0.01 to 2% by weight relative to the total weight of the oxidizing agent.

In the oxidizing agent comprising an aqueous hydrogen peroxide solution, the concentration ratio of the hydrogen peroxide to the at least one stabilizer may range from 0.05:1 to 1,000:1, such as from 0.1:1 to 500:1 and further such as from 1:1 to 200:1.

The oxidizing agent may be present in the composition used for the present invention or may be applied to keratin fibers independently as the form of an oxidizing composition.

The amount of the oxidizing agent(s) in the composition used for the present invention or the oxidizing composition may range from 0.0001 to 10% by weight, preferably 0.001 to 10% by weight, and more preferably 0.01 to 5% by weight, relative to the total weight of the composition.

It is preferable that the composition used for the present invention contain at least one organic compound which is liquid at 25 °C and atmospheric pressure (760 mmHg) with a value of Hansen solubility parameter ( $\delta H$ ) of less than 16 MPa<sup>1/2</sup> at 25 °C. Two or more types of the organic compound may be used in combination. The organic compound is preferably capable of functioning as an organic solvent.

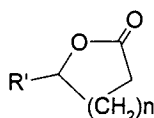
According to one particular embodiment, the  $\delta H$  value is preferably less than 15 MPa<sup>1/2</sup> at 25 °C, more preferably less than 14.5 MPa<sup>1/2</sup> at 25 °C, and further more preferably less than 14 MPa<sup>1/2</sup> at 25 °C. According to one particularly preferred embodiment, the  $\delta H$  value is greater than 0. According to one variant, the  $\delta H$  value may be greater than 3 MPa<sup>1/2</sup> at 25 °C, preferably greater than 4 MPa<sup>1/2</sup> at 25 °C, and more preferably greater than 5 MPa<sup>1/2</sup> at 25 °C.

The organic compounds, such as organic solvents, having a value of the Hansen solubility parameter  $\delta H$  as defined previously are, for example, described in the reference work "Hansen solubility parameters--A user's handbook", Charles M. Hansen, CRC Press, 2000, pages 167 to 185.

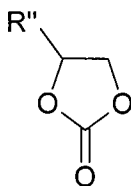
This value takes into account the solubility parameter  $\delta H$  linked to the formation of hydrogen bonds. It is recalled that there are three main types of interactions in organic compounds, non-polar interactions, permanent dipole-dipole interactions and hydrogen bonding type interactions, the latter being the subject of the parameter that defines the organic compound

preferably used in the present invention.

It is preferable that the organic compound be selected from the group consisting of C<sub>5</sub>-C<sub>30</sub> alkanols; alcohol ethers, particularly C<sub>1</sub>-C<sub>4</sub> ether of C<sub>5</sub>-C<sub>30</sub> alcohols, preferably saturated,  
 5 optionally interrupted by one or more non vicinal ether groups; aliphatic esters of C<sub>1</sub>-C<sub>4</sub> carboxylic acids and C<sub>3</sub>-C<sub>10</sub> monoalcohols or C<sub>3</sub>-C<sub>10</sub> polyols, optionally interrupted by one or more non vicinal ether groups; aromatic ethers, particularly C<sub>6</sub>-C<sub>10</sub>, of C<sub>1</sub>-C<sub>6</sub> alkyl, optionally bearing a hydroxyl group; alkanol with aryl or oxyaryl substituting group, particularly wherein the aryl part is a C<sub>6</sub>-C<sub>10</sub> aryl, preferably C<sub>6</sub>, and the alkanol is a C<sub>1</sub>-C<sub>4</sub> alkyl; lactones particularly of  
 10 formula (I):



wherein R' represents a hydrogen, a (C<sub>1</sub>-C<sub>8</sub>) alkyl group, a (C<sub>1</sub>-C<sub>4</sub>) hydroxyalkyl group, n means 1,  
 15 2 or 3; alkylene carbonate of formula (II) :



wherein R'' represents a hydrogen atom, a (C<sub>1</sub>-C<sub>8</sub>) alkyl group, a (C<sub>1</sub>-C<sub>4</sub>) hydroxyalkyl group.  
 20

As the alkylene carbonate, mention may be made of ethylene carbonate (R''=H), propylene carbonate (R''=CH<sub>3</sub>), glycerol carbonate (R''=CH<sub>2</sub>OH), or else butylene carbonate (R''=CH<sub>2</sub>CH<sub>3</sub>). Among the alkylene carbonates, propylene carbonate is preferred.

25 It is also preferable that the organic compound be selected from propyleneglycol derivatives, aromatic alcohols and alkylene carbonates.

As the propyleneglycol derivatives, mention may be made of propyleneglycol ethers having at least one free alcohol functional moiety, or propyleneglycol esters having at least one ether  
 30 moiety.

The term "aromatic alcohol" means an alcohol having at least one hydroxyl group which does not directly bond to an aromatic moiety such as a benzene ring. As the aromatic alcohols, mention may be made of benzyl alcohol, phenyl ethanol, and phenyl propanol.  
 35

In particular, as the organic compound, mention may be made of the compounds in the following table.

Name	Chemical formula	$\delta H$
Dipropylene glycol methyl ether	$\text{CH}_3\text{O}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_2\text{H}$	11.2
Tripropylene glycol methyl ether	$\text{CH}_3\text{O}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_3\text{H}$	10.4
Propylene glycol n-butyl ether (PnB)	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$	9.2
Propylene glycol n-propyl ether (PnP)	$\text{C}_9\text{H}_7\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$	9.2
Dipropylene glycol monomethyl ether acetate	$\text{CH}_3\text{COO}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_2\text{CH}_3$	8.0
Benzyl alcohol	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	13.7
Ethylene glycol 2-ethylhexyl ether	$\text{C}_8\text{H}_{17}\text{OCH}_2\text{CH}_2\text{OH}$	5.1
2-pentanol	$\text{CH}_3\text{CH}(\text{OH})\text{C}_3\text{H}_7$	13.3

The composition used for the present invention may contain the organic compound(s) which is/are liquid at 25 °C and atmospheric pressure (760 mmHg) with a value of Hansen solubility parameter of less than  $16 \text{ MPa}^{1/2}$  at 25 °C in an amount of 0.1 to 80% by weight, preferably 1 to 50% by weight, and more preferably 2 to 30% by weight, relative to the total weight of the composition.

The composition used for the present invention may contain water. Preferably, the amount of water in the composition used for the present invention may be at least equal to 40% by weight relative to the total weight of the composition. More preferably, the amount of water may be at least equal to 70% relative to the total weight of the composition.

The composition used for the present invention may contain at least one additional organic solvent different from the compounds with the value of the component  $\delta H$  of the Hansen solubility parameter as defined previously. By way of example, mention may be made of  $\text{C}_1$ - $\text{C}_4$  lower alkanols, such as ethanol and isopropanol; polyols such as propylene glycol or glycerol and mixtures thereof.

The amount of the above additional organic solvent(s) in the composition used for the present invention may vary between around 0.1 and 80% by weight, preferably between around 0.5 and 50% by weight, and more preferably between 1 and 30% by weight, relative to the total weight of the composition.

The compositions used for the present invention may also contain various adjuvants conventionally used in compositions for dyeing hair, such as anionic, non-ionic, cationic, amphoteric or zwitterionic polymers, or mixtures thereof, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, conditioning agents, film-forming agents, ceramides, preservatives and opacifying agents.

By way of conditioning agent, mention may be made of branched or unbranched, volatile or non-volatile linear or cyclic silicones. These silicones may be in the form of oils, resins or gums, they may in particular be polyorganosiloxanes that are insoluble in the cosmetically acceptable medium.

Organopolysiloxanes are defined in greater detail in the work by Walter Noll, "Chemistry and

Technology of Silicones" (1968) Academic Press. They may be volatile or non-volatile.

When they are volatile, the silicones are more particularly chosen from those having a boiling point between 60 °C and 260 °C.

5 By way of conditioning agent, use can also be made of polymers such as the polyquaterniums 22, 6, 10, 11, 35 and 37 and hexadimethrine chloride.

10 The concentration of conditioning agent(s) in the composition used for the present invention may vary from 0.01 to 10% by weight, preferably from 0.05 to 5% by weight, and more preferably from 0.1 to 3% by weight, relative to the total weight of the composition.

The compositions used for the present invention may contain, in addition, at least one thickening agent also known as "rheology modifiers". This agent may be mineral or organic.

15 The organic thickening agents may be chosen from fatty acid amides (coconut diethanolamide or monoethanol-amide, oxyethylenated alkyl ether carboxylic acid monoethanolamide), polymeric thickeners such as cellulose thickeners (hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose), guar gum and its derivatives (hydroxypropyl guar), gums of microbial origin (xanthan gum, scleroglucan gum), homopolymers crosslinked with acrylic acid or acrylamidopropanesulfonic acid and neutral, anionic, amphoteric or cationic associative polymers (polymers comprising hydrophilic zones, and hydrophobic zones having a fatty chain, that are capable, in an aqueous medium, of reversibly associating with one another or with other molecules).

25 According to one particular embodiment, the thickener is polymeric and is chosen from cellulose thickeners (hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose), guar gum and its derivatives (hydroxypropyl guar), gums of microbial origin (xanthan gum, scleroglucan gum), homopolymers crosslinked with acrylic acid or acrylamidopropanesulfonic acid.

30 The composition used for the present invention may furthermore contain at least one surfactant.

The surfactant(s) may be selected from the following (i) to (iv).

35 (i) Anionic Surfactant(s)

An "anionic surfactant" is understood to mean a surfactant only comprising anionic groups as ionic or ionizable groups. These groups are preferably chosen among the  $-C(O)OH$ ,  $-C(O)O^-$ ,  $-SO_3H$ ,  $-S(O)_2O^-$ ,  $-OS(O)_2OH$ ,  $-OS(O)_2O^-$ ,  $-P(O)OH_2$ ,  $-P(O)_2O^-$ ,  $-P(O)O_2^-$ ,  $-P(OH)_2$ ,  $=P(O)OH$ ,  $-P(OH)O^-$ ,  $=P(O)O^-$ ,  $=POH$ ,  $=PO^-$  groups, where the anionic parts comprise a cationic counter-ion such as an alkaline metal, an alkaline-earth metal or ammonium.

45 The following can be listed as anionic surfactants which can be used in the composition according to the invention: alkyl sulfates, alkyl ether sulfates, alkylamidoether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates, alkyl sulfonates, alkyl amide sulfonates, alkyl aryl sulfonates, alpha-olefin

sulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkyl amide sulfosuccinates, alkyl sulfoacetates, acylsarcosinate, acylglutamates, alkyl sulfosuccinamates, acylisethionates, N-acyltaurates, alkyl and polyglycoside polycarboxylic acid monoester salts, acyllactylates, D-galactoside uronic acid salts, alkyl ether carboxylic acid salts, alkylaryl ether  
5 carboxylic acid salts, alkylamido ether carboxylic acid salts, and the corresponding unsalted forms of all these compounds, where the alkyl and acyl groups of all these compounds comprise from 6 to 40 carbon atoms and the aryl group designates a phenyl group.

10 These compounds can be oxyethylenated and then comprise preferably from 1 to 50 ethylene oxide units.

The salts of C<sub>6</sub>-C<sub>24</sub> alkyl and polyglycoside-polycarboxylic acid monoesters can be chosen among the C<sub>6</sub>-C<sub>24</sub> alkyl polyglycoside citrates, C<sub>6</sub>-C<sub>24</sub> alkyl polyglycoside tartrates and the C<sub>6</sub>-C<sub>24</sub> alkyl polyglycoside sulfosuccinates.

15 When the anionic surfactant(s) is/are in salt form, they can be chosen from alkaline metal salts such as sodium or potassium salts and preferably sodium, ammonium salts, amine salts and in particular amino alcohols, or alkaline-earth metal salts such as magnesium salts.

20 The following can be cited in particular as examples of amino alcohol salts: mono-, di- and tri-ethanolamine salts, mono-, di- or tri-isopropanolamine salts, and the salts of 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propanediol and tris(hydroxy-methyl)amino methane.

25 Preferably the alkaline or alkaline earth metal salts and in particular the sodium or magnesium salts are used.

30 Among the cited anionic surfactants, the use of (C<sub>6</sub>-C<sub>24</sub>)alkyl sulfates, (C<sub>6</sub>-C<sub>24</sub>)alkyl ether sulfates comprising from 2 to 50 ethylene oxide units, especially in the form of alkaline metal, ammonium, amino alcohol and alkaline-earth metal salts, or a mixture of these compounds, is preferred.

35 In particular, the use of (C<sub>12</sub>-C<sub>20</sub>)alkyl sulfates, (C<sub>12</sub>-C<sub>20</sub>)alkylether sulfates comprising from 2 to 20 ethylene oxide units, especially in the form of alkaline metal, ammonium, amino alcohol and alkaline-earth metal salts, or a mixture of these compounds, is preferred. Better still, the use of sodium lauryl ether sulfate with 2.2 mol of ethylene oxide is preferred.

#### (ii) Non-Ionic Surfactant(s)

40 The non-ionic surfactants are themselves also compounds which are well known per se (in this respect see, in particular, "Handbook of Surfactants" by M. R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178). Thus, they may especially be chosen from (non-limiting list) alcohols,  $\alpha$ -diols or alkylphenols that are polyethoxylated or polypropoxylated, having a fatty chain comprising, for example 8 to 18 carbon atoms, the number of ethylene oxide or propylene oxide groups possibly ranging, in particular, from 2 to 50. Mention may also be  
45 made of the copolymers of ethylene and propylene oxide, the condensates of ethylene and



propylene oxide with fatty alcohols; polyethoxylated fatty amides preferably having from 2 to 30 mol of ethylene oxide, polyglycerolated fatty amides comprising, on average, 1 to 5, and in particular 1.5 to 4, glycerol groups; oxyethylenated esters of sorbitan fatty acids having from 2 to 30 mol of ethylene oxide; sucrose fatty acid esters, polyethylene glycol fatty acid esters, alkyl polyglycosides, N-alkylglucamine derivatives, amine oxides such as oxides of (C<sub>10</sub>-C<sub>14</sub>) alkylamines or oxides of N-acylamino-propylmorpholine.

(iii) Amphoteric or Zwitterionic Surfactant(s)

The amphoteric or zwitterionic surfactants may especially be (non-limiting list) derivatives of aliphatic secondary or tertiary amines in which the aliphatic radical is a linear or branched chain comprising 8 to 18 carbon atoms and containing at least one water-solubilizing anionic group (for example carboxylate, sulfonate, sulfate, phosphate or phosphonate); mention may also be made of (C<sub>8</sub>-C<sub>20</sub>)alkyl betaines, sulfobetaines, (C<sub>8</sub>-C<sub>20</sub>)alkylamido-(C<sub>1</sub>-C<sub>6</sub>) alkyl betaines or (C<sub>8</sub>-C<sub>20</sub>)alkylamido(C<sub>1</sub>-C<sub>6</sub>)alkyl sulfobetaines.

Among the amine derivatives, mention may be made of the products sold under the name MIRANOL, as described in U.S. Pat. Nos. 2,528,378 and 2,781,354 and classified in the CTFA dictionary, 3rd edition, 1982, under the names Amphocarboxyglycinates and Amphocarboxypropionates.

These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names Disodium Cocoamphodiacetate, Disodium Lauroamphodiacetate, Disodium Caprylamphodiacetate, Disodium Capryloamphodiacetate, Disodium Cocoamphodipropionate, Disodium Lauroamphodipropionate, Disodium Capryl-amphodipropionate, Disodium Capryloamphodipropionate, Lauroamphodipropionic acid, Cocoamphodipropionic acid.

By way of example, mention may be made of the cocoamphodiacetate sold under the trade name MIRANOL® C2M concentrate by Rhodia Chimie.

(iv) Cationic Surfactants

Among the cationic surfactants, mention may, in particular, be made (non-limiting list) of: salts of primary, secondary or tertiary fatty amines, optionally polyoxyalkylenated; quaternary ammonium salts such as tetraalkylammonium, alkylamidoalkyltrialkylammonium, trialkylbenzylammonium, trialkylhydroxyalkylammonium or alkylpyridinium chlorides or bromides; imidazoline derivatives; or oxides of amines having a cationic nature.

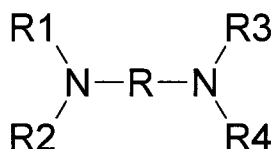
The amount of surfactant(s) present in the composition used for the process of the present invention may vary from 0.01 to 40% by weight, preferably from 0.5 to 30% by weight, relative to the total weight of the composition.

The pH of the composition applied to the keratin fibers is generally between 2 and 13, preferably between 3 and 11, and more preferably between 7 and 11. It may be adjusted to the desired value using acidifying or basifying agents commonly used in dyeing keratinous fibers or else

using conventional buffer systems.

Among the acidifying agents, mention may be made, by way of example, of mineral or organic acids such as hydrochloric acid, ortho-phosphoric acid, sulfuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid, lactic acid and sulfonic acids.

Among the basifying agents, mention may be made, by way of example, of ammonium hydroxide, alkali metal carbonates, alkanolamines such as mono-, di- and triethanolamines and also their derivatives, sodium or potassium hydroxide and compounds of formula below:



wherein R denotes an alkylene such as propylene optionally substituted by a hydroxyl or a C<sub>1</sub>-C<sub>4</sub> alkyl radical, and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently denote a hydrogen atom, an alkyl radical or a C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radical, which may be exemplified by 1,3-propanediamine and derivatives thereof. Arginine, urea and monoethanolamine are preferable.

(Keratin Fiber Treatment Process)

The process for treating keratin fibers according to the present invention can be performed by: applying onto the keratin fibers the composition as described above; then placing the keratin fibers in an occlusive space; and then heating the keratin fibers to from 50 to 250 °C,

According to the present invention relating to the treatment process for keratin fibers, keratin fibers such as hair are subjected to a specific heating process which is performed in an occlusive space.

The heating process can be performed by any heating means which can be freely controlled to realize the temperature desired for the process.

The heating process may preferably be performed by using a special heating device or devices that can form an occlusive space to restrict the evaporation of evaporable components such as water in the above-described composition from keratin fibers and keep a predetermined temperature in the heating device throughout the process.

If the evaporable components such as water in the above-described composition evaporate from the keratin fibers, most of the heat energy applied to the keratin fibers will be consumed by the evaporation, and therefore the temperature of the keratin fibers cannot increase up to the predetermined temperature until all evaporable components in the composition evaporate.

The above heating device may comprise a heat energy source being either in contact with keratin

fibers or apart from keratin fibers, and at least one means to form an occlusive space surrounding the keratin fibers.

The heat energy source is used to heat keratin fibers. The heat energy source may be at least one heater providing at least one selected from the group consisting of hot air, hot steam, high frequency induction heating, microwave heating, infrared ray irradiation, laser, and flash lamp irradiation.

The occlusive space may be formed by at least one coating means. A plurality of coating means may be used. The coating means may be rigid or flexible.

The coating means may comprise at least one member selected from the group consisting of a film and a sheet. The material of the film or the sheet is not limited. For example, the film or the sheet may comprise a thermoplastic or thermosetting resin, a paper, a textile, a bonnet, a metal foil such as aluminum foil, and the like.

For example, the film or sheet may be set on a heating rod, a heating bar or a heating plate which is covered by keratin fibers.

According to the present invention, the coating means may comprise the heat energy source. Therefore, for example, the film or sheet which includes a heater may be set on a rod, a bar, or a plate which is covered by keratin fibers.

The occlusive conditions can restrict the evaporation of evaporable components such as water in the above-described composition applied to keratin fibers, and therefore the temperature of the keratin fibers can be increased higher than that obtainable by a conventional heating process or device for the keratin fibers in open conditions. Furthermore, the keratin fibers can be heated effectively, and the keratin fibers can be heated evenly.

According to one variation of the present invention, the occlusive space may comprise apertures, the surface area of which is less than 5%, preferably less than 3% and more particularly less than 0.5% of the total surface area of the coating means. According to this variation, the total surface area of the coating means comprises the surface area of, when it is present, an opening means for the coating means.

The apertures may be passages, holes or orifices, which may allow an exchange of air between the occlusive space and the exterior thereof, especially when the reaction such as forming vapor inside the occlusive space is too great. On the other hand, a person skilled in the art could form the apertures such that the diffusion of heat in the occlusive space is not impaired.

The keratin fibers can be heated at 50°C to 230 °C, preferably 60 °C to 200 °C, more preferably 60 °C to 150 °C, more preferably 60 °C to 90 °C, during the step of heating the keratin fibers.

The heating process may be performed for an appropriate time which is required to treat the keratin fibers. The time length for the heating process is not limited, but it may be from 1 minute

to 2 hours, preferably 1 minute to 1 hour, and more preferably 1 minute to 30 minutes. For example, the time for heating may be from 5 to 20 minutes, preferably 10 to 15 minutes.

5 The keratin fibers may be rinsed after the step of applying the composition onto the keratin fibers and/or after the step of heating the keratin fibers.

According to one embodiment of the process for treating keratin fibers according to the present invention, mechanical tension may be applied to the keratin fibers.

10 If mechanical tension is provided to keratin fibers, the treatment process according to the present invention may be performed as follows.

15 First, keratin fibers are subjected to mechanical tension. The mechanical tension can be applied to the keratin fibers by any means to deform the keratin fibers to an intended shape. For example, the mechanical tension may be provided by at least one reshaping or mechanically tensioning means selected from the group consisting of a curler, a roller, a clip, a plate and an iron. The reshaping or mechanically tensioning means may comprise at least one heater as described above. If the keratin fibers are rolled around a curler, this rolling-up may be performed on the entire length of the keratin fibers or, for example, on half the length of the keratin fibers. Depending on, 20 for example, the desired hairstyle shape and amount of curls, the rolling-up may be performed with more or less thick locks.

25 Next, the above-described composition is applied to the keratin fibers. The application of the composition may be performed by any means, such as a brush and a comb. The keratin fibers to which the mechanical tension has been applied should be treated with the composition. It may be possible that the keratin fibers are left as they are for a certain amount of time, if necessary.

30 Lastly, the above-described heating process is performed. The heat energy is applied to the keratin fibers under occlusive conditions as described above.

This process for permanent deformation of keratin fibers may be performed without any step of oxidizing the keratin fibers. Therefore, the time required for the process according to the present invention can be shorter than that for a conventional process which needs an oxidizing step. Furthermore, damage to the keratin fibers by the oxidizing step can be avoided.

35 The keratin fibers may be rinsed after the step of applying the composition onto the keratin fibers and/or after the step of heating the keratin fibers.

One embodiment of the treatment process according to the present invention may comprise:

- 40 a) a step of placing keratin fibers under mechanical tension by rolling them up on at least one reshaping or mechanically tensioning means so as to form curls;
- b) a step of applying the above-described composition to the keratin fibers;
- c) an optional step of rinsing the keratin fibers,
- 45 d) a step of placing at least one coating means on the reshaping or mechanically tensioning means or vice versa to form one or more occlusive spaces; and

- e) a step of heating the keratin fibers at a temperature of between 50 and 250 °C, preferably for 1 minute to 2 hours. However, the time for the heating should not be limited.

In this process, the temperature can be set, adjusted and regulated by using one or more heating means, and may be measured with a thermo-measurement probe such as Digital Surface Sensor Module, reference MT-144, sold by Sakaguchi E.H VOC Corp (Japan), set on the keratin fibers. Normally, the probe is set on a single keratin fiber. However, it is advantageous that the probe be set on the part of the keratin fibers which directly contacts with the occlusive space, and more preferably, the probe be set on the part of the keratin fibers which directly contacts with the occlusive space and forms the curl end of the keratin fibers, if a curler is used.

Preferably, the temperature is measured at atmospheric pressure of 101,325 Pa.

According to the present invention, the temperature of the keratin fibers may be constant with a fluctuation of  $\pm 2$  or  $3$  °C over the head, if the keratin fibers are hair, of an individual, and the probe may be set on any type of keratin fibers.

If the keratin fibers are hair, according to the present invention, the constant temperature with a fluctuation of  $\pm 2$  or  $3$  °C can be obtained for any type of hair, and the temperature of the hair can be controlled to be constant  $\pm 2$  or  $3$  °C during the heating of the hair at a certain temperature. Thus, the hair style becomes uniform and homogeneous for the entirety of the hair, and a further excellent hair style can be finally obtained.

Advantageously, the coating means may comprise one or more thermal insulating materials, and more advantageously, the coating means may consist of the material(s).

The term "thermal insulating material" means any material which has an electric conductivity of 0 to  $1 \text{ W/m}^\circ\text{C}$  (PVC:  $0.17 \text{ W/m}^\circ\text{C}$ ).

Preferably, the heating means may be adjusted such that the temperature measured on the keratin fibers is  $50^\circ\text{C}$  or more, more preferably  $55^\circ\text{C}$  to less than  $150^\circ\text{C}$ , and further more preferably less than  $100^\circ\text{C}$ . It is preferable that the heating be performed by heating via electrical resistance.

Advantageously, the coating means is impermeable with regard to the composition used in the step b).

In the above embodiment, at least one of the reshaping or mechanical tensioning means and at least one of the covering means may include a heater.

In the above embodiment, "occlusive space" means that when the coating means is placed on the reshaping or mechanical tensioning means, or vice versa, they together form a closed structure in which heat can diffuse, but heat cannot diffuse out of or is difficult to diffuse out of the closed structure. It is preferable that the coating means and the reshaping or mechanical tensioning means can form the occlusive space when they are set on the head, if the keratin fibers are hair.

The occlusive space may form a condensation cage in which water and a component or components in the composition used in the step b) may evaporate from the keratin fibers, adhere to the wall of the coating means, and drop onto the keratin fibers. This cycle may be repeated during the heating of the keratin fibers. Thus, the keratin fibers can be always kept wet, and drying and deterioration of the keratin fibers will be prevented.

The formation of the occlusive space is an important characteristic of the present invention, because the keratin fibers in the occlusive space can be kept wet and the temperature of the keratin fibers can be kept constant.

Preferably, the process of the present invention may comprise an additional step of tightening the coating means on the head of an individual, if the keratin fibers are hair, by an elastic cord, an extensible band, or a stretch.

According to the process of the present invention, because of the occlusive space in which the composition can be continuously condensed on the keratin fibers, the amount of a cosmetic component or components in the composition is advantageously reduced as compared to the processes in the prior art. The amount of the cosmetic component(s) may be 0.3 to 3 % by weight of the composition.

In a preferred embodiment, a coating means may be placed on each hair curler as the reshaping or mechanically tensioning means, if the keratin fibers are hair. In other words, each of the hair curlers, if two or more hair curlers are used, may be covered individually by a coating means. It is advantageous to cover each hair curler because leaking to the scalp of the composition which has been applied onto keratin fibers in the step b) can be prevented.

In another preferred embodiment, a coating means may cover all hair curlers, if two or more hair curlers are used. In other words, the coating means may cover the entirety of the head if the keratin fibers are hair.

Advantageously, the occlusive space formed in the step d) may be maintained during the step e). In other words, the coating means may be removed only after the step e) or after the stopping of the heating in the step e).

If necessary, the composition may be applied to keratin fibers before applying mechanical tension to the keratin fibers. It may be possible that the keratin fibers are left as they are for a certain amount of time, if necessary, before and/or after applying mechanical tension to the keratin fibers, before and/or after applying the above-described composition to the keratin fibers, and before and/or after heating the keratin fibers.

After the above step e), if necessary, the keratin fibers may be fixed by oxidation after being taken out from the coating means.

(Use and Products)

The present invention also relates to use of a composition for treating keratin fibers at a temperature from 50 to 250 °C in an occlusive space, comprising at least one oxidative dye as mentioned above in an amount of 0.001% by weight or more of the composition. This composition may have the same technical features as those of the composition described above.

5 The composition may comprise at least one oxidizing agent.

The present invention also relates to a kit for treating keratin fibers, comprising:  
a device comprising

at least one coating means to form an occlusive space, and

10 at least one heater to heat the keratin fibers to from 50 to 250 °C in the occlusive space;

and

a composition comprising at least one oxidative dye in an amount of 0.001% by weight or more of the composition, which may optionally comprise at least one oxidizing agent.

15 The coating means and the heater, as well as the composition in the kit, may be the same as those described above.

#### EXAMPLE

20 The present invention will be described in more detail by way of examples, which however should not be construed as limiting the scope of the present invention.

#### **Evaluation 1**

25 Two hair swatches of natural or permed Caucasian hair with 90% white hair were treated with Majirêve 5.52 Coloring (a composition comprising an oxidative dye) sold by L'Oreal Professional.

As a control (Control 1), each of one of the natural hair swatches and one of the permed hair swatches was left for 30 minutes at room temperature.

30

As an example of the present invention (Example 1), each of the other natural or permed hair swatch was rolled on a curler composed of a 1.7 cm diameter polyethylene cylinder covering an electric resistance. Then, the hair swatch on the curler was further covered with a polyvinylchloride plastic film, and the curler was plugged with electrical connection into a Digital Perm device (Oohiro, model ODIS-2) delivering 10 W of power per curler. Then, the hair swatch was heated for 30 minutes at 90 °C.

35

At the end of the developping time, heating of the curler was stopped. Then, after removing the plastic film, the hair was unrolled. All of the hair swatches were rinsed, wash with a shampoo, rinsed and then dried under a dryer.

40

It was found that all the natural and permed hair swatches had mahogany color.

It was also found that the color of the hair swatches according to Example 1 was less selective and more intense than that of the hair swatches according to Control 1. In particular, the Chinese hair

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swatch colored in accordance with Example 1 had further less selective and more brilliant color than that colored according to Control 1.

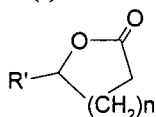


## CLAIMS

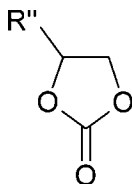
1. A process for treating keratin fibers comprising the steps of:  
applying onto the keratin fibers a composition comprising at least 0.001% by weight,  
5 relative to the total weight of the composition, of one or more oxidative dyes;  
placing the keratin fibers in an occlusive space; and  
heating the keratin fibers to from 50 to 250 °C.
2. The process according to Claim 1, further comprising the step of rinsing the keratin fibers  
10 after the step of applying the composition onto the keratin fibers and/or after the step of  
heating the keratin fibers.
3. The process according to Claim 1 or 2, further comprising providing the keratin fibers with  
15 mechanical tension.
4. The process according to any one of Claims 1 to 3, wherein the occlusive space is formed  
by at least one coating means.
5. The process according to Claim 4, wherein the coating means is rigid or flexible.
- 20 6. The process according to Claim 4 or 5, wherein the coating means comprises at least one  
member selected from the group consisting of a film and a sheet.
7. The process according to any one of Claims 1 to 6, wherein the keratin fibers are heated at  
25 60 °C to 150 °C during the step of heating the keratin fibers.
8. The process according to any one of Claims 1 to 7, wherein the keratin fibers are heated by  
at least one heater providing at least one selected from the group consisting of hot air, hot  
30 steam, high frequency induction heating, microwave heating, infrared ray irradiation, laser,  
and flash lamp irradiation.
9. The process according to Claim 8, wherein the coating means comprises the heater.
10. The process according to any one of Claims 1 to 9, wherein the oxidative dye is selected  
35 from oxidation bases and couplers.
11. The process according to Claim 10, wherein the oxidation bases are selected from ortho-  
and para-phenylenediamines, double bases, ortho- and para-aminophenols, heterocyclic  
40 bases and acid addition salts thereof.
12. The process according to Claim 10, wherein the couplers are selected from  
meta-aminophenols, meta-phenylenediamines, meta-diphenols, naphthols, heterocyclic  
couplers and acid addition salts thereof.
- 45 13. The process according to any one of Claims 1 to 12, wherein the composition comprises at

least one organic compound which is liquid at 25 °C and atmospheric pressure (760 mmHg) with a value of Hansen solubility parameter ( $\delta H$ ) of less than  $16 \text{ MPa}^{1/2}$  at 25°C.

14. Process according to claim 13, wherein the organic compound is chosen among C<sub>5</sub>-C<sub>30</sub> alkanols; alcohol ethers, particularly C<sub>1</sub>-C<sub>4</sub> ether of C<sub>5</sub>-C<sub>30</sub> alcohols, preferably saturated, optionally interrupted by one or more non vicinal ether groups; aliphatic esters of C<sub>1</sub>-C<sub>4</sub> carboxylic acids and C<sub>3</sub>-C<sub>10</sub> monoalcohols or C<sub>3</sub>-C<sub>10</sub> polyols, optionally interrupted by one or more non vicinal ether groups; aromatic ethers, particularly C<sub>6</sub>-C<sub>10</sub>, of C<sub>1</sub>-C<sub>6</sub> alkyl, optionally bearing a hydroxyl group; alkanol with aryl or oxyaryl substituting group, particularly wherein the aryl part is a C<sub>6</sub>-C<sub>10</sub> aryl, preferably C<sub>6</sub>, and the alkanol is a C<sub>1</sub>-C<sub>4</sub> alkyl; lactones particularly of formula (I)



wherein R' represents a hydrogen, a (C<sub>1</sub>-C<sub>8</sub>) alkyl group, a (C<sub>1</sub>-C<sub>4</sub>) hydroxyalkyl group, n means 1, 2 or 3; alkylene carbonate of formula (II) :



wherein R'' represents a hydrogen atom, a (C<sub>1</sub>-C<sub>8</sub>) alkyl group, a (C<sub>1</sub>-C<sub>4</sub>) hydroxyalkyl group.

15. The process according to any one of Claims 1 to 14, wherein the composition comprises the oxidative dye in an amount of 0.001 to 30% by weight, relative to the total weight of the composition.
16. The process according to any one of Claims 1 to 15, wherein the composition comprises at least one synthetic direct dye and/or at least one natural direct dye.
17. The process according to any one of Claims 1 to 16, wherein the composition comprises at least one oxidizing agent.
18. A kit for treating keratin fibers, comprising:  
 a device comprising  
 at least one coating means to form an occlusive space, and  
 at least one heater to heat the keratin fibers to from 50 to 250 °C in the occlusive space;  
 and  
 a composition comprising at least one oxidative dye in an amount of 0.001% by weight or more, relative to the total weight of the composition, optionally comprising at least one oxidizing agent.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/JP2012/055312

A. CLASSIFICATION OF SUBJECT MATTER INV. A61K8/22 A61Q5/10 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, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/229520 A1 (JAVET MANUELA [CH] ET AL) 25 September 2008 (2008-09-25)	1,2,4-8, 10-12, 15,16,18
Y	paragraphs [0006], [0008], [0009], [0018], [0022], [0023], [0025], [0030], [0031]	1-18
Y	----- US 2009/159093 A1 (YU KENT [US]) 25 June 2009 (2009-06-25) paragraphs [0038], [0039], [0041] claim 19 ----- -/--	1-12, 15-18
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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	Date of mailing of the international search report	
22 January 2013	31/01/2013	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Lenzen, Achim	

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/JP2012/055312

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/074144 A1 (OREAL [FR]; DE BONI MAXIME [JP]; TAKAHASHI HIROSHI [JP]) 23 June 2011 (2011-06-23) page 2, line 1 - line 36 page 3, line 32 - page 4, line 11 page 4, line 20 - line 27 page 8, line 7 - line 23 -----	1-12, 15-18
Y	JP 2000 189230 A (KAO CORP) 11 July 2000 (2000-07-11) paragraphs [0007], [0009] figures 1-3 claim 1 -----	1-12, 15-18
Y	EP 2 359 804 A2 (OREAL [FR]) 24 August 2011 (2011-08-24) paragraphs [0095] - [0100] examples 1-6 -----	13,14

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2012/055312

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EP 2359804	A2	24-08-2011	NONE
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