AUSTRALIA
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PATENT REQUEST : STANDARD PATENT

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

Applicant(s) and Nominated Person(s): L'ORÉAL

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FRANCE

Invention Title: PROCESS FOR THE TWO-STEP DIRECT DYEING OF KERATIN FIBRES USING BASIC DIRECT DYES.

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BASIC CONVENTION APPLICATION DETAILS
Application No: 9715413
Country: FR
Application Date: 5 December 1997

DATED: 27 November 1998

L'ORÉAL
GRiffith Hack
Melbourne Office

R. J. STRICKLAND
Patent Attorney for and on behalf of the Applicant
NOTICE OF ENTITLEMENT

I/We L'ORÉAL

of 14, RUE ROYALE
PARIS 75008
FRANCE

being the applicant(s) in respect of an application for a patent for an invention entitled PROCESS FOR THE TWO-STEP DIRECT DYEING OF KERATIN FIBRES USING BASIC DIRECT DYES, state the following:

1. The nominated person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):
   
   The nominated person would be entitled to have assigned to it a patent granted to the inventor in respect of the said invention.

2. The nominated person(s) has/have, for the following reasons, gained entitlement from the applicant(s) of the basic application(s) listed on the patent request form:
   
   The applicant and nominated person is the basic applicant.

3. The basic application(s) listed on the request form is/are the first application(s) made in a Convention country in respect of the invention.

DATE: 27 November 1998

L'ORÉAL

GRIFFITH HACK
MELBOURNE OFFICE

R. J. STRICKLAND

Patent Attorney for and on behalf of the applicant
The invention relates to a process for the two-stage direct dyeing of keratin fibres, in particular human keratin fibres such as the hair, characterized in that, in a first step, the keratin fibres are bleached, and, in a second step, a dye composition containing, in an aqueous medium, at least one partially dissolved basic direct dye is then applied to the keratin fibres, the said dye composition being ready to use or resulting from the mixing, at the time of use, of at least one pulverulent composition (P) containing at least one basic direct dye and an aqueous composition (A).
Invention Title:
PROCESS FOR THE TWO-STEP DIRECT DYEING OF KERATIN FIBRES USING BASIC DIRECT DYES.

The following statement is a full description of this invention, including the best method of performing it known to me/us:
PROCESS FOR THE TWO-STEP DIRECT DYEING OF KERATIN FIBRES USING BASIC DIRECT DYES

The invention relates to a process for the two-stage direct dyeing of keratin fibres, in particular human keratin fibres such as the hair, characterized in that, in a first step, the keratin fibres are bleached, and, in a second step, a dye composition, containing, in an aqueous medium, at least one partially dissolved basic direct dye is then applied to the keratin fibres, the said dye composition being ready to use or resulting from the mixing, at the time of use, of at least one pulverulent composition (P) containing at least one basic direct dye and an aqueous composition (A).

It is well known to dye keratin fibres, and in particular human hair, with dye compositions containing direct dyes and in particular nitrobenzene direct dyes. However, when direct dyes are incorporated into dye compositions, they have the drawback of giving colourings which are not sufficiently fast, in particular with respect to shampooing. Furthermore, the colourings obtained generally lack intensity and are too dull.

In order to overcome this problem, it has already been proposed to bleach keratin fibres prior to any step of application of direct dyes. However, although the application of direct dyes to bleached keratin fibres leads to colourings which are less dull
than those obtained without pre-bleaching the fibres, this nevertheless gives colourings which are not sufficiently chromatic or intense and are non-uniform, i.e. they show local differences in intensity.

It is in seeking to overcome these problems that the Applicant has now discovered, surprisingly, that it is possible to obtain intense, very chromatic and uniform colourings which also have good resistance with respect to atmospheric agents such as light and bad weather, and with respect to perspiration and the various treatments to which the hair may be subjected (washing, permanent-waving), by carrying out a process of two-stage direct dyeing of keratin fibres which consists, in a first step, in bleaching the keratin fibres, and, in a second step, in then applying to these fibres a dye composition containing, in an aqueous medium, at least one partially dissolved basic direct dye, the said dye composition being ready to use or resulting from the mixing, at the time of use, of at least one pulverulent composition (P) containing at least one basic direct dye and an aqueous composition (A).

The dyeing process in accordance with the invention can also dye the keratin fibres in short dye-application times.

This discovery forms the basis for the present invention.

The subject of the present invention is thus
a process for the two-step direct dyeing of keratin fibres, and in particular human keratin fibres such as the hair, characterized in that, in a first step, the keratin fibres are bleached, and, in a second step, a dye composition containing, in an aqueous medium, at least one partially dissolved basic direct dye is then applied to the keratin fibres, the said dye composition being ready to use or resulting from the mixing, at the time of use, of at least one pulverulent composition (P) containing at least one basic direct dye and an aqueous composition (A).

According to the invention, the fact that the basic direct dye(s) present in the dye composition applied during the second step of the process in accordance with the invention is (are) partially dissolved either means that the basic direct dye(s) is (are) in supersaturation, i.e. they have an amount by weight which is greater than their solubility limit in the aqueous dyeing medium used, or means that the basic direct dye(s) is (are) partially or totally adsorbed onto or coated with an insoluble inorganic or organic filler present in the dye composition.

According to the invention, the first step of the process in accordance with the invention is a bleaching step which leads to a shade (after bleaching) preferably having a tone height of greater than or equal to 6.

In the keratin fibre dyeing sector, the
colour of the keratin fibres can be expressed in tone heights ranging from 1 to 10 and corresponding to the following shades:

<table>
<thead>
<tr>
<th>Tone height</th>
<th>Corresponding shade</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Extremely light blonde</td>
</tr>
<tr>
<td>9</td>
<td>Very light blonde</td>
</tr>
<tr>
<td>8</td>
<td>Light blonde</td>
</tr>
<tr>
<td>7</td>
<td>Blonde</td>
</tr>
<tr>
<td>6</td>
<td>Dark blonde</td>
</tr>
<tr>
<td>10</td>
<td>Light chestnut</td>
</tr>
<tr>
<td>5</td>
<td>Chestnut</td>
</tr>
<tr>
<td>4</td>
<td>Dark chestnut</td>
</tr>
<tr>
<td>3</td>
<td>Brown</td>
</tr>
<tr>
<td>2</td>
<td>Black</td>
</tr>
</tbody>
</table>

Preferably, the bleaching step leads to a shade which shows a colour difference of greater than or equal to 2 tones when compared with the colour of the fibres before bleaching. The results are proportionately better the closer the tone heights are, after the bleaching step, to values of 9 or 10.

Any type of method for bleaching keratin fibres can be used according to the process of the invention.

According to a first embodiment of the process of the invention, the bleaching can be carried out by applying an oxidizing composition containing at least one oxidizing agent.
The time required to obtain the desired bleaching is generally between 15 and 60 minutes and even more particularly between 30 and 45 minutes.

The nature of the oxidizing agent present in the oxidizing composition is not critical. Among these oxidizing agents, mention may be made in particular of hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates, persulphates and percarbonates, and polythionates, and mixtures thereof.

The oxidizing composition can be in liquid or creamy form, the said oxidizing composition being ready to use or resulting from the mixing, at the time of use, of one or more aqueous compositions or of one or more aqueous compositions with one or more pulverulent compositions, the oxidizing agent being present in the aqueous composition(s) and/or in the pulverulent composition(s).

When the oxidizing agent is present in the pulverulent composition, this composition can then be in granular or coated form, as is described, for example, in patent applications FR-A-2,703,588, FR-A-2,703,589, FR-A-2,715,065 and FR-A-2,716,804 in the name of the Applicant and the content of which forms an integral part of the present application.

The pH of the oxidizing composition is preferably between 5 and 12 and even more particularly between 8 and 11, and it can be adjusted to the desired value using acidifying or basifying agents which are
well known in the state of the art in the bleaching of keratin fibres.

Among the basifying agents, mention may be made, for example, of aqueous ammonia, alkali metal carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide or the compounds described in patent application EP-A-512,879 in the name of the Applicant, and among which mention may be made in particular of 1,3-diaminopropane, N,N'-diethyl-1,3-diaminopropane, N,N-diethyl-1,3-diaminopropane, N,N-dimethyl-1,3-diaminopropane, 2-hydroxy-1-(N,N-diethyl)amino-3-aminopropane and 2-hydroxy-1,3-diaminopropane.

The acidifying agents are conventionally, for example, inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, carboxylic acids such as tartaric acid, citric acid or lactic acid, or sulphonic acids.

The oxidizing composition used according to the process in accordance with the invention can also contain one or more adjuvants used conventionally in compositions for bleaching keratin fibres, such as surfactants, polymers, inorganic or organic thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners, film-forming agents, ceramides, preserving agents and opacifiers.
When the bleaching step using the oxidizing composition is complete, the keratin fibres are preferably rinsed with water before the second step of applying the dye composition containing the partially dissolved basic direct dye(s). The rinsing can also be followed by shampooing in order to remove any traces of oxidizing agent.

According to a second embodiment of the process of the invention, the bleaching step can be carried out by irradiating the keratin fibres with laser light in the form of pulses which are powerful enough to degrade the melanin contained in the keratin fibres and thus lead to the bleaching.

This method of bleaching by laser irradiation is described in the patent applications EP-A-685,220 and EP-A-685,180 by the Applicant, the content of which forms an integral part of the present application.

The basic direct dye(s) which can be used in the dye composition used during the second step of the process in accordance with the invention is (are) preferably chosen from basic aminoanthraquinone dyes, basic mono- or diazo dyes, basic azomethine dyes, basic naphthoquinone dyes and basic dyes containing ethylenic monounsaturations.

As examples, mention may be made in particular of [8-[(p-aminophenyl)azo]-7-hydroxy-2-naphthyl]trimethylammonium chloride (also known as Basic Brown 16 or Arianor Mahogany 306002 in the Color
Index), the combination of 3-[(4-amino-6-bromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-2-naphthyl)amino]-N,N,N-trimethylbenzenaminium chloride and of 3-[(2,6-dibromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-3-naphthyl)amino]-N,N,N-trimethylbenzenaminium chloride (also known as Basic Blue 99 or Arianor Steel Blue 306004 in the Color Index), 7-hydroxy-8-[(2-methoxy-phenyl)azo]-N,N,N-trimethyl-2-naphthalenaminium chloride (also known as Basic Red 76 or Arianor Madder Red in the Color Index), 8-[(4-amino-2-nitrophenyl)azo]-7-hydroxy-2-naphthyl]trimethylammonium chloride (also known as Basic Red 118 in the Color Index), the combination of 8-[(4-amino-3-nitrophenyl)azo]-7-hydroxy-2-naphthyl]trimethylammonium chloride and of 8-[(4-amino-2-nitrophenyl)azo]-7-hydroxy-2-naphthyl]trimethylammonium chloride (also known as Brown 17 or Arianor Sienna Brown 306001 in the Color Index), 3-[(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo]-N,N,N-trimethylbenzenaminium chloride (also known as Basic Yellow 57 or Arianor Straw Yellow 306005 in the Color Index), 1-(γ-aminopropyl)aminoanthraquinone hydrochloride, 1-N-(methylmorpholiniumpropyl)-amino-4-hydroxyanthraquinone methyl sulphate and Basic Orange 69 (Color Index name).

The basic direct dye(s) can also be chosen from:

a) the compounds of formula (I) below:
in which:

D represents a nitrogen atom or a -CH group,

R₁ and R₂, which may be identical or different,

represent a hydrogen atom; a C₁-C₄ alkyl radical which can be substituted with a -CN, -OH or -NH₂ radical or form, with a carbon atom of the benzene ring, a heterocycle optionally containing oxygen or nitrogen, which can be substituted with one or more C₁-C₄ alkyl radicals; a 4'-aminophenyl radical,

R₃ and R'₃, which may be identical or different,

represent a hydrogen atom or a halogen atom chosen from chlorine, bromine, iodine and fluorine, or a cyano, C₁-C₄ alkoxy or acetyloxy radical,

X⁻ represents an anion preferably chosen from chloride, methyl sulphate and acetate,

A represents a group chosen from structures A₁ to A₉ below:

![Chemical Structure](image.png)
in which $R_4$ represents a $C_1-C_4$ alkyl radical which can be substituted with a hydroxyl radical and $R_5$ represents a $C_1-C_4$ alkoxy radical, with the proviso that when $D$ represents $-\text{CH}_2$, $A$ represents $A_4$ or $A_{13}$ and $R_3$ is other than an alkoxy radical, then $R_1$ and $R_2$ do not simultaneously denote a hydrogen atom;
b) the compounds of formula (XI) below:
can be substituted with a -CN radical or with an amino group, a 4’-aminophenyl radical or forms with R₆ a heterocycle, optionally containing oxygen and/or nitrogen, which can be substituted with a C₁-C₄ alkyl radical,

R₆ and R₉, which may be identical or different,

represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a C₁-C₄ alkyl or C₁-C₄ alkoxy radical or a -CN radical,

X⁻ represents an anion preferably chosen from chloride, methyl sulphate and acetate,

B represents a group chosen from the structures B₁ to B₆ below:
in which \( R_{10} \) represents a \( C_1-C_4 \) alkyl radical and \( R_{11} \) and 
\( R_{12} \), which may be identical or different, represent a 
hydrogen atom or a \( C_1-C_4 \) alkyl radical;

c) the compounds of formulae (III) and (III') below:

\[
\begin{align*}
\text{(III)} & : E\overbrace{D_1\equiv D_2}^{(N)_m} \text{-} \text{R}_{13} \\
\text{(III')} & : E\overbrace{D_1\equiv D_2}^{(N)_m} \text{-} \text{R}_{17} 
\end{align*}
\]

in which:

\( R_{13} \) represents a hydrogen atom, a \( C_1-C_4 \) alkoxy radical, a 
halogen atom such as bromine, chlorine, iodine or 
fluorine or an amino radical,

\( R_{14} \) represents a hydrogen atom, a \( C_1-C_4 \) alkyl radical or 
forms, with a carbon atom of the benzene ring, a 
heterocycle optionally containing oxygen and/or 
substituted with one or more \( C_1-C_4 \) alkyl groups,

\( R_{15} \) represents a hydrogen atom or a halogen atom such as 
bromine, chlorine, iodine or fluorine,
$R_{16}$ and $R_{17}$, which may be identical or different, represent a hydrogen atom or a $C_1-C_4$ alkyl radical, $D_1$ and $D_2$, which may be identical or different, represent a nitrogen atom or a $-CH$ group, $m = 0$ or $1$, it being understood that when $R_{13}$ represents an unsubstituted amino group, then $D_1$ and $D_2$ simultaneously represent a $-CH$ group and $m = 0$, $X^-$ represents an anion preferably chosen from chloride, methyl sulphate and acetate, $E$ represents a group chosen from the structures $E_1$ to $E_8$ below:

![Chemical Structures]

$E_1$, $E_2$, $E_3$, $E_4$, $E_5$
in which \( R' \) represents a \( \text{C}_1-\text{C}_4 \) alkyl radical;

when \( m = 0 \) and \( D_1 \) represents a nitrogen atom, then \( E \) can also denote a group of structure \( E_9 \) below:

\[
\text{E9}
\]

in which \( R' \) represents a \( \text{C}_2-\text{C}_4 \) alkyl radical;

\[ \text{G—N=N—J} \quad \text{(IV)} \]

in which:

the symbol \( \text{G} \) represents a group chosen from the structures \( \text{G}_1 \) to \( \text{G}_5 \) below:
in which structures $G_1$ to $G_3$:

$R_{18}$ denotes a $C_1$-$C_4$ alkyl radical, a phenyl radical which can be substituted with a $C_1$-$C_4$ alkyl radical or a halogen atom chosen from chlorine, bromine, iodine and fluorine;

$R_{19}$ denotes a $C_1$-$C_4$ alkyl radical or a phenyl radical;

$R_{20}$ and $R_{21}$, which may be identical or different, represent a $C_1$-$C_4$ alkyl radical, a phenyl radical or together form, in $G_1$, a benzene ring substituted with one or more $C_1$-$C_4$ alkyl, $C_1$-$C_4$ alkoxy or $NO_2$ radicals, or together form, in $G_2$, a benzene ring optionally substituted with one or more $C_1$-$C_4$ alkyl, $C_1$-$C_4$ alkoxy or $NO_2$ radicals;

$R_{20}$ can also denote a hydrogen atom;

Z denotes an oxygen or sulphur atom or a group $-NR_{19}$;
M represents a -CH, -CR (R denoting C₁-C₄ alkyl) or -NR₂₂(X⁻)ᵣ group;
K represents a -CH, -CR (R denoting C₁-C₄ alkyl) or -NR₂₂(X⁻)ᵣ group;
P represents a -CH, -CR (R denoting C₁-C₄ alkyl) or -NR₂₂(X⁻)ᵣ group; r denotes zero or 1;
R₂₂ represents an atom O⁻, a C₁-C₄ alkoxy radical or a C₁-C₄ alkyl radical;
R₂₃ and R₂₄, which may be identical or different,
represent a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C₁-C₄ alkyl or C₁-C₄ alkoxy radical or an -NO₂ radical;
X⁻ represents an anion preferably chosen from chloride, iodide, methyl sulphate, ethyl sulphate, acetate and perchlorate;
with the proviso that,
if R₂₂ denotes O⁻, then r denotes zero;
if K or P or M denotes -N-(C₁-C₄)alkyl X⁻, then R₂₃ or R₂₄ is other than a hydrogen atom;
if K denotes -NR₂₂(X⁻)ᵣ, then M=P=-CH or -CR;
if M denotes -NR₂₂(X⁻)ᵣ, then K=P=-CH or -CR;
if P denotes -NR₂₂(X⁻)ᵣ, then K=M and denote -CH or -CR;
if Z denotes a sulphur atom with R₂₁ denoting C₁-C₄ alkyl, then R₂₆ is other than a hydrogen atom;
if Z denotes -NR₂₂ with R₁₉ denoting C₁-C₄ alkyl, then at least one of the radicals R₁₈, R₂₆ or R₂₁ in the group of structure G₂ is other than a C₁-C₄ alkyl radical;
the symbol $J$ represents:

- (a) a group of structure $J_1$ below:

![Structure $J_1$](image)

in which structure $J_1$:

$R_{25}$ represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a $C_1$-$C_4$ alkyl or $C_1$-$C_4$ alkoxy radical, a radical $-\text{OH}$, $-\text{NO}_2$, $-\text{NHR}_{28}$, $-\text{NR}_{29}$, or $-\text{NHCO}(C_1-C_4)$alkyl, or forms, with $R_{26}$, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

$R_{25}$ represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a $C_1$-$C_4$ alkyl or $C_1$-$C_4$ alkoxy radical, or forms, with $R_{27}$ or $R_{28}$, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

$R_{26}$ represents a hydrogen atom, an $-\text{OH}$ radical, an $-\text{NHR}_{28}$ radical or an $-\text{NR}_{29}$ radical;

$R_{28}$ represents a hydrogen atom, a $C_1$-$C_4$ alkyl radical, a $C_1$-$C_4$ monohydroxyalkyl radical, a $C_2$-$C_4$ polyhydroxyalkyl radical or a phenyl radical;

$R_{28}$ and $R_{30}$, which may be identical or different, represent a $C_1$-$C_4$ alkyl radical, a $C_1$-$C_4$ monohydroxyalkyl radical or a $C_2$-$C_4$ polyhydroxyalkyl
radical;
-(b) a 5- or 6-membered heterocyclic group containing nitrogen, which can contain other hetero atoms and/or carbonyl groups and can be substituted with one or more C₁-C₄ alkyl, amino or phenyl radicals, and in particular a group of structure J₂ below:

\[
\begin{array}{c}
\text{R₃₁} \\
\text{(Y) ----- N} \\
\text{Uₙ} \\
\text{O} \\
\text{R₃₂}
\end{array}
\]

in which structure J₂:
R₃₁ and R₃₂, which may be identical or different, represent a hydrogen atom, a C₁-C₄ alkyl radical or a phenyl radical;
Y denotes a -CO- radical or a radical \( \text{CH}_3 \) \( \text{C} \)

n = 0 or 1 with, when n denotes 1, U denoting a -CO- radical.

In the structures (I) to (IV) defined above, the C₁-C₄ alkyl or alkoxy group preferably denotes methyl, ethyl, butyl, methoxy or ethoxy.

The basic direct dyes of formulae (I), (II), (III) and (III') which can be used in the dye composition used during the second step of the process
in accordance with the invention are known compounds and are described, for example, in the patent applications WO 95/01772, WO 95/15144 and EP-A-0,714,954.

Among the basic direct dyes of formula (I), mention may be made more particularly of the compounds corresponding to structures (II) to (IS2) below:

\[ \text{Structure (I1):} \]
\[
\begin{array}{c}
\text{CH}_3 \\
\text{N} = \text{N} \\
\text{CH}_3 \\
\text{N} = \text{N} \\
\text{CH}_3 \\
\text{NH} - \text{CH}_3 \\
\text{Cl}^-
\end{array}
\]  

\[ \text{Structure (I2):} \]
\[
\begin{array}{c}
\text{CH}_3 \\
\text{N} = \text{N} \\
\text{CH}_3 \\
\text{N} = \text{N} \\
\text{CH}_3 \\
\text{NH} - \text{CH}_3 \\
\text{Cl}^-
\end{array}
\]  

\[ \text{Structure (I3):} \]
\[
\begin{array}{c}
\text{H}_3\text{C} - \text{N}^+ \\
\text{CH} = \text{CH} \\
\text{N} - \text{CH}_3 \\
\text{Cl}^-
\end{array}
\]  

\[ \text{Structure (I4):} \]
\[
\begin{array}{c}
\text{NH} - \text{CH}_3 \\
\text{N} = \text{N} \\
\text{CH}_3 \\
\text{N} = \text{N} \\
\text{CH}_3 \\
\text{Cl}^-
\end{array}
\]
\[
\text{CH}_3\text{C}_l\text{C}H\text{H}_3\text{N=N=O}_H\text{N}_3\text{Cl}^-\quad (15)
\]
\[
\text{CH}_3\text{C}_l\text{C}H\text{H}_3\text{N=N=O}_H\text{N}_3\text{Cl}^-\quad (16)
\]
\[
\text{H}_3\text{C}_l\text{C}_l\text{C}H\text{H}_3\text{N=N=O}_H\text{N}_3\text{Cl}^-\quad (17)
\]
\[
\text{N=N=O}_H\text{N}_3\text{Cl}^-\quad (18)
\]
\[
\text{N=N=O}_H\text{N}_3\text{Cl}^-\quad (19)
\]
(125)

(126)

(127)

(128)

(129)

(130)
Among the compounds of structures (II) to (I52) described above, the compounds particularly preferred are those corresponding to the structures (II), (I2), (I14) and (I31).

Among the basic direct dyes of formula (II), mention may be made more particularly of the compounds corresponding to the structures (III) to (III2) below:
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\[ \text{CH}_3 \text{N}^+ - \text{N} = \text{N} - \text{N}^+ \text{N} - \text{CH}_3 \text{Cl}^- \quad (113) \]

\[ \text{H}_3 \text{C} - \text{N}^+ - \text{N} = \text{N} - \text{N}^+ - \text{H}_3 \text{C} \text{Cl}^- \quad (114) \]

\[ \text{H}_3 \text{C} - \text{C} - \text{N}^+ - \text{N} = \text{N} - \text{N}^+ - \text{H}_3 \text{C} \text{C} \text{SO}_4^- \quad (116) \]

\[ \text{CH}_3 \text{S}_2 \text{O}_4^- \quad (117) \]
Among the basic direct dyes of formula (III), mention may be made more particularly of the compounds
corresponding to the structures (III1) to (III18) below:

(III1)

(III2)

(III3)

(III4)

(III5)
(III7) Cl

(III6) CH₃COO (III6)

(III5) CH₃COO (III5)

(III4) CH₃ (III4)

(III3) CH₃SO₂ (III3)

(III2) Cl (III2)

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Among the specific compounds of the structures (III) to (III8) described above, the compounds most particularly preferred are those corresponding to the structures (III4), (III5) and (III13).

Among the basic direct dyes of formula (III'), mention may be made more particularly of the compounds corresponding to the structures (III'1) to (III'3) below:

Among the basic direct dyes of formula (III'), mention may be made more particularly of the compounds corresponding to the structures (III'1) to (III'3) below:
Among the cationic direct dyes of formula (IV) which can be used in the dye compositions in accordance with the invention, mention may be made more particularly of the compounds of structures (IV)₁ to (IV)₇, below:
\[
\text{(IV)}_1
\]

\[
\text{(IV)}_2
\]

\[
\text{(IV)}_3
\]

\[
\text{(IV)}_4
\]
(IV)_{11}

(IV)_{12}

(IV)_{13}

(IV)_{14}

(IV)_{15}
(IV)_{22}

(IV)_{23}

(IV)_{24}

(IV)_{25}

(IV)_{26}
\[
\begin{align*}
\text{(IV)}_{40} & \quad \text{Pyridinium \( \text{CH}_3\text{SO}_4^- \)} \\
\text{(IV)}_{41} & \quad \text{Pyridinium \( \text{CH}_3\text{SO}_4^- \)} \\
\text{(IV)}_{42} & \quad \text{Pyridinium \( \text{C}_2\text{H}_5\text{SO}_4^- \)} \\
\text{(IV)}_{43} & \quad \text{Pyridinium \( \text{Br}^- \)}
\end{align*}
\]
The aqueous medium of the dye composition consists solely of water or of a mixture of water and at least one cosmetic adjuvant chosen from the various adjuvants commonly used for dyeing keratin fibres, such as solvents, surfactants, polymers, inorganic or organic thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners, film-forming agents, ceramides, preserving agents and opacifiers.

According to the invention, the water preferably represents from 20 to 95% by weight relative to the total weight of the dye composition and even more preferably from 40 to 90% by weight relative to this weight.

According to the process of the invention, the dye composition can be ready to use or prepared at
the time of use by mixing at least one pulverulent composition (P) containing at least one basic direct dye, and at least one aqueous composition (A).

The aqueous composition (A) can consist solely of water or of a mixture of water and one or more cosmetic adjuvants such as those mentioned above.

In the pulverulent composition (P), the basic direct dye(s) can constitute, by itself (themselves), all of the pulverulent composition, or can be dispersed in an excipient, as powder, of organic nature and/or of inorganic nature. This powder preferably has a particle size of less than 350 \( \mu \text{m} \).

The organic excipient can be of synthetic or plant origin and chosen in particular from crosslinked or non-crosslinked synthetic polymers, polysaccharides such as celluloses and modified or unmodified starches, as well as natural products containing them such as sawdust, or plant gums (guar gum, carob gum, xanthan gum, etc.).

The inorganic excipient can consist of metal oxides such as titanium oxides, aluminium oxides, kaolin, talc, silicates, mica and silicas.

An advantageously preferred excipient consists of sawdust such as Epicea sawdust.

The water-insoluble products which can constitute this inorganic or organic excipient can also be present in the dye composition as adsorption agent for the basic direct dye(s).
The pulverulent composition (P) can also contain binders or coating products in an amount preferably not exceeding 3% by weight approximately relative to the total weight of the said pulverulent composition.

These binders are preferably oils or liquid fats of mineral, synthetic, animal or plant origin.

The pulverulent composition can optionally also contain other adjuvants, in powder form, in particular surfactants of any nature and hair conditioners.

Needless to say, a person skilled in the art will take care to select the optional complementary compound(s) mentioned above, such that the advantageous properties intrinsically associated with the dye composition according to the invention, or with the pulverulent composition, are not, or are not substantially, adversely affected by the addition(s) envisaged.

According to the invention, the dye composition used during the second step of the process is applied to the keratin fibres for however long a dye-application time is necessary to obtain the colouring in the desired intensity, which is generally between 2 and 45 minutes and even more particularly between 3 and 10 minutes.

Concrete examples illustrating the invention will now be given without, however, being limiting in
EXAMPLES

EXAMPLES 1 to 3

The various compositions below were prepared:

Oxidizing composition: (common to Examples 1, 2 and 3)

At the time of use, the following were mixed together:

- 48 g of a powdered oxidizing composition containing:
  - 70% by weight of a mixture of sodium persulphate and potassium persulphate
  - 12% by weight of sodium metasilicate, and
  - 7% of ammonium chloride

- 30 ml of a cream containing nonionic surfactants and 12 g of aqueous ammonia containing 20% NH₃.

- and 30 ml of oxidizing milk having a pH of 2.0 and a hydrogen peroxide titre of 40 volumes (12% by weight).

Dye compositions:

At the time of use, the following were mixed together:

- 60 g of an aqueous composition (A) consisting of:
  - cetylstearyl alcohol 7 g
  - ethanol 2 g
  - coconut acid diethanolamide freed of the head fraction, sold under the name Comperlan KD by the company Henkel
- sodium cocoylamidoethylamine-N-hydroxyethyl-N-propionate
- Preserving agents and fragrances
- demineralized water

*: A.M. = Active material

40 g of water, and

3.5 g of a pulverulent composition (P) consisting of

(contents in grams):

<table>
<thead>
<tr>
<th>Example</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(γ-Aminopropyl)aminoanthraquinone</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>hydrochloride (basic direct dye)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basic Red 76 (basic direct dye)</td>
<td>-</td>
<td>45.7</td>
<td>-</td>
</tr>
<tr>
<td>Basic Red 51 (basic direct dye)</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Liquid petroleum jelly</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Ground Epicea sawdust qs</td>
<td>100 g</td>
<td>100 g</td>
<td>100 g</td>
</tr>
</tbody>
</table>

The bleaching oxidizing composition was applied to three locks of dark chestnut hair for 40 minutes at room temperature. The locks of hair were bleached 6 tones, to a very light blonde.

After this first bleaching step, the locks of hair were rinsed, washed with shampoo, rinsed again and then dried.

Each of the dye compositions described above was then applied to each of the locks of hair thus
bleached, for 5 minutes.

After rinsing and drying, the locks of hair were dyed in the shades featured in the table below:

<table>
<thead>
<tr>
<th>EXAMPLE</th>
<th>SHADE OBTAINED</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Intense fuchsia</td>
</tr>
<tr>
<td>2</td>
<td>Intense coppery red</td>
</tr>
<tr>
<td>3</td>
<td>Intense fuchsia</td>
</tr>
</tbody>
</table>

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word “comprising” is used in the sense of “including”, i.e. the features specified may be associated with further features in various embodiments of the invention.
THE CLAIMS DEFINING THE INVENTION ARE AS follows:

1. Process for the two-step direct dyeing of keratin fibres, and in particular human keratin fibres such as the hair, characterized in that, in a first step, the keratin fibres are bleached, and, in a second step, a dye composition containing, in an aqueous medium, at least one partially dissolved basic direct dye is then applied to the keratin fibres, the said dye composition being ready to use or resulting from the mixing, at the time of use, of at least one pulverulent composition (P) containing at least one basic direct dye and an aqueous composition (A).

2. Process according to Claim 1, characterized in that the basic direct dye(s) is (are) in supersaturation.

3. Process according to Claim 1, characterized in that the basic direct dye(s) is (are) partially or totally adsorbed onto or coated with an insoluble inorganic or organic filler present in the dye composition.

4. Process according to any one of the preceding claims, characterized in that the first step is a bleaching step which leads to a shade having a tone height of greater than or equal to 6.

5. Process according to Claim 4, characterized in that the bleaching step leads to a shade which shows a colour difference of greater than or equal to 2 tones when compared with the colour of
the fibres before bleaching.

6. Process according to any one of the preceding claims, characterized in that the bleaching is carried out by applying an oxidizing composition containing at least one oxidizing agent.

7. Process according to Claim 6, characterized in that the oxidizing agent is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts and polythionates, and mixtures thereof.

8. Process according to either of Claims 6 and 7, characterized in that the oxidizing composition is in liquid or creamy form, the said oxidizing composition being ready to use or resulting from the mixing, at the time of use, of one or more aqueous compositions or of one or more aqueous compositions with one or more pulverulent compositions, the oxidizing agent being present in the aqueous composition(s) and/or in the pulverulent composition(s).

9. Process according to any one of Claims 6 to 8, characterized in that the oxidizing composition has a pH of between 5 and 12.

10. Process according to any one of Claims 1 to 5, characterized in that the bleaching is carried out by irradiating the keratin fibres with laser light in the form of pulses which are powerful enough to degrade the melanin contained in the keratin fibres.
11. Process according to any one of the preceding claims, characterized in that the basic direct dye(s) is (are) chosen from basic aminoanthraquinone dyes, basic mono- or diazo dyes, basic azomethine dyes, basic naphthoquinone dyes and basic dyes containing ethylenic monounsaturations.

12. Process according to Claim 11, characterized in that the dyes are chosen from

- \[8-[(p\text{-aminophenyl})\text{azo}] \text{-7-hydroxy-2-naphthyl}]\text{-trimethylammonium chloride (also known as Basic Brown 16 or Arianor Mahogany 306002 in the Color Index), the combination of 3-[(4-amino-6-bromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-2-naphthyl)\text{amino}]\text{-N,N,N-trimethylbenzenaminium chloride and of 3-[(2,6-dibromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-3-naphthyl)\text{amino}]\text{-N,N,N-trimethylbenzenaminium chloride (also known as Basic Blue 99 or Arianor Steel Blue 306004 in the Color Index), 7-hydroxy-8-[(2-methoxyphenyl)\text{azo}]\text{-N,N,N-trimethyl-2-naphthalenaminium chloride (also known as Basic Red 76 or Arianor Madder Red in the Color Index),}]

- \[8-[(4-amino-2-nitrophenyl)\text{azo}] \text{-7-hydroxy-2-naphthyl}]\text{-trimethylammonium chloride (also known as Basic Red 118 in the Color Index), the combination of \[8-[(4-amino-3-nitrophenyl)\text{azo}] \text{-7-hydroxy-2-naphthyl]}\text{trimethylammonium chloride and of \[8-[(4-amino-2-nitrophenyl)\text{azo}] \text{-7-hydroxy-2-naphthyl]}\text{trimethylammonium chloride (also known as Brown 17 or Arianor Sienna Brown 306001 in the Color Index), 3-[(4,5-dihydro-3-methyl-5-oxo-}]}
1-phenyl-1H-pyrazol-4-yl)azo]-N,N,N-trimethyl-benzenaminium chloride (also known as Basic Yellow 57 or Arianor Straw Yellow 306005 in the Color Index),
1-(γ-aminopropyl)aminoanthraquinone hydrochloride,
1-N-(methylmorpholiniumpropyl)amino-4-hydroxyanthraquinone methyl sulphate and Basic Orange 69 (Color Index name).

13. Process according to any one of Claims 1 to 10, characterized in that the basic direct dye(s) is (are) chosen from:

a) the compounds of formula (I) below:

\[
\begin{align*}
\text{A} & \equiv \text{D} \equiv \text{D} \\
& \equiv \text{N} \\
& \equiv \text{X} \\
& \equiv \text{R}_1 \\
& \equiv \text{R}_2 \\
& \equiv \text{R}_3 \\
& \equiv \text{R}'_3
\end{align*}
\]

in which:
D represents a nitrogen atom or a -CH group,
R₁ and R₂, which may be identical or different,
represent a hydrogen atom; a C₁-C₄ alkyl radical which can be substituted with a -CN, -OH or -NH₂ radical or form, with a carbon atom of the benzene ring, a heterocycle optionally containing oxygen or nitrogen, which can be substituted with one or more C₁-C₄ alkyl radicals; a 4'-aminophenyl radical,
R₃ and R'₃, which may be identical or different, represent a hydrogen atom or a halogen atom chosen from chlorine, bromine, iodine and fluorine, or a cyano,
C\textsubscript{1}-C\textsubscript{4} alkoxy or acetyloxy radical,

X\textsuperscript{-} represents an anion preferably chosen from chloride, methyl sulphate and acetate,

A represents a group chosen from structures A\textsubscript{1} to A\textsubscript{12} below:
in which $R_4$ represents a $C_1$-$C_4$ alkyl radical which can be substituted with a hydroxyl radical and $R_5$ represents a $C_1$-$C_4$ alkoxy radical, with the proviso that when $D$ represents $-CH$, $A$ represents $A_4$ or $A_{13}$ and $R_3$ is other than an alkoxy radical, then $R_1$ and $R_2$ do not simultaneously denote a hydrogen atom;

b) the compounds of formula (II) below:
in which:

- $R_6$ represents a hydrogen atom or a $C_1$-$C_4$ alkyl radical,
- $R_7$ represents a hydrogen atom, an alkyl radical which can be substituted with a -CN radical or with an amino group, a 4'-aminophenyl radical or forms with $R_6$ a heterocycle, optionally containing oxygen and/or nitrogen, which can be substituted with a $C_1$-$C_4$ alkyl radical,
- $R_8$ and $R_9$, which may be identical or different,
- represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a $C_1$-$C_4$ alkyl or $C_1$-$C_4$ alkoxy radical or a -CN radical,
- $X^-$ represents an anion preferably chosen from chloride, methyl sulphate and acetate,

$B$ represents a group chosen from the structures $B_1$ to $B_6$ below:

![Diagram](image-url)
in which \( R_{10} \) represents a \( C_1-C_4 \) alkyl radical and \( R_{11} \) and 
\( R_{12} \), which may be identical or different, represent a 
hydrogen atom or a \( C_1-C_4 \) alkyl radical;

c) the compounds of formulae (III) and (III') below:

in which:

\( R_{13} \) represents a hydrogen atom, a \( C_1-C_4 \) alkoxy radical, a 
halogen atom such as bromine, chlorine, iodine or 
fluorine \( \cdot \) : an amino radical,

\( R_{14} \) represents a hydrogen atom, a \( C_1-C_4 \) alkyl radical or 
forms, with a carbon atom of the benzene ring, a 
heterocycle optionally containing oxygen and/or 
substituted with one or more \( C_1-C_4 \) alkyl groups,

\( R_{15} \) represents a hydrogen atom or a halogen atom such as 
bromine, chlorine, iodine or fluorine,
$R_1$, $R_2$, which may be identical or different, represent a hydrogen atom or a C$_1$-C$_4$ alkyl radical, $D_1$ and $D_2$, which may be identical or different, represent a nitrogen atom or a -CH group, $m = 0$ or 1, it being understood that when $R_3$ represents an unsubstituted amino group, then $D_1$ and $D_2$ simultaneously represent a -CH group and $m = 0$, $X^-$ represents an anion preferably chosen from chloride, methyl sulphate and acetate, $E$ represents a group chosen from the structures $E_1$ to $E_8$ below:
in which \( R' \) represents a \( C_1-C_4 \) alkyl radical;

when \( m = 0 \) and \( D_1 \) represents a nitrogen atom, then \( E \) can also denote a group of structure \( E_9 \) below:

\[
E_9
\]

in which \( R' \) represents a \( C_1-C_4 \) alkyl radical;

5 d) the compounds of formula (IV) below:

\[
G - N \equiv N - J \quad (IV)
\]

in which :

the symbol \( G \) represents a group chosen from the structures \( G_1 \) to \( G_3 \) below:
in which structures $G_1$ to $G_3$:

$R_{18}$ denotes a C$_1$-C$_4$ alkyl radical, a phenyl radical which can be substituted with a C$_1$-C$_4$ alkyl radical or a halogen atom chosen from chlorine, bromine, iodine and fluorine;

$R_{19}$ denotes a C$_1$-C$_4$ alkyl radical or a phenyl radical;

$R_{20}$ and $R_{21}$, which may be identical or different, represent a C$_1$-C$_4$ alkyl radical, a phenyl radical or together form, in $G_1$, a benzene ring substituted with one or more C$_1$-C$_4$ alkyl, C$_1$-$C_4$ alkoxy or NO$_2$ radicals, or together form, in $G_2$, a benzene ring optionally substituted with one or more C$_1$-C$_4$ alkyl, C$_1$-$C_4$ alkoxy or NO$_2$ radicals;

$R_{20}$ can also denote a hydrogen atom;

$Z$ denotes an oxygen or sulphur atom or a group $-NR_{19}$;
M represents a -CH, -CR (R denoting C₁-C₄ alkyl) or 
-NR₂₂(X')ₜ group;
K represents a -CH, -CR (R denoting C₁-C₄ alkyl) or 
-NR₂₂(X')ₜ group;
P represents a -CH, -CR (R denoting C₁-C₄ alkyl) or 
-NR₂₂(X')ₜ group; r denotes zero or 1;
R₂₂ represents an atom O⁻, a C₁-C₄ alkoxy radical or a 
C₁-C₄ alkyl radical;
R₂₃ and R₂₄, which may be identical or different, 
represent a hydrogen atom, a halogen atom chosen from 
chlorine, bromine, iodine and fluorine, a C₁-C₄ alkyl or 
C₁-C₄ alkoxy radical or an -NO₂ radical;
X⁻ represents an anion preferably chosen from chloride, 
iodide, methyl sulphate, ethyl sulphate, acetate and 
perchlorate;
with the proviso that,
if R₂₂ denotes O⁻, then r denotes zero;
if K or P or M denotes -N-(C₁-C₄)alkyl X⁻, then R₂₃ or R₂₄ 
is other than a hydrogen atom;
if K denotes -NR₂₂(X')ₜ, then M=P=-CH or -CR;
if M denotes -NR₂₂(X')ₜ, then K=P=-CH or -CR;
if P denotes -NR₂₂(X')ₜ, then K=M and denote -CH or -CR;
if Z denotes a sulphur atom with R₂₁ denoting C₁-C₄ 
alkyl, then R₂₀ is other than a hydrogen atom;
if Z denotes -NR₂₂ with R₁₉ denoting C₁-C₄ alkyl, then at 
least one of the radicals R₁₈, R₂₀ or R₂₁ of G₂ is other 
than a C₁-C₄ alkyl radical;
the symbol J represents:
-(a) a group of structure J₁ below:

\[
\begin{array}{c}
\text{J₁} \\
R_{25} \quad R_{26} \\
R_{27}
\end{array}
\]

in which structure J₁:

R₄₅ represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C₁-C₄ alkyl or C₁-C₄ alkoxy radical, a radical -OH, -NO₂, -NH₂, -NH₃, -NR₃, -NR₂R₄, or -NHCO(C₁-C₄)alkyl, or forms, with R₂₆, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

R₅₆ represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C₁-C₄ alkyl or C₁-C₄ alkoxy radical, or forms, with R₂₇ or R₃₈, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

R₂₇ represents a hydrogen atom, an -OH radical, an -NH₃ radical or an -NR₂₆ radical;

R₃₈ represents a hydrogen atom, a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical, a C₁-C₄ polyhydroxyalkyl radical or a phenyl radical;

R₄₈ and R₉₀, which may be identical or different, represent a C₁-C₄ alkyl radical, a C₁-C₄ monohydroxyalkyl radical or a C₁-C₄ polyhydroxyalkyl radical;

-(b) a 5- or 6-membered heterocyclic group containing
nitrogen, which can contain other hetero atoms and/or carbonyl groups and can be substituted with one or more C_1-C_4 alkyl, amino or phenyl radicals, and in particular a group of structure J_2 below:

![Structure J_2](image)

in which structure J_2:
R_{31} and R_{32}, which may be identical or different, represent a hydrogen atom, a C_1-C_4 alkyl radical or a phenyl radical;

Y denotes a -CO- radical or a radical \(\text{CH}_3\) \(\text{C}\);

n = 0 or 1 with, when n denotes 1, U denoting a -CO- radical.

14. Process according to any one of the preceding claims, characterized in that the aqueous medium of the dye composition consists solely of water or of a mixture of water and at least one cosmetic adjuvant chosen from solvents, surfactants, polymers, inorganic or organic thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners, film-forming
agents, ceramides, preserving agents and opacifiers.

15. Process according to any one of the preceding claims, characterized in that the water represents from 20 to 95% by weight of the total weight of the dye composition.

16. Process according to any one of the preceding claims, characterized in that, in the pulverulent composition (P), the basic direct dye(s) constitute, by themselves, all of the pulverulent composition, or are dispersed in an excipient, as powder, of organic nature and/or of inorganic nature.

17. Process according to Claim 16, characterized in that the excipient is sawdust.

18. Process according to any one of the preceding claims, characterized in that the dye composition is applied for a dye-application time of between 2 and 45 minutes.

19. Process according to Claim 18, characterized in that the dye-application time is between 3 and 10 minutes.

Dated this 27th day of November 1998

L'ORÉAL
By their Patent Attorneys

GRIFFITH HACK
Fellows Institute of Patent Attorneys of Australia
The invention relates to a process for the two-stage direct dyeing of keratin fibres, in particular human keratin fibres such as the hair, characterized in that, in a first step, the keratin fibres are bleached, and, in a second step, a dye composition containing, in an aqueous medium, at least one partially dissolved basic direct dye is then applied to the keratin fibres, the said dye composition being ready to use or resulting from the mixing, at the time of use, of at least one pulverulent composition (P) containing at least one basic direct dye and an aqueous composition (A).
END