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(54) Title: COMPOSITION COMPRISING AT LEAST ONE ANTHRONE DERIVATIVE AND ONE BASIFYING AGENT, AND METHOD FOR DYEING KERATINOUS FIBRES STARTING FROM THE COMPOSITION

(57) Abstract: A subject-matter of the invention is a composition for the dyeing of keratinous fibres comprising at least one anthrone derivative and at least one basifying agent, the use of the composition in hair dyeing and the use of the composition in a dyeing method. The dyeing method according to the invention makes it possible to dye keratinous fibres with anthrone derivatives under mild oxidizing conditions, even without using an oxidation base and an aromatic amine, while covering a broad palette of colours. The dyeing under oxidizing conditions observed operates under mild conditions of oxidation and/or of alkaline agent, in particular exposed to the air.



WO 2011/045404 A2

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**COMPOSITION COMPRISING AT LEAST ONE ANTHRONE DERIVATIVE
AND ONE BASIFYING AGENT, AND METHOD FOR DYEING
KERATINOUS FIBRES STARTING FROM THE COMPOSITION**

5 A subject-matter of the invention is a composition for the dyeing of keratinous fibres comprising at least one anthrone derivative and at least one basifying agent, the use of the composition in hair dyeing and the use of the composition in a dyeing method.

10

It is known to obtain "permanent" colourings with dyeing compositions comprising oxidation dye precursors, generally known as oxidation bases, such as ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are colourless or weakly coloured compounds which, in combination with oxidizing products, can give rise, by an oxidative condensation process, to coloured compounds. It is also known that 15 it is possible to vary the shades obtained by combining these oxidation bases with couplers or colouring modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds, such as 25 indole compounds. This oxidation dyeing method consists in applying, to the keratinous fibres, bases or a mixture of bases and of couplers with hydrogen peroxide (H_2O_2 or aqueous hydrogen peroxide solution) as oxidizing agent, in allowing to diffuse and then in 30 rinsing the fibres. The colourings which result therefrom are permanent, powerful and resistant to external agents, in particular to light, bad weather, washing operations, perspiration and rubbing actions.

35 The oxidation bases and oxidation couplers make it possible to obtain a rich palette of colours but they generally require the presence i) of aromatic amine, ii) of hydrogen peroxide, as oxidizing agent, or iii) of ammonia, thus causing annoyance due to the smell of

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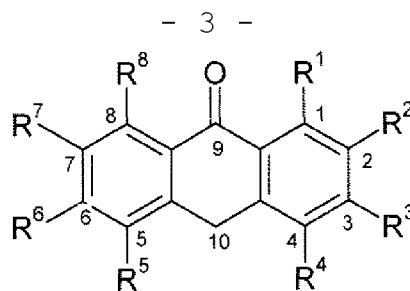
the ammonia and damage to the fibres due to the presence of hydrogen peroxide.

Furthermore, disadvantages can be encountered with
5 oxidation dyeing, such as staining and problems of discomfort.

Anthrones are known for their role of antioxidant. 1,8-
dihydroxyanthrone derivatives substituted in 10
10 position with an aryl group and 1-hydroxy-8-acyloxy-10-
acylanthrone derivatives have furthermore been used to
treat acne, dandruff, seborrhoea and hair loss
(US 4 755 530 and US 4 889 865). Some anthrones
optionally substituted by a glycosyl group have also
15 been described in hair dyeing (DE 10260880,
US 2005/0144740, JP 08-337516 and JP 2-040317). The
colourings obtained do not give satisfactory results,
in particular in terms of persistence, of chromaticity,
of power or of homogeneity of the colouring, this being
20 the case under mild conditions.

There thus exists a real need to produce colourings
under milder conditions than those conventionally used
and with reduced damage to the keratinous fibres,
25 indeed without damaging the fibres, while providing
colourings which withstand external agents (light, bad
weather, shampooing) and which are persistent and
homogeneous while remaining powerful and chromatic,
this being achieved if possible in the absence of an
30 unpleasant smell or in the presence of one which has
been greatly weakened.

This aim is achieved by the present invention, a
subject-matter of which is a method for dyeing
35 keratinous fibres, in particular the hair, employing
i) one or more anthrone derivative(s) of formula **(I)**:



(II)

its salts of inorganic or organic bases, its optical isomers, its geometric isomers, its tautomers and/or its solvates, such as the hydrates;

in which formula **(I)**:

• **R¹** to **R⁸** represent, independently of one another:

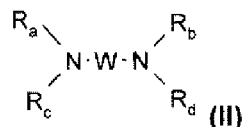
- a hydrogen atom,
- a hydroxyl radical,
- 10 - a C₁-C₆ alkyl or C₂-C₆ alkenyl radical, it being possible for said alkyl or alkenyl radical to be functionalized by one or more hydroxyl or carboxyl -C(O)OH radicals,
- a carboxyl radical,
- 15 - a (C₁-C₄)alkoxycarbonyl radical,
- an -OR⁹ radical in which **R⁹** represents:
 - a C₁-C₄ alkyl radical,
 - a (C₁-C₄)alkylcarbonyl radical,
- a sugar, particularly 1,5 anhydrohexitol, fructose, galactose, sucrose, glucose, maltose and mannose,
- 20 and

ii) one or more basifying agent(s), either together with the anthrone derivative(s) of formula **(I)** in the same stage, or applied separately before or after that of the anthrone derivative(s) of formula **(I)** to the keratinous fibres; preferably i) the anthrone derivative(s) of formula **(I)** and ii) the basifying agent(s) occur together in a cosmetic composition, which is applied to the keratinous fibres in a single stage;

in which the basifying agent(s) is (are) preferably chosen from ammonia, alkanolamines, such as mono-, di- and triethanolamines, alkali metal carbonate salts,

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guanidine, imidazole, sodium hydroxide, potassium hydroxide, calcium hydroxide, arginine and the compounds of the following formula **(II)**:



5

in which formula **(II)**:

- **W** is a (C₁-C₁₀)alkylene radical optionally interrupted by one or more heteroatoms such as oxygen atom, or by one or more groups NR wherein R represents an hydrogen atom, or (hydroxyl)(C₁-C₆)alkyl group, the said alkylene radical is optionally substituted by one or more hydroxyl or (C₁-C₄)alkyl group ;

W represents especially a propylene radical optionally substituted by a hydroxyl group or a C₁-C₄ alkyl radical;

- **R_a**, **R_b**, **R_c** and **R_d**, which are identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical;

and in particular the basifying agent(s) is (are) chosen from ethanolamine, carbonate salts, guanidine, imidazole, calcium hydroxide and arginine.

Another subject-matter of the invention is the use of compounds of formula (I) as defined above in dyeing keratinous fibres, in particular human keratinous fibres, such as the hair.

Another subject-matter of the invention is a cosmetic composition which comprises i) one or more anthrone derivatives of formula **(I)** as defined above and ii) one or more basifying agent(s) as defined above.

Another subject-matter of the invention is a device comprising from 2 to 5 compartments comprising from 2 to 5 compositions, in which compartments the following ingredients are distributed:

- 5 -

- i) one or more anthrone derivative(s) of formula (I),
- ii) one or more basifying agent(s), and
- iii) optionally one or more chemical oxidizing
5 agent(s),
- iv) and/or oxidation catalysts and
- v) optionally one or more mordant(s).

10 The method according to the invention makes it possible to dye keratinous fibres under mild conditions while covering a broad palette of colours.

15 Furthermore, the composition according to the invention exhibits the advantage of dyeing human keratinous fibres, with results for colourings which are powerful, chromatic and resistant to washing operations, perspiration, sebum and light, without detrimentally affecting said fibres. The colouring method according to the invention makes it possible to access colours
20 which are natural in appearance. The colourings obtained starting from the method additionally give colours which are homogeneous from the root to the tip of a fibre (low colouring selectivity).

25 Within the meaning of the present invention and unless otherwise indicated:

- The "alkyl" radicals are saturated, linear or branched, generally C₁-C₄, hydrocarbon radicals, such
30 as methyl, ethyl, propyl and butyl.
- The "alkenyl" radicals are unsaturated, linear or branched, hydrocarbon radicals comprising one or two π double bonds which may or may not be conjugated; the generally C₂-C₅ alkenyl group preferably comprises
35 just one double bond, such as 2-methylbut-2-enyl (CH₃)₂C=CH-CH₂-.
- The "alkylene" radicals are divalent saturated, linear or branched hydrocarbon radicals, generally C₁-

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C₁₀, preferably (C₂-C₆)alkylene, such as ethylene, propylene and butylene;

the latter being optionally interrupted by one or more heteroatoms and/or being optionally substituted

5 such as: (A) $-(CR'R''_2)_n-X-(CR'R''_2)_p-$ or (B) $-(CR'R''_2)_n-X-(CR'R''_2)_p-Y-(CR'R''_2)_q-$ wherein

➤ n, p and q, identical or different, each representing an integer between 1 to 4 ; with in

10 (A) n + p representing an integer between 2 and 6 or (B) n + p + q representing an integer between 3 and 6;

➤ X and Y, identical or different, represent a bond, an heteroatom such as oxygen atom or NR with R representing an hydrogen atom, or (hydroxyl) (C₁-C₆)alkyl group, preferably X = Y; and

15 ➤ R' and R'', identical or different, represent an hydrogen atom or a group selected from hydroxyl and (C₁-C₆)alkyl such as methyl;

preferably alkylene radical represents (A) with more particularly R' and R'' representing an hydrogen atom.

- The "alkoxy" radicals are alkyloxy radicals with alkyl as defined above, preferably C₁-C₄ alkyl, such as methoxy, ethoxy, propoxy and butoxy.

25 - The "heterocycle optionally substituted by an oxo group" is a heterocycle fused to the 1,8-dihydroxynaphthalene ring system via the R₁ and R₂ radicals, said heterocycle comprising from 5 to 7 ring members and from 1 to 3 heteroatoms chosen from oxygen, sulphur or nitrogen atoms and being able to additionally comprise an oxo or carbonyl group and an unsaturation preferably conjugated with the oxo group.

35 - The term "mild conditions" is understood to mean without the simultaneous use, in the method or in the composition according to the invention, of chemical oxidizing agent other than air, of a large amount of basifying agent exhibiting an unpleasant smell and of the presence of oxidation bases and couplers of

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- aromatic amine type. The method of the invention is carried out under mild conditions, i.e. the composition applied to the hair according to the invention does not comprise ammonia. The composition comprises a basifying agent which does not present a problem of smell and a small amount of, indeed even no, chemical oxidizing agent and a small amount of, indeed even no, oxidation bases and couplers derived from aromatic amine.
- 10 - For the notion of "chemical oxidizing agents", see "The oxidizing agents and oxidation catalysts" below.

i) Anthrone derivative of formula (I):

- 15 According to a preferred embodiment of the invention, the anthrone derivative(s) of formula **(I)** are such are **R₁** to **R₈** cannot represent a sugar.

A particular form of the invention relates to anthrone derivatives of formula **(I)** for which **R¹** to **R⁸** represent, independently of one another:

- a hydrogen atom,
- a hydroxyl radical,
- a C₁-C₄ alkyl radical,
- 25 - a (C₁-C₄)alkoxycarbonyl radical,
- an -OR⁹ radical in which **R⁹** represents:
 - a C₁-C₄ alkyl radical, or
 - a (C₁-C₄)alkylcarbonyl radical.

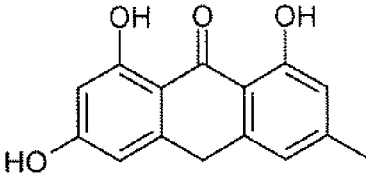
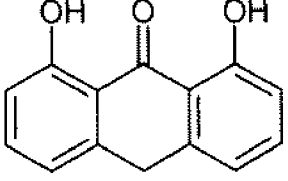
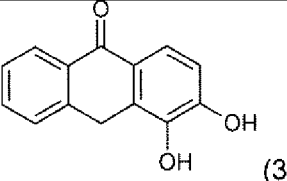
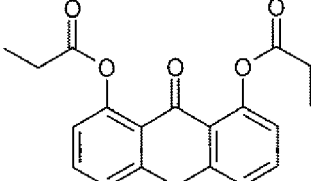
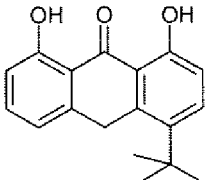
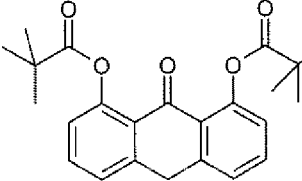
30 More particularly, the anthrone derivatives of formula **(I)** are such that:

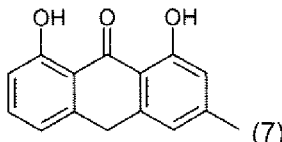
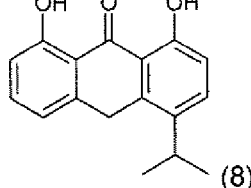
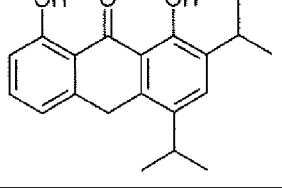
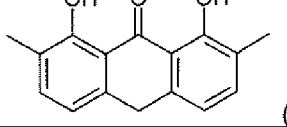
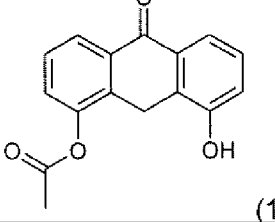
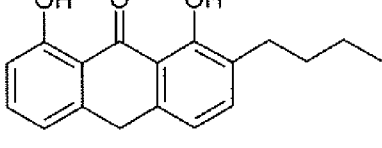
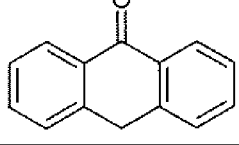
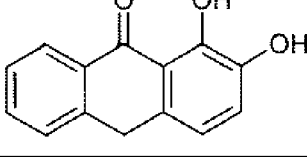
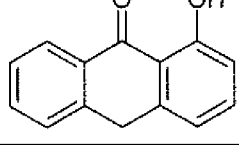
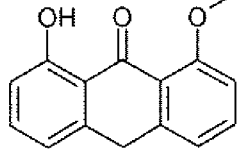
- **R¹** and **R⁸** represent, independently of one another:
 - a hydrogen atom,
 - 35 - a hydroxyl radical,
 - a (C₁-C₄)alkoxycarbonyl radical,
 - an -OR⁹ radical in which **R⁹** represents:
 - a C₁-C₂ alkyl radical, or
 - a (C₁-C₄)alkylcarbonyl radical,

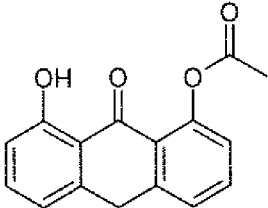
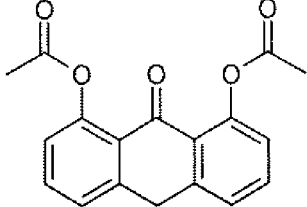
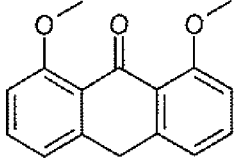
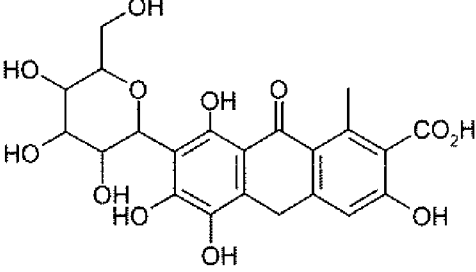
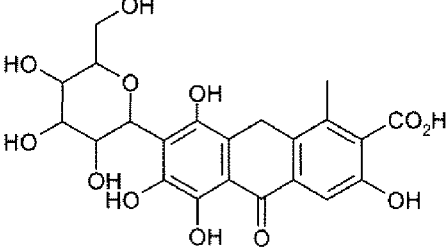
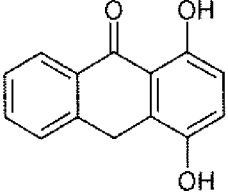
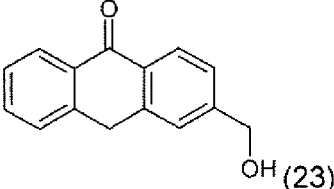
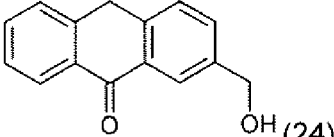
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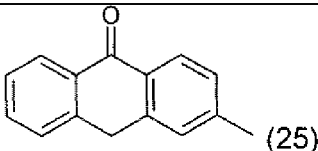
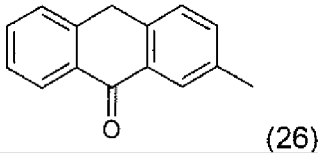
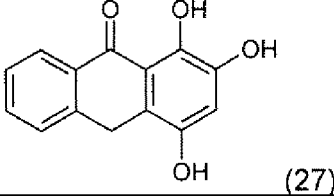
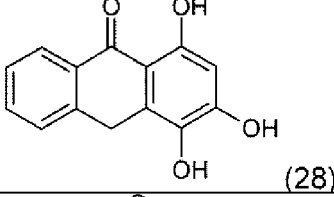
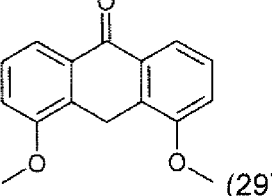
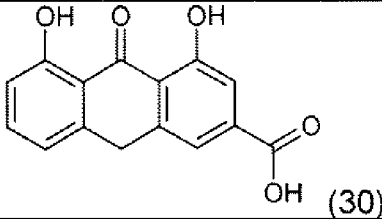
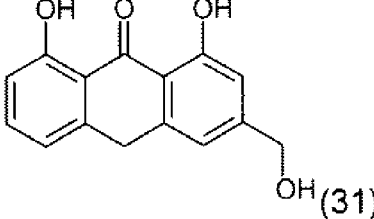
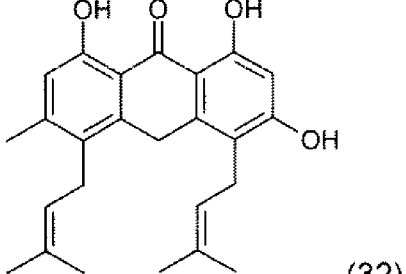
- R^2 , R^3 and R^4 independently represent:
 - a hydrogen atom,
 - a hydroxyl radical,
 - a saturated C_1 - C_4 alkyl radical,
- 5 • R^5 and R^6 represent a hydrogen atom,
- R^7 represents:
 - a hydrogen atom,
 - a saturated C_1 - C_5 alkyl radical.

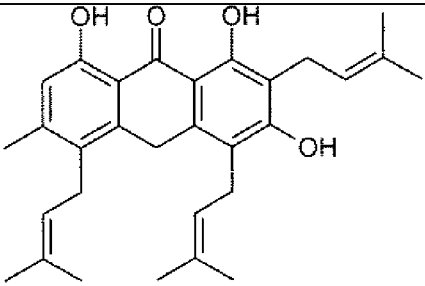
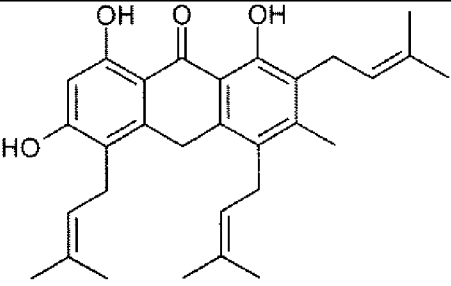
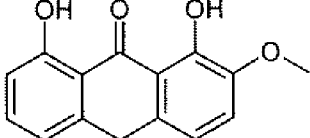
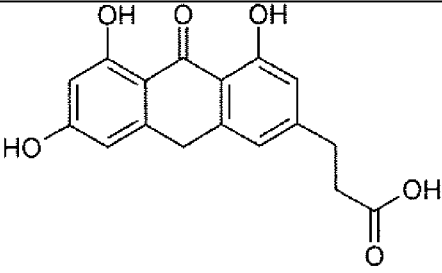
10 More particularly, the compounds according to the invention are chosen from those below:

 (1)	1,3,8-trihydroxy-6-methyl-10H-anthracen-9-one or <i>"emodin anthrone"</i>
 (2)	1,8-dihydroxy-10H-anthracen-9-one
 (3)	3,4-dihydroxy-10H-anthracen-9-one
 (4)	Propionic acid 9-oxo-8-propionyloxy-9,10-dihydroanthracen-1-yl ester
 (5)	4-tert-butyl-1,8-dihydroxy-10H-anthracen-9-one
 (6)	2,2-dimethylpropionic acid 8-(2,2-dimethylpropionyloxy)-9-oxo-9,10-dihydroanthracen-1-yl ester

 (7)	1,8-dihydroxy-3-methyl-10 <i>H</i> -anthracen-9-one
 (8)	1,8-dihydroxy-4-isopropyl-10 <i>H</i> -anthracen-9-one
 (9)	1,8-dihydroxy-2,4-diisopropyl-10 <i>H</i> -anthracen-9-one
 (10)	1,8-dihydroxy-2,7-dimethyl-10 <i>H</i> -anthracen-9-one
 (11)	Acetic acid 8-hydroxy-10-oxo-9,10-dihydroanthracen-1-yl ester
 (12)	2-butyl-1,8-dihydroxy-10 <i>H</i> -anthracen-9-one
 (13)	10 <i>H</i> -anthracen-9-one
 (14)	1,2-dihydroxy-10 <i>H</i> -anthracen-9-one
 (15)	1-hydroxy-10 <i>H</i> -anthracen-9-one
 (16)	1-hydroxy-8-methoxy-10 <i>H</i> -anthracen-9-one

 (17)	Acetic acid 8-hydroxy-9-oxo-9,10-dihydroanthracen-1-yl ester
 (18)	Acetic acid 8-acetoxy-9-oxo-9,10-dihydroanthracen-1-yl ester
 (19)	1,8-dimethoxy-10H-anthracen-9-one
 (20)	1,5-anhydro-1-(7-carboxy-1,3,4,6-tetrahydroxy-8-methyl-9-oxo-9,10-dihydroanthracen-2-yl)hexitol
 (21)	1,5-anhydro-1-(7-carboxy-1,3,4,6-tetrahydroxy-8-methyl-10-oxo-9,10-dihydroanthracen-2-yl)hexitol
 (22)	1,4-dihydroxy-10H-anthracen-9-one
 (23)	3-hydroxymethyl-10H-anthracen-9-one
 (24)	2-hydroxymethyl-10H-anthracen-9-one

 (25)	3-methyl-10 <i>H</i> -anthracen-9-one
 (26)	2-methyl-10 <i>H</i> -anthracen-9-one
 (27)	1,2,4-trihydroxy-10 <i>H</i> -anthracen-9-one
 (28)	1,3,4-trihydroxy-10 <i>H</i> -anthracen-9-one
 (29)	4,5-dimethoxy-10 <i>H</i> -anthracen-9-one
 (30)	4,5-dihydroxy-10-oxo-9,10-dihydroanthracene-2-carboxylic acid
 (31)	1,8-dihydroxy-3-hydroxymethyl-10 <i>H</i> -anthracen-9-one
 (32)	1,3,8-trihydroxy-6-methyl-4,5-bis(3-methylbut-2-enyl)-10 <i>H</i> -anthracen-9-one

 (33)	1,3,8-trihydroxy-6-methyl-2,4,5-tris(3-methylbut-2-enyl)-10<i>H</i>-anthracen-9-one
 (34)	1,6,8-trihydroxy-3-methyl-2,4,5-tris(3-methylbut-2-enyl)-10<i>H</i>-anthracen-9-one
 (35)	1,8-dihydroxy-2-methoxy-10<i>H</i>-anthracen-9-one
 (36)	3-(4,5,7-trihydroxy-10-oxo-9,10-dihydroanthracen-2-yl)propionic acid

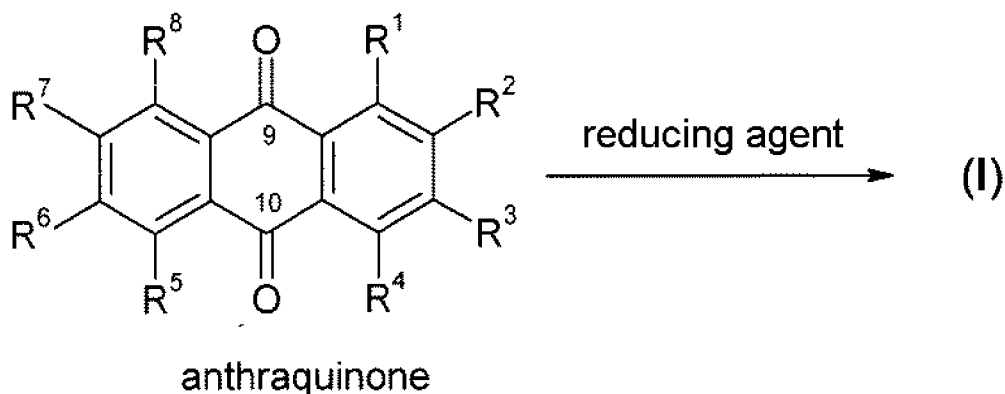
and their optical isomers, their geometrical isomers, their tautomers, their hydrates and their addition salts with an organic or inorganic base.

- 5 The preferred compounds of formula **(I)** are chosen from the compounds (1), (2), (3), (5), (7), (10), (12), (13), (14), (15), (16), (17), (18), (19), (23), (24), (25), (26), (31) and (35). More preferably, the compounds of formula **(I)** are chosen from (1), (3), (5),
 10 (7), (10), (12), (14), (15), (16), (17), (18), (19), (23), (24), (25), (26), (31) and (35).

The anthrone derivatives of formula **(I)** used in the invention can be natural, synthetic and/or commercially
 15 available. The compounds of formula **(I)** can be synthesized by the synthetic routes described in the literature. The compounds of formula **(I)** can be

- 13 -

obtained very simply from the corresponding anthraquinones via a reduction stage:



5

The most conventionally used reducing agents are:

- Na₂S₂O₄: *Bioorganic & Medicine Chemistry*, 14(2), 418-425, 2006
Journal of Organic Chemistry, 61(8), 2853-2856, 1996
- H₂, PtO₂, HCl, EtOH: *Tetrahedron Letters*, 36(13), 2331-2334, 1995
- SnCl₂, HCl, AcOH: *Natural Product Communications*, 2(1), 67-70, 2007
- SnCl₂, HBr, AcOH: *European Journal of Organic Chemistry*, (5), 1200-1206, 2006
- Cu, H₂SO₄: *Journal of the American Chemical Society*, 127(50), 17612-17613, 2005
- Sn, HCl, AcOH: *Bulletin of the Chemical Society of Japan*, 78(5), 917-928, 2005

According to a specific embodiment of the invention, the composition comprises one or more synthetic anthrone derivative(s) of formula **(I)** which do(es) not exist in nature.

According to one embodiment, the natural anthrone derivatives of formula **(I)** result from animal, bacterial, fungal, algal or plant extracts used in their entirety or partially. More particularly, the derivative is emodin anthrone (compound of formula (1))

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as defined above. These natural anthrone derivatives of formula **(I)** can be obtained from extracts, the purification of which can be carried out by simple extraction without chemical treatment or chemical
5 reaction.

Mixtures of extracts can also be used.

According to a preferred form, the anthrone derivative
10 or derivatives of formula **(I)** are solely natural extracts.

The natural extracts according to the invention can be provided in the form of powders or liquids. Preferably,
15 the extracts of the invention are provided in the form of powders.

According to the invention, the synthetic and/or natural anthrone derivative(s) of formula **(I)** and/or
20 the natural extract(s) used in the composition according to the invention preferably represent(s) from 0.001 to 20% by weight of the total weight of the composition or compositions comprising the anthrone derivative or derivative(s) of formula **(I)** or the
25 extract or extracts.

As regards the pure anthrone derivatives of formula **(I)**, the content in the composition or compositions comprising them is preferably between 0.001 and 5% by
30 weight of each of these compositions.

As regards the extracts, the content in the composition or compositions comprising the extracts as such is preferably between 0.001 and 20% by weight of each of
35 these compositions.

ii) cosmetic composition:

- 15 -

The cosmetic composition according to the invention is cosmetically acceptable for the dyeing of keratinous fibres, i.e. it comprises a dyeing vehicle which generally comprises water or a mixture of water and of one or more organic solvents or a mixture of organic solvents.

The term "organic solvent" is understood to mean an organic substance capable of dissolving or dispersing another substance without modifying it chemically.

The organic solvents:

Mention may be made, as organic solvent, for example, of lower C₁-C₄ alkanols, such as ethanol and isopropanol; polyols and polyol ethers, such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monomethyl ether or hexylene glycol, and aromatic alcohols, such as benzyl alcohol or phenoxyethanol.

The organic solvents are present in proportions preferably of between 1 and 40% by weight approximately, with respect to the total weight of the dyeing composition, and more preferably still between 5 and 30% by weight approximately.

The adjuvants:

The composition or compositions of the dyeing method in accordance with the invention can also include various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surface-active agents or their mixtures, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or their blends, inorganic or organic thickening agents, and in particular anionic, cationic, nonionic and amphoteric polymeric associative

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thickeners, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioning agents, such as, for example, volatile or nonvolatile and modified or unmodified
5 silicones, film-forming agents, ceramides, preservatives or passifying agents.

Said adjuvants are preferably chosen from surface-active agents, such as anionic or nonionic surfactants
10 or their mixtures, and inorganic or organic thickening agents.

The above adjuvants are generally present in an amount of, for each of them, between 0.01 and 40% by weight, with respect to the weight of the composition,
15 preferably between 0.1 and 20% by weight, with respect to the weight of the composition.

Of course, a person skilled in the art would take care to choose this or these optional additional compounds so that the advantageous properties intrinsically attached to the composition in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

25

The additional dyes:

The composition comprising one or more anthrone derivatives of formula **(I)** as defined above can also
30 comprise one or more additional direct dyes. These direct dyes are, for example, chosen from those conventionally used in direct dyeing, among which may be mentioned all the aromatic and/or nonaromatic dyes commonly used, such as neutral, acid or cationic
35 nitrobenzene direct dyes, neutral, acid or cationic azo direct dyes, natural direct dyes other than the anthrone derivatives of formula **(I)**, neutral, acid or cationic quinone and in particular anthraquinone direct dyes, azine, triarylmethane or indoamine direct dyes,

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methines, styryls, porphyrins, metalloporphyrins, phthalocyanines, methane cyanines and fluorescent dyes. All these additional dyes are different from the anthrone derivatives of formula **(I)** according to the invention.

Mention may be made, among natural direct dyes, of lawsone, juglone, indigo, isatin, curcumin, spinulosin, apigenidine or orceins. Use may also be made of extracts or decoctions comprising these natural dyes, and in particular cataplasms or henna-based extracts.

The additional direct dye or dyes used in the composition preferably represents from 0.001 to 10% by weight approximately of the total weight of the composition or compositions comprising them and more preferably still from 0.05 to 5% by weight approximately.

The cosmetic composition according to the invention comprising one or more anthrone derivatives of formula **(I)** as defined above can also employ or comprise one or more oxidation bases and/or one or more couplers conventionally used for the dyeing of keratinous fibres.

Mention may be made, among the oxidation bases, of paraphenylenediamines, bisphenylalkylenediamines, paraaminophenols, bis-paraaminophenols, ortho-aminophenols, heterocyclic bases and their addition salts.

Mention may in particular be made, among these couplers, of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene couplers, heterocyclic couplers and their addition salts.

The oxidation base or bases present in the composition or compositions are generally each present in an amount

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of between 0.001 and 10% by weight of the total weight of the corresponding composition or compositions.

According to another specific embodiment of the invention, the composition according to the invention does not comprise an oxidation base.

According to yet another embodiment, the composition does not comprise a coupler. Preferably, the composition according to the invention does not comprise oxidation bases or couplers of aromatic amine type.

The cosmetic composition of the invention can be provided in various formulation forms, such as a powder, a lotion, a foam, a cream or a gel, or in any other form appropriate for carrying out dyeing of keratinous fibres. It can also be packaged as a propellant-free pump-action spray or under pressure in an aerosol container in the presence of a propellant and form a foam.

The pH of the composition

According to a specific form of the invention, the pH of the composition comprising the anthrone derivative or derivatives of formula **(I)** is greater than 7 and preferably between 8 and 12, particularly between 9 and 11, especially between 9 and 9.5.

The pH of the composition according to the invention can be adjusted to the desired value using acidifying or basifying agents commonly used in the dyeing of keratinous fibres or else using conventional buffer systems.

Mention may be made, among the acidifying agents of the compositions used in the invention, by way of example, of inorganic or organic acids, such as hydrochloric

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acid, orthophosphoric acid, sulphuric acid, carboxylic acids, such as acetic acid, tartaric acid, citric acid or lactic acid, or sulphonic acids.

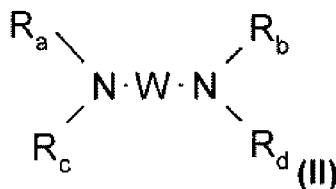
5 *The basifying agents*

The composition according to the invention comprises one or more basifying agents. According to a specific embodiment of the invention, the composition comprises
10 a small amount of, indeed even no, basifying agent which exhibits an unpleasant smell, such as ammonia.

When the composition comprises ammonia, the latter preferably occurs in a content of between 0.005 and 5%
15 by weight, with respect to the total weight of said composition, more particularly between 0.05 and 3% by weight, in particular between 1 and 2% by weight, with respect to the total weight of the composition.

20 According to another specific embodiment of the invention, the composition does not comprise ammonia.

The basifying agent not exhibiting an unpleasant smell is preferably chosen from alkanolamines, such as mono-,
25 di- and triethanolamines, alkali metal carbonate salts, guanidine, imidazole, sodium hydroxide, potassium hydroxide, calcium hydroxide, arginine and the compounds of the following formula **(II)**:



30

in which formula **(II)**:

- **W** is a (C₂-C₆)alkylene radical optionally interrupted
35 by one or more heteroatoms such as oxygen atom, or by

- 20 -

one or more groups NR wherein R represents an hydrogen atom, or (hydroxyl)(C₁-C₆)alkyl group, the said alkylene radical is optionally substituted by one or more hydroxyl or (C₁-C₄)alkyl group ;

5 W represents preferably a propylene radical optionally substituted by a hydroxyl group or a C₁-C₄ alkyl radical;

- R_a, R_b, R_c and R_d, which are identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical.

More particularly, the basifying agent(s) is (are) chosen from ethanolamine, carbonate salts, guanidine, imidazole, calcium hydroxide, sodium hydroxide and arginine.

The basifying agent not exhibiting an unpleasant smell preferably occurs in a content of between 0.001 and 10% by weight, with respect to the total weight of said composition, more particularly between 0.01 and 5% by weight. According to a preferred embodiment of the invention, the basifying agent is a hydroxide, such as sodium hydroxide, and particularly in a content of between 0.001 and 1% by weight, with respect to the total weight of said composition, in particular between 0.01 and 0.05% by weight, with respect to the total weight of said composition.

The oxidizing agents and oxidation catalysts

30 According to a specific form of the invention, the composition comprises a chemical oxidizing agent. The term "chemical oxidizing agent" is understood to mean an oxidizing agent other than atmospheric oxygen (O₂), such as hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, such as perborates and persulphates, or several system(s) which generate(s) hydrogen peroxide, such as:

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- polymer complexes which can release hydrogen peroxide, such as polyvinylpyrrolidone/H₂O₂, which are provided in particular in the form of powders, and the other polymer complexes described in
5 US 5 008 093, US 3 376 110 and US 5 183 901;
- metal peroxides which, in water, generate hydrogen peroxide, such as calcium peroxide or magnesium peroxide;
- oxidases which produce hydrogen peroxide in the
10 presence of an appropriate substrate (for example, glucose in the case of glucose oxidase or uric acid with uricase), and also enzymes, among which may be mentioned peroxidases, 2-electron oxidoreductases, such as uricases, and 4-electron oxygenases, such as
15 laccases.

The use of hydrogen peroxide is particularly preferred.

The chemical oxidizing agent is found in the
20 composition particularly in proportions of between 0.001 and 12%, with respect to the total weight of the composition.

According to another specific embodiment of the
25 invention, the composition does not comprise a chemical oxidizing agent. The oxidation and the appearance of the colour then take place solely with atmospheric oxygen.

30 According to another alternative form, the composition additionally comprises an oxidation catalyst. By way of example, this catalyst can be chosen from manganese (Mn), zinc (Zn), iron (Fe) or copper (Cu) salts. The catalysts are found in the composition in particular in
35 proportions of between 0.001 and 10%, with respect to the total weight of the composition.

The mordants

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The composition according to the invention can additionally comprise a mordant or mordanting agent conventionally used in the textile industry which is cosmetically acceptable, preferably in the form of metal salts, such as iron, aluminium, titanium, calcium, manganese, copper, zinc or strontium salts. By way of example, the mordant can be iron sulphate, manganese gluconate, copper sulphate, zinc gluconate, calcium chloride, magnesium chloride, potassium titanyl oxalate or strontium acetate. The mordants are found in the composition in particular in proportions of between 0.001 and 10%, with respect to the total weight of the composition.

iii) Single- or multistage dyeing method

A subject-matter of the invention is the dyeing method employing i) one or more anthrone derivative(s) of formula **(I)**, by their application to keratinous fibres, as defined above and ii) one or more basifying agent(s) as defined above. The method can be carried out in one or more stages.

According to a preferred form of the dyeing method according to the invention, the method uses neither oxidation bases nor couplers. More particularly, the method does not involve an oxidation base or a coupler of aromatic amine type.

The process additionally employs ii) one or more basifying agent(s). Said basifying agent is as defined above and can either be employed with the anthrone derivative(s) of formula **(I)** simultaneously in the same stage or can be applied separately, before or after that of the anthrone derivative(s) of formula **(I)**, to the keratinous fibres. Preferably, i) the anthrone derivative(s) of formula **(I)** and ii) the basifying agent(s) are found together in a cosmetic composition,

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which is applied to the keratinous fibres in a single stage.

According to a specific embodiment of the invention,
5 the method of the invention employs a small amount of, even no, basifying agent which exhibits an unpleasant smell, such as ammonia.

When the process involves ammonia, it is preferably
10 present in a content of between 0.005 and 5% by weight, with respect to the total weight of the composition comprising i) the anthrone derivative(s) of formula **(I)** and ii) the ammonia, more particularly between 0.05 and 3% by weight, in particular between 1 and 2% by weight,
15 with respect to the total weight of the composition.

The basifying agent is present preferably in an amount such that the pH of the composition is between 8 and 12, more particularly between 9 and 11, in particular
20 between 9 and 9.5.

According to another preferred embodiment of the dyeing method, the basifying agent(s) is (are) such that it (they) do not exhibit(s) an unpleasant smell. In
25 particular, they are other than ammonia. For example, said agent(s) is (are) chosen from alkanolamines, such as mono-, di- and triethanolamines, alkali metal carbonate salts, guanidine, imidazole, sodium hydroxide, potassium hydroxide, calcium hydroxide,
30 arginine and the compounds of formula **(II)** as defined above.

The basifying agent(s) not exhibiting an unpleasant smell is (are) preferably present in a content of
35 between 0.001 and 10% by weight, with respect to the total weight of said composition comprising i) the anthrone derivative(s) of formula **(I)** and ii) the basifying agent(s), more particularly between 0.01 and 5% by weight.

According to a preferred embodiment of the invention, the basifying agent is a hydroxide, such as sodium hydroxide, particularly in a content of between 0.001 and 1% by weight, with respect to the total weight of said composition comprising i) the anthrone derivative(s) of formula **(I)** and ii) the hydroxide(s) in particular between 0.01 and 0.05% by weight, with respect to the total weight of said composition.

10

More particularly, the basifying agent(s) not exhibiting an unpleasant smell is (are) chosen from ethanolamine, carbonate salts, guanidine, imidazole, sodium hydroxide and arginine.

15

According to a specific form of the invention, the dyeing method additionally employs iii) one or more chemical oxidizing agent(s) as defined above. More particularly, the chemical oxidizing agent(s) is (are) hydrogen peroxide. Said agent(s) can be employed before or after the application of the anthrone derivative(s) of formula **(I)** to the keratinous fibres. According to another alternative form, the chemical oxidizing agent(s) are employed simultaneously with the anthrone derivative(s) of formula **(I)** on the keratinous fibres. Preferably, the chemical oxidizing agent(s) is (are) found in the same cosmetic composition which comprises the anthrone derivative(s) of formula **(I)**, which is applied to the keratinous fibres in a single stage.

25

Preferably, the chemical oxidizing agent is present in a proportion of between 0.001 and 12%, with respect to the total weight of the composition.

30

According to another preferred alternative form of the method of the invention, the oxidation is carried out with atmospheric oxygen in the absence of any chemical oxidizing agent. In other words, no stage of the dyeing

35

- 25 -

method involves an oxidizing agent other than atmospheric oxygen.

5 According to another preferred embodiment of the dyeing method, said method additionally employs iv) one or more oxidation catalyst(s). By way of example, this catalyst can be manganese gluconate or zinc gluconate.

10 The leave-in time in order for the oxidation to be carried out exposed to the air is between 3 and 120 minutes. Preferably, after application of the composition comprising the anthrone derivatives of formula **(I)**, the composition is left to act for 10 to 60 minutes.

15 According to another specific embodiment of the dyeing method, said method additionally employs v) one or more mordant(s) conventionally used. This treatment in particular takes place either before the application of
20 the composition according to the invention, comprising the anthrone derivative(s) of formula **(I)** as defined above, or after the dyeing method. By way of example, the mordant can be iron sulphate.

25 The application can be carried out in one or more stages, under oxidizing and basic conditions.

30 According to a specific method of the invention, the composition which comprises the anthrone derivatives of formula **(I)** also comprises basifying agents other than ammonia and additionally comprises chemical oxidizing agents.

35 According to another specific dyeing method of the invention, the composition which comprises the anthrone derivatives of formula **(I)** also comprises basifying agents other than ammonia and does not comprise a chemical oxidizing agent. In this case, the reaction takes place solely with atmospheric oxygen.

According to another alternative form, the composition which comprises the anthrone derivatives of formula **(I)** also comprises ammonia or sodium hydroxide at a pH of between 8 and 12, particularly between 9 and 11, in particular between 9 and 9.5, and additionally comprises chemical oxidizing agents.

According to another alternative form, the composition which comprises the anthrone derivatives of formula **(I)** also comprises ammonia at a pH of between 8 and 12, particularly between 9 and 11, in particular between 9 and 9.5, and does not comprise a chemical oxidizing agent.

A preferred alternative form of the invention relates to a dyeing method in which the composition which comprises the anthrone derivatives of formula **(I)** also comprises ammonia and does not comprise a chemical oxidizing agent. In this case, the reaction takes place solely with atmospheric oxygen.

A specific alternative form of the invention consists of a dyeing method in which the keratinous fibres are treated with i) the anthrone derivative(s) of formula **(I)** as defined above, ii) one or more basifying agents, iii) one or more oxidizing agent(s), iv) optionally one or more oxidation catalyst(s) and v) optionally one or more mordant(s) in different stages.

According to another preferred alternative form, the ingredients i) to v) occur in a cosmetic composition which is applied in a single stage to the keratinous fibres.

The leave-in time after application of the composition according to the invention comprising the anthrone derivative(s) of formula **(I)** as defined above and between each stage of treatment with the basifying

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agent(s), with optionally the oxidation catalyst(s) and with optionally the mordant(s) is set at between 3 and 120 minutes, preferably between 10 and 60 minutes and more particularly between 15 and 45 minutes.

5

Whatever the form of application, the application temperature is generally between ambient temperature (15 to 25°C) and 80°C and more particularly between 15 and 45°C. Thus, it is advantageously possible, after
10 application of the composition according to the invention, to subject the hair to a heat treatment by heating at a temperature of between 30 and 60°C. In practice, this operation can be carried out using a hood hairdryer, a handheld hairdryer, a dispenser of
15 infrared radiation and other conventional heating devices.

Use may be made, both as means for heating and smoothing the hair, of a heating iron at a temperature
20 of between 60 and 220°C and preferably between 120 and 200°C.

A specific form of the invention relates to a dyeing method which is carried out at ambient temperature
25 (25°C).

According to a preferred embodiment of the dyeing method, once the ingredients i) to v) have been applied to the fibres, the ingredients are left standing for
30 between 15 and 60 minutes, in particular 30 minutes, and then the fibres are rinsed with water, washed with a conventional shampoo and dried. More particularly, a cosmetic composition comprises the ingredients i) to v) and is applied to the fibres in one stage and then left
35 standing for 30 minutes, and then the fibres are rinsed with water, washed with a conventional shampoo and dried.

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In all the specific forms and the alternative forms of the methods described above, the compositions mentioned are ready-to-use compositions which can result from the mixing at the time of use of two or more compositions and in particular of compositions present dyeing kits.

iv) Dyeing device or kit:

Another subject-matter of the invention is a dyeing kit or multicompartment device. Advantageously, this device comprises from 2 to 5 compartments comprising from 2 to 5 compositions, in which compartments the following ingredients i) to v) are distributed:

- i) one or more anthrone derivative(s) of formula **(I)** as defined above,
- ii) one or more basifying agent(s) as defined above, and
- iii) optionally one or more chemically oxidizing agent(s),
- iv) and/or oxidation catalysts and
- v) optionally one or more mordant(s).

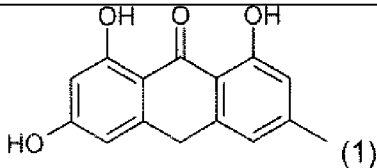
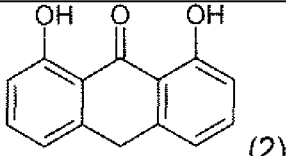
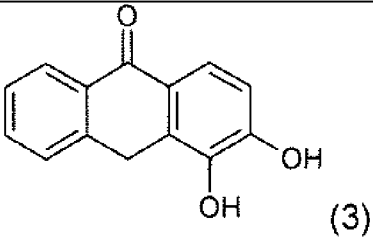
The compositions of the device according to the invention are packaged in separate compartments optionally accompanied by appropriate application means which are identical or different, such as brushes, including fine brushes, or sponges.

The device mentioned above can also be equipped with a means which makes it possible to deliver the desired mixture to the hair, for example such as the devices described in patent FR 2 586 913.

DYEING EXAMPLES**Aqueous hydrogen peroxide solution + aqueous ammonia protocol**

- 5 1 ml of 20% aqueous ammonia solution and then 1 ml of 6% aqueous hydrogen peroxide solution are added to a mixture comprising 300 mg of compound **(I)** in 4 ml of water and 4 ml of ethanol.
- 10 This solution is applied to a 0.5 g lock of natural hair comprising 90% of white hairs. The preparation is left standing for 30 minutes and then the lock is rinsed with water, washed with a shampoo and dried.
- The following dyeing results are obtained:

15

Compounds of formula (I)	Dyeing result
 (1) 1,3,8-trihydroxy-6-methyl-10H-anthracen-9-one	light brown
 (2) 1,8-dihydroxy-10H-anthracen-9-one	dark brown
 (3) 3,4-dihydroxy-10H-anthracen-9-one	purple

Aqueous hydrogen peroxide solution + sodium hydroxide solution protocol

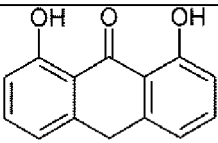
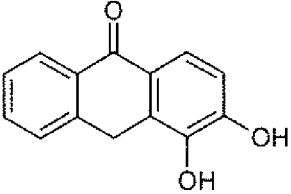
- 1 ml of 0.1 mol/l sodium hydroxide solution and then
- 20 1 ml of 6% aqueous hydrogen peroxide solution are added

- 30 -

to a mixture comprising 300 mg of compound **(I)** in 4 ml of water and 4 ml of ethanol.

This solution is applied to a 0.5 g lock of natural hair comprising 90% of white hairs. The preparation is left standing for 30 minutes and then the lock is rinsed with water, washed with a shampoo and dried.

The following dyeing results are obtained:

Compounds of formula (I)	Dyeing result
 (2) 1,8-dihydroxy-10H-anthracen-9-one	light beige
 (3) 3,4-dihydroxy-10H-anthracen-9-one	purple-red

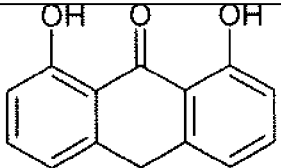
10 Air + sodium hydroxide solution protocol

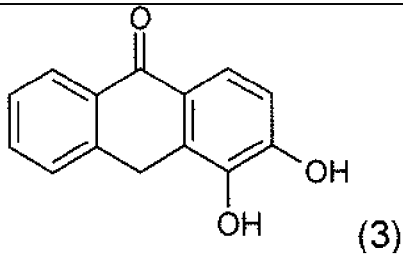
2 ml of 0.01 mol/l sodium hydroxide solution are added to a mixture comprising 300 mg of compound **(I)** in 4 ml of water and 4 ml of ethanol.

This solution is applied to a 0.5 g lock of natural hair comprising 90% of white hairs. The preparation is oxidized with atmospheric oxygen for 30 minutes and then the lock is rinsed with water, washed with a shampoo and dried.

The following dyeing results are obtained:

20

Compounds of formula (I)	Dyeing result
 (2) 1,8-dihydroxy-10H-anthracen-9-one	light beige

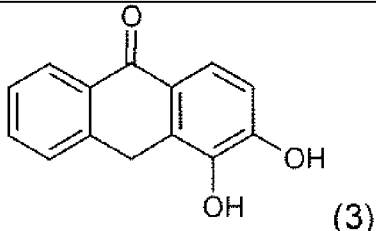
 3,4-dihydroxy-10<i>H</i>-anthracen-9-one	pinkish
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Air + K₂CO₃ protocol

Potassium carbonate is added to a mixture comprising 300 mg of compound **(I)** in 4 ml of water and 4 ml of ethanol to achieve a pH of 9.5.

This solution is applied to a 0.5 g lock of natural hair comprising 90% of white hairs. The preparation is oxidized with atmospheric oxygen for 30 minutes and then the lock is rinsed with water, washed with a shampoo and dried.

The following dyeing results are obtained:

Compounds of formula (I)	Dyeing result
 3,4-dihydroxy-10<i>H</i>-anthracen-9-one	purple

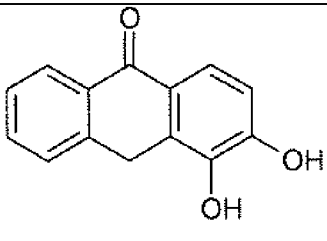
Air + imidazole protocol

Imidazole is added to a mixture comprising 300 mg of compound **(I)** in 4 ml of water and 4 ml of ethanol to achieve a pH of 6.5.

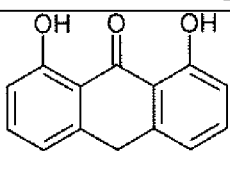
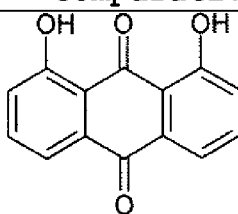
This solution is applied to a 0.5 g lock of natural hair comprising 90% of white hairs. The preparation is oxidized with atmospheric oxygen for 30 minutes and then the lock is rinsed with water, washed with a shampoo and dried.

The following dyeing results are obtained:

Compounds of formula (I)	Dyeing result
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 (3) 3,4-dihydroxy-10<i>H</i>-anthracen-9-one	orange
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COMPARATIVE TEST

Invention	Comparative
 (2) 1,8-dihydroxy-10<i>H</i>-anthracen-9-one	

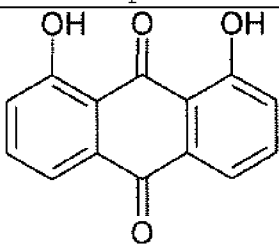
5 Aqueous ammonia solution + aqueous hydrogen peroxide solution protocol

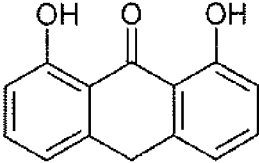
1 ml of 20% aqueous ammonia solution and then 1 ml of 6% aqueous hydrogen peroxide solution are added to a mixture comprising 300 mg of compound of formula (2) in 4 ml of water and 4 ml of ethanol: method of the invention. For the comparative, the same mixture is prepared, apart from the fact that the compound of formula (2) is replaced with the comparative.

Each composition is applied to a 0.5 g lock of natural hair comprising 90% of white hairs. The preparations are subsequently left standing for 30 minutes at 50°C and then each lock is rinsed with water, washed with a shampoo and then dried.

The following dyeing results are obtained:

20

Compounds	Dyeing result
 Comparative	golden yellow

 (2) 1,8-dihydroxy-10 <i>H</i> -anthracen-9-one	natural dark brown
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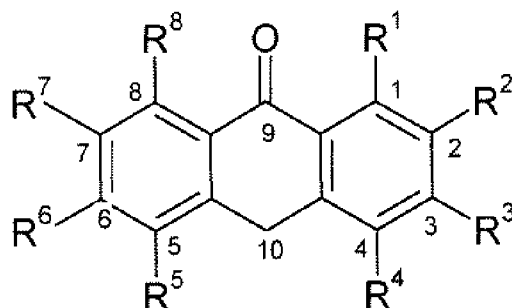
It thus appears, surprisingly, that the colouring obtained with the composition comprising a compound of formula **(I)** according to the invention is more powerful, more chromatic, has a natural appearance and makes it possible to achieve different colours than that obtained with the comparative composition.

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CLAIMS

1. Method for dyeing keratinous fibres, employing i)
one or more anthrone derivative(s) of formula **(I)**:

5

**(I)**

its salts of inorganic or organic bases, its optical
isomers, its geometric isomers, its tautomers and/or
10 its solvates, such as the hydrates;
in which formula **(I)**:

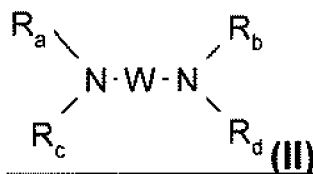
- **R¹** to **R⁸** represent, independently of one another:
 - a hydrogen atom,
 - a hydroxyl radical,
 - 15 - a C₁-C₆ alkyl or C₂-C₆ alkenyl radical, it being possible for said alkyl or alkenyl radical to be functionalized by one or more hydroxyl or carboxyl -C(O)OH radicals,
 - a carboxyl radical,
 - 20 - a (C₁-C₄)alkoxycarbonyl radical,
 - an -OR⁹ radical in which **R⁹** represents:
 - a C₁-C₄ alkyl radical,
 - a (C₁-C₄)alkylcarbonyl radical,
 - a sugar, particularly 1,5 anhydrohexitol, fructose,
 - 25 galactose, sucrose, glucose, maltose and mannose;
- and which employs ii) one or more basifying agent(s), either together with the anthrone derivative(s) of formula **(I)** in the same stage, or applied separately before or after that of the anthrone derivative(s) of formula **(I)** to the keratinous fibres; preferably i) the
30 anthrone derivative(s) of formula **(I)** and ii) the

- 35 -

basifying agent(s) occur together in a cosmetic composition, which is applied to the keratinous fibres in a single stage;

in which the basifying agent(s) is (are) preferably
 5 chosen from ammonia, alkanolamines, such as mono-, di- and triethanolamines, alkali metal carbonate salts, guanidine, imidazole, sodium hydroxide, potassium hydroxide, calcium hydroxide, arginine and the compounds of the following formula **(II)**:

10



in which formula **(II)**:

- **W** is a (C₁-C₁₀)alkylene radical optionally interrupted
 15 by one or more heteroatoms such as oxygen atom, or by one or more groups NR wherein R represents an hydrogen atom, or (hydroxyl)(C₁-C₆)alkyl group, the said alkylene radical is optionally substituted by one or more hydroxyl or (C₁-C₄)alkyl group ;

20 - **R_a**, **R_b**, **R_c** and **R_d**, which are identical or different, represent a hydrogen atom or a C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl radical;

and in particular the basifying agent(s) is (are)
 25 chosen from ethanolamine, carbonate salts, guanidine, imidazole, calcium hydroxide and arginine.

2. Dyeing method according to the preceding claim, in which the anthrone derivative(s) of formula **(I)** are such that **R¹** to **R⁸** represent, independently of one
 30 another:

- a hydrogen atom,
- a hydroxyl radical,
- a saturated C₁-C₄ alkyl radical,
- a (C₁-C₄)alkoxycarbonyl radical,
- 35 - an -OR⁹ radical in which **R⁹** represents:

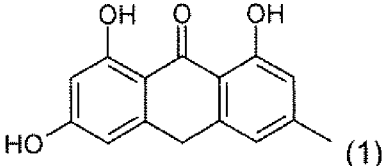
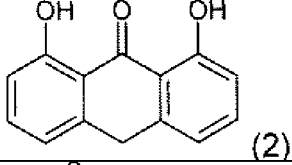
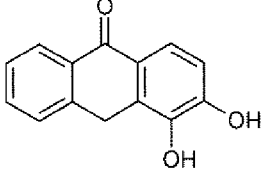
- 36 -

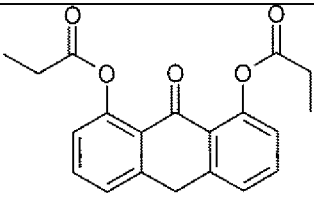
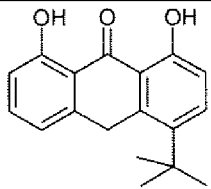
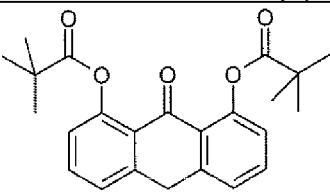
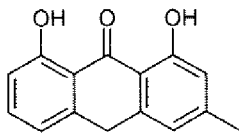
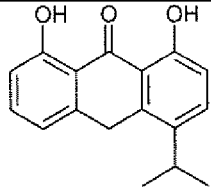
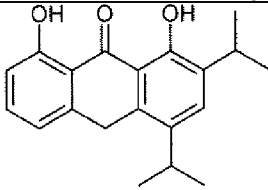
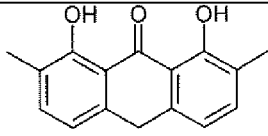
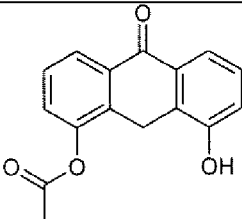
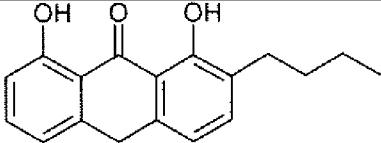
- a C₁-C₄ alkyl radical, or
- a (C₁-C₄)alkylcarbonyl radical.

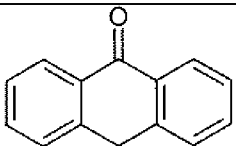
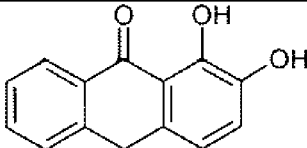
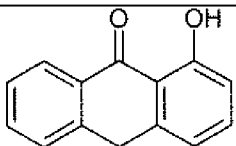
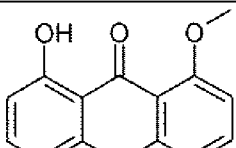
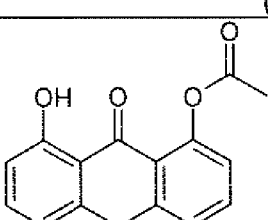
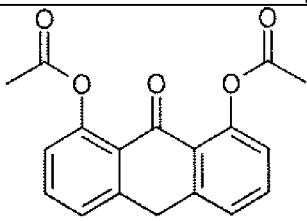
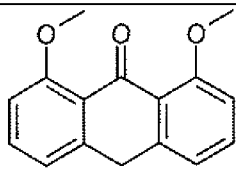
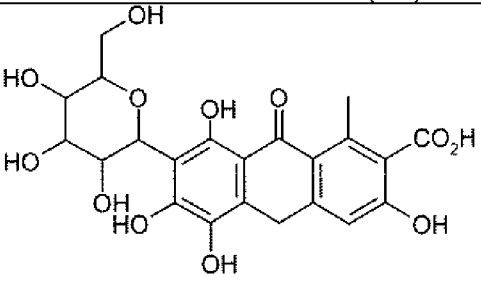
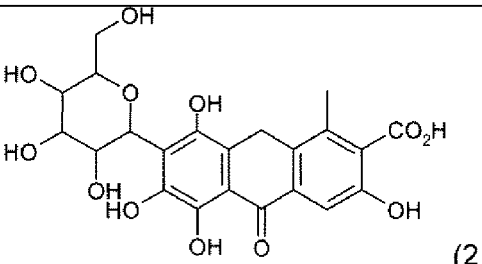
3. Dyeing method according to the preceding claim, in which the anthrone derivative(s) of formula **(I)** are such that:

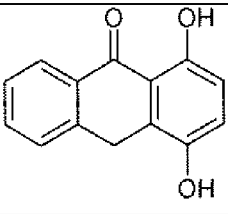
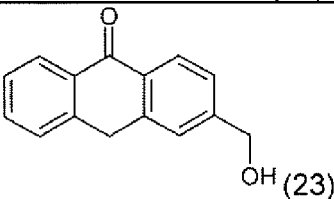
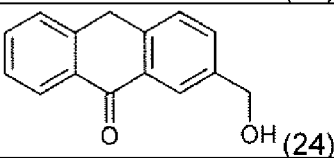
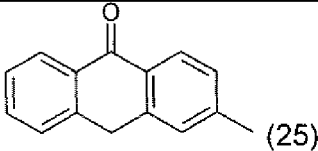
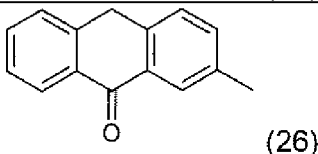
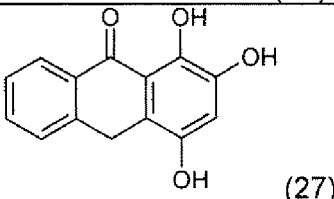
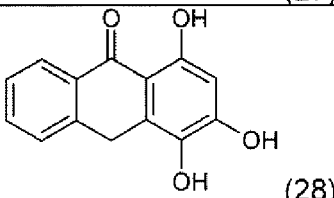
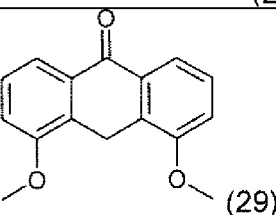
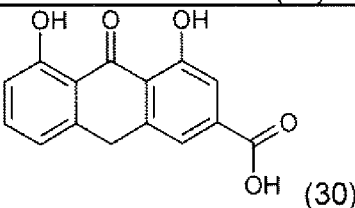
- **R**¹ and **R**⁸ represent, independently of one another:
 - a hydrogen atom,
 - a hydroxyl radical,
 - a (C₁-C₄)alkoxycarbonyl radical,
 - an -OR⁹ radical in which **R**⁹ represents:
 - a C₁-C₂ alkyl radical, or
 - a (C₁-C₄)alkylcarbonyl radical,
- **R**², **R**³ and **R**⁴ independently represent:
 - a hydrogen atom,
 - a hydroxyl radical,
 - a saturated C₁-C₄ alkyl radical,
- **R**⁵ and **R**⁶ represent a hydrogen atom, and
- **R**⁷ represents:
 - a hydrogen atom,
 - a saturated C₁-C₅ alkyl radical.

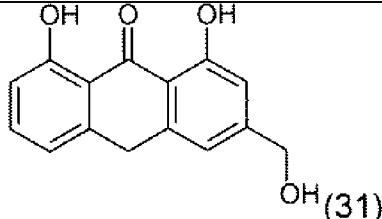
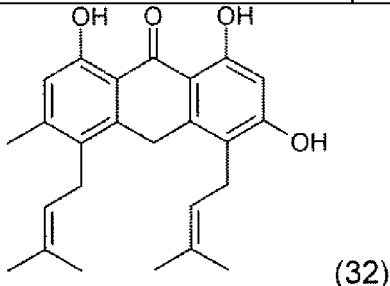
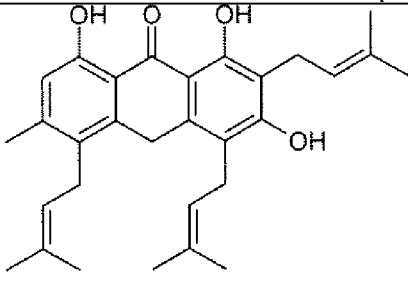
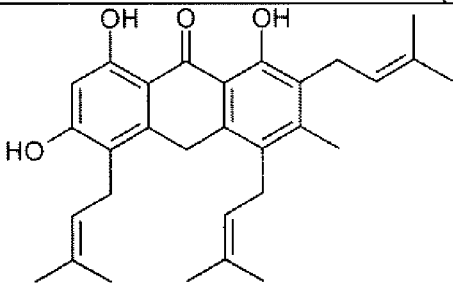
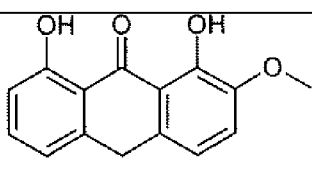
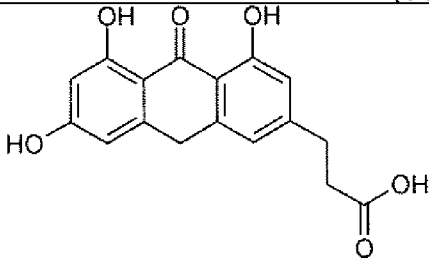
4. Dyeing method according to any one of the preceding claims, in which the anthrone derivative(s) of formula **(I)** are chosen from those below:

	1,3,8-trihydroxy-6-methyl-10H-anthracen-9-one or "emodin anthrone"
	1,8-dihydroxy-10H-anthracen-9-one
	3,4-dihydroxy-10H-anthracen-9-one

 (4)	Propionic acid 9-oxo-8-propionyloxy-9,10-dihydroanthracen-1-yl ester
 (5)	4-tert-butyl-1,8-dihydroxy-10H-anthracen-9-one
 (6)	2,2-dimethylpropionic acid 8-(2,2-dimethylpropionyloxy)-9-oxo-9,10-dihydroanthracen-1-yl ester
 (7)	1,8-dihydroxy-3-methyl-10H-anthracen-9-one
 (8)	1,8-dihydroxy-4-isopropyl-10H-anthracen-9-one
 (9)	1,8-dihydroxy-2,4-diisopropyl-10H-anthracen-9-one
 (10)	1,8-dihydroxy-2,7-dimethyl-10H-anthracen-9-one
 (11)	Acetic acid 8-hydroxy-10-oxo-9,10-dihydroanthracen-1-yl ester
 (12)	2-butyl-1,8-dihydroxy-10H-anthracen-9-one

 (13)	10 <i>H</i> -anthracen-9-one
 (14)	1,2-dihydroxy-10 <i>H</i> -anthracen-9-one
 (15)	1-hydroxy-10 <i>H</i> -anthracen-9-one
 (16)	1-hydroxy-8-methoxy-10 <i>H</i> -anthracen-9-one
 (17)	Acetic acid 8-hydroxy-9-oxo-9,10-dihydroanthracen-1-yl ester
 (18)	Acetic acid 8-acetoxy-9-oxo-9,10-dihydroanthracen-1-yl ester
 (19)	1,8-dimethoxy-10 <i>H</i> -anthracen-9-one
 (20)	1,5-anhydro-1-(7-carboxy-1,3,4,6-tetrahydroxy-8-methyl-9-oxo-9,10-dihydroanthracen-2-yl)hexitol
 (21)	1,5-anhydro-1-(7-carboxy-1,3,4,6-tetrahydroxy-8-methyl-10-oxo-9,10-dihydroanthracen-2-yl)hexitol

	1,4-dihydroxy-10 <i>H</i> -anthracen-9-one
	3-hydroxymethyl-10 <i>H</i> -anthracen-9-one
	2-hydroxymethyl-10 <i>H</i> -anthracen-9-one
	3-methyl-10 <i>H</i> -anthracen-9-one
	2-methyl-10 <i>H</i> -anthracen-9-one
	1,2,4-trihydroxy-10 <i>H</i> -anthracen-9-one
	1,3,4-trihydroxy-10 <i>H</i> -anthracen-9-one
	4,5-dimethoxy-10 <i>H</i> -anthracen-9-one
	4,5-dihydroxy-10-oxo-9,10-dihydroanthracene-2-carboxylic acid

 (31)	1,8-dihydroxy-3-hydroxymethyl-10H-anthracen-9-one
 (32)	1,3,8-trihydroxy-6-methyl-4,5-bis(3-methylbut-2-enyl)-10H-anthracen-9-one
 (33)	1,3,8-trihydroxy-6-methyl-2,4,5-tris(3-methylbut-2-enyl)-10H-anthracen-9-one
 (34)	1,6,8-trihydroxy-3-methyl-2,4,5-tris(3-methylbut-2-enyl)-10H-anthracen-9-one
 (35)	1,8-dihydroxy-2-methoxy-10H-anthracen-9-one
 (36)	3-(4,5,7-trihydroxy-10-oxo-9,10-dihydroanthracen-2-yl)propionic acid

and their optical isomers, their geometrical isomers, their tautomers, their hydrates and their addition salts with an organic or inorganic base.

- 5 **5.** Dyeing method according to the preceding claim, in which the anthrone derivative(s) of formula **(I)** are the compounds (1), (2), (3), (5), (7), (10), (12), (13),

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(14), (15), (16), (17), (18), (19), (23), (24), (25), (26), (31) and (35); and are preferably chosen from (1), (3), (5), (7), (10), (12), (14), (15), (16), (17), (18), (19), (23), (24), (25), (26), (31) and (35).

5

6. Dyeing method according to any one of the preceding claims, in which the basifying agent or agents is (are) present in an amount such that the pH of the composition is between 8 and 12 and particularly between 9 and 11, in particular between 9 and 9.5.

7. Dyeing method according to any one of the preceding claims, in which said method does not employ ammonia.

15

8. Dyeing method according to any one of Claims 1 to 6, in which said method employs ammonia as basifying agent ii) which is preferably present in a content of between 0.005 and 5% by weight, with respect to the total weight of the composition comprising i) the anthrone derivative(s) of formula **(I)** and ii) the ammonia.

9. Dyeing method according to any one of the preceding claims, in which said method employs iii) one or more chemical oxidizing agent(s) other than atmospheric oxygen (O₂), such as hydrogen peroxide, urea peroxide, alkali metal bromates, persalts, such as perborates and persulphates, or several system(s) which generate(s) hydrogen peroxide, such as:

30

- polymer complexes which can release hydrogen peroxide;
- metal peroxides which, in water, generate hydrogen peroxide, such as calcium peroxide or magnesium peroxide;
- oxidases which produce hydrogen peroxide in the presence of an appropriate substrate (for example, glucose in the case of glucose oxidase or uric acid with uricase), and also enzymes, among which may be

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mentioned peroxidases, 2-electron oxidoreductases, such as uricases, and 4-electron oxygenases, such as laccases.

5 **10.** Dyeing method according to any one of the preceding claims, in which said method employs iii) one or more chemical oxidizing agent(s) which is (are) applied simultaneously with i) the anthrone derivative(s) of formula **(I)** to the keratinous fibres;
10 preferably, the chemical oxidizing agent(s) is (are) found in the same cosmetic composition which comprises the anthrone derivative(s) of formula **(I)**, which composition is applied to the keratinous fibres in a single stage.

15 **11.** Dyeing method according to any one of Claims 1 to 8, in which said method does not employ a chemical oxidizing agent, the oxidation being carried out solely with atmospheric oxygen.

20 **12.** Dyeing method according to any one of the preceding claims, which does not employ an oxidation base and/or coupler of aromatic amine type.

25 **13.** Dyeing method according to any one of the preceding claims, which employs iv) one or more oxidation catalyst(s), such as manganese (Mn), zinc (Zn), iron (Fe) or copper (Cu) salts.

30 **14.** Dyeing method according to any one of the preceding claims, which employs v) one or more mordant(s) chosen from metal salts, such as iron, aluminium, titanium, calcium, manganese, copper, zinc or strontium salts, particularly iron sulphate,
35 manganese gluconate, copper sulphate, zinc gluconate, calcium chloride, magnesium chloride, potassium titanyl oxalate or strontium acetate.

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15. Cosmetic composition comprising i) one or more anthrone derivative(s) of formula **(I)** as defined in any one of Claims 1 to 5 and ii) one or more basifying agent(s) as defined in any one of Claims 1 to 8 and optionally the ingredients iii) to v) as defined in any one of Claims 9 to 14.

16. Use of the composition according to the preceding claim in the dyeing of keratinous fibres.

10

17. Multicompartment device comprising from 2 to 5 compartments comprising from 2 to 5 compositions, in which compartments the following ingredients i) to v) are distributed:

- 15 - i) one or more anthrone derivative(s) of formula **(I)** as defined in any one of Claims 1 to 5,
- ii) one or more basifying agent(s) as defined in any one of Claims 1 to 6, and
- iii) optionally one or more chemical oxidizing agent(s) as defined in Claim 8,
20 - iv) and/or oxidation catalysts as defined in Claim 12 and
- v) optionally one or more mordant(s) as claimed in Claim 13.