(CONVENTION. By one or more persons and/or a Company.) 652741 Form 4.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address(es).

I/We(1) L'OREAL
of 14, avenue Royale F-75008 Paris, France

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled:(2)
PROCESS FOR DYEING KERATINOUS FIBRES, AT ACID pH, USING 5,6- OR 7-MONOHYDROXYINDOLES AND THE COMPOSITIONS EMPLOYED

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered(3)
9002975

(3) Here insert number(s) of basic application(s).

(4) Here insert Name of basic Country or Countries, and basic date or dates.

for a patent or similar protection made in(4) France
on 8th March 1990

My/Our address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS 290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this 7th day of March 19 91

(5) Signature(s) of Applicant(s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

L'OREAL

by (5)

Louis C. Gebhardt
Registered Patent Attorney

To: THE COMMISSIONER OF PATENTS.

AUSTRALIA PATENT OFFICE MB WATERMARK PATENT & TRADEMARK ATTORNEYS

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Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by(1) L'OREAL

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled:(2) PROCESS FOR DYEING KERATINOUS FIBRES, AT ACID pH, USING 6- OR 7-MONOHYDROXYINDOLES AND THE COMPOSITIONS EMPLOYED

(3) Here insert full Name and Address, of Company official authorized to make declaration.

I,(3) Josiane PLOT

of 14, avenue Royale, F-75008 Paris, France

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in(4) France

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

on the 8th day of March 19 90, by L'OREAL

~~on the xx day of xx by xx~~

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3.(5) JEAN COTTERET, 15 Allee des Meuniers F-78480 Verneuil-sur-Seine and MARIE PASCALE AUDOUSSET, 106, rue Baudin F-92300 Levallois-Perret, France

~~I~~s/are the actual inventor s of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of the invention from the said actual inventors

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Paris, France

this 25th day of February 1991

(6) Signature.

(6)

AU9172692

(12) PATENT ABRIDGMENT (11) Document No. AU-B-72692/91
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 652741

(54) Title
PROCESS FOR DYEING KERATINOUS FIBRES, AT ACID PH, USING 5-6- OR 7-MONOHYDROXYINDOLES AND THE COMPOSITIONS EMPLOYED

International Patent Classification(s)
(51)[5] **D06P 001/642** **A61K 007/13** **D06P 001/32**

(21) Application No. : **72692/91** (22) Application Date : **07.03.91**

(30) Priority Data

(31) Number (32) Date (33) Country
90 02975 **08.03.90** **FR FRANCE**

(43) Publication Date : **12.09.91**

(44) Publication Date of Accepted Application : **08.09.94**

(71) Applicant(s)
L'OREAL

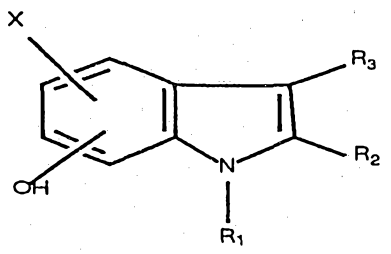
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(56) Prior Art Documents
AU 65977/90 A61K 007/13 C07D 209/08
AU 65892/90 A61K 007/13
AU 41207/89 A61K 007/13 C09B 007/02

(57) Claim

1. Process for dyeing keratinous fibres, for instance human keratinous fibres, for example hair, characterised in that there is applied to these fibres a composition containing, in a suitable dyeing medium, at least one indole-based coupler, of the formula:



(I)

in which R_1 designates a hydrogen atom or a C_1-C_4 alkyl radical; R_2 and R_3, which may be identical or different, designate a hydrogen atom, a C_1-C_4 lower alkyl radical, a carboxyl radical or an alkoxycarbonyl radical; X designates a hydrogen atom, a C_1-C_4 lower alkyl radical, a C_1-C_{18} alkoxy radical, a halogen atom, a C_2-C_{20} acyloxy radical or an acetylamino group; the OH group occupying the 5- or 6- or 7- positions of the aromatic ring; as well as the salts of these compounds;

.../2

an oxidation dye precursor;

an oxidising agent;

the pH of the composition applied to the fibres being less than 7.

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PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

Application Number: 72692/91
Lodged: 7th March 1991

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

Name of Applicant : L'OREAL

Address of Applicant : 14, avenue Royale F-75008 Paris, France

Actual Inventor : JEAN COTTERET and MARIE PASCALE AUDOUSSET

Address for Service : WATERMARK PATENT & TRADEMARK ATTORNEYS.
LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA

Complete Specification for the invention entitled:

PROCESS FOR DYEING KERATINOUS FIBRES, AT ACID pH, USING 5-, 6- OR 7-MONOHYDROXYINDOLES AND THE COMPOSITIONS EMPLOYED

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

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Process for dyeing keratinous fibres, at acid pH, using 5-,6- or 7-monohydroxyindoles and the compositions employed.

The present invention relates to a new process for dyeing keratinous fibres, in particular human keratinous fibres, using 5-,6- or 7-hydroxyindoles in combination with oxidation bases and an oxidising agent in acid medium, and to compositions employed during this process.

The dyeing of keratinous fibres, and in particular human hair, using tinctorial compositions containing oxidation dye precursors and in particular p-phenylenediamines or ortho- or para-aminophenols generally called "oxidation bases" and possessing an alkaline pH is known.

It is also known that it is possible to vary the hues obtained with these oxidation bases by combining them with couplers otherwise called colour modifiers, chosen in particular from among aromatic meta-diamines, meta-aminophenols and meta-diphenols.

The aim generally is to obtain colorations with good resistance to light, washing, perspiration and to adverse weather conditions, in particular by the choice of couplers and/or oxidation bases which allow such results to be obtained.

The Applicant has just discovered that the use of 5-,6- and/or 7-monohydroxyindole derivatives combined with oxidation bases resulted in colorations possessing an improved tinctorial ability when this combination was applied to hair in the presence of an oxidising agent at acid pH. The colorations thus obtained possess, moreover, an excellent resistance to light, washing, perspiration and adverse weather conditions.

These results are particularly surprising when they are compared to those obtained with conventional couplers of the benzene series mentioned above where a loss of tinctorial ability and decreased resistance is often observed when the procedure is carried out at acid pH.

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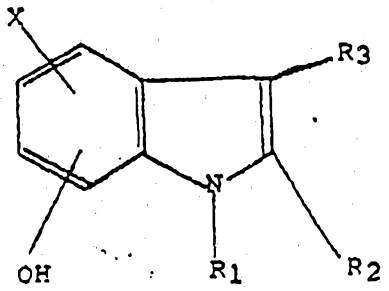
The subject of the present invention therefore is a process for dyeing keratinous fibres, in particular human keratinous fibres such as hair, which comprises the application to these fibres of at least one composition containing a 5-6- and/or 7-monohydroxyindole derivative, an oxidation dye precursor otherwise called an oxidation base and an oxidising agent, at acid pH.

Another subject of the invention is a two-component dyeing agent, one of whose components comprises the 5-6- or 7-monohydroxyindole derivative and the oxidation dye precursor and the other the oxidising agent.

Another subject of the invention is the composition which is ready for use, containing the various agents which are used for the dyeing of hair in acid medium.

Other subjects of the invention will emerge from reading the description and the examples which follow.

The process for dyeing keratinous fibres and in particular human keratinous fibres such as hair, in accordance with the invention, is essentially characterised in that there is applied to these fibres at least one composition containing, in a suitable dyeing medium, an indole-based coupler, of the formula:



(I)

in which R_1 designates a hydrogen atom or a C_1-C_4 alkyl radical; R_2 and R_3, which may be identical or different, designate a hydrogen atom, a C_1-C_4 lower alkyl radical, a carboxyl radical or an alkoxycarbonyl radical; X designates a hydrogen atom, a C_1-C_4 lower alkyl radical, a C_1-C_{18} alkoxy radical, a halogen atom, a C_2-C_{20} acyloxy

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radical or an acetylamino group; the OH group occupying the 5- or 6- or 7- positions of the aromatic ring; as well as the salts of these compounds;

at least one oxidation dye precursor or oxidation base;

at least one oxidising agent; the pH of the composition applied to the fibres being less than 7.

The preferred compounds of the formula (I), used in accordance with the invention, are the compounds in which the alkyl radical preferably designates methyl or ethyl; the alkoxycarbonyl radical designates methoxy or ethoxycarbonyl; the alkoxy radical designates methoxy, ethoxy, butoxy or hexadecyloxy; the acyloxy radical designates acetoxy or tetradecanoyloxy.

Among these compounds, the following may be mentioned: 6-hydroxyindole, 6-hydroxy-3-methoxycarbonylindole, 6-hydroxy-1-methyl-3-methoxycarbonylindole, 6-hydroxy-1-methyl-2,3-dimethoxycarbonylindole, 6-hydroxy-1,2-dimethylindole, 6-hydroxy-2-methylindole, 6-hydroxy-2-carboxyindole, 6-hydroxy-2,3-dimethylindole, 6-hydroxy-3-carboxyindole, 6-hydroxy-3-ethoxycarbonylindole, 6-hydroxy-2-ethoxycarbonylindole, 6-hydroxy-3-methylindole, 6-hydroxy-1-methylindole, 6-hydroxy-5-acetoxyindole, 6-hydroxy-5-methoxyindole, 6-hydroxy-5-methoxy-2-methylindole, 6-hydroxy-5-butoxyindole, 6-hydroxy-5-methoxyindole-2-carboxylic acid, 6-hydroxy-5-methoxy-2,3-dimethylindole, 6-hydroxy-7-methoxyindole, 6-hydroxy-5-tetradecanoyloxyindole, 6-hydroxy-5-hexadecyloxyindole, 7-hydroxyindole, 7-hydroxy-3-methylindole, 7-hydroxy-4-methoxy-2,3-dimethylindole, 6-hydroxy-5-methoxy-1-methylindole, 6-hydroxy-7-methylindole, 6-hydroxy-2-ethoxycarbonyl-5-methoxyindole, 6-hydroxy-2-methoxycarbonyl-5-butylindole, 6-hydroxy-2,3-dimethyl-5-(acetylamino)indole, 5-hydroxy-2-methyl-3-ethoxycarbonylindole and 5-hydroxy-2-carboxyindole.

The salts are chosen more particularly from among the acid addition salts, such as hydrochloric acid, sulphuric acid and the like.

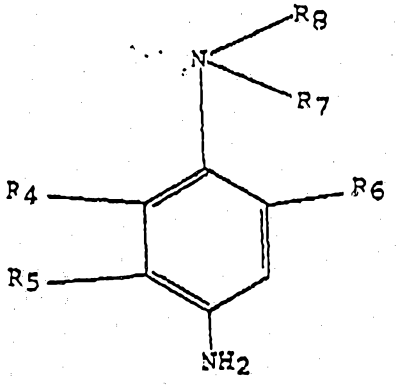
The 5- or 6- or 7-hydroxyindoles which are more

particularly preferred are chosen from among 6-hydroxyindole, N-methyl-6-hydroxyindole, 2-carboxy-6-hydroxyindole, N-methyl-5-methoxy-6-hydroxyindole, 7-hydroxyindole, 7-methyl-6-hydroxyindole, 2-methyl-5-methoxy-6-hydroxyindole, 2,3-dimethyl-5-methoxy-6-hydroxyindole, 5-methoxy-6-hydroxyindole, 5-acetoxy-6-hydroxyindole, 7-methoxy-6-hydroxyindole, 2-carboxy-5-methoxy-6-hydroxyindole, 3-methyl-7-hydroxyindole, 5-hydroxyindole, 3-methyl-5-hydroxyindole, 2-ethoxycarbonyl-5-hydroxyindole, 2,3-dimethyl-5-hydroxy-6-methoxyindole and 5-hydroxy-6-methoxyindole.

The oxidation dye precursors or oxidation bases are known compounds in themselves which are not dyes in themselves and which form a dye by a process of oxidative condensation either with themselves or in the presence of a coupler or modifier. These compounds generally contain an aromatic ring bearing functional groups, formed either by two amino groups or by an amino group and a hydroxyl group; these groups being in the para or ortho position with respect to one another.

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

Among the para-phenylenediamines, the compounds of the formula (II) may be mentioned more particularly:



(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; 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 attached, a piperidino or morpholino heterocycle, on the condition that R_4 or R_6 represents a hydrogen atom when R_7 and R_8 do not represent a hydrogen atom, as well as the salts of these compounds.

Among the compounds of the formula (II) which are particularly preferred, the following may be mentioned: p-phenylenediamine, p-toluylenediamine, methoxy-paraphenylenediamine, chloro-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,5-dimethylpara-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-ethyl-N-carbamylmethylaniline, 3-methyl-4-amino-N-ethyl-N-carbamylmethylaniline, 4-amino-N-ethyl-N-β-piperidinoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-piperidinoethylaniline, 4-amino-N-ethyl-N-β-morpholinoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-morpholinoethylaniline, 4-amino-N-ethyl-N-β-acetylaminoethylaniline, 4-amino-N-(β-methoxyethyl)aniline, 3-methyl-4-amino-N-ethyl-N-β-acetylaminoethylaniline, 4-amino-N-ethyl-N-β-mesylaminoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-mesylaminoethylaniline, 4-amino-N-ethyl-N-β-sulphoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-sulphoethylaniline, N-[(4'-amino)phenyl]morpholine and N-[(4'-amino)phenyl]-piperidine.

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

Among the p-aminophenols, the following may be mentioned: 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 ortho type oxidation dye precursors are chosen from among 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 chosen, preferably, from among hydrogen peroxide, urea peroxide, alkaline metal bromates and per salts, such as perborates and persulphates. Hydrogen peroxide is particularly preferred.

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

The compounds of formula (I) of the 5-,6- or 7-hydroxyindole family are present in the composition applied to the keratinous fibres, preferably in proportions of between 0.01 and 3.5% by weight relative to the total weight of the composition.

The compositions defined above, which are applied in the dyeing of keratinous fibres, may also contain, in addition to the heterocyclic couplers of the 5-,6- or 7-hydroxyindole family of formula (I), other couplers

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which are known in themselves, such as meta-diphenols, meta-aminophenols, meta-phenylenediamines, meta-acylaminophenols, meta-ureidophenols, meta-carbalkoxy-aminophenols or α-naphthol or couplers containing an active methylene group, such as β-ketonic compounds and pyrazolones.

Among these couplers which may be used in addition to the couplers of the 5-, 6- or 7-dihydroxyindole family of formula (I), the following may be mentioned more particularly: 2,4-dihydroxyphenoxyethanol, 2,4-dihydroxyanisole, meta-aminophenol, resorcinol, resorcinol monomethyl ether, 2-methylresorcinol, 2-methyl-5-N-(β-hydroxyethyl)aminophenol, 2-methyl-5-N-(β-mesylaminoethyl)aminophenol, 6-hydroxybenzomorpholine, 2,4-diaminoanisole, 2,4-diaminophenoxyethanol, 6-amino-benzomorpholine, [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, 2-methyl-5-aminophenol, 2,6-dimethyl-3-aminophenol, 3,4-methylenedioxyphenol and 3,4-methylenedioxyaniline and their salts.

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

Among these surface-active agents, the following may be mentioned: alkylbenzenesulphonates, alkylnaphthalenesulphonates, the sulphates, ether sulphates and sulphonates of fatty alcohols, quaternary ammonium salts such as trimethylcetylammonium bromide, cetylpyridinium bromide, the ethanolamides of optionally oxyethylenated fatty acids, polyoxyethylenated acids, alcohols or amines, polyglycerolated alcohols, polyoxyethylenated or polyglycerolated alkylphenols, as well as polyoxyethylenated alkylsulphates.

The tinctorial compositions are generally aqueous, but they may also contain organic solvents for solubilising compounds which may not be sufficiently soluble in water. Among these solvents, the following may be mentioned by way of example: C_2-C_4 lower alkanols such

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as ethanol and isopropanol, glycerol, glycols or glycol ethers, such as 2-butoxyethanol, ethylene glycol, propylene glycol, diethylene glycol monoethyl ether and monomethyl ether, as well as aromatic alcohols such as benzyl alcohol or phenoxyethanol, or mixtures of these solvents.

The composition applied to hair may also contain thickening agents chosen in particular from among sodium alginate, gum arabic, cellulose derivatives such as methylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxymethylcellulose, carboxymethylcellulose, optionally crosslinked acrylic acid polymers and xanthan gum. Inorganic thickening agents such as bentonite may also be used.

The composition may also contain antioxidants chosen in particular from among 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 keratinous fibres, such as penetrating agents, sequestering agents, preservatives, buffers, perfumes and the like.

The compositions used in the process contain neither iodide ion nor nitrite ion in sufficient quantity to oxidise the coupler of formula (I) and the oxidation base.

The composition applied to hair may be presented in various forms, such as liquids, creams, gels or any other suitable form for carrying out capillary dyeing. It may be packaged in aerosol canisters in the presence of a propellant.

Another subject of the invention is the ready-for-use composition which is employed in the process defined above.

According to a particularly preferred embodiment, the process comprises a preliminary stage consisting in storing in a separate form, on the one hand, the composition containing, in a suitable dyeing medium, the indole-based coupler of the formula (I) defined above and the oxidation dye precursors in the form of a composition ~~component~~

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(A) and, on the other, a composition (B) containing the oxidising agent such as defined above and carrying out their extemporaneous mixing before applying this mixture to keratinous fibres, as indicated above.

The composition applied to keratinous fibres is obtained in particular from a mixture of 10 to 90% of the composition (A) with 90 to 10% of the composition (B) containing an oxidising agent, the percentages being by weight relative to the total weight of the resulting composition.

Another subject of the invention is the use in keratinous fibres dyeing for example hair, of a composition (A) containing, in a suitable dyeing medium, an indole-based coupler of 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 4 to 12, in association with a composition (B) containing, in a suitable dyeing medium, an oxidising agent, the pH of the compositions (A) and (B) being such that after mixing in proportions of 90 to 10% for the composition (A) and of 10 to 90% for composition (B), said proportions being by weight relative to the total weight of the resulting composition, free of iodide ions the resulting composition has a pH of less than 7.

In this embodiment, the composition (A) which contains at least the indole-based derivative of the 5-,6- or 7-hydroxyindole family 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 by means of alkalising agents normally used in the dyeing of keratinous fibres, such as ammonium hydroxide, alkaline carbonates, alkanolamines such as the mono-, di- and triethanolamines as well as their derivatives or conventional acidifying agents, such as inorganic or organic acids, such as hydrochloric, tartaric, citric and phosphoric acids.

This composition may contain the various other adjuvants mentioned above, particularly couplers other than the couplers of the 5-, 6- or 7-hydroxyindole family of the formula (I) already mentioned above.

All of the oxidation dye precursors of the para and/or ortho type as well as the couplers are preferably present in proportions of between 0.3 and 7% by weight relative to the total weight of the composition (A). The concentration of compounds of formula (I) may vary between 0.05 and 4% by

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weight relative to the total weight of the composition A.

The surface-active agents are present in the composition (A) in proportions of 0.1 to 55% by weight. The solvent agents optionally present in addition to water are present in proportions of between 0.5 and 40% by weight and in particular between 5 and 30% by weight relative to the total weight of the composition (A). The thickening agents are preferably present in proportions of between 0.1 and 5% and in particular between 0.2 and 3% by weight. The antioxidants mentioned above are preferably present in the composition (A) in proportions of between 0.02 and 1.5% by weight relative to the total weight of the composition (A).

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

It may be presented in the form of more or less thick liquids, milk or gel.

This two-component dyeing agent may be packaged in a multi-compartment device or dyeing kit, or any other multi-compartment packaging system one of whose compartments contains the composition (A) and the second compartment contains the composition (B); these devices may be equipped with a means permitting the desired mixture to be delivered to the hair, such as the devices described more particularly in US Patent 4 823 985 by the Applicant.

Another subject of the invention is the use, as a coupler, of 5-, 6- or 7-hydroxyindole derivatives of the formula (I) for the dyeing in acid medium of keratinous fibres, in combination with oxidation dye precursors.

In accordance with the invention, the dyeing process consists in applying the mixture obtained to the hair, in allowing to settle for 3 to 40 minutes, then in rinsing the hair and optionally carrying out a shampooing.

It is also possible, in accordance with the

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invention, to apply separately a composition containing the indole-based coupler of formula (I), the oxidation dye precursor and the oxidising agent, in a manner such that the mixture which forms in situ on the fibres has a pH of less than 7, as defined above.

The following examples are intended to illustrate the invention without, as a result, implying any limitation.

EXAMPLES 1 to 23

The dyeing of hair is carried out by applying to grey hair which is 90% white a mixture of equal weights of the dyeing composition (A) and the oxidising composition (B), prepared immediately before use.

This mixture has the pH indicated in the table of examples which follow. This mixture is allowed to act for 30 minutes, then the hair is rinsed, and a shampooing is carried out After drying, the hair is dyed in the hue defined at the bottom of the table herein.

A) Dyeing composition (component A)	1	2	3
6-hydroxy-5-acetoxyindole	0.573		
6-hydroxy-N-methylindole		0.441	
6-hydroxy-5-methoxy-2-methylindole			0.708
Para-phenylenediamine	0.324		
2,6-dimethyl-para-phenylene-diamine		0.657	
2-methyl-para-phenylene-diamine, 2 HCl			0.488
Monoethanolamine qs pH	9.7	8.9	9.2
Dye mixture 1	X		
Dye mixture 2		X	X
Water qs to	100	100	100
B) Oxidising composition (component B)			
20 volumes hydrogen peroxide solution			
Phosphoric acid qs pH	1	1	1
pH mixture w/w A + B	4.3	6.7	6.7
Hues obtained	ashen iridescent dark blond	iridescent coppery dark blond	dull ash chest-nut

A) Dyeing composition (component A)	4	5	6
6-hydroxy-2-carboxyindole	0.354		
6-hydroxy-5-methoxy-2,3-dimethylindole		0.573	
7-hydroxy-3-methylindole			0.294
Para-phenylenediamine	0.216		0.216
2,6-dimethyl-para-phenylene-diamine		0.657	
3-(β-hydroxyethylamino)-6-methylphenol	0.05		
Meta-aminophenol	0.05		
γ-naphthol	0.05		
Monoethanolamine qs pH	9	8.9	9.2
Dye mixture 2	X	X	X
Water qs to	100	100	100
B) Oxidising composition (component B)			
20 volumes hydrogen peroxide solution			
Phosphoric acid qs pH	1	1	1
pH mixture w/w A + B	6.5	6.4	6.7
Hues obtained	pearly beige auburn	ash dark blond	beige blond

A) Dyeing composition (component A)	7	8	9
6-hydroxyindole	0.532		
6-hydroxy-7-methoxyindole		0.489	
7-hydroxyindole			0.399
Para-aminophenol	0.432		
2,6-dimethyl-para-phenylene-diamine		0.657	
Para-phenylenediamine			0.327
Monoethanolamine qs pH	9.2	9.4	9.8
Dye mixture 1		X	X
Dye mixture 2	X		
Water qs to	100	100	100
B) Oxidising composition (component B)			
20 volumes hydrogen peroxide solution			
Phosphoric acid qs pH	1	1.5	1.5
pH mixture w/w A + B	6.7	6.6	5
Hues obtained	golden very light blond	blue	chest-nut

A) <u>Dyeing composition</u> (component A)	10	11
6-hydroxyindole		0.399
6-hydroxy-5-methoxy-N-methylindole	0.531	
2,6-dimethyl-para-phenylenediamine	0.657	0.657
Monoethanolamine qs pH	8.9	9.8
Dye mixture 1		X
Dye mixture 2	X	
Water qs to	100	100
B) <u>Oxidising composition</u> (component B)		
20 volumes hydrogen peroxide solution		
Phosphoric acid qs pH	1	1.5
pH mixture p/p A + B	6.3	6.5
Hues obtained	iridescent mahogany dark blond	light coppery intense red

A) Dyeing composition (component A)	12	13	14	15
6-hydroxyindole				
6-hydroxy-7-methylindole	0.44			
2-carboxy-5-methoxy-6-hydroxyindole		0.62		
5-methoxy-6-hydroxyindole			0.49	
5-acetoxy-6-hydroxyindole				0.57
2,3-dimethyl-5-acetylamino-6-hydroxyindole				
Para-phenylenediamine	0.32	0.32	0.32	
2,6-dimethyl-para-phenylenediamine, 2 HCl				0.63
2-methoxymethyl-para-aminophenol				
Monoethanolamine qs pH	9.2	9.2	9.2	8.7
Dye mixture 3	X	X	X	X
Water qs to	100	100	100	100
B) Oxidising composition (component B)				
20 volumes hydrogen peroxide solution				
Phosphoric acid qs pH	1	1	1	1
pH mixture w/w A + B	6.8	6.8	6.8	6.3
Hues obtained on permanent-waved hair which is 90% white	red mahogany chestnut	ashen iridescent auburn	intense red iridescent	iridescent dark purple

A) Dyeing composition (component A)	16	17	18
6-hydroxyindole		0.4	
6-hydroxy-7-methylindole			
2-carboxy-5-methoxy-6-hydroxyindole			
5-methoxy-6-hydroxyindole			
5-acetoxy-6-hydroxyindole	0.57		
2,3-dimethyl-5-acetylamino-6-hydroxyindole			0.65
Para-phenylenediamine			
2,6-dimethyl-para-phenylene-diamine, 2 HCl			0.63
2-methoxymethyl-para-aminophenol	0.46	0.46	
Monoethanolamine qs pH	9.3	9.3	9.1
Dye mixture 3	X	X	X
Water qs to	100	100	100
B) Oxidising composition (component B)			
20 volumes hydrogen peroxide solution			
Phosphoric acid qs pH	1	1.5	1
pH mixture w/w A + B	6.5	6.9	6.6
Hues obtained on permanent-waved hair which is 90% white	ash beige light blond	golden ash very light natural blond	ash auburn

A) Dyeing composition (component A)	19	20	21
5-hydroxyindole	0.399		
3-methyl-5-hydroxyindole		0.44	
2-ethoxycarbonyl-5-hydroxyindole			0.615
2,3-dimethyl-5-hydroxy-6-methoxyindole			
5-hydroxy-6-methoxyindole			
Para-phenylenediamine	0.324		
2,6-dimethyl-para-phenylenediamine, 2 HCl			0.627
Para-aminophenol		0.327	
Monoethanolamine qs pH	9.2	9.2	9.1
Dye mixture 3	X	X	X
Water qs to	100	100	100
B) Oxidising composition (component B)			
20 volumes hydrogen peroxide solution			
Phosphoric acid qs pH	1	1	1
pH mixture w/w A + B	6.6	6.6	6.5
Hues obtained on natural hair which is 90% white	dark purple	pearly beige	light dark purple ash

A) <u>Dyeing composition</u> (component A)	22	23
5-hydroxyindole		
3-methyl-5-hydroxyindole		
2-ethoxycarbonyl-5-hydroxy-indole		
2,3-dimethyl-5-hydroxy-6-methoxyindole		0.573
5-hydroxy-6-methoxyindole	0.489	
Para-phenylenediamine		
2,6-dimethyl-para-phenylene-diamine, 2 HCl	0.627	0.627
Para-aminophenol		
Monoethanolamine qs pH	9	9
Dye mixture 3	X	X
Water qs to	100	100
B) <u>Oxidising composition</u> (component B)		
20 volumes hydrogen peroxide solution		
Phosphoric acid qs pH	1	1
pH mixture w/w A + B	6.7	6.6
Hues obtained on natural hair which is 90% white	blue	ashen dull grey

DYE MIXTURE No. 1

-	Nonylphenol containing 4 moles of ethylene oxide, sold under the name SINNOPAL NP4 by the company HENKEL	25.5 g
-	Nonylphenol containing 9 moles of ethylene oxide, sold under the name SINNOPAL NP9 by the company HENKEL	17.5 g
-	Ethylene glycol butyl ether	7.0 g
-	Propylene glycol	11.0 g
-	Ethyl alcohol	2.0 g
-	Monoethanolamine lauryl ether sulphate, sold under the name SACTIPON 2 OM 29 by the company LEVER and containing 28% AS	5.0 g AS
-	Sodium metabisulphite in aqueous solution containing 35% AS	0.46 g AS
-	Sodium acetate	0.8 g
-	Antioxidant, sequestering agent, qs	

DYE MIXTURE No. 2

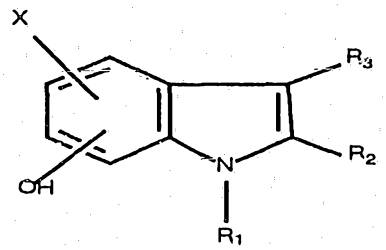
-	Polyglycerolated oleic alcohol containing 2 moles of glycerol	4.0 g
-	Polyglycerolated oleic alcohol containing 4 moles of glycerol, 78% AS	5.69 g AS
-	Oleic acid	3.0 g
-	Oleic amine 2 OE sold under the name ETHOMEEN O 12 by the company AKZO	7.0 g
-	Diethylaminopropyl laurylaminosuccinamate, sodium salt containing 55% AS	3.0 g AS
-	Oleic alcohol	5.0 g
-	Coconut acid diethanolamide	12.0 g
-	Propylene glycol	4.0 g
-	Ethyl alcohol	7.0 g
-	Propylene glycol monomethyl ether	9.0 g
-	Sodium bisulphite in aqueous solution containing 35% AS	0.46 g AS
-	Ammonium acetate	0.8 g
-	Antioxidant, sequestering agent, qs	

DYE MIXTURE No. 3

-	Polyglycerolated oleic alcohol containing 2 moles of glycerol	4.0 g
-	Polyglycerolated oleic alcohol containing 4 moles of glycerol, 78% AS	5.69 g AS
-	Oleic acid	3.0 g
-	Oleic amine 2 OE sold under the name ETHOMEEN O 12 by the company AKZO	7.0 g
-	Diethylaminopropyl laurylaminosuccinamate, sodium salt containing 55% AS	3.0 g AS
-	Oleic 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
-	Sodium metabisulphite in aqueous solution containing 35% AS	0.46 g AS
-	Ammonium acetate	0.8 g
-	Antioxidant, sequestering agent, qs	

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for dyeing keratinous fibres, for instance human keratinous fibres, for example hair, characterised in that there is applied to these fibres a composition free of iodide ions containing, in a suitable dyeing medium, at least one indole-based coupler, of the formula:



(I)

in which R_1 designates a hydrogen atom or a C_1-C_4 alkyl radical; R_2 and R_3, which may be identical or different, designate a hydrogen atom, a C_1-C_4 lower alkyl radical, a carboxyl radical or an alkoxycarbonyl radical; X designates a hydrogen atom, a C_1-C_4 lower alkyl radical, a C_1-C_{18} alkoxy radical, a halogen atom, a C_2-C_{20} acyloxy radical or an acetylamino group; the OH group occupying the 5- or 6- or 7- positions of the aromatic ring; as well as the salts of these compounds;

an oxidation dye precursor;

an oxidising agent;

the pH of the composition applied to the fibres being less than 7.

2. Process according to claim 1, characterised in that the compounds of formula (I) are chosen from among the compounds in which the alkyl radical designates methyl or ethyl; the alkoxycarbonyl radical designates methoxy or ethoxycarbonyl; the alkoxy radical designates methoxy, ethoxy, butoxy or hexadecyloxy; the acyloxy radical designates acetoxy or tetradecanoyloxy.

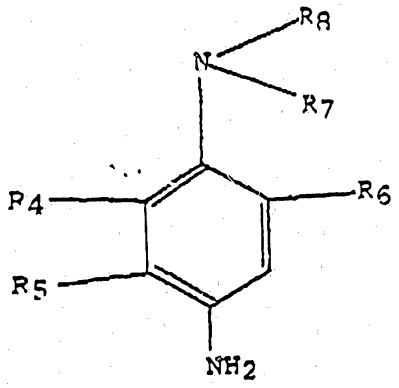
3. Process according to claim 2, characterised in that the compounds of formula (I) are chosen from among 6-hydroxyindole, 6-hydroxy-3-methoxycarbonylindole,

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6-hydroxy-1-methyl-3-methoxycarbonylindole, 6-hydroxy-1-methyl-2,3-dimethoxycarbonylindole, 6-hydroxy-1,2-dimethylindole, 6-hydroxy-2-methylindole, 6-hydroxy-2-carboxyindole, 6-hydroxy-2,3-dimethylindole, 6-hydroxy-3-carboxyindole, 6-hydroxy-3-ethoxycarbonylindole, 6-hydroxy-2-ethoxycarbonylindole, 6-hydroxy-3-methylindole, 6-hydroxy-1-methylindole, 6-hydroxy-5-acetoxyindole, 6-hydroxy-5-methoxyindole, 6-hydroxy-5-methoxy-2-methylindole, 6-hydroxy-5-butoxyindole, 6-hydroxy-5-methoxyindole-2-carboxylic acid, 6-hydroxy-5-methoxy-2,3-dimethylindole, 6-hydroxy-7-methoxyindole, 6-hydroxy-5-tetradecanoyloxyindole, 6-hydroxy-5-hexadecyloxyindole, 7-hydroxyindole, 7-hydroxy-3-methylindole, 7-hydroxy-4-methoxy-2,3-dimethylindole, 6-hydroxy-5-methoxy-1-methylindole, 6-hydroxy-7-methylindole, 6-hydroxy-2-ethoxycarbonyl-5-methoxyindole, 6-hydroxy-2-methoxycarbonyl-5-butylindole, 6-hydroxy-2,3-dimethyl-5-(acetylamino)-indole, 5-hydroxy-2-methyl-3-ethoxycarbonylindole and 5-hydroxy-2-carboxyindole.

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

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



(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; 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 attached, a piperidino or morpholino heterocycle, on the condition that R_4 or R_6 represents a hydrogen atom when R_7 and R_8 do not represent a hydrogen atom, as well as the salts of these compounds.

6. Process according to Claim 4 or 5, characterised in that the compounds of formula (II) are chosen from among p-phenylenediamine, p-toluylenediamine, methoxy-para-phenylenediamine, chloro-para-phenylenediamine, 2,6-dimethyl-para-phenylènediamine, 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-ethyl-N-carbamylmethylaniline, 3-methyl-4-amino-N-ethyl-N-carbamylmethylaniline, 4-amino-N-ethyl-N-β-piperidinoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-piperidinoethylaniline, 4-amino-N-ethyl-N-β-morpholinoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-morpholinoethylaniline, 4-amino-N-ethyl-N-β-acetylaminoethylaniline, 4-amino-N-(β-methoxyethyl)aniline, 3-methyl-4-amino-N-ethyl-N-β-acetylaminoethylaniline, 4-amino-N-ethyl-N-β-mesylaminoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-mesylaminoethylaniline, 4-amino-N-ethyl-N-β-sulphoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-sulphoethylaniline, N-[(4'-amino)phenyl]morpholine and N-[(4'-amino)phenyl]-piperidine, in the form of a free base or salts.

7. Process according to Claim 4, ~~or 5,~~ characterised in that the p-aminophenols are chosen from among p-aminophenol, 2-methyl-4-aminophenol, 3-methyl-4-aminophenol,

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

9. Process according to any one of Claims 1 to 8, characterised in that the oxidising agent is chosen from among hydrogen peroxide, urea peroxide, alkaline metal bromates and per salts.

10. Process 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. Process 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 5-, 6- or 7-hydroxyindole family of formula (I), other couplers chosen from among meta-diphenols, meta-aminophenols, meta-phenylenediamines, meta-acylaminophenols, meta-ureidophenols, meta-carbalkoxyaminophenols or α-naphthol or couplers containing an active methylene group chosen from among β-ketonic compounds and pyrazolones.

12. Process according to Claim 11, characterised in that the couplers are chosen from among 2,4-dihydroxyphenoxyethanol, 2,4-dihydroxyanisole, meta-aminophenol, resorcinol, resorcinol monomethyl ether, 2-methylresorcinol, 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, 2-methyl-5-aminophenol, 2,6-dimethyl-3-aminophenol, 3,4-methylene-

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dioxyphenol and 3,4-methylenedioxyaniline and their salts.

13. Process according to any one of claims 1 to 12, characterised in that the composition contains anionic, cationic, non-ionic or amphoteric surface-active agents or their mixtures; thickening agents, antioxidants and/or any other cosmetically acceptable adjuvant.

14. Process according to any one of claims 1 to 13, characterised in that the suitable dyeing medium consists of water or a mixture of water and a solvent chosen from among C_2-C_4 lower alkanols, glycerol, glycols or glycol ethers, diethylene glycol monoethyl ether and monomethyl ether, aromatic alcohols or phenoxy ethanol, or their mixtures.

15. Use in keratinous fibres dyeing for example hair, of a composition (A) containing, in a suitable dyeing medium, an indole-based coupler of 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 4 to 12, in association with a composition (B) containing, in a suitable dyeing medium, an oxidising agent, the pH of the compositions (A) and (B) being such that after mixing in proportions of 90 to 10% being such that after mixing in proportions of 90 to 10% for the composition (A) and of 10 to 90% for composition (B), said proportions being by weight relative to the total weight of the resulting composition, is free of iodide ions and the resulting composition has a pH of less than 7.

16. Use according to claim 15, characterised in that the composition (A) has a pH of between 3 and 10.5.

17. Use according to claim 15 or 16, characterised in that the composition (A) contains the para and/or ortho type oxidation dye precursors as wel as the couplers in proportions of between 0.3 and 7% by weight relative to the total weight of the composition (A).

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18. Use according to any one of claims 15 to 17, charcterised in that the concentration of compounds of formula (I) is between 0.05 and 4% by weight relative to the total weight of the composition (A).

19. Use according to any one of claims 15 to 18, characterised in that the composition (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, thickening agents 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.

20. Use according to any one of claims 15 to 19, characterised in that the composition (B) has a pH which has a minimum value of 1 and is less than 7.

21. Process for dyeing keratinous fibres for example hair, characterised in that it comprises a first stage consisting in storing a dyeing agent as defined in any one of claims 15 to 20 and in carrying out, before application, the mixing of compositions (A) and (B) in proportions of 10 to 90% for composition (A) and of 90 to 10% for composition (B), said proportions being by weight relative to the total weight of a resulting composition, so as to obtain a composition free of iodide ions which has a pH of less than 7 and applying this mixture to the keratinous fibres immediately after preparation.

22. Dyeing process according to any one of claims 1 to 14, characterised in that the composition is applied to the hair and allowed to settle for 3 to 40 minutes, the hair is rinsed and shampooing is optionally carried out before rinsing again and drying.

23. Use, as couplers, of 5-, 6- or 7-hydroxyindole derivatives of the formula (I) as defined in any one of claims 1 to 3 for the dyeing in acid medium of keratinous fibres, in combination with oxidation dye precursors in the presence of an oxidising agent.

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24. Ready for use composition for dyeing keratinous fibres, as employed in the process according to any one of claims 1 to 14.

25. Composition according to claim ~~26~~ 24, containing the compound of formula I in proportions of 0.01 to 3.5% by weight relative to the total weight of the composition.

DATED this 14th day of December, 1993.

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