AUSTRALIA 654994

P/00/001 28/5/91
Section 29

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

I/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.

[71] Applicant: L'OREAL

Address: 14, rue Royale F-75008 Paris, France

[70] Nominated Person: L'OREAL

Address: 14, rue Royale F-75008 Paris, France

[54] Invention Title: USE OF INDOLE DERIVATIVES AS COUPLERS IN DYEING KERATINOUS FIBRES

[72] Name(s) of actual inventor(s): JEAN COTTERET

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of The Atrium, 290 Burwood Road, Hawthorn, Victoria 3122, Australia Attorney Code: WM

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
9100640	France	FR	21st January 1991

Drawing number recommended to accompany the abstract .....

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

Louis C. Gebhardt

20th January 1991
(Date)

Registered Patent Attorney

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Section 29 (1)
Regulation 3.1 (2)

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

We, L'OREAL, of 14, rue Royale F-75008 Paris, France, being the applicant in respect of Application No. 10355/92 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 inventor.

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

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Louis C. Gebhardt

Registered Patent Attorney

27th September, 1994

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AU9210355

(12) PATENT ABRIDGMENT (11) Document No. AU-B-10355/92
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 654994

(54) Title
USE OF INDOLE DERIVATIVES AS COUPLERS IN DYEING KERATINOUS FIBRES

International Patent Classification(s)
(51)[5] **A61K 007/13**

(21) Application No. : **10355/92** (22) Application Date : **20.01.92**

(30) Priority Data

(31) Number	(32) Date	(33) Country
91 00640	**21.01.91**	**FR FRANCE**

(43) Publication Date : **23.07.92**

(44) Publication Date of Accepted Application : **01.12.94**

(71) Applicant(s)
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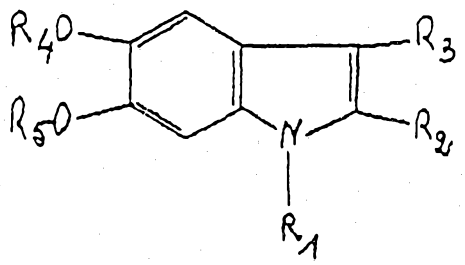
(57) Claim

1. Use of an indole derivative corresponding to the formula (I):



(I)

in which:

R_1 denotes a hydrogen atom or a C_1-C_4 alkyl group,

R_2 and R_3, which are identical or different, denote a hydrogen atom or a C_1-C_4 alkyl group or a carboxyl or C_1-C_4 alkoxycarbonyl group,

R_4 and R_5, which are identical or different, denote a C_1-C_4 alkyl group, a C_2-C_{20} acyl group, an aryl group, or else R_4 and R_5, together with the oxygen atoms and the two carbon atoms to which they are attached, form a ring optionally containing a carbonyl group or a methylene group unsubstituted or substituted by one or two alkyl or alkoxy or alkylamino groups, it being possible for R_4 and R_5 simultaneously to denote hydrogen,

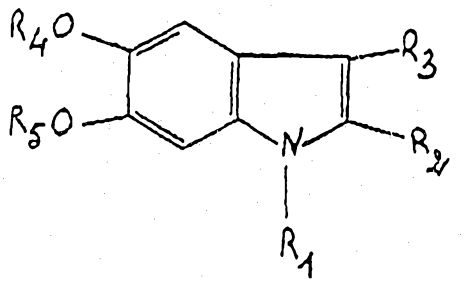
and the addition salts of inorganic or organic acids, as well as the corresponding alkali, alkaline-earth metal or amine salts,

.../2

as a coupler for the oxidation dyeing of keratinous fibres, and in particular of hair, using para and/or ortho oxidation dye precursors.

11. Dye composition for keratinous fibres, characterised in that it contains in a medium appropriate for dyeing:

a) at least one coupler of formula (I):



(I)

in which:

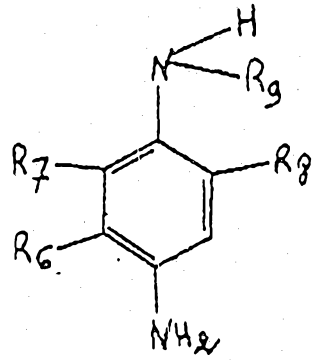
R_1 denotes a hydrogen atom or a C_1-C_4 alkyl group,

R_2 and R_3, which are identical or different, denote a hydrogen atom or a C_1-C_4 alkyl group or a carboxyl or C_1-C_4 alkoxycarbonyl group,

R_4 and R_5, which are identical or different, denote a C_1-C_4 alkyl group, a C_2-C_{20} acyl group, an aryl group, or else R_4 and R_5, together with the oxygen atoms and the two carbon atoms to which they are attached, form a ring optionally containing a carbonyl group or a methylene group unsubstituted or substituted by one or two alkyl or alkoxy or alkylamino groups, it being possible for R_4 and R_5 simultaneously to denote hydrogen,

and the addition salts of inorganic or organic acids, as well as the corresponding alkali, alkaline-earth metal or amine salts;

b) at least one para and/or ortho oxidation dye precursor chosen from para-aminophenols, heterocylic precursors, ortho-aminophenols, ortho-phenylenediamines, so-called "double" bases and para-phenylenediamines corresponding to the formula (IV):



(IV)

in which:

R_6, R_7 and R_8, which are identical or different, denote a hydrogen or halogen atom, an alkyl radical containing from 1 to 4 carbon atoms or an alkoxy radical containing from 1 to 4 carbon atoms,

R_9 denotes a hydrogen atom or an alkyl, carbamylalkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbalkoxyaminoalkyl, piperidinoalkyl or morpholinoalkyl radical, these alkyl or alkoxy groups containing from 1 to 4 carbon atoms, and the salts of these compounds;

c) at least one oxidising agent, this composition containing no iodide ion.

P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

654994

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: USE OF INDOLE DERIVATIVES AS COUPLERS IN DYEING KERATINOUS FIBRES

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

Use of indole derivatives as couplers in dyeing keratinous fibres.

The present invention relates to the use of indole derivatives as couplers for dyeing keratinous fibres and in particular for dyeing human hair, and to the compositions and to the dyeing processes used.

It is known to dye keratinous fibres, in particular human hair, with dyeing compositions containing precursors of oxidation dyes and in particular p-phenylenediamines and ortho- or para-aminophenols, generally called "oxidation bases".

It is also known that it is possible to vary the shades obtained with these oxidation bases by combining them with couplers which are also called colour modifiers, generally chosen from aromatic meta-diamines, meta-aminophenols and meta-diphenols.

In the field of hair dyeing there is a requirement for oxidation dye precursors or couplers making it possible to impart to the hair, in an oxidising medium, a colour which has a satisfactory resistance to light, to washing, to inclement weather and to perspiration.

The Applicant has just found, and this is what forms the subject matter of the invention, that the use of 5,6-dihydroxyindole or of some of its derivatives as couplers, with oxidation dye precursors, makes it possible to obtain, after application to keratinous fibres and in particular to human hair, colours of very varied shades exhibiting particularly remarkable resistance to light, washing, inclement weather and perspiration, epecially when they are employed with p-phenylenediamine and its derivatives. In addition, these dyes do not stain the scalp.

A subject of the invention consists, therefore, of this use.

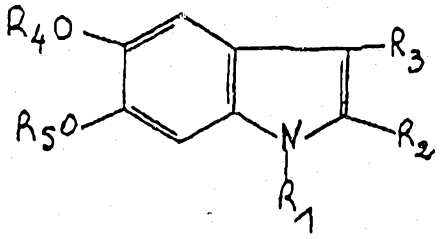
Another subject of the invention is oxidation dye compositions intended to be employed for dyeing keratinous fibres, in which the indole derivatives defined

hereinafter act as couplers, and containing at least one oxidation dye precursor of the para and/or ortho type and at least one oxidising agent.

Another subject of the invention consists of the process for dyeing keratinous fibres, in particular human hair, using this coupler.

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

The indole compounds employed as couplers in the oxidation dyeing of keratinous fibres and in particular of human hair, in the presence of at least one para and/or ortho oxidation dye precursor, correspond to the formula:



(I)

in which:

R_1 denotes a hydrogen atom or a C_1-C_4 alkyl group,

R_2 and R_3, which are identical or different, denote a hydrogen atom or a C_1-C_4 alkyl group or a carboxyl or C_1-C_4 alkoxycarbonyl group,

R_4 and R_5, which are identical or different, denote a C_1-C_4 alkyl group, a C_2-C_{20} acyl group, an aryl group, or else R_4 and R_5, together with the oxygen atoms and the two carbon atoms to which they are attached, form a ring optionally containing a carbonyl group or a methylene group unsubstituted or substituted by one or two alkyl or alkoxy or alkylamino groups, it being possible for R_4 and R_5 simultaneously to denote hydrogen,

and the addition salts of inorganic or organic acids, as well as the corresponding alkali, alkaline-earth metal or amine salts.

Among the compounds of formula (I) the preferred compounds are the compounds in which the alkyl radical denotes methyl or ethyl, the alkoxycarbonyl radical

denotes methoxy or ethoxycarbonyl, and the acyloxy radical denotes acetoxy or tetradecanoyloxy.

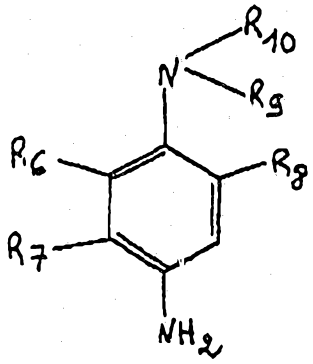
Among the preferred compounds of (I) there may be mentioned 5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, 1,2-dimethyl-5,6-dihydroxyindole, 2-ethoxycarbonyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dimethoxyindole, 5,6-dimethoxyindole, 5-methoxy-6-acetoxyindole, 5,6-dibenzyloxyindole and 2-carboxy-5,6-dihydroxyindole.

The dye precursors of para or ortho type are compounds which are not themselves dyes but which form a dye by a process of oxidative condensation, either with themselves or in the presence of a coupler or modifier.

These compounds contain functional groups, either two amino groups or an amino group and a hydroxyl group in para or ortho position, relative to each other.

The precursors of para type are chosen in particular from para-phenylenediamines, para-aminophenols, heterocyclic para precursors such as 2,5-diaminopyridine, 2-hydroxy-5-aminopyridine, tetraaminopyrimidine, 4,5-diamino-1-methylpyrazole, 2-dimethylamino-4,5,6-triaminopyridimidine and the so-called "double" bases.

By way of para-phenylenediamines there may be mentioned the compounds corresponding to the formula (II) below:



(II)

in which:

R_6, R_7 and R_8, which are identical or different, denote a hydrogen or halogen atom, an alkyl radical containing 1 to 4 carbon toms, or an alkoxy radical containing 1 to 4

carbon atoms,
R_9 and R_{10}, which are identical or different, denote a hydrogen atom or an alkyl, hydroxyalkyl, alkoxyalkyl, carbamylalkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbalkoxyaminoalkyl, piperidinoalkyl, morpholinoalkyl or phenyl radical optionally substituted by an amino group in the para position,
these alkyl or alkoxy groups containing from 1 to 4 carbon atoms, or else R_9 and R_{10}, together with the nitrogen atom to which they are bonded, form a piperidino or morpholino heterocylic ring, provided that R_6 and R_8 denote a hydrogen atom when R_9 and R_{10} do not denote a hydrogen atom, and the salts of these compounds.

Among the compounds of formula (II) there may be mentioned more particularly p-phenylenediamine, p-tolylenediamine, methoxy-para-phenylenediamine, chloro-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-dimethyl-5-methoxy-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-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, N-[(4'-amino)phenyl]piperidine, 2-hydroxyethyl-para-phenylenediamine, fluoro-para-phenylenediamine,

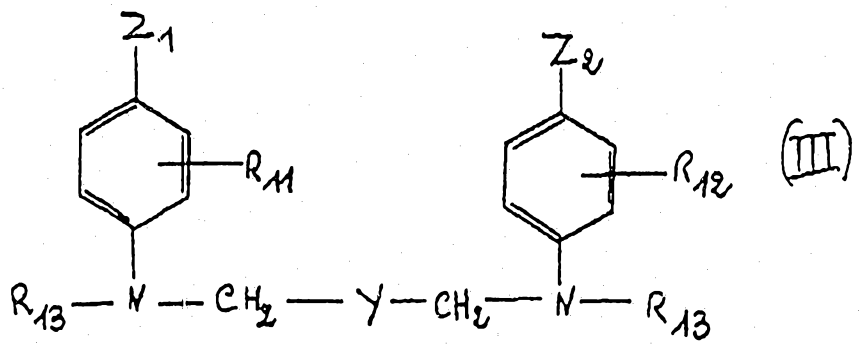
carboxy-para-phenylenediamine, sulpho-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, 2-n-propyl-para-phenylenediamine, hydroxy-2-n-propyl-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl,β-hydroxyethyl)-para-phenylenediamine, N-(dihydroxypropyl)-para-phenylenediamine, N-4'-aminophenyl-para-phenylenediamine and N-phenyl-para-phenylenediamine.

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

Among the p-aminophenols there 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, 2-methoxymethyl-4-aminophenol, 2-aminomethyl-4-aminophenol and 2-β-hydroxyethylaminomethyl-4-aminophenol.

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

The so-called double bases are bisphenylenealkylenediamines corresponding to the formula:



in which:

Z_1 and Z_2, which are identical or different, denote

hydroxyl or NHR_{14} groups where R_{14} denotes a hydrogen atom or a lower alkyl radical,

R_{11} and R_{12}, which are identical or different, denote either hydrogen atoms or halogen atoms or else alkyl groups,

R_{13} denotes a hydrogen atom or an alkyl, hydroxyalkyl or aminoalkyl group in which the amino residue may be substituted by one or two alkyl groups,

Y denotes a radical chosen from the following radicals: $-(CH_2)_n-$, $(CH_2)_m-O-(CH_2)_m-$, $-(CH_2)_m-CHOH-(CH_2)_m$, $-(CH_2)_m-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}-(CH_2)_m$.

n is an integer between 0 and 8 and m an integer between 0 and 4, it being possible for this so-called double base to be in the form of its addition salts with acids.

The alkyl or alkoxy radicals preferably denote a group containing 1 to 4 carbon atoms and especially methyl, ethyl, propyl, methoxy or ethoxy.

Among the compounds of formula (III) there may be mentioned N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diamino-2-propanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine and N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)-ethylenediamine.

In addition to the indole coupler of formula (I) defined above it is also optionally possible to employ other couplers which are known per se, such as meta-diphenols, meta-aminophenols, meta-phenylenediamines, meta-acylaminophenols, meta-ureidophenols, meta-carbalkoxyaminophenols, α-naphthol, couplers containing an active methylene group, such as β-ketonic compounds and pyrazolones, and heterocyclic couplers or 4-hydroxyindole and 6- or 7-hydroxyindole.

Among these couplers there may be mentioned more particularly 2,4-dihydroxyphenoxyethanol, 2,4-dihydroxyanisole, meta-aminophenol, resorcinol monomethyl ether,

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, 1-amino-3,4-methylenedioxybenzene, 1-hydroxy-3,4-methylenedioxybenzene, 2-chloro-6-methyl-3-aminophenol, 2-methyl-3-aminophenol, 2-chlororesorcinol, resorcinol, 6-methoxy-3-hydroxyethylaminoaniline, 1-ethoxy-2-bis(β-hydroxyethyl)amino-4-aminobenzene, 3-diethylaminophenol, 1,3-dihydroxy-2-methylbenzene, 1-hydroxy-2,4-dichloro-3-aminobenzene, 4,6-hydroxyethoxy-1,3-diaminobenzene, 4-methyl-6-ethoxy-1,3-diaminobenzene, 4-chloro-6-methyl-3-aminophenol, 6-chloro-3-trifluoroethylaminophenol and their salts.

Direct dyes such as azo or anthraquinone dyes or nitro derivatives of the benzene series may also be used together with the abovementioned compounds, as is well known in the state of the art, especially with a view to shading or enriching in glints the colours provided by the oxidation dye precursors and the coupler of formula (I).

When using the coupler of formula (I) in accordance with the invention, no use is made together with these couplers of any quinone derivative from the class of benzoquinones and naphthoquinones capable of oxidising the compound of formula (I), nor of any iodide ions in a quantity liable to oxidise the compound of formula (I) and the oxidation dye precursor in the presence of the coupler.

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

The abovementioned indole coupler of formula (I) is used as a coupler in oxidation dye compositions

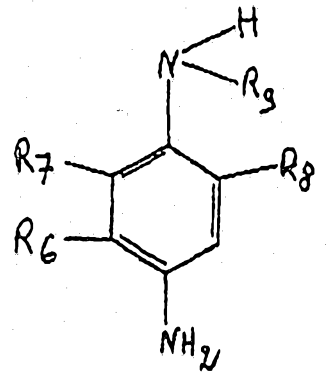
containing, in a medium which is suitable for dyeing, in addition at least one para and/or ortho oxidation dye precursor and optionally other couplers and direct dyes mentioned and at least one oxidising agent.

These compositions must not contain any iodide ion in proportions liable to oxidise the oxidation dye precursor and the coupler of formula (I).

The dye compositions which form another subject of the invention are essentially characterised in that they contain, in a medium suitable for dyeing:

a) at least one coupler of formula (I)

b) at least one para and/or ortho oxidation dye precursor chosen from para-aminophenols, heterocylic precursors, ortho-aminophenols, ortho phenylenediamines, so-called "double" bases as defined above and para-phenylenediamines corresponding to the formula (IV):



(IV)

in which:

R_6, R_7 and R_8, which are identical or different, denote a hydrogen or halogen atom, an alkyl radical containing from 1 to 4 carbon atoms or an alkoxy radical containing from 1 to 4 carbon atoms,

R_9 denotes a hydrogen atom or an alkyl, carbamylalkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbalkoxyaminoalkyl, piperidinoalkyl or morpholinoalkyl radical, these alkyl or alkoxy groups containing from 1 to 4 carbon atoms, and the salts of these compounds.

Among the compounds of formula (IV) there may be mentioned p-phenylenediamine, p-tolylenediamine, methoxy-para-phenylenediamine, chloro-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,5-dimethyl-para-phenyl-

enediamine, 2-methyl-5-methoxy-para-phenylenediamine and 2,6-dimethyl-5-methoxy-para-phenylenediamine.

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

c) at least one oxidising agent defined above.

These compositions do not contain any iodide ion in quantities liable to oxidise the precursors and the couplers present.

All the oxidation dye precursors of para and/or ortho type and the couplers employed in the dye compositions in accordance with the invention preferably represent from 0.1 to 10% by weight relative to the total weight of the said composition. The concentration of indole compounds of formula (I) may vary between 0.05 and 3.5% by weight relative to the total weight of the composition.

The pH of the composition applied to keratinous fibres, in particular to hair, has a value which is generally between 3 and 11.

This pH is adjusted by employing acidifying or alkalifying agents which are well known in the field of hair dyeing.

In their preferred form of embodiment, the dye compositions in accordance with the invention generally contain anionic, cationic, nonionic or amphoteric surface-active agents or mixtures thereof. Among these surface-active agents there may be mentioned alkylbenzenesulphonates, alkylnaphthalenesulphonates, sulphates, ether sulphates and fatty alcohol sulphonates, quaternary ammonium salts such as trimethylcetylammonium bromide and cetylpyridinium bromide, optionally oxyethylenated fatty acid ethanolamides, polyoxyethylenated acids, alcohols or amines, polyglycerolated alcohols, polyoxyethylenated or polyglycerolated alkylphenols and polyoxyethylenated alkyl sulphates.

These surface-active agents are present in the

compositions employed in accordance with the invention in proportions of between 0.5 and 55% by weight and preferably between 2 and 50% by weight, relative to the total weight of the composition.

These compositions may also contain organic solvents to solubilise the compounds which might not be sufficiently soluble in water.

As examples of these solvents there may be mentioned C_1-C_4 lower alkanols such as ethanol and isopropanol, glycerol, glycols or glycol ethers such as 2-butoxyethanol, ethylene glycol, propylene glycol, diethylene glycol monoethyl ether and monomethyl ether and aromatic alcohols such as benzyl alcohol or phenoxyethanol and similar products or mixtures thereof.

The solvents are preferably present in proportions of between 1 and 40% by weight and in particular between 50 and 30% by weight relative to the total weight of the composition.

The thickening agents which may be added to the compositions in accordance with the invention may be chosen from sodium alginate, gum arabic, cellulose derivatives, acrylic acid polymers and xanthan gum. Inorganic thickening agents such as bentonite can also be employed.

These thickening agents are preferably present in proportions of between 0.1 and 5% and in particular between 0.2 and 3% by weight relative to the total weight of the composition.

The antioxidant agents which may be present in the compositions are chosen in particular from sodium sulphite, thioglycolic acid, sodium bisulphite, dihydroascorbic acid, hydroquinone and homogentisic acid. These antioxidant agents are present in the composition in proportions of between 0.05 and 1.5% by weight relative to the total weight of the composition.

These compositions may also contain other cosmetically acceptable adjuvants such as, for example, penetrating agents, sequestering agents, perfumes, buffers and the like.

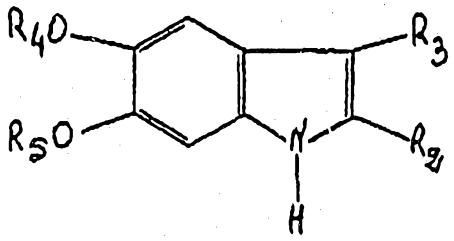
The compositions employed in accordance with the invention may be presented in various forms such as in the form of liquids, creams, gels or any other appropriate form for performing a dyeing of keratinous fibres and especially of human hair. These compositions may also be packaged in aerosol bottles in the presence of a propellent agent.

In accordance with the invention, the process consists in applying to the keratinous fibres a composition prepared at the time of use, containing at least one coupler of formula (I), at least one oxidation dye precursor of para type and at least one oxidising agent other than iodide ions in a quantity which is sufficient to develop a colour.

A 20-volume aqueous hydrogen peroxide solution is preferably employed. The mixture obtained is applied to the hair and is left in place for 10 to 40 minutes, preferably 15 to 30 minutes, after which the hair is rinsed, washed with shampoo, rinsed again and dried.

The compounds of formula (I) which are employed preferably when the composition applied to the hair has a pH lower than 9 are 5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 1,2-dimethyl-5,6-dihydroxyindole, 2-carboxy-5,6-dihydroxyindole, 2-ethoxycarbonyl-5,6-dihydroxyindole, 5-methoxy-6-acetoxyindole, 5,6-dibenzyloxyindole and 5,6-dimethoxyindole.

When the composition applied to the hair has a pH higher than 9, the indole derivative is preferably a derivative corresponding to the formula:



(V)

in which:

R_2 denotes hydrogen, alkyl or alkoxycarbonyl,
R_3 denotes hydrogen or alkyl,
R_4 and R_5, which are identical or different, denote alkyl or acyl,
provided that when R_4 and R_5 denote alkyl, at least one group R_2 and R_3 is other than hydrogen,
it being possible for R_4 and R_5 together to denote hydrogen.

Among the compounds of formula (V) preference is given to 5,6-dihydroxyindole, 2-ethoxycarbonyl-5,6-dihydroxyindole and 5-methoxy-6-acetoxyindole.

Another form of embodiment of the invention consists in applying separately a composition (A) containing the indole coupler of formula (I) and the oxidation dye precursor, and then, after rinsing, a composition (B) containing the oxidising agent other than iodide ions.

It is also possible, in accordance with the invention, to apply separately the compositions containing the oxidation dye precursor and then, after rinsing, to apply a composition containing the indole coupler of formula (I) and the oxidising agent.

The conditions of application and of drying or washing are similar to those indicated above.

The following examples are intended to illustrate the invention without, however, being limiting in character.

EXAMPLES 1 to 12

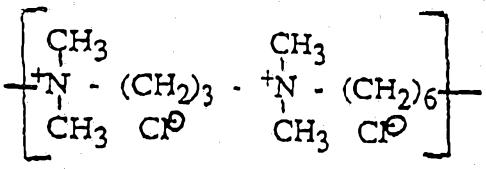
Hair dyeing is performed by applying to permanent-waved or natural grey hair containing 90% of white an ad hoc mixture of the dye composition (A) and of the oxidising composition (B).

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

in g	1	2	3	4	5	6	7	8
A) Dye composition								
5,6-Dihydroxyindole	0.447							
2-Methyl-5,6-dihydroxyindole.HBr		0.732						
3-Methyl-5,6-dihydroxyindole			0.489					
2-Carboxy-5,6-dihydroxyindole				0.579				
5,6-Dimethoxyindole					0.532			
2,3-Dimethyl-5,6-dimethoxyindole						0.616		
1,2-Dimethyl-5,6-dihydroxyindole							0.489	
5-Methoxy-6-acetoxyindole								0.615
para-Phenylenediamine	0.324			0.324			0.324	
2,6-Dimethyl-para-phenylenediamine.2HCl		0.657			0.657	0.657		0.657
para-Aminophenol			0.327					
Monoethanolamine q.s. pH	9.1	8.8	9.1	8.9	8.6	9.1	9.1	8.75
Carrier 2	X	X	X	X	X	X	X	X
Water q.s.	100	100	100	100	100	100	100	100
B) Oxidising composition								
20-volume hydrogen peroxide solution								
Phosphoric acid q.s. pH	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
pH w/w mixture A+B	6.7	6.2	6.7	6.7	6.1	6.7	6.7	6.4
Shades obtained on 90% white natural hair	auburn chestnut	matt ashen	coppery golden blonde	natural iridescent mahogany	slightly golden iridescent ashen	golden beige blonde	warm iridescent chestnut	purple-violet light chestnut

in g	9	10	11	12
A) Dye composition				
5,6-Dihydroxyindole	0.149		0.596	
2-Ethoxycarbonyl-5,6-dihydroxyindole		0.221		
5-Methoxy-6-acetoxyindole				0.41
para-Phenylenediamine	0.216			0.216
2,6-Dimethyl-para-phenylenediamine.2HCl				
para-Aminophenol			0.436	
meta-Aminophenol		0.109		
3-(β-Hydroxyethylamino)-6-methylphenol	0.167			
2-Methyl-para-phenylenediamine.2HCl		0.366		
α-Naphthol		0.144		
Ethyl alcohol	30			
20% aqueous ammonia q.s. pH	11.2			
pH		10.4	10.5	10.5
Carrier 1		X	X	X
Water q.s.	100	100	100	100
B) Oxidising composition				
20-volume hydrogen peroxide solution				
Phosphoric acid q.s. pH	3	3	3	3
pH w/w mixture 1/3A+2/3B	10		10	10
pH w/w mixture A+B		9.8		
Shades obtained on permanent-waved 90% white hair	ashen mahogany	subdued violet	coppery chestnut	coppery mahogany

COLOUR CARRIER 1

- Octyldodecanol sold by Henkel under the name Eutanol G	8.0 g
- Oleic acid	20.0 g
- Monoethanolamine lauryl ether sulfate sold by Henkel under the name of Sipon LM 35	3.0 g
- Ethyl alcohol	10.0 g
- Benzyl alcohol	10.0 g
- Cetylstearyl alcohol oxyethylenated with 33 moles of ethylene oxide, sold by Seppic under the name of Simulsol GS	2.4 g
- Ethylenediaminetetraacetic acid	0.2 g
- Cationic polymer consisting of repeat units: 	2.2 g
- Monoethanolamine	7.5 g
- Linoleic acid diethanolamide sold by Henkel under the name of Comperlan F	8.0 g
- 20% ammonia	10.2 g
- Sodium metabisulphite as 35% aqueous solution	0.45 g
- Hydroquinone	0.15 g
- 1-Phenyl-3-methyl-5-pyrazolone	0.2 g

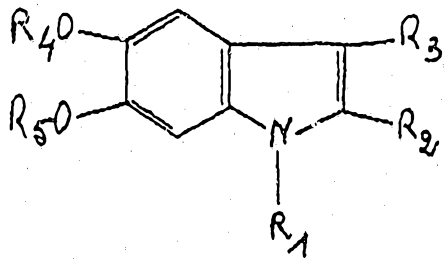
COLOUR CARRIER 2

- Oleic alcohol polyglycerolated with 2 moles of glycerol	4.0 g
- Oleic alcohol polyglycerolated with 4 moles of glycerol	5.71 g AS
- Oleic acid	3.0 g
- Oleylamine oxyethylenated with 2 moles of ethylene oxide, sold by Akzo under the name Ethomeen O 12	7.0 g
- Diethylaminopropyl laurylaminosuccinamate, sodium salt	3.0 g AS
- Oleylamine 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 as aqueous solution	0.45 g AS
- Ammonium acetate	0.8 g
- Antioxidant, sequestering agent q.s.	

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

CLAIMS

1. Use of an indole derivative corresponding to the formula (I):



(I)

in which:

R_1 denotes a hydrogen atom or a C_1-C_4 alkyl group,

R_2 and R_3, which are identical or different, denote a hydrogen atom or a C_1-C_4 alkyl group or a carboxyl or C_1-C_4 alkoxycarbonyl group,

R_4 and R_5, which are identical or different, denote a C_1-C_4 alkyl group, a C_2-C_{20} acyl group, an aryl group, or else R_4 and R_5, together with the oxygen atoms and the two carbon atoms to which they are attached, form a ring optionally containing a carbonyl group or a methylene group unsubstituted or substituted by one or two alkyl or alkoxy or alkylamino groups, it being possible for R_4 and R_5 simultaneously to denote hydrogen,

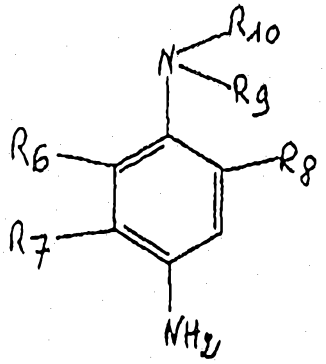
and the addition salts of inorganic or organic acids, as well as the corresponding alkali, alkaline-earth metal or amine salts,

as a coupler for the oxidation dyeing of keratinous fibres, and in particular of hair, using para and/or ortho oxidation dye precursors.

2. Use according to claim 1, characterised in that the indole compound of formula (I) is chosen from 5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, 1,2-dimethyl-5,6-dihydroxyindole, 2-ethoxycarbonyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dimethoxyindole, 5,6-dimethoxyindole, 5-methoxy-6-acetoxyindole, 5,6-dibenzyloxyindole and 2-carboxy-5,6-dihydroxyindole.

3. Use according to claim 1 or 2, characterised in that the oxidation dye precursor is chosen from the

dye precursors of para type, corresponding to the formula:



(II)

in which:

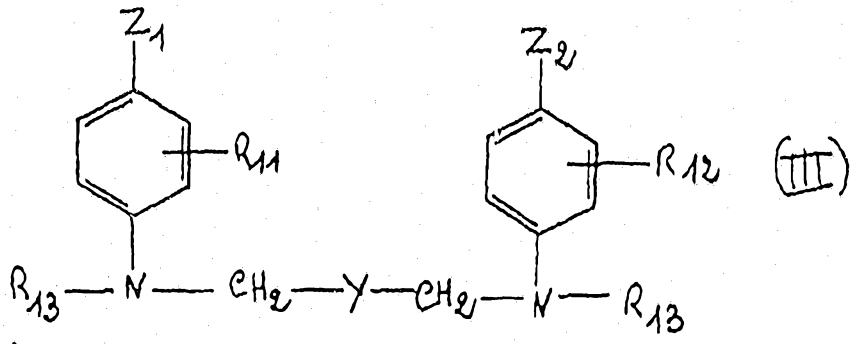
R_6, R_7 and R_8, which are identical or different, denote a hydrogen or halogen atom, an alkyl radical containing 1 to 4 carbon toms, or an alkoxy radical containing 1 to 4 carbon atoms,

R_9 and R_{10}, which are identical or different, denote a hydrogen atom or an alkyl, hydroxyalkyl, alkoxyalkyl, carbamylalkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbalkoxyaminoalkyl, piperidinoalkyl, morpholinoalkyl or phenyl radical optionally substituted by an amino group in the para position,

these alkyl or alkoxy groups containing from 1 to 4 carbon atoms, or else R_9 and R_{10}, together with the nitrogen atom to which they are bonded, form a piperidino or morpholino heterocylic ring, provided that R_5 and R_8 denote a hydrogen atom when R_9 and R_{10} do not denote a hydrogen atom, and the salts of these compounds.

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

5. Use according to any one of Claims 1 to 4, characterised in that the oxidation dye precursors are chosen from so-called "double" bases which are bis-phenylenealkylenediamines corresponding to the formula (III):



(III)

in which:

Z_1 and Z_2, which are identical or different, denote hydroxyl or NHR_{14} groups where R_{14} denotes a hydrogen atom or a lower alkyl radical,

R_{11} and R_{12}, which are identical or different, denote either hydrogen atoms or halogen atoms or else alkyl groups,

R_{13} denotes a hydrogen atom or an alkyl, hydroxyalkyl or aminoalkyl group in which the amino residue may be substituted by one or two alkyl groups,

Y denotes a radical chosen from the following radicals: $-(CH_2)_n-$, $(CH_2)_m-O-(CH_2)_m-$, $-(CH_2)_m-CHOH-(CH_2)_m$, $-(CH_2)_m-\underset{\displaystyle CH_3}{\overset{|}{N}}-(CH_2)_m$.

n is an integer between 0 and 8 and m an integer between 0 and 4, it being possible for this so-called double base to be in the form of its addition salts with acids.

6. Use according to any one of Claims 1 to 5, characterised in that other couplers are used in addition to the indole coupler of formula (I).

7. Use according to Claim 6, characterised in that the other couplers used in addition to the indole coupler of formula (I) are chosen from meta-diphenols, meta-aminophenols, meta-phenylenediamines, meta-acylaminophenols, meta-ureidophenols, meta-carbalkoxyaminophenols, α-napthol, couplers containing an active methylene group which are chosen from β-ketonic compounds, pyrazolones, heterocyclic couplers, 4-hydroxyindole, 6-hydroxyindole and 7-hydroxyindole.

8. Use according to any one of Claims 1 to 7, characterised in that, in addition, direct dyes chosen from azo or anthraquinone dyes or nitro derivatives of

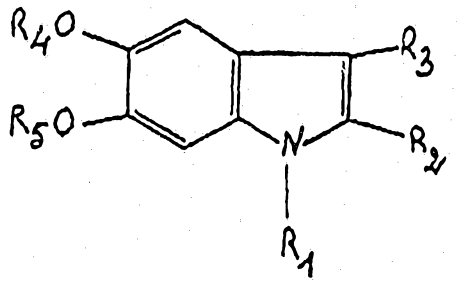
the benzene series are used.

9. Use according to any one of Claims 1 to 8, characterised in that the coupler of formula (I) is used in the presence of an oxidising agent chosen from hydrogen peroxide, urea peroxide, alkali metal bromates and persalts.

10. Use according to any one of Claims 1 to 9, characterised in that the indole compound of formula (I) employed as coupler is used with the aid of oxidation dye compositions containing, in a medium which is suitable for dyeing, at least one para and/or ortho oxidation dye precursor, at least the indole compound as coupler of formula (I), and optionally other couplers and other direct dyes and at least one oxidising agent other than iodide ions.

11. Dye composition for keratinous fibres, characterised in that it contains in a medium appropriate for dyeing:

a) at least one coupler of formula (I):



(I)

in which:

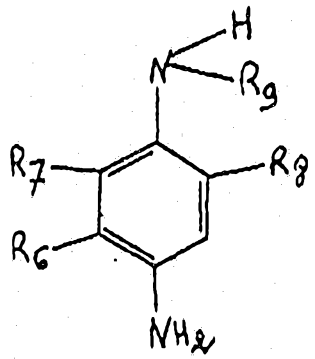
R_1 denotes a hydrogen atom or a C_1-C_4 alkyl group,

R_2 and R_3, which are identical or different, denote a hydrogen atom or a C_1-C_4 alkyl group or a carboxyl or C_1-C_4 alkoxycarbonyl group,

R_4 and R_5, which are identical or different, denote a C_1-C_4 alkyl group, a C_2-C_{20} acyl group, an aryl group, or else R_4 and R_5, together with the oxygen atoms and the two carbon atoms to which they are attached, form a ring optionally containing a carbonyl group or a methylene group unsubstituted or substituted by one or two alkyl or alkoxy or alkylamino groups, it being possible for R_4 and R_5 simultaneously to denote hydrogen,

and the addition salts of inorganic or organic acids, as well as the corresponding alkali, alkaline-earth metal or amine salts;

b) at least one para and/or ortho oxidation dye precursor chosen from para-aminophenols, heterocylic precursors, ortho-aminophenols, ortho-phenylenediamines, so-called "double" bases and para-phenylenediamines corresponding to the formula (IV):



(IV)

in which:

R_6, R_7 and R_8, which are identical or different, denote a hydrogen or halogen atom, an alkyl radical containing from 1 to 4 carbon atoms or an alkoxy radical containing from 1 to 4 carbon atoms,

R_9 denotes a hydrogen atom or an alkyl, carbamylalkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbalkoxyaminoalkyl, piperidinoalkyl or morpholinoalkyl radical, these alkyl or alkoxy groups containing from 1 to 4 carbon atoms, and the salts of these compounds;

c) at least one oxidising agent, this composition containing no iodide ion.

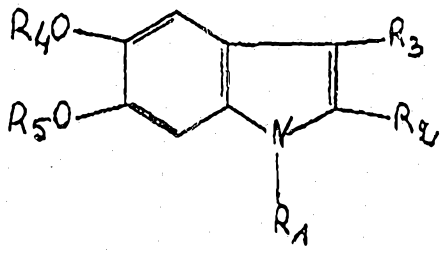
12. Composition according to Claim 11, characterised in that in that the para-phenylenediamines of formula (IV) are chosen from p-phenylenediamine, p-tolylenediamine, methoxy-para-phenylenediamine, chloro-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine and 2,6-dimethyl-5-methoxy-para-phenylenediamine, in the form of free base or in the form of salts.

13. Composition according to either of Claims 11

and 12, characterised in that the oxidation dye precursors of para and/or ortho type and the couplers of formula (I) are employed in proportions of between 0.1 and 10% by weight relative to the total weight of the composition, the concentration of indole compounds of formula (I) being between 0.05 and 3.5% by weight relative to the total weight of the composition.

14. Composition according to any one of Claims 11 to 13, characterised in that the pH is between 3 and 11.

15. Process for dyeing keratinous fibres, in particular hair, characterised in that oxidation dye precursors of para type are coupled in the presence of an oxidising agent with a coupler corresponding to the formula (I):



in which:

R_1 denotes a hydrogen atom or a C_1-C_4 alkyl group,

R_2 and R_3, which are identical or different, denote a hydrogen atom or a C_1-C_4 alkyl group or a carboxyl or C_1-C_4 alkoxycarbonyl group,

R_4 and R_5, which are identical or different, denote a C_1-C_4 alkyl group, a C_2-C_{10} acyl group, an aryl group, or else R_4 and R_5, together with the oxygen atoms and the two carbon atoms to which they are attached, form a ring optionally containing a carbonyl group or a methylene group unsubstituted or substituted by one or two alkyl or alkoxy or alkylamino groups, it being possible for R_4 and R_5 simultaneously to denote hydrogen,

and the addition salts of inorganic or organic acids, as well as the corresponding alkali, alkaline-earth metal or amine salts.

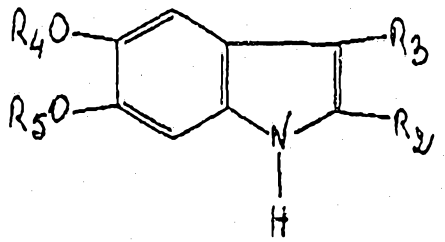
16. Process according to Claim 15, characterised in that the composition is applied to keratinous fibres,

in particular to hair, that this composition is left in place for 10 to 40 minutes, after which the hair is rinsed, washed with shampoo, rinsed again and dried.

17. Use according to any one of Claims 1 to 10, characterised in that the dyeing is performed at a pH lower than 9.

18. Use according to Claim 17, characterised in that the coupler is chosen from 5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 1,2-dimethyl-5,6-dihydroxyindole, 2-carboxy-5,6-dihydroxyindole, 2-ethoxycarbonyl-5,6-dihydroxyindole, 5-methoxy-6-acetoxyindole, 5,6-dibenzyloxyindole and 5,6-dimethoxyindole.

19. Use according to any one of claims 1 to 10, characterised in that keratinous fibres are dyed at a pH higher than 9, the indole derivative of formula (I) being chosen from the compounds of formula (V):



(V)

in which:

R_2 denotes hydrogen, alkyl or alkoxycarbonyl,

R_3 denotes hydrogen or alkyl,

R_4 and R_5, which are identical or different, denote alkyl or acyl,

provided that when R_4 and R_5 denote alkyl, at least one group R_2 and R_3 is other than hydrogen, it being possible for R_4 and R_5 together to denote hydrogen.

20. Process for dyeing keratinous fibres, in particular human hair, characterised in that there are applied separately, on the one hand, a composition (A)

containing the indole coupler as defined in either of claims 1 and 2, and a para and/or ortho oxidation dye precursor as defined in any one of claims 1 to 5, optionally another coupler and then, after rinsing, a composition (B) containing an oxidising agent.

21. Process for dyeing keratinous fibres, in particular hair, characterised in that there are applied separately a composition (A) containing a para and/or ortho oxidation dye precursor as defined in any one of claims 1 to 5 and then, after rinising, a composition (B) containing an indole compound of formula (I) and the oxidising agent.

DATED this 20th day of January 1992.

L'OREAL

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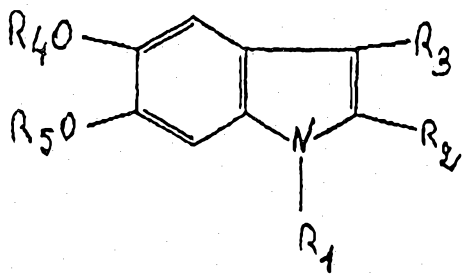
ABSTRACT - FR 542

Use of indole derivatives as couplers in dyeing keratinous fibres.

The invention relates to the use of an indole derivative corresponding to the formula (I):



(I)

in which:

R_1 denotes a hydrogen atom or a C_1-C_4 alkyl group,

R_2 and R_3 denote a hydrogen atom or a C_1-C_4 alkyl group or a carboxyl or C_1-C_4 alkoxycarbonyl group,

R_4 and R_5, which are identical or different, denote a C_1-C_4 alkyl group, a C_2-C_{20} acyl group, an aryl group, or else R_4 and R_5, together with the oxygen atoms and the two carbon atoms to which they are attached, form a ring optionally containing a carbonyl group or a methylene group unsubstituted or substituted by one or two alkyl or alkoxy or alkylamino groups, it being possible for R_4 and R_5 simultaneously to denote hydrogen,

and the addition salts of inorganic or organic acids, as well as the corresponding alkali, alkaline-earth metal or amine salts,

as a coupler for the oxidation dyeing of keratinous fibres, and in particular of hair, using para and/or ortho oxidation dye precursors, and to the compositions and methods of use.