

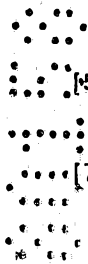
PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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[54] Invention Title: METHOD FOR DYEING KERATINOUS FIBRES USING 4-HYDROXYINDOLE DERIVATIVES AT ACID pH AND COMPOSITIONS USED

[72] Name(s) of actual inventor(s): JEAN COTTERET and MARIE PASCALE AUDOUSSET

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BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
9008570	France	Fr	5th July 1990

TICK IF APPLICABLE

For the purposes of Section 40, the specification relies on Section 6 of the Act (Microorganisms).

Drawing number recommended to accompany the abstract

F026390 04/07/91

By our/ny Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Louis C. Gebhardt

Registered Patent Attorney

.....
3rd July 1991
(Date)

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT
(To be filed before acceptance)

We, L'OREAL

of, 14, rue Royale, F-75008 Paris, FRANCE

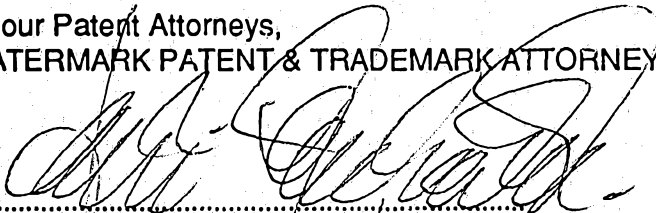
being the applicant in respect of Application No. 80158/91 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventor by virtue of a contract of employment with the inventors.

The person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS



10 March 1994

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Louis C. Gebhardt
Registered Patent Attorney

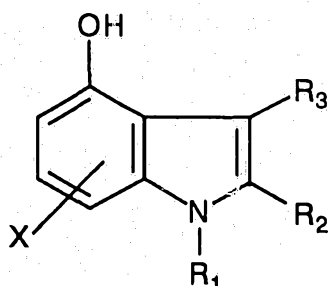


AU91E0158

(12) PATENT ABRIDGMENT (11) Document No. AU-B-80158/91
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 654281

- (54) Title
METHOD FOR DYEING KERATINOUS FIBRES USING 4-HYDROXYINDOLE DERIVATIVES AT ACID PH AND COMPOSITIONS USED
- (51)⁵ International Patent Classification(s)
A61K 007/13
- (21) Application No. : **80158/91** (22) Application Date : **04.07.91**
- (30) Priority Data
- (31) Number (32) Date (33) Country
90 08570 05.07.90 FR FRANCE
- (43) Publication Date : **09.01.92**
- (44) Publication Date of Accepted Application : **03.11.94**
- (71) Applicant(s)
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- (56) Prior Art Documents
AU 65892/90 A61K
- (57) Claim

1. Method for dyeing keratinous fibres, in particular human keratinous fibres such as hair, characterised in that a composition containing, in a medium appropriate for dyeing, at least one coupler corresponding to the formula:



in which R₁ denotes a hydrogen atom or a C₁-C₄ alkyl radical; R₂ and R₃, which may be identical or different, denote a hydrogen atom, a C₁-C₄ alkyl radical, a carboxyl radical or an alkoxy carbonyl radical; and X denotes a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₁₈ alkoxy radical, a halogen atom or an acetylamino group; at least one of the groups X, R₁, R₂ and R₃ being other than hydrogen; as well as the salts of these compounds;

- at least one oxidation dye precursor; and
- at least one oxidising agent; is applied to said fibres, the pH of the composition applied to the fibres being less than 7.

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(10) 654281

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26. Use of 4-hydroxyindole derivatives corresponding to the formula (I) as defined in any one of Claims 1 to 3 as couplers for dyeing keratinous fibres in an acid medium, in combination with oxidation dye precursors.

3. Method according to claim 2, characterised in that the compounds of formula (I) are chosen from 4-hydroxy-5-methoxyindole, 4-hydroxy-2-ethoxycarbonyl-5-ethoxyindole, 4-hydroxy-2-methyl-5-ethoxyindole, 4-hydroxy-7-methoxy-2, 3-dimethylindole, 4-hydroxy-5-methylindole, 4-hydroxy-5-ethoxyindole and 4-hydroxy-1-methyl-5-ethoxyindole.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:

Lodged:

654281

Complete Specification Lodged:

Accepted:

Published:



Priority :



Related Art :



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**WATERMARK PATENT & TRADEMARK ATTORNEYS.
LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA**

Complete Specification for the invention entitled:

**METHOD FOR DYEING KERATINOUS FIBRES USING 4-HYDROXYINDOLE DERIVATIVES
AT ACID pH AND COMPOSITIONS USED**

The following statement is a full description of this invention, including the best method of performing it known to :-

US

Method for dyeing keratinous fibres using 4-hydroxyindole derivatives at acid pH and compositions used.

5 The present invention relates to a new method for dyeing keratinous fibres, in particular human keratinous fibres, using 4-hydroxyindole derivatives in combination with oxidation bases and an oxidising agent in an acid medium and to the compositions used in the course of this method.

10 It is known to dye keratinous fibres and in particular human hair using tinctorial compositions containing, in an alkaline medium, oxidation dye precursors and in particular p-phenylenediamines or ortho- or para-aminophenols, generally termed "oxidation bases".

15 It is also known that the shades obtained with these oxidation bases can be varied by combining said bases with couplers, also termed colour modifiers, chosen, in particular, from aromatic meta-diamines, meta-aminophenols and meta-diphenols.

20 The Applicant has just discovered that the use of 4-hydroxyindole derivatives in combination with oxidation bases led, when this combination was applied to the hair in the presence of an oxidising agent and at acid pH, to dyeings having an improved tinctorial power. The dyeings thus obtained also have an excellent stability to light, to washing, to perspiration and to the weather.

25 These results are particularly surprising when they are compared with those obtained with conventional couplers of the benzene series mentioned above, where a loss of tinctorial power and a lower stability is often found when the method is carried out at acid pH.

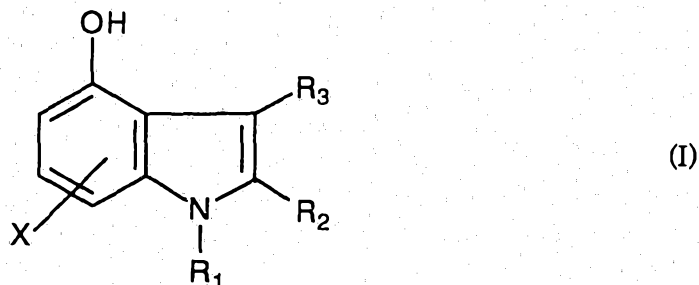
30 The present invention therefore relates to a method for dyeing keratinous fibres, in particular human keratinous fibres such as hair, comprising the application to these fibres of at least one composition containing a hydroxyindole compound of formula (I) as defined below, an oxidation dye precursor, also termed oxidation base, and an oxidising agent, at acid pH.

The invention also relates to a two-component agent for dyeing, one of which components comprises the 4-hydroxyindole derivative and the oxidation dye precursor and the other comprises the oxidising agent at an acid pH, and in amounts such that the mixture has an acid pH.

- 5 The invention also relates to the ready-to-use composition containing the various agents used for dyeing hair in an acid medium.

Further subjects of the invention will become apparent on reading the description and the examples which follow.

The method for dyeing keratinous fibres and in particular human
10 keratinous fibres such as hair, according to the invention, is essentially characterised in that a composition containing, in a medium appropriate for dyeing, at least one coupler corresponding to the formula:



- in which R_1 denotes a hydrogen atom or a C_1 - C_4 alkyl radical; R_2 and R_3 , which
15 may be identical or different, denote a hydrogen atom, a C_1 - C_4 alkyl radical, a carboxyl radical or an alkoxy carbonyl radical; and X denotes a hydrogen atom, a C_1 - C_4 alkyl radical, a C_1 - C_{18} alkoxy radical, a halogen atom or an acetylamino group; at least one of the groups X, R_1 , R_2 and R_3 being other than hydrogen; as well as the salts of these compounds;
- 20 at least one oxidation dye precursor or oxidation base; and
at least one oxidising agent; is applied to said fibres, the pH of the composition applied to the fibres



being less than 7.

The preferred compounds corresponding to the formula (I), used according to the invention, are the compounds in which the alkyl radical denotes methyl or ethyl and the alkoxy-carbonyl radical denotes methoxy-carbonyl or ethoxy-carbonyl.

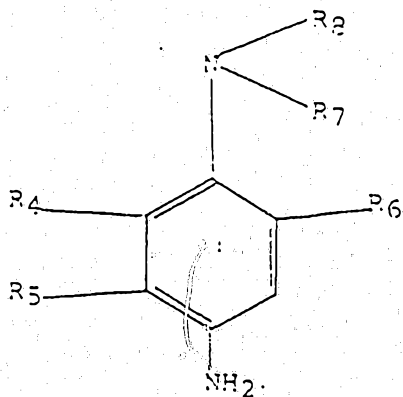
Amongst these compounds, the following may be mentioned: 4-hydroxy-5-ethoxyindole, 4-hydroxy-5-methoxyindole, 4-hydroxy-1-methyl-5-ethoxyindole, 4-hydroxy-2-ethoxycarbonyl-5-ethoxyindole, 4-hydroxy-2-methyl-5-ethoxyindole, 4-hydroxy-7-methoxy-2,3-dimethylindole and 4-hydroxy-5-methylindole.

The salts are chosen more particularly from the hydrochlorides or hydrobromides.

The oxidation dye precursors or oxidation bases are known compounds which are not themselves dyes and which form a dye by means of an oxidative condensation process, either on themselves or in the presence of a coupler or modifier. These compounds generally comprise an aromatic ring carrying functional groups consisting: either of two amino groups; or of an amino group and a hydroxyl group; these groups being in the para- or ortho-position relative to one another.

The oxidation dye precursors of the para type, used according to the invention, are chosen more particularly from para-phenylenediamines, para-aminophenols and para heterocyclic precursors, such as 2,5-diaminopyridine, 2-hydroxy-5-aminopyridine and 2,4,5,6-tetraaminopyrimidine.

Para-phenylenediamines which may be mentioned are the compounds corresponding to the formula (II):



(II)

in which R_4 , R_5 and R_6 , which may be identical or different, represent a hydrogen or halogen atom, an alkyl radical having from 1 to 4 carbon atoms or an alkoxy radical having from 1 to 4 carbon atoms; and R_7 and R_8 , which may be identical or different, represent a hydrogen atom or an alkyl, hydroxyalkyl, alkoxyalkyl, carbamyl-alkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbalkoxyaminoalkyl, piperidinoalkyl, or morpholinoalkyl radical; these alkyl or alkoxy groups having from 1 to 4 carbon atoms, or R_7 and R_8 form, together with the nitrogen atom to which they are bonded, a piperidino or morpholino heterocycle, on condition that R_4 or R_6 represents a hydrogen atom when R_7 and R_8 do not represent a hydrogen atom, and the salts of these compounds.

Particularly preferred compounds corresponding to the formula (II) which may be mentioned are p-phenylenediamine, 2-methyl-p-phenylenediamine, methoxy-para-phenylenediamine, chloro-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-dimethyl-5-methoxy-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, 3-methyl-4-amino-N,N-diethylaniline, N,N-di-(β -hydroxyethyl)para-phenylenediamine, 3-methyl-4-amino-N,N-di-(β -hydroxyethyl)aniline, 3-chloro-4-amino-N,N-di-(β -hydroxyethyl)aniline, 4-amino-N,N-(ethyl, carbamylmethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, carbamylmethyl)aniline, 4-amino-N,N-(ethyl, β -piperidinoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -piperidinoethyl)aniline, 4-amino-N,N-(ethyl, β -morpholinoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -morpholinoethyl)aniline, 4-amino-N,N-(ethyl, β -acetylaminoethyl)aniline, 4-amino-N-(β -methoxyethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -acetylaminoethyl)aniline, 4-amino-N,N-(ethyl, β -mesylaminoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -mesylaminoethyl)aniline, 4-amino-N,N-(ethyl, β -sulphoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -sulphoethyl)aniline, N-[(4'-amino)phenyl]morpholine and N-[(4'-amino)phenyl]piperidine.

These oxidation dye precursors of the para type may be introduced into the tinctorial composition either in the form of the free base or in the form of salts, such as in the form of the hydrochloride, hydrobromide or sulphate.

p-Aminophenols which may be mentioned are p-aminophenol, 2-methyl-4-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 2-(β -hydroxyethyl)-4-aminophenol, 2-methoxy-4-aminophenol, 3-methoxy-4-aminophenol, 2,5-dimethyl-4-aminophenol and 2-methoxymethyl-4-aminophenol.

The oxidation dye precursors of the ortho type are chosen from ortho-aminophenols, such as 1-amino-2-hydroxybenzene, 6-methyl-1-hydroxy-2-aminobenzene and 4-methyl-1-amino-2-hydroxybenzene, and ortho-phenylenediamines.

The oxidising agent is preferably chosen from hydrogen peroxide, urea peroxide, alkali metal bromates and persalts such as perborates and persulphates. Hydrogen peroxide is particularly preferred.

The compositions of the invention do not contain either iodide ions or nitrite ions in an amount sufficient to oxidise the indole derivative of formula (I) and the oxidation dye precursor.

The pH of the composition applied to the keratinous fibres, in particular the hair, has a value of below 7 and is preferably between 3 and 6.9. This pH is adjusted using acidifying agents well known in the field of dyeing of keratinous fibres, and in particular of human hair, such as inorganic acids, such as hydrochloric acid or phosphoric acid, or organic acids, such as carboxylic acids, such as tartaric acid or citric acid.

The compounds of formula (I) are present in the composition applied to the keratinous fibres in proportions of preferably between 0.01 and 3.5% by weight relative to the total weight of the composition.

The compositions, defined above, applied in the dyeing of keratinous fibres may also contain, in addition to the heterocyclic couplers of formula (I), other couplers known per se, such as meta-diphenols, meta-aminophenols, meta-phenylenediamines, meta-N-acylaminophenols, meta-ureidophenols, meta-carbalkoxyaminophenols, α -naphthol and couplers containing an active methylene group, such as the diketone compounds and pyrazolones.

Amongst these couplers which may be used in addition to the couplers of formula (I), the following may be mentioned: 2,4-dihydroxyphenoxyethanol, 2,4-dihydroxyanisole, meta-aminophenol, resorcinol, resorcinol monomethyl ether, 2-methylresorcinol, pyrocatechol, 2-methyl-5-N-(β -hydroxyethyl)aminophenol, 2-methyl-5-N-(β -mesylaminoethyl)aminophenol, 6-hydroxybenzomorpholine, 2,4-diaminoanisole, 2,4-diaminophenoxyethanol, 6-aminobenzomorpholine, [2-N-(β -hydroxyethyl)-amino-4-amino]-phenoxyethanol, 2-amino-4-N-(β -hydroxyethyl)aminoanisole, (2,4-diamino)phenyl- β , γ -dihydroxypropyl ether, 2,4-diaminophenoxyethylamine, 1,3-dimethoxy-2,4-diaminobenzene, 2-methyl-5-aminophenol, 2,6-dimethyl-3-aminophenol, 3,4-methylenedioxyphenol and 3,4-methylenedioxyaniline and their salts.

The tinctorial compositions of the invention may also contain direct dyes such as the derivatives of the benzene series, azo dyes, anthraquinone dyes, triphenylmethane and its derivatives, or xanthene or azine dyes. They may also contain rapid oxidation dyes.

These compositions may also contain anionic, cationic, nonionic or amphoteric surface-active agents or their mixtures.

Amongst these surface-active agents, the following may be mentioned: fatty alcohol alkylbenzenesulphonates, alkyl-naphthalenesulphonates, sulphates, ether-sulphates and sulphonates, quaternary ammonium salts, such as trimethylcetyl ammonium bromide, cetylpyridinium bromide, optionally oxyethylenated fatty acid ethanolamides, polyoxyethylenated acids, alcohols or

amines, polyglycerolated alcohols, polyoxyethylenated or polyglycerolated alkylphenols and polyoxyethylenated alkyl sulphates.

5 The tinctorial compositions are generally aqueous but they may also contain organic solvents in order to dissolve compounds which would not be sufficiently soluble in water. Among these solvents, the following may be mentioned as examples: C₂-C₄ lower alkanols, such as ethanol and isopropanol, glycerol, glycols or glycol
10 ethers, such as 2-butoxyethanol, ethylene glycol, propylene glycol, diethylene glycol monoethyl ether and monomethyl ether, and propylene glycol monoethyl ether and monomethyl ether, and also aromatic alcohols, such as benzyl alcohol or phenoxyethanol, or mixtures of these
15 solvents.

The composition applied to the hair may also contain thickeners chosen in particular from sodium alginate, gum arabic, cellulose derivatives, such as methyl cellulose, hydroxyethyl cellulose, hydroxypropyl
20 cellulose, hydroxymethyl cellulose and carboxymethyl cellulose, optionally crosslinked acrylic acid polymers and xanthan gum. It is also possible to use inorganic thickeners such as bentonite.

The composition may also contain antioxidants, chosen in particular from sodium sulphite, thioglycolic acid, sodium bisulphite, ascorbic acid and hydroquinone, as well as other cosmetically acceptable adjuvants when the composition is intended to be used for dyeing human
25 keratinous fibres, such as penetrating agents, sequestering agents, preservatives, buffers, perfumes, and the like.
30

The composition applied to the hair may be in diverse forms, such as liquids, creams or gels or in any other form appropriate for carrying out hair dyeing. It
35 may be packaged in an aerosol can in the presence of a propellant.

The invention also relates to the ready-to-use composition used in the method defined above.

According to a preferred embodiment, the method

comprises a preliminary step consisting in storing separately on the one hand the composition containing, in a medium appropriate for dyeing, the coupler corresponding to the formula (I) defined above and the oxidation dye precursors, in the form of a component (A), and, on the other hand, a composition containing the oxidising agent as defined above, in the form of a component (B), and in preparing a mixture thereof for use before applying this mixture to the keratinous fibres, as indicated above.

The composition applied to the keratinous fibres results from a mixture of 10 to 90% of the component (A) with 90 to 10% of the component (B) containing an oxidising agent.

The invention also relates to an agent for dyeing keratinous fibres, in particular hair, essentially characterised in that it comprises at least two components, one of the components consisting of the component (A) defined above and the other consisting of the component (B), also defined above, the pH of the components (A) and (B) being such that, after mixing in proportions of 90 to 10% in respect of component (A) and of 10 to 90% in respect of component (B), the resulting composition has a pH of less than 7.

The component (A) does not contain either iodide ions or nitrite ions in an amount sufficient to oxidise the indole derivative of formula (I) and the oxidation dye precursor.

In this embodiment the component (A), which contains at least the coupler of formula (I) and an oxidation dye precursor, may have a pH of between 3 and 10.5 and may be adjusted to the chosen value using alkalinising agents customarily used in dyeing keratinous fibres, such as ammonia, alkali metal carbonates or alkanolamines, such as mono-, di- and triethanolamines and their derivatives, or conventional acidifying agents, such as inorganic acids, such as hydrochloric or phosphoric acid, or organic acids, such as carboxylic acids, such as tartaric or citric acid.

This composition may contain the various other adjuvants mentioned above, in particular couplers other than the couplers derived from 4-hydroxyindole and corresponding to the formula (I) already mentioned above.

5 The system comprising oxidation dye precursors of the para and/or ortho type and also the couplers are present in proportions of preferably between 0.05 and 7% by weight relative to the total weight of the component (A). The concentration of compounds of formula
10 (I) may vary between 0.01 and 4% by weight relative to the total weight of the component (A).

15 The surface-active agents are present in the component (A) in proportions of 0.1 to 55% by weight. If the mixture contains solvents in addition to water, the latter are present in proportions of between 0.5 and 40% by weight, and in particular of between 5 and 30% by weight, relative to the total weight of the component (A). The thickeners are preferably present in proportions of between 0.1 and 5%, and in particular of between 0.2
20 and 3%, by weight. The antioxidants mentioned above are preferably present in the component (A) in proportions of between 0.02 and 1.5% by weight relative to the total weight of the component (A).

25 The component (B) containing the oxidising agent as defined above has a pH of less than 7. This pH may have a minimum value of 1 and it is preferably between 1.5 and 3.5. This component (B) may be acidified using the same type of acidifying agents as those used for the component (A).

30 It may be in the form of a liquid thickened to a greater or lesser extent or of a milk or gel.

35 This two-component dyeing agent may be packaged in a multi-compartment device or dyeing kit, or any other multi-compartment packaging system in which one compartment contains the component (A) and the second compartment contains the component (B); these devices may be fitted with means permitting the desired mixture to be delivered onto the hair, such as the devices described in the Applicant's Patent US-A-4 823 985.

The invention also relates to the use of 4-hydroxyindole derivatives corresponding to the formula (I) as a coupler for dyeing keratinous fibres in an acid medium, in combination with oxidation dye precursors.

5 According to the invention, the dyeing method consists in applying the mixture obtained to the hair, leaving it on the hair for 3 to 40 minutes, then rinsing the hair and optionally shampooing.

10 It is also possible, according to the invention, separately to apply a composition containing the coupler of formula (I), the oxidation dye precursor and the oxidising agent in such a way that the mixture forming in situ on the fibres has a pH of less than 7, as defined above.

15 The following examples are intended to illustrate the invention without, however, having a limiting character.

EXAMPLES 1 to 6

20 Hair is dyed by applying a mixture, prepared for use, of the dyeing composition (A) and the oxidising composition (B) to grey hair which is 90% white.

25 This mixture has the pH indicated in the table of examples which follow. This mixture is allowed to act for 30 minutes and the hair is then rinsed and shampooed. After drying, the hair is dyed in the shade specified at the bottom of the table.

in g	1	2	3
A) <u>Dyeing composition</u> 2,3-dimethyl-7-methoxy- 4-hydroxyindole	0.573	0.191	0.573
2,6-dimethyl-para- phenylenediamine.2HCl			0.657
Para-phenylenediamine		0.324	
Para-aminophenol	0.327		
2-methyl-5-N-(β -hydroxyethyl)- aminophenol		0.167	
Monoethanolamine qs pH	9.2	9.9	8.9
Carrier 1		X	
Carrier 2	X		X
Water qs	100	100	100
B) <u>Oxidising composition</u> 20 volume hydrogen peroxide solution			
Phosphoric acid qs pH	1.2	1.3	1.2
pH of wt/wt A + B mixture	6.5		6.4
pH of 1/3 A + 2/3 B mixture		4.4	
<u>Shades obtained:</u>	iri- descent light blond	light ash blond	grey

in g	4	5	6
A) <u>Dyeing composition</u> 2,3-dimethyl-7-methoxy- 4-hydroxyindole	0.191		
4-hydroxy-5-methoxyindole		0.489	0.489
2,6-dimethyl-para- phenylenediamine.2HCl		0.657	
Para-phenylenediamine			0.324
2-methyl-para- phenylenediamine.2HCl	0.366		
Meta-aminophenol	0.109		
α -naphthol	0.144		
Monoethanolamine qs pH	9.7	8.9	9.1
Carrier 1	X		
Carrier 2		X	X
Water qs	100	100	100
B) <u>Oxidising composition</u> 20 volume hydrogen peroxide solution			
Phosphoric acid qs pH	1.3	1.2	1.2
pH of wt/wt A + B mixture	6.0	6.4	6.5
<u>Shades obtained:</u>	matt very light blond	purple	red- purple

EXAMPLE 7

DYEING COMPOSITION

- 2,5-diaminonitrobenzene 0.3 g
- 4-hydroxy-5-ethoxyindole 0.3 g
- 5 - Para-phenylenediamine 0.4 g
- 1-methyl-2-hydroxy-4-aminobenzene 0.1 g
- Sodium lauryl ether sulphate containing
2 moles of ethylene oxide, sold as a
formulation containing 28% of AS 4.2 g AS
- 10 - Oxyethylenated nonylphenol containing
9 moles of ethylene oxide 1.0 g
- Ethylene glycol monobutyl ether 9.5 g
- Monoethanolamine qs pH=8.4
- Sodium metabisulphite containing 35% 0.45 g AS
- 15 of AS
- Sequestering agent qs
- Water qs 100 g

Weight for weight mixture with an oxidising composition: 20 volume hydrogen peroxide solution, the pH of which is adjusted to 1.3 using phosphoric acid.

20 Spontaneous pH of the mixture: 6.3.

This mixture is applied for 30 minutes to permanent-waved grey hair. After rinsing and shampooing, the hair is dyed red ash chestnut.

25

EXAMPLE 8

DYEING COMPOSITION

- 4-hydroxy-5-methylindole 0.45 g
- 2,6-dimethyl-1,4-diamino-
benzene.2 HCl 0.64 g
- 30 - Carrier 2
- Monoethanolamine qs pH=8.9
- Water qs 100 g

OXIDISING COMPOSITION

35 20 volume hydrogen peroxide solution adjusted to pH 1.2 using phosphoric acid.

Grey hair which is 90% white is dyed by applying a weight for weight mixture of the dyeing composition and the oxidising composition. The pH of the mixture is 6.4.

After leaving on the hair for 30 minutes, the hair is rinsed, washed with shampoo, rinsed again and then dried. The hair is dyed iridescent purple-violet.

DYEING CARRIER 1

- | | | |
|----|---|-----------|
| 5 | - Nonylphenol containing 4 moles of ethylene oxide, sold under the name SINNOPAL NP4 by HENKEL | 25.5 g |
| | - Nonylphenol containing 9 moles of ethylene oxide, sold under the name SINNOPAL NP9 by HENKEL | 17.5 g |
| 10 | - Ethylene glycol monoethyl ether | 7.0 g |
| | - Propylene glycol | 10.5 g |
| | - Dipropylene glycol | 0.5 g |
| | - Ethyl alcohol | 2.0 g |
| 15 | - Monoethanolamine lauryl ether sulphate, sold under the name SACTIPON 2 OM 29 by LEVER as a formulation containing 28% of AS | 4.2 g AS |
| | - Sodium alkyl ether sulphate containing 28% of AS | 0.8 g AS |
| 20 | - Aqueous sodium metabisulphite solution containing 35% of AS | 0.45 g AS |
| | - Sodium acetate | 0.8 g |
| | - Antioxidant, sequestering agent qs | |

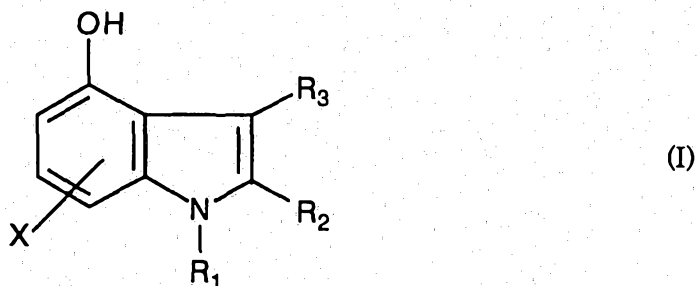
DYEING CARRIER 2

- | | | |
|----|--|-----------|
| 25 | - Polyglycerolated oleyl alcohol containing 2 moles of glycerol | 4.0 g |
| | - Polyglycerolated oleyl alcohol containing 4 moles of glycerol, containing 78% of AS | 5.69 g AS |
| | - Oleic acid | 3.0 g |
| 30 | - Oleylamine containing 2 moles of ethylene oxide, sold under the name ETHOMEEN O 12 by AKZO | 7.0 g |
| | - Diethylaminopropyl laurylamino succinamate, sodium salt containing 55% of AS | 3.0 g AS |
| 35 | - Oleyl alcohol | 5.0 g |
| | - Oleic acid diethanolamide | 12.0 g |
| | - Propylene glycol | 3.5 g |

- Ethyl alcohol 7.0 g
- Dipropylene glycol 0.5 g
- Propylene glycol monomethyl ether 9.0 g
- Aqueous sodium metabisulphite solution
5 containing 35% of AS 0.45 g AS
- Ammonium acetate 0.8 g
- Antioxidant, sequestering agent qs

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Method for dyeing keratinous fibres, in particular human keratinous fibres such as hair, characterised in that a composition containing, in a medium appropriate for dyeing, at least one coupler corresponding to the formula:



in which R_1 denotes a hydrogen atom or a C_1 - C_4 alkyl radical; R_2 and R_3 , which may be identical or different, denote a hydrogen atom, a C_1 - C_4 alkyl radical, a carboxyl radical or an alkoxy carbonyl radical; and X denotes a hydrogen atom, a C_1 - C_4 alkyl radical, a C_1 - C_{18} alkoxy radical, a halogen atom or an acetylamino group; at least one of the groups X, R_1 , R_2 and R_3 being other than hydrogen; as well as the salts of these compounds;

- at least one oxidation dye precursor; and
- at least one oxidising agent; is applied to said fibres, the pH of the composition applied to the fibres being less than 7.

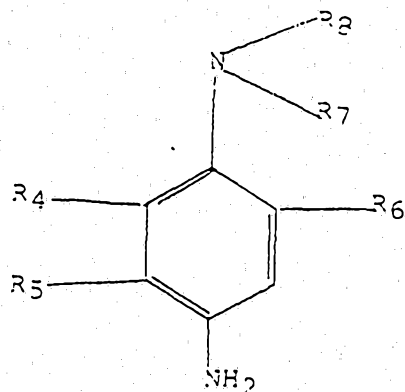
2. Method according to claim 1, characterised in that the compounds of formula (I) are chosen from the compounds in which the alkyl radical denotes methyl or ethyl and the alkoxy carbonyl radical denotes methoxycarbonyl or ethoxycarbonyl.

3. Method according to claim 2, characterised in that the compounds of formula (I) are chosen from 4-hydroxy-5-methoxyindole, 4-hydroxy-2-ethoxycarbonyl-5-ethoxyindole, 4-hydroxy-2-methyl-5-ethoxyindole, 4-hydroxy-7-methoxy-2, 3-dimethylindole, 4-hydroxy-5-methylindole, 4-hydroxy-5-ethoxyindole and 4-hydroxy-1-methyl-5-ethoxyindole.



4. Method according to any one of Claims 1 to 3, characterised in that the oxidation dye precursors are chosen from para-phenylenediamines, para-aminophenols and para heterocyclic precursors.

5. Method according to Claim 4, characterised in that the para-phenylenediamines are chosen from the compounds corresponding to the formula:



10 in which R_4 , R_5 and R_6 , which may be identical or different, represent a hydrogen or halogen atom, an alkyl radical having from 1 to 4 carbon atoms or an alkoxy radical having from 1 to 4 carbon atoms; and R_7 and R_8 , which may be identical or different, represent a hydrogen atom or an alkyl, hydroxyalkyl, alkoxyalkyl, carbamylalkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbalkoxyaminoalkyl, piperidinoalkyl, or morpholinoalkyl radical; these alkyl or alkoxy groups having from 1 to 4 carbon atoms, or R_7 and R_8 form, together with the nitrogen atom to which they are bonded, a piperidino or morpholino heterocycle, on condition that R_4 or R_6 represents a hydrogen atom when R_7 and R_8 do not represent a hydrogen atom, and the salts of these compounds.

25 6. Method according to Claim 4 or 5, characterised in that the compounds of formula (II) are chosen from p-phenylenediamine, 2-methyl-p-phenylenediamine, methoxy-para-phenylenediamine, chloro-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-dimethyl-5-methoxy-para-phenylenediamine, N,N-dimethyl-para-

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phenylenediamine, 3-methyl-4-amino-N,N-diethylaniline, N,N-di-(β -hydroxyethyl)para-phenylenediamine, 3-methyl-4-amino-N,N-di-(β -hydroxyethyl)aniline, 3-chloro-4-amino-N,N-di-(β -hydroxyethyl)aniline, 4-amino-N,N-(ethyl, carbamylmethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, carbamylmethyl)aniline, 4-amino-N,N-(ethyl, β -piperidinoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -piperidinoethyl)aniline, 4-amino-N,N-(ethyl, β -morpholinoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -morpholinoethyl)aniline, 4-amino-N,N-(ethyl, β -acetylaminoethyl)aniline, 4-amino-N-(β -methoxyethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -acetylaminoethyl)aniline, 4-amino-N,N-(ethyl, β -mesylaminoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -mesylaminoethyl)aniline, 4-amino-N,N-(ethyl, β -sulphoethyl)aniline, 3-methyl-4-amino-N,N-(ethyl, β -sulphoethyl)aniline, N-[(4'-amino)phenyl]morpholine and N-[(4'-amino)phenyl]piperidine, in the form of the free base or of salts.

7. Method according to Claim 4 or 5, characterised in that the p-aminophenols are chosen from p-aminophenol, 2-methyl-4-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 2-(β -hydroxyethyl)-4-aminophenol, 2-methoxy-4-aminophenol, 3-methoxy-4-aminophenol, 2,5-dimethyl-4-aminophenol and 2-methoxymethyl-4-aminophenol.

8. Method according to any one of Claims 1 to 3, characterised in that the oxidation dye precursors are oxidation dye precursors of the ortho type chosen from ortho-aminophenols and ortho-phenylenediamines.

9. Method according to any one of Claims 1 to 8, characterised in that the oxidising agent is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates and persalts.

10. Method according to any one of Claims 1 to 9, characterised in that the pH of the composition applied to the keratinous fibres is between 3 and 6.9.

11. Method according to any one of Claims 1 to 10,

characterised in that the composition used for dyeing keratinous fibres contains, in addition to the heterocyclic couplers of the family of 4-hydroxyindoles of formula (I), other couplers chosen from meta-diphenols, meta-aminophenols, meta-phenylenediamines, meta-N-acylaminophenols, meta-ureidophenols, meta-carbalkoxyaminophenols, α -naphthol and couplers containing an active methylene group chosen from diketone compounds and pyrazolones.

12. Method according to Claim 11, characterised in that the couplers are chosen from 2,4-dihydroxy-phenoxyethanol, 2,4-dihydroxyanisole, meta-aminophenol, resorcinol, resorcinol monomethyl ether, 2-methyl-resorcinol, pyrocatechol, 2-methyl-5-N-(β -hydroxy-ethyl)aminophenol, 2-methyl-5-N-(β -mesylaminoethyl)-aminophenol, 6-hydroxybenzomorpholine, 2,4-diaminoanisole, 2,4-diaminophenoxyethanol, 6-aminobenzomorpholine, [2-N-(β -hydroxyethyl)amino-4-amino]-phenoxyethanol, 2-amino-4-N-(β -hydroxyethyl)-aminoanisole, (2,4-diamino)phenyl- β,γ -dihydroxypropyl ether, 2,4-diaminophenoxyethylamine, 1,3-dimethoxy-2,4-diaminobenzene, 2-methyl-5-aminophenol, 2,6-dimethyl-3-aminophenol, 3,4-methylenedioxyphenol and 3,4-methylene-dioxyaniline and their salts.

13. Method according to any one of Claims 1 to 12, characterised in that the composition contains direct dyes and/or rapid oxidation dyes.

14. Method according to any one of Claims 1 to 13, characterised in that the composition contains anionic, cationic, nonionic or amphoteric surface-active agents or their mixtures; thickeners, antioxidants and/or any other cosmetically acceptable adjuvant.

15. Method according to any one of Claims 1 to 14 characterised in that the medium appropriate for dyeing consists of water or a mixture of water and a solvent chosen from C₂-C₄ lower alkanols, glycerol, glycols, glycol ethers and aromatic alcohols or their mixtures.

16. Agent for dyeing keratinous fibres and in particular hair, when used in the method as claimed in any one of Claims 1 to 15 characterised in that said agent comprises at



5 least two components: a component (A) consisting of a composition containing, in a medium appropriate for dyeing, an indole coupler corresponding to the formula (I) as defined in any one of Claims 1 to 3 and an oxidation dye precursor as defined in any one of Claims 1 and 4 to 8, and a component (B) consisting of a composition containing an oxidising agent in a medium appropriate for dyeing, the pH of the components (A) and (B) being such that, after mixing in proportions of 90 to 10% in respect of component (A) and of 10 to 90% in respect of component (B), the resulting composition has a pH of less than 7.

17. Agent according to Claim 16, characterised in that the component (A) has a pH of between 3 and 10.5.

15 18. Agent according to Claim 16 or 17, characterised in that the component (A) contains the oxidation dye precursors of the para and/or ortho type and also the couplers, in proportions of between 0.5 and 7% by weight relative to the total weight of the component (A).

20 19. Agent according to any one of Claims 16 to 18, characterised in that the concentration of compounds of formula (I) is between 0.01 and 4% by weight relative to the total weight of the component (A).

25 20. Agent according to any one of Claims 16 to 19, characterised in that the component (A) contains surface-active agents in proportions of 0.1 to 55% by weight, solvents in addition to water in proportions of between 0.5 and 40% by weight, thickeners in proportions of between 0.1 and 5% by weight, antioxidants in proportions of between 0.02 and 1.5% by weight and/or any other cosmetically acceptable adjuvant.

30 21. Agent according to any one of Claims 16 to 20, characterised in that the component (B) has a pH which has a minimum value of 1 and less than 7.

35 22. Method for dyeing keratinous fibres and in particular hair, characterised in that it comprises a first step consisting in storing a dyeing agent as defined in any one of Claims 16 to 21 and, before application, in mixing the components (A) and (B) in

proportions of 10 to 90% in respect of component (A) and of 90 to 10% in respect of component (B), so as to obtain a composition having a pH of less than 7, and applying this mixture immediately after preparation to the keratinous fibres.

23. Use in the method of any one of claims 1 to 15 of a multi-compartment device or dyeing kit which comprises at least two compartments, a first compartment of which contains the component (A) as defined in any one of Claims 16 to 20 and the second compartment contains the component (B) as defined in Claims 16 and 21.

24. Use of a multi-compartment device or dyeing kit according to Claim 23, characterised in that said device or dyeing kit is fitted with means permitting the desired mixture of components (A) and (B) to be delivered onto the hair.

25. Dyeing method according to any one of Claims 1 to 15, characterised in that the composition is applied to the hair and in that it is left on the hair for 3 to 40 minutes, in that the hair is rinsed and in that shampooing is optionally carried out before rinsing again and drying.

26. Use of 4-hydroxyindole derivatives corresponding to the formula (I) as defined in any one of Claims 1 to 3 as couplers for dyeing keratinous fibres in an acid medium, in combination with oxidation dye precursors.

27. Ready-to-use composition for dyeing keratinous fibres, as used in the method according to any one of Claims 1 to 15.

28. Composition according to Claim 27, containing the compound of formula (I) in proportions of from 0.01 to 3.5% by weight relative to the total weight of the composition.

DATED this 29th day of July, 1994

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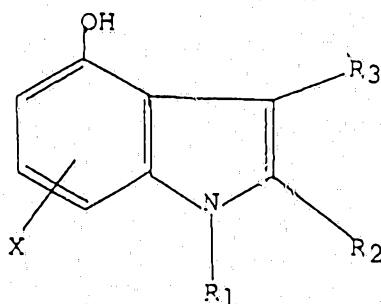


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ABSTRACT - EXT.531

Method for dyeing keratinous fibres using 4-hydroxyindole derivatives at acid pH and compositions used.

Method for dyeing keratinous fibres, in particular human keratinous fibres such as hair, characterised in that a composition containing, in a medium appropriate for dyeing, at least one 4-hydroxyindole derivative of formula:



in which R_1 denotes hydrogen or C_1-C_4 alkyl; R_2 and R_3 , which may be identical or different, denote hydrogen, C_1-C_4 alkyl, carboxyl or alkoxy-carbonyl; and X denotes hydrogen, C_1-C_4 alkyl, C_1-C_{18} alkoxy, halogen or acetyl-amino; at least one of the groups X, R_1 , R_2 and R_3 being other than hydrogen;

as well as the salts of these compounds;

- at least one oxidation dye precursor; and
- at least one oxidising agent; is applied to said fibres, the pH of the composition applied to the fibres being less than 7.