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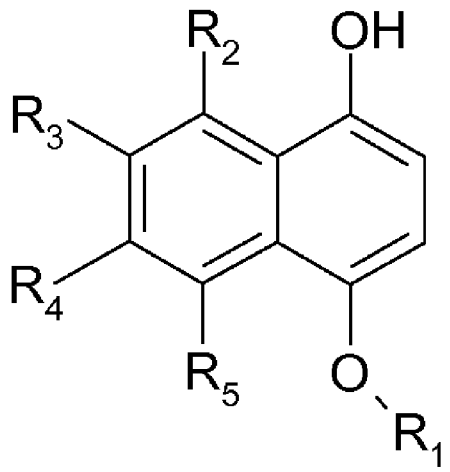
(54) **Title**: METHOD FOR THE TWO-STEP DYEING OF KERATIN FIBRES, BY APPLICATION OF A COMPOSITION COMPRISING A NAPHTALENE DERIVATIVE, THEN ALKALINE TREATMENT.



(II)

(57) **Abstract**: One subject of the present invention is a method for the two-step dyeing of keratin fibres, comprising the application: (1) in a first step, of a composition A comprising one or more organic compounds (I) having a value of the Hansen solubility parameter δ_H of less than or equal to 16 $MPa^{1/2}$ and having a molecular weight of less than 250 g/mol, and one or more naphthalene derivatives of formula (II): (2) then, in a second step, of a composition B having a pH greater than or equal to 8. Another subject of the invention is a device suitable for implementing such a method.

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Method for the two-step dyeing of keratin fibres, by application of a composition comprising a naphthalene derivative, then alkaline treatment.

One subject of the present invention is a novel method for dyeing human keratin fibres such as the hair comprising, in a first step, the application to the fibres of a composition comprising a particular derivative of naphthalene as a mixture with a specific organic compound then, in a second step, the treatment of said fibres with an alkaline composition.

Another subject of the invention is the multicompartment device or "dyeing kit", intended for implementing the dyeing method according to the invention.

Two main methods are known for dyeing human keratin fibres and in particular the hair.

The first, known as oxidation dyeing or permanent dyeing, consists in employing one or more oxidation dye precursors, more particularly one or more oxidation bases, optionally combined with one or more couplers.

Usually, oxidation bases are chosen from *ortho*-phenylenediamines or *para*-phenylenediamines, *ortho*-aminophenols or *para*-aminophenols, and also certain heterocyclic compounds. These oxidation bases are colourless or weakly coloured compounds which, combined with oxidizing products, make it possible to obtain, by an oxidative condensation process, coloured species which remain trapped inside the fibre.

In a manner known *per se*, it is possible to vary the shades obtained with these oxidation bases by combining them with one or more couplers or dye modifiers, the latter being chosen in particular from aromatic *meta*-diamines, *meta*-aminophenols, *meta*-diphenols and certain heterocyclic compounds, such as indole compounds

The variety of molecules employed as oxidation bases and couplers makes it possible to obtain a rich palette of colours.

The oxidation dyeing methods are generally carried out by applying the oxidation dye precursors (one or more oxidation bases, optionally combined with one or more couplers) to the keratin fibres in the presence of an oxidizing agent such as, in particular, hydrogen peroxide (or aqueous hydrogen peroxide solution) which is mixed with the dye composition just before the use thereof.

The resulting colourings are generally powerful and have good resistance especially to shampooing.

However, the conditions of implementation are capable of leading to a degradation of the keratin fibres. In the long term, the latter are degraded to a greater or lesser degree and have a tendency to become rough, dull, brittle and difficult to style, especially in the case of repeated dyeing.

The second dyeing method, known as direct or semi-permanent dyeing, comprises the application of direct dyes, which are dye molecules that have an affinity for the fibres, even in the absence of oxidizing agent added to the compositions comprising them.

The direct dyes generally employed are chosen from nitrobenzene, anthraquinone, nitropyridine, azo, methine, azomethine, xanthene, acridine, azine or triarylmethane direct dyes. The chemical species employed can be non-ionic, anionic (acid dyes) or cationic (basic dyes). Direct dyes can also be natural dyes.

The method conventionally used consists in applying a composition containing the direct dye(s) to the fibres, leaving it in, then rinsing the fibres.

However, the colourings which result therefrom are colourings which are particularly chromatic but temporary or semi-permanent due to the nature of the interactions which bind the direct dyes to the keratin fibre, and their desorption from the fibre is responsible for their low dyeing power and for their poor resistance to washing operations or to light.

Thus, the known hair-dyeing methods, whether in the direct dyeing or oxidation dyeing field, are capable of being improved.

In particular, there is a need to provide methods for dyeing human keratin fibres that make it possible to respect the nature of these fibres, and in particular to avoid the degradation thereof, while

offering powerful colourings that withstand external agents, in particular washing, perspiration, light, UV radiation, bad weather, chemical treatments (for example, permanent-wave treatment), and rubbing.

This need is felt in particular with blue dyes, the resistance of which to light and to UV radiation is generally not very satisfactory.

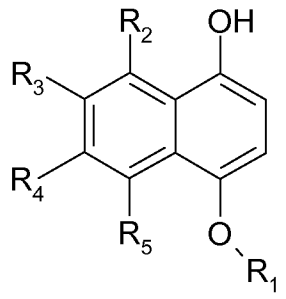
Finally, the colouring obtained should also be chromatic, homogeneous, and not very selective, that is to say should make it possible to obtain the minimal differences in coloration along a single keratin fibre, which in general is differently sensitized (i.e. damaged) between its tip and its root.

Patent application EP 2 793 408 in the name of the Applicant describes a method for the oxidation dyeing of keratin fibres that consists in applying, to these fibres, a dye composition having a pH greater than or equal to 8 and that results from the extemporaneous mixing of a dye composition A comprising at least one 4-substituted 1-naphtol and of an oxidizing composition B containing at least one oxidizing agent.

However, the Applicant has now just discovered that it is possible to obtain a colouring of keratin fibres that corresponds to the aforementioned objectives by applying separately and staggered over time (in two steps), firstly a composition A comprising the combination of a particular organic compound as defined below and of a specific derivative of naphthalene, then an alkaline composition B.

One subject of the present invention is therefore a method for the two-step dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, comprising the application to the fibres:

(1) in a first step, of a composition A comprising one or more organic compounds (I) having a value of the Hansen solubility parameter δ_H of less than or equal to 16 $MPa^{1/2}$ and having a molecular weight of less than 250 g/mol, and one or more naphthalene derivatives of formula (II):



(II)

in which:

- R_1 represents a saturated or unsaturated, linear or branched, hydrocarbon-based group comprising from 1 to 30 carbon atoms which may contain one or more saturated, unsaturated or aromatic rings, and which may contain one or more halogen atoms and/or oxygen atoms;
- R_2, R_3, R_4 and R_5, which are identical or different, represent a hydrogen atom; a halogen atom; a hydroxyl radical; a C_1 to C_{30} alkyl, C_1 to C_{30} alkyloxy, benzyloxy, C_2 to C_{30} acyl, C_2 to C_{30} acyloxy or benzoyloxy radical, it being possible for these radicals to be unsusbstituted or substituted with one or more halogen atoms and/or with one or more hydroxyl groups;

(2) then, in a second step, of a composition B having a pH greater than or equal to 8.

In the formula (II) above, the expression "halogen atom" denotes, in particular, chlorine, bromine and fluorine atoms.

Preferably, the R_1 radical is a benzyl radical or an alkyl radical comprising from 1 to 10 carbon atoms and possibly being uninterrupted or interrupted by one or more oxygen atoms, it being possible for said benzyl or alkyl radical to be unsusbstituted or substituted with one or more halogen atoms and/or with one or more hydroxyl groups, and/or with one or more –OR' alkoxy groups with R' denoting an alkyl radical comprising from 1 to 4 carbon atoms.

Particularly preferably, the R_1 radical is a benzyl radical, or an alkyl radical comprising from 1 to 4 carbon atoms.

Also preferably, the R_2, R_3, R_4 and R_5 radicals, which are identical or different, represent a hydrogen atom; a halogen atom; a hydroxyl radical; a C_1 to C_{10} alkyl, C_1 to C_{10} alkyloxy, benzyloxy, C_2 to C_{10} acyl or C_2 to C_{10} acyloxy radical, it being possible for these

radicals to be unsusbstituted or substituted with one or more halogen atoms and/or with one or more hydroxyl groups.

More preferably still, the R_2, R_3, R_4 and R_5 radicals, which are identical or different, represent a hydrogen atom; a halogen atom; a hydroxyl radical; a C_1 to C_4 alkyl, C_1 to C_4 alkyloxy, C_2 to C_4 acyl or benzyloxy radical, it being possible for these radicals to be unsusbstituted or substituted with one or more halogen atoms.

According to one particularly preferred embodiment, the R_2, R_3, R_4 and R_5 radicals all represent a hydrogen atom.

Among the compounds of formula (II) capable of being used in accordance with the dyeing method according to the invention, mention may more particularly be made of:

- 4-acetoxy-5-chloro-6-methyl-7-acetyl-8-hydroxynaphtalen-1-ol,
- 4-acetoxy-6-methyl-7-acetyl-8-hydroxynaphtalen-1-ol,
- 4-acetoxy-8-benzyloxynaphtalen-1-ol,
- 4-benzyloxynaphtalen-1-ol,
- 4,8-dibenzyloxy-6-methylnaphtalen-1-ol,
- 4,8-dibenzyloxynaphtalen-1-ol,
- 4-benzyloxy-8-(2-chloro)ethoxynaphtalen-1-ol,
- 4-benzyloxy-8-isopropyloxynaphtalen-1-ol,
- 4-benzyloxy-8-methoxynaphtalen-1-ol,
- 4-(2,2,2-trifluoroethoxy)naphtalen-1-ol,
- 4-(2-bromo)ethoxynaphtalen-1-ol,
- 4-(2-bromo)ethoxy-5-methoxynaphtalen-1-ol,
- 4-(2-bromo)ethoxy-8-methoxynaphtalen-1-ol,
- 4-(2-chloro)ethoxynaphtalen-1-ol,
- 4-(2-chloro)ethoxy-8-methoxynaphtalen-1-ol
- 4-(2-methoxy)ethoxynaphtalen-1-ol
- 4-(1,4,7-trioxaheptyl)naphtalen-1-ol,
- 4-(1,4,7-trioxaoctyl)naphtalen-1-ol,
- 4-(1,4,7,10-tetraoxadecyl)naphtalen-1-ol,
- (4-hydroxy-1-naphtalenyl)oxyacetic acid,
- 4-methoxynaphtalen-1-ol,
- 4-methoxy-5-chloronaphtalen-1-ol,
- 4-methoxy-5-chloro-8-benzyloxynaphtalen-1-ol,
- 4,8-dimethoxy-5-chloronaphtalen-1-ol,

- 4-methoxy-5-methylnaphtalen-1-ol,
- 4-methoxy-5-benzyloxynaphtalen-1-ol,
- 4-methoxy-5-benzyloxy-7-methylnaphtalen-1-ol,
- 4-methoxy-5-hydroxynaphtalen-1-ol,
- 4-methoxy-5-hydroxy-7-methylnaphtalen-1-ol,
- 4-methoxy-5-isopropyloxynaphtalen-1-ol,
- 4,5-dimethoxynaphtalen-1-ol,
- 4,5-dimethoxy-6-benzyloxynaphtalen-1-ol,
- 4,5-dimethoxy-7-methylnaphtalen-1-ol,
- 4,5-dimethoxy-8-chloronaphtalen-1-ol,
- 4-methoxy-6-methylnaphtalen-1-ol,
- 4-methoxy-6-methyl-7-acetyl-8-hydroxynaphtalen-1-ol,
- 4-methoxy-6,7-dimethylnaphtalen-1-ol,
- 4-methoxy-6-methyl-8-benzyloxynaphtalen-1-ol,
- 4-methoxy-6-methyl-8-hydroxynaphtalen-1-ol,
- 4,8-dimethoxy-6-methylnaphtalen-1-ol,
- 4-methoxy-6-ethoxynaphtalen-1-ol,
- 4-methoxy-6,7-diethoxynaphtalen-1-ol,
- 4-methoxy-7-methylnaphtalen-1-ol,
- 4,8-dimethoxy-7-benzyloxynaphtalen-1-ol,
- 4-methoxy-7-ethoxynaphtalen-1-ol,
- 4-methoxy-8-chloronaphtalen-1-ol,
- 4-methoxy-8-methylnaphtalen-1-ol,
- 4-methoxy-8-benzyloxynaphtalen-1-ol,
- 4-methoxy-8-hydroxynaphtalen-1-ol,
- 4-methoxy-8-isopropyloxynaphtalen-1-ol,
- 4,8-dimethoxynaphtalen-1-ol,
- 4-ethoxynaphtalen-1-ol,
- 4-propyloxynaphtalen-1-ol,
- 4-isopropyloxynaphtalen-1-ol,
- 4-butoxynaphtalen-1-ol,
- 4-isobutoxynaphtalen-1-ol,
- 4-*sec*-butoxy-naphtalen-1-ol,
- 4-isoamoxynaphtalen-1-ol,
- 4-bis(2-chloroisopropyloxy)naphtalen-1-ol,
- 4-cyclohexyloxynaphtalen-1-ol,

- 4-octyloxynaphtalen-1-ol,
- 4-(2-chloropropoxy)naphtalen-1-ol,
- isopropyliden-4,5-dioxynaphtalen-1-ol,
- and mixtures of these compounds.

Among the compounds of formula (II) mentioned above, the following are very particularly preferred:

- 4-methoxynaphtalen-1-ol,
- 4-ethoxynaphtalen-1-ol, and
- 4-isopropyloxynaphtalen-1-ol,
- and mixtures thereof.

More preferably still, the compound of formula (II) is 4-methoxynaphtalen-1-ol.

The compound(s) of formula (II) used in accordance with the method of the invention preferably represent from 0.001 to 5% by weight of composition A, and more preferably from 0.01 to 2% by weight, relative to the total weight of this composition.

The composition A according to the invention also comprises one or more organic compounds (I) having a value of the Hansen solubility parameter δ_H of less than or equal to 16 $MPa^{1/2}$, preferably less than 16 $MPa^{1/2}$, more preferably between 4 and 15 $MPa^{1/2}$ and more preferably still between 8 and 15 $MPa^{1/2}$, and a molecular weight of less than 250 g/mol.

Preferably, the organic compounds (I) are liquid at a temperature of 25°C and at atmospheric pressure (760 mmHg, or 1.013×10^5 Pa).

The organic compound(s) having a value of the Hansen solubility parameter δ_H as defined previously are, for example, described in the reference work "Hansen Solubility Parameters: A User's Handbook" by Charles M. HANSEN, second edition, CRC Press, 2007, pages 347 to 483, or else in the work "Handbook of Solubility Parameters and Other Cohesion Parameters", CRC Press, pages 95 to 121 and pages 177 to 185.

This value of the solubility parameter δ_H is linked to the formation of hydrogen bonds.

In particular, the work "Handbook of Solubility Parameters and Other Cohesion Parameters", CRC Press, pages 95 to 121 and pages 177 to 185, gives the equation $\delta H = (\sum -^{z}U_h/V)^{1/2}$

where

$^{z}U_h$ (in $J.mol^{-1}$) describes the contributions of the functional group in question in the solubility parameters linked to the hydrogen bonds (values in table 14, page 183); this parameter $^{z}U_h$ is also described in the work "The relation between surface tension and solubility parameter in liquids", Bagda, E, Farbe Lack, 84, 212, 1978; and

V is the volume of the molecule.

It should be noted that the value of the solubility parameter δH is usually given for a temperature of 25°C.

Said organic compound(s) (I) may especially be chosen from alkanols, aliphatic esters, ethers, aromatic alcohols, alkylaryl alcohols, aromatic acids, aliphatic acids, the alkylene carbonates such as propylene carbonate, lactones such as γ-butyrolactone, and mixtures thereof.

Preferably said organic compound(s) (I) are chosen from the alkanols, aliphatic esters, ethers, aromatic alcohols, alkylaryl alcohols, alkylene carbonates, aliphatic acids, and mixtures thereof.

More preferably still, said organic compound(s) (I) are chosen from 1-octanol, 1-decanol, tridecyl alcool, dipropylene glycol monomethyl ether acetate, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monomethyl ether, ethylene glycol 2-ethylhexyl ether, 3-phenyl-1-propanol, 2-phenyl-1-propanol, benzyl alcohol, benzyloxyethanol, phenoxyethanol, propylene carbonate, and mixtures of these compounds.

The organic compound (I) is particularly preferably chosen from aromatic alcohols, and more preferably still benzyl alcohol.

The organic compound(s) (I) generally represent from 0.1 to 20% by weight, preferably from 1 to 10% by weight, relative to the total weight of composition A.

Composition A may be acidic, neutral or basic. Preferably, it is acidic or neutral, that is to say it has a pH preferably of less than or equal to 7.

Such an acid pH may especially be adjusted by incorporating one or more acidifying agents into composition A.

Among the acidifying agents, mention may be made, by way of example, of mineral or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid, lactic acid, benzoic acid and sulphonic acids.

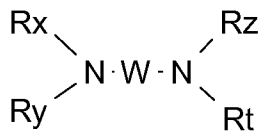
The application of composition A is followed by the application of a composition B having a pH greater than or equal to 8 to the fibres.

Preferably, composition B comprises one or more alkalinizing agent(s).

The expression "alkalinizing agent" is understood, within the meaning of the invention, to mean any compound which, by its presence in the composition, increases the pH of the composition by at least 0.05 of a pH unit and preferably by at least 0.1 of a pH unit.

The alkalinizing agent may in particular be a mineral or organic base.

Among the alkalinizing agents, mention may be made, by way of example, of aqueous ammonia, alkali metal carbonates, alkanolamines such as monoethanolamines, diethanolamines and triethanolamines and also derivatives thereof, sodium or potassium hydroxides, and compounds of formula (III) below:



(III)

in which W is a C_1-C_6 alkylene residue optionally substituted with a hydroxyl group or a C_1-C_6 alkyl radical; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a C_1-C_6 alkyl, C_1-C_6 hydroxyalkyl or C_1-C_6 aminoalkyl radical.

Mention may be made, by way of such compounds of formula (III), of 1,3-diaminopropane, 1,3-diamino-2-propanol, spermine and spermidine.

As alkalinizing agent, aqueous ammonia is particularly preferred.

Preferably, composition B has a pH ranging from 8.5 to 11.5.

Compositions A and B are formulated in a cosmetically acceptable medium, which is generally constituted of water or a mixture of water and of at least one organic solvent different from the organic compounds (I) described above, in order to solubilize the compounds which might not be sufficiently soluble in water. As organic solvent, mention may be made, for example, of C_1 to C_4 alkanols, such as ethanol and isopropanol; glycerol; and mixtures thereof.

Such organic solvents may be present in proportions preferably between 1 and 40% by weight relative to the total weight of each composition in which they are contained, and more preferably between 5 and 30% by weight.

According to one advantageous embodiment of the present invention, composition B also contains one or more oxidizing agent(s).

This oxidizing agent may be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibres, and among which mention may be made of hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts such as for example persulphates, perborates and percarbonates of alkali or alkaline-earth metals, for instance sodium, potassium or magnesium, enzymes such as peroxidases and 2-electron or 4-electron oxidoreductases.

The use of hydrogen peroxide is particularly preferred. This may advantageously be used in aqueous solution (aqueous hydrogen peroxide solution), the titer of which may vary, more particularly, from 1 to 40 volumes, and more preferably still from 5 to 40 volumes.

When hydrogen peroxide is used, the concentration of hydrogen peroxide in composition B preferably ranges from 0.3 to 12% by weight, relative to the total weight of this composition.

When composition B comprises an oxidizing agent, according to one particular embodiment this oxidizing agent may be incorporated

into said composition B just before the application of this composition to the keratin fibres.

According to the present invention, the application of composition A to the fibres may be separated from the application of composition B to these same fibres by an intermediate wringing and/or rinsing step.

Preferably, the applications of the respective compositions A and B are not separated by an intermediate rinsing step.

Moreover, the application of composition B to the fibres is preferably followed by a step of rinsing said fibres.

Composition A remains applied to the keratin fibres by observing a preferential leave-in time that ranges from 30 seconds to 90 minutes, preferably from 10 to 60 minutes, before the application of composition B, and at a temperature which may range from room temperature (around 25°C) to 60°C.

Composition B preferably remains applied to the keratin fibres by observing a leave-in time that preferably ranges from 5 seconds to 40 minutes, preferably from 10 to 30 minutes, and preferably at room temperature (around 25°C).

According to one particular embodiment of the invention, composition A may also contain one or more oxidation bases.

The optional oxidation base(s) are chosen from the oxidation bases conventionally used for the oxidation dyeing of keratin fibres, and are preferably chosen from *para*-phenylenediamines, bisphenylalkylenediamines, *para*-aminophenols, *ortho*-aminophenols, heterocyclic bases and their addition salts with an acid.

Mention may more particularly be made, among the heterocyclic bases that can be used as oxidation bases in the composition in accordance with the invention, of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

When they are present, the oxidation base(s) preferably represent from 0.001 to 15% by weight of the total weight of composition A and more preferably still from 0.01 to 5% by weight of this weight.

Composition A used in the method according to the invention may also comprise one or more couplers, so as to vary or enrich with

highlights the shades obtained with the compounds of formula (II) in accordance with the invention.

The couplers that can be used in the composition may be chosen from the couplers conventionally used in oxidation dyeing, and among which mention may especially be made of *meta*-phenylenediamines, *meta*-aminophenols, *meta*-diphenols and heterocyclic couplers such as, for example, indole derivatives, indoline derivatives and their addition salts with an acid.

When they are present, these couplers preferably represent from 0.001 to 10% by weight of the total weight of composition A and more preferably still from 0.01 to 5% by weight of this weight.

The addition salts with an acid of the oxidation bases and/or of the couplers that can be used in composition A may especially be chosen from hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, tosylates, benzenesulphonates, lactates and acetates.

The composition A used according to the method of the invention may also comprise one or more direct dyes, chosen from natural and non-natural direct dyes.

The expression "natural dye" is understood to mean any dye or dye precursor which occurs naturally and which is produced either by extraction (and optionally purification) from a plant matrix or by chemical synthesis.

The natural dyes suitable in particular for the implementation of the invention may be chosen, for example and non-limitingly, from carminic acid, kermesic acid, isatin, chlorophyllins, hematein, hematoxylin, brazilin, brazilein, extracts of sorghum, betanin, flavonoids, orceins or anthocyanins.

Use may also be made of extracts or decoctions containing these natural dyes and in particular henna-based extracts.

The composition may also comprise one or more non-natural direct dyes, chosen from ionic or non-ionic species, preferably cationic or non-ionic species.

Mention may be made, as examples of suitable additional direct dyes, of azo, methine, carbonyl, azine, nitro(hetero)aryl or

tri(hetero)arylmethane direct dyes, porphyrins and phthalocyanines, alone or as mixtures.

When they are present, the directs dye(s) represent from 0.01 to 20% by weight, and preferably from 0.5 to 10% by weight, relative to the total weight of the composition A.

According to one particularly preferred embodiment of the invention, composition A contains at least one compound chosen from isatin and isatin derivatives, thio-isatin and thio-isatin derivatives, oxindole and oxindole derivatives, thio-oxindole and thio-oxindole derivatives.

The latter compound(s) may advantageously be present in a content ranging from 0.01 to 10% by weight, and preferably from 0.05 to 5% by weight, relative to the total weight of composition A.

Compositions A and B in accordance with the invention may also comprise one or more cosmetic adjuvants.

These cosmetic adjuvants may, for example, be chosen from anionic, cationic, non-ionic, amphoteric or zwitterionic polymers or mixtures thereof; anionic, non-ionic, cationic or amphoteric surfactants; pigments; mineral thickeners; antioxidants; penetrants; sequestrants; fragrances; dispersants; conditioning agents such as, for example, cations, cationic or amphoteric polymers, chitosans or modified or unmodified, volatile or non-volatile silicones; film-forming agents; ceramides; preservatives; stabilizers; and opacifiers.

Of course, a person skilled in the art will be sure to choose this or these optional additional compound(s) so that the advantageous properties intrinsically linked to the dyeing method in accordance with the invention are not, or not substantially, impaired by the envisaged addition(s).

The above adjuvants may in general be present in an amount, for each of them, between 0 and 20% by weight relative to the total weight of each composition.

According to one preferred embodiment of the invention, composition A also contains one or more thickening polymers.

The expression “thickening polymer” is understood, within the meaning of the present invention, to mean any polymer, the presence of which in the composition makes it possible to increase the viscosity

thereof by at least 100 cP at a temperature of 25°C and at a shear rate of 1 s^{-1}, this viscosity possibly being determined by a rheometer or a cone and plate viscometer.

The thickening polymers may very particularly be 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) and crosslinked homopolymers of acrylic acid or of acrylamidopropane-sulphonic acid.

The thickening polymers may also be chosen from associative thickening polymers, that is to say polymers for which the chemical structure comprises at least one hydrophilic zone and at least one hydrophobic zone.

Such associative polymers may be of non-ionic or ionic nature, and are preferably anionic or cationic.

The content of thickening polymers, if they are present, usually varies from 0.05% to 5% by weight, relative to the total weight of composition A.

According to one equally preferred embodiment of the invention, composition A also contains one or more surfactants. This or these surfactant(s) may be non-ionic, anionic, cationic, amphoteric or zwitterionic.

The surfactants may thus represent from 0.01 to 50% by weight, preferably from 0.1 to 25% by weight, relative to the total weight of composition A.

Equally advantageously, composition A may also comprise one or more conditioning agents.

By way of example, mention may be made of volatile or non-volatile, branched or unbranched, cyclic or linear silicones. These silicones may be in the form of oils, resins or gums, they may in particular be polyorganosiloxanes.

Organopolysiloxanes aret defined in more 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.

As conditioning agent, cationic polymers such as, in particular, polyquaterniums 22, 6, 10, 11, 35 and 37 and hexadimethrine chloride are very particularly preferred.

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

Another subject of the invention is a multicompartment device or "kit" for dyeing, comprising at least a first compartment containing a composition A as described above, and at least a second compartment containing a composition B as described above.

According to one variant, the device according to the invention comprises at least three compartments: at least a first compartment containing a composition A as described above, at least a second compartment containing a composition B as described above and that does not contain oxidizing agent, and at least a third compartment containing a composition that contains at least one oxidizing agent as described above. Composition B with no oxidizing agent and the composition that contains the oxidizing agent(s) are such that the final composition resulting from the mixing of these two compositions has a pH greater than or equal to 8.

All these devices may be equipped with a means that makes it possible to deliver the desired mixture to the hair, such as the devices described in patent FR 2586913.

The examples that follow are intended to illustrate the invention without, however, limiting the scope thereof.

In all these examples, all the quantities are given in percent by weight of active material relative to the total weight of the composition, unless otherwise indicated.

Example 1

Dyeing composition A1 is prepared according to the invention, the formulation of which is given in Table 1 below:

Dyeing gel

	A1
4-methoxy-1-naphthol [1]	1 g
Benzyl alcohol	5 g
Ethanol	15 g
Hydroxyethyl cellulose (MW: 720 000) [2]	2 g
pH agent	qs for pH = 2.7
Fragrance	Qs
Water	qs for 100 g

[1] 4-methoxy-1-naphthol, CAS=84-85-5

[2] NATROSOL 250 MR sold by Aqualon

Pairs of locks of hair comprising 90% of permed, natural white hairs are treated for 45 minutes at 40°C with composition A1.

The locks are then wrung out, and then again treated for 15 minutes at room temperature with a weight-for-weight (50/50) mixture of an aqueous ammoniacal solution containing 2% by weight of ammonia, and an aqueous oxidizing composition containing 30 volumes of hydrogen peroxide having a pH of 2.2.

The pH of the composition resulting from this mixture is greater than 10.

The locks are then rinsed, shampooed and dried.

Intense and long-lasting blue colouring of the locks is obtained.

Example 2

Dyeing compositions A2, A3 and A4 are prepared according to the invention, the formulations of which are given in Table 2 below.

Dyeing gels

Composition	A2	A3	A4
4-methoxy-1-naphthol [1]	0.5 g	0.5 g	0.5 g
Ethanol	16 g	15 g	10 g
Benzyl alcohol	1 g	-	-
3-phenyl-1-propanol	0.5 g	-	-
2-phenyl-1-ethanol	1 g	-	-
Benzoic acid	0.5 g	-	-
Decanol	-	5 g	-
Propylene glycol butyl ether	-	-	6 g
Sodium lauryl sulphate	-	2 g	-
Hydroxyethyl cellulose (MW: 720 000) [2]	2 g	2 g	2 g
pH agent	qs for pH = 2.7	qs for pH = 2.7	qs for pH = 2.7
Fragrance	qs	qs	qs
Water	qs for 100 g	qs for 100 g	qs for 100 g

[1] 4-methoxy-1-naphthol, CAS=84-85-5
[2] NATROSOL 250 MR from Aqualon

Pairs of locks of hair comprising 90% of permed, natural white hairs are treated for 30 minutes at 40°C with these compositions A2 to A4.

The locks are then wrung out, and then again treated for 15 minutes at room temperature with a weight-for-weight (50/50) mixture of an aqueous ammoniacal solution containing 2% by weight of ammonia, and an aqueous oxidizing composition containing 20 volumes of hydrogen peroxide.

The pH of the composition resulting from this mixture is greater than 10.

The locks are then rinsed, shampooed and dried.

Powerful and long-lasting blue colourings are obtained.

Example 3

Dyeing compositions A5 and A6 are prepared according to the invention, the formulations of which are given in Table 3 below.

Dyeing gels

	A5	A6
4-methoxy-1-naphthol [1]	0.5 g	0.5 g
Isatin	0.5 g	0.5 g
Oxindole	-	0.5 g
Ethanol	15 g	15 g
Benzyl alcohol	5 g	5 g
Hydroxyethyl cellulose (MW: 720 000) [2]	2 g	2 g
pH agent	qs for pH = 2.7	qs for pH = 2.7
Fragrance	qs	qs
Water	qs for 100 g	qs for 100 g

[1] 4-methoxy-1-naphthol, CAS=84-85-5
[2] NATROSOL 250 MR from Aqualon

Pairs of locks of hair comprising 90% of permed, natural white hairs are treated for 45 minutes at 40°C with these compositions A5 and A6.

The locks are then wrung out, and then again treated for 15 minutes at room temperature with an aqueous ammoniacal solution containing 2% by weight of ammonia, and having a pH greater than 10.

The locks are then rinsed, shampooed and dried.

Powerful and long-lasting red colourings are obtained.

Example 4

Dyeing compositions A7 to A10 are prepared according to the invention, the formulations of which are given in Table 4 below.

Dyeing gels

	A7	A8	A9	A10
4-methoxy-1-naphthol [1]	0.5 g	0.5 g	0.5 g	0.5 g
Curcumin	0 .5 g	0 .5 g	0 .5 g	0 .5 g
Orcein	0.3 g	0.3 g	0.3 g	0.3 g
Chlorophyllin	0.15 g	0.15 g	0.15 g	0.15 g
Sorghum	0.02 g	0.02 g	0.02 g	0.02 g
Laccaic acid	0.01 g	0.01 g	0.01 g	0.01 g
Ethanol	15 g	16 g	15 g	10 g
Benzyl alcohol	5 g	1 g	-	-
3-phenyl-1-propanol	-	0.5 g	-	-
2-phenyl-1-ethanol	-	1 g	-	-
Benzoic acid	0.5 g	0.5 g	-	-
Decanol	-	-	5 g	-
Propylene glycol butyl ether	-	-	-	6 g
Sodium lauryl sulphate	-	-	2 g	2 g
Hydroxyethyl cellulose (MW: 720 000) [2]	2 g	2 g	2 g	2 g
pH agent	qs for pH = 2.7	qs for pH = 2.7	qs for pH = 2.7	qs for pH = 2.7
Fragrance	qs	qs	qs	qs
Water	qs for 100 g	qs for 100 g	qs for 100 g	qs for 100 g

[1] 4-methoxy-1-naphthol, CAS=84-85-5

[2] NATROSOL 250 MR from Aqualon

Pairs of locks of hair comprising 90% of permed, natural white hairs are treated for 30 minutes at 40°C with these compositions A7 to A10.

The locks are then wrung out, and then again treated for 15 minutes at room temperature with a weight-for-weight (50/50) mixture of an aqueous ammoniacal solution containing 2% by weight of ammonia, and an aqueous oxidizing composition containing 20 volumes of hydrogen peroxide.

The pH of the composition resulting from this mixture is greater than 10.

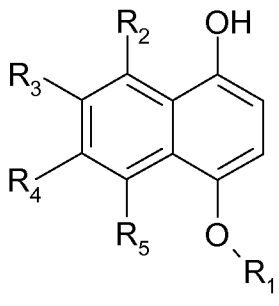
The locks are then rinsed, shampooed and dried.

Powerful and long-lasting brown colourings are obtained.

CLAIMS

1. Method for the two-step dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, comprising the application to the fibres:

(1) in a first step, of a composition A comprising one or more organic compounds (I) having a value of the Hansen solubility parameter δ_H of less than or equal to 16 $MPa^{1/2}$ and having a molecular weight of less than 250 g/mol, and one or more naphthalene derivatives of formula (II):



(II)

in which:

- R_1 represents a saturated or unsaturated, linear or branched, hydrocarbon-based group comprising from 1 to 30 carbon atoms which may contain one or more saturated, unsaturated or aromatic rings, and which may contain one or more halogen atoms and/or oxygen atoms;
- R_2, R_3, R_4 and R_5, which are identical or different, represent a hydrogen atom; a halogen atom; a hydroxyl radical; a C_1 to C_{30} alkyl, C_1 to C_{30} alkyloxy, benzyloxy, C_2 to C_{30} acyl, C_2 to C_{30} acyloxy or benzoyloxy radical, it being possible for these radicals to be unsusbstituted or substituted with one or more halogen atoms and/or with one or more hydroxyl groups;

(2) then, in a second step, of a composition B having a pH greater than or equal to 8.

2. Method according to Claim 1, characterized in that in the formula (II):

- the R_1 radical is a benzyl radical or an alkyl radical comprising from 1 to 10 carbon atoms and possibly being uninterrupted or interrupted by one or more oxygen atoms, it being possible for said benzyl or alkyl radical to be unsusbstituted or substituted with one or more halogen atoms and/or with one or more hydroxyl groups, and/or with one or more –OR' alkoxy groups with R' denoting an alkyl radical comprising from 1 to 4 carbon atoms, and

- the R_2, R_3, R_4 and R_5 radicals, which are identical or different, represent a hydrogen atom; a halogen atom; a hydroxyl radical; a C_1 to C_{10} alkyl, C_1 to C_{10} alkyloxy, benzyloxy, C_2 to C_{10} acyl or C_2 to C_{10} acyloxy radical, it being possible for these radicals to be unsusbstituted or substituted with one or more halogen atoms and/or with one or more hydroxyl groups.

3. Method according to any one of the preceding claims, characterized in that the compound of formula (II) is chosen from:

- 4-acetoxy-5-chloro-6-methyl-7-acetyl-8-hydroxynaphthalen-1-ol,
- 4-acetoxy-6-methyl-7-acetyl-8-hydroxynaphthalen-1-ol,
- 4-acetoxy-8-benzyloxynaphthalen-1-ol,
- 4-benzyloxynaphthalen-1-ol,
- 4,8-dibenzyloxy-6-methylnaphthalen-1-ol,
- 4,8-dibenzyloxynaphthalen-1-ol,
- 4-benzyloxy-8-(2-chloro)ethoxynaphthalen-1-ol,
- 4-benzyloxy-8-isopropyloxynaphthalen-1-ol,
- 4-benzyloxy-8-methoxynaphthalen-1-ol,
- 4-(2,2,2-trifluoroethoxy)naphthalen-1-ol,
- 4-(2-bromo)ethoxynaphthalen-1-ol,
- 4-(2-bromo)ethoxy-5-methoxynaphthalen-1-ol,
- 4-(2-bromo)ethoxy-8-methoxynaphthalen-1-ol,
- 4-(2-chloro)ethoxynaphthalen-1-ol,
- 4-(2-chloro)ethoxy-8-methoxynaphthalen-1-ol
- 4-(2-methoxy)ethoxynaphthalen-1-ol
- 4-(1,4,7-trioxaheptyl)naphthalen-1-ol,
- 4-(1,4,7-trioxaoctyl)naphthalen-1-ol,
- 4-(1,4,7,10-tetraoxadecyl)naphthalen-1-ol,
- (4-hydroxy-1-naphthalenyl)oxyacetic acid,
- 4-methoxynaphthalen-1-ol,

- 4-methoxy-5-chloronaphthalen-1-ol,
- 4-methoxy-5-chloro-8-benzyloxynaphthalen-1-ol,
- 4,8-dimethoxy-5-chloronaphthalen-1-ol,
- 4-methoxy-5-methylnaphthalen-1-ol,
- 4-methoxy-5-benzyloxynaphthalen-1-ol,
- 4-methoxy-5-benzyloxy-7-methylnaphthalen-1-ol,
- 4-methoxy-5-hydroxynaphthalen-1-ol,
- 4-methoxy-5-hydroxy-7-methylnaphthalen-1-ol,
- 4-methoxy-5-isopropyloxynaphthalen-1-ol,
- 4,5-dimethoxynaphthalen-1-ol,
- 4,5-dimethoxy-6-benzyloxynaphthalen-1-ol,
- 4,5-dimethoxy-7-methylnaphthalen-1-ol,
- 4,5-dimethoxy-8-chloronaphthalen-1-ol,
- 4-methoxy-6-methylnaphthalen-1-ol,
- 4-methoxy-6-methyl-7-acetyl-8-hydroxynaphthalen-1-ol,
- 4-methoxy-6,7-dimethylnaphthalen-1-ol,
- 4-methoxy-6-methyl-8-benzyloxynaphthalen-1-ol,
- 4-methoxy-6-methyl-8-hydroxynaphthalen-1-ol,
- 4,8-dimethoxy-6-methylnaphthalen-1-ol,
- 4-methoxy-6-ethoxynaphthalen-1-ol,
- 4-methoxy-6,7-diethoxynaphthalen-1-ol,
- 4-methoxy-7-methylnaphthalen-1-ol,
- 4,8-dimethoxy-7-benzyloxy-naphthalen-1-ol,
- 4-methoxy-7-ethoxynaphthalen-1-ol,
- 4-methoxy-8-chloronaphthalen-1-ol,
- 4-methoxy-8-methylnaphthalen-1-ol,
- 4-methoxy-8-benzyloxynaphthalen-1-ol,
- 4-methoxy-8-hydroxynaphthalen-1-ol,
- 4-methoxy-8-isopropyloxynaphthalen-1-ol,
- 4,8-dimethoxynaphthalen-1-ol,
- 4-ethoxynaphthalen-1-ol,
- 4-propyloxynaphthalen-1-ol,
- 4-isopropyloxynaphthalen-1-ol,
- 4-butoxynaphthalen-1-ol,
- 4-isobutoxynaphthalen-1-ol,
- 4-*sec*-butoxynaphthalen-1-ol,

- 4-isoamoxynaphthalen-1-ol,
- 4-bis(2-chloro-isopropyloxy)naphthalen-1-ol,
- 4-cyclohexyloxynaphthalen-1-ol,
- 4-octyloxynaphthalen-1-ol,
- 4-(2-chloropropoxy)naphthalen-1-ol,
- isopropyliden-4,5-dioxynaphthalen-1-ol,
- and mixtures of these compounds,

and preferably from:

- 4-methoxynaphthalen-1-ol,
- 4-ethoxynaphthalen-1-ol, and
- 4-isopropyloxynaphthalen-1-ol,
- and mixtures thereof.

4. Method according to any one of the preceding claims, characterized in that the compound(s) of formula (II) represent from 0.001 to 5% by weight of the composition A, and preferably from 0.01 to 2% by weight, relative to the total weight of this composition.

5. Method according to any one of the preceding claims, characterized in that the organic compound(s) (I) have a value of the Hansen solubility parameter δ_H of less than 16 $MPa^{1/2}$, preferably between 4 and 15 $MPa^{1/2}$ and more preferably between 8 and 15 $MPa^{1/2}$.

6. Method according to any one of the preceding claims, characterized in that the organic compound(s) (I) are chosen from alkanols, aliphatic esters, ethers, aromatic alcohols, alkylaryl alcohols, aromatic acids, aliphatic acids, the alkylene carbonates such as propylene carbonate, lactones such as γ-butyrolactone, and mixtures thereof.

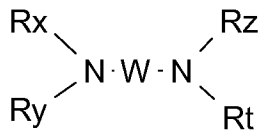
7. Method according to any one of the preceding claims, characterized in that the organic compound(s) (I) are chosen from 1-octanol, 1-decanol, tridecyl alcool, dipropylene glycol monomethyl ether acetate, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monomethyl ether, ethylene glycol 2-ethylhexyl ether, 3-phenyl-1-propanol, 2-phenyl-1-propanol,

benzyl alcohol, benzyloxyethanol, phenoxyethanol, propylene carbonate, and mixtures of these compounds.

8. Method according to any one of the preceding claims, characterized in that the organic compound(s) (I) represent from 0.1 to 20% by weight, preferably from 1 to 10% by weight, relative to the total weight of composition A.

9. Method according to any one of the preceding claims, characterized in that composition B comprises one or more alkalinizing agent(s).

10. Method according to the preceding claim, characterized in that the alkalinizing agent(s) are chosen from aqueous ammonia, alkali metal carbonates, alkanolamines such as monoethanolamines, diethanolamines and triethanolamines and also derivatives thereof, sodium or potassium hydroxides, and compounds of formula (III) below:



(III)

in which W is a C_1-C_6 alkylene residue optionally substituted with a hydroxyl group or a C_1-C_6 alkyl radical; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a C_1-C_6 alkyl, C_1-C_6 hydroxyalkyl or C_1-C_6 aminoalkyl radical.

11. Method according to either one of the preceding Claims 9 and 10, characterized in that composition B contains aqueous ammonia.

12. Method according to any one of the preceding claims, characterized in that composition B has a pH ranging from 8.5 to 11.5.

13. Method according to any one of the preceding claims, characterized in that composition B also contains one or more oxidizing agent(s), chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts, enzymes such as peroxidases and 2-electron or 4-electron oxidoreductases, and preferably hydrogen peroxide.

14. Method according to the preceding claim, characterized in that the oxidizing agent is incorporated into composition B just before the application of this composition to the keratin fibres.

15. Multicompartment device or "kit" for dyeing, comprising at least a first compartment containing a composition A as defined in any one of Claims 1 to 8, and at least a second compartment containing a composition B as defined in any one of Claims 1 and 9 to 12.

16. Device according to the preceding claim, characterized in that it comprises at least three compartments:

- at least a first compartment containing said composition A,
- at least a second compartment containing said composition B, this composition not containing oxidizing agent, and
- at least a third compartment containing a composition that contains at least one oxidizing agent,

composition B with no oxidizing agent and the composition that contains the oxidizing agent(s) being such that the final composition resulting from the mixing of these two compositions has a pH greater than or equal to 8.