particular for hair, the said composition contacting at
 Datagram composition for keratin fibres, and in

2. A
We hereby apply for the grant of a Patent for an invention entitled:

META-PHENYLENEDIAMINES AND THE PROCESS FOR THEIR MANUFACTURE, DYEING COMPOSITIONS IN WHICH THEY ARE PRESENT AND CORRESPONDING DYEING PROCESS.

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered 30.14pt1 for a patent or similar protection made in FRANCE on 1st July, 1980.

My address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, Our 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 29th day of June, 1981

L’OREAL

By: T.A. Barnes

Reg'd Patent Attorney

To: The Commissioner of Patents.
COMMONWEALTH OF AUSTRALIA
Patents Act 1952-1969

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

In support of the Convention Application made by

L'OREAL

(hereinafter referred to as the applicant) for a Patent for an invention entitled:

META-PHENYLENEDIAMINES AND THE PROCESS FOR THEIR MANUFACTURE, DYEING COMPOSITIONS IN WHICH THEY ARE PRESENT AND CORRESPONDING DYING PROCESS

I, (3) ANDRE VIOUT,
of 14, rue Royale,
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 France on the 1st day of July 1980, by L'OREAL.

3. Andree BUGAUT née ORMANDEY, of 7, rue des Abondances, 92100 Boulogne, and Jean-Jacques VANDENBOSSCHE, of 6, rue Léon Richer, 93601 Aulnay-Sous-Bois both of France,

are the actual inventors 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 said Andree BUGAUT née ORMANDEY and Jean-Jacques VANDENBOSSCHE.

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 17th day of June 1981

To: THE COMMISSIONER OF PATENTS.
I. Chemical compound of the general formula (I):

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{NH}_2
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{N} \\
\text{H}_2
\end{array}
\end{array}
\begin{array}{c}
\begin{array}{c}
\text{H}
\end{array}
\end{array}
\]

in which formula Z represents either a polyhydroxyalkyl radical in which the alkyl group contains from 3 to 6 carbon atoms, the said radical containing 2 or 3 hydroxyl groups, or an alkyl chain interrupted by from one to three oxygen atoms and containing from one to three hydroxyl groups, the said alkyl chain containing from 4 to 8 carbon atoms, or the corresponding salts with acids.
7. Dyeing composition for keratin fibres, and in particular for hair, the said composition containing at least one oxidation base, in a cosmetically acceptable carrier, characterised in that it contains, as the coupler, at least one compound of the formula (I) or a corresponding salt with an acid.
The following statement is a full description of this invention, including the best method of performing it known to us.
META-PHENYLENEDIAMINES AND THE PROCESS FOR THEIR MANUFACTURE, DYEING COMPOSITIONS IN WHICH THEY ARE PRESENT AND CORRESPONDING DYEING PROCESS

The present invention relates to new meta-phenylenediamines, the process for their preparation, dyeing compositions, for keratin fibres, in which they are present, and a hair-dyeing process using the said dyeing compositions.

In the field of the dyeing of keratin fibres such as hair or fur, meta-phenylenediamines have an important function which has been known for a long time; they form part of the class of compounds commonly referred to as "couplers". In association with para-phenylenediamines or para-aminophenols, which are compounds referred to as "oxidation bases", couplers give rise, in an oxidising alkaline medium, to coloured indamines, indoanilines or indophenols.

The association of meta-phenylenediamines with para-phenylenediamines, in an oxidising alkaline medium and more particularly in the presence of hydrogen peroxide, gives rise to indamines capable of imparting very strong blue colorations to keratin fibres. Furthermore, when associated with para-aminophenols, meta-phenylenediamines give, in an oxidising alkaline medium, indoanilines which impart, to keratin fibres, red colorations containing a greater or lesser degree of purple.
Thus, as couplers, meta-phenylenediamines have a dual function in hair dyeing, namely the provision of blue and the provision of red, that is to say the provision of two fundamental colours which are essential for obtaining not only blacks and greys, but also ashen or coppery chestnuts.

Despite its important function, this category of couplers has hitherto been limited in practice to a very restricted number of compounds. This over-restricted number is explained by the fact that the only compounds which can be selected for the dyeing of keratin fibres are those which make it possible to obtain dye of good quality, that is to say dyes which do not change with time, and, in particular, do not change when subjected either to light or to adverse weather conditions.

Moreover, in the case of hair dyes, the couplers used must have the advantage of being very harmless and, in particular, must be virtually non-mutagenic in the Ames test on Salmonella typhimurium (TA 1538, TA 98, TA 100, TA 1537 and TA 1535, in the absence or presence of "S9 MIX" activated by "Arochlor 1254").

The object of the present invention is thus to describe new chemical compounds capable of constituting meta-phenylenediamine couplers which can be used in dyeing compositions for keratin fibres. The compounds according to the invention can be used particularly in hair dyeing because they not only possess the dyeing
properties of a good coupler, but they also have the advantage of being very harmless and are non-mutagenic in the Ames test as defined above. French Patent Application 2,362,116 has already proposed meta-phenylene-diamines which give satisfactory results in hair dyeing, and the aim of the invention is to describe other metaphenylenediamines of the same type, and also their use.

The present invention thus relates to the new industrial product consisting of a chemical compound of the general formula (I):

\[
\begin{array}{c}
\text{O} \\
\text{NH}_2 \\
\text{NH}_2
\end{array}
\]

in which formula Z represents either a polyhydroxyalkyl radical in which the alkyl group contains from 3 to 6 carbon atoms, the said radical containing 2 or 3 hydroxyl groups, or an alkyl chain interrupted by at least one oxygen atom and containing from one to three hydroxyl groups, the said alkyl chain containing from 4 to 8 carbon atoms, or to the corresponding salts with acids.

The hydroxyl group (or groups) of the alkyl chain may or may not be at the end of the chain.
The present invention also relates to a process for the preparation of the compounds of the formula (I) defined above. In this process, a halogen derivative of the formula \(X - Z\), \(X\) being a halogen and \(Z\) having the meanings indicated above for the definition of the formula (I), is reacted with an alkali metal salt of 2-acetylaminoo-4-nitrophenol so as to condense the radical \(Z\) onto the nucleus, an alkali metal halide being eliminated, the nitro group of the product obtained is then reduced and, finally, the product is deacetylated to obtain the compound of the formula (I).

In a preferred embodiment, the halogen \(X\) which is used is chlorine and the alkali metal is potassium; the reduction of the nitro group is carried out in alcoholic solution, under reflux, by means of zinc powder in the presence of ammonium chloride.

The present invention also relates to the new industrial product consisting of a dyeing composition for keratin fibres, and in particular for hair, the said composition containing at least one oxidation base, in a cosmetically acceptable carrier, and being characterised in that it contains, as the coupler, at least one compound of the formula (I) or a corresponding salt with an acid.

In general, the meta-phenylenediamines of the formula (I) are present in the dyeing composition according to the invention in a proportion of between 0.001 and
2.8% by weight, relative to the total weight of the composition.

The meta-phenylenediamines according to the invention can be incorporated into dyeing compositions together with oxidation bases consisting of:

A. The para-phenylenediamines of the general formula (II):

\[
\begin{array}{c}
\text{N} \\
\text{R_1} \\
\text{R_2} \\
\text{R_3} \\
\text{R_4} \\
\text{R_5} \\
\text{NH}_2
\end{array}
\]

(II)

or the corresponding salts with acids, in which formula R₁, R₂ and R₃ are identical or different and represent a hydrogen atom, an alkyl radical having from 1 to 4 carbon atoms or an alkoxy radical having from 1 to 2 carbon atoms, and R₄ and R₅ are identical or different and represent a hydrogen atom, an alkyl or hydroxyalkyl radical, an alkoxyalkyl radical in which the alkoxy group contains from 1 to 2 carbon atoms, or a carbamylalkyl, mesylaminoalkyl, acetylaminoalkyl, ureidoalkyl, carbethoxyaminoalkyl, aminoalkyl, monoalkylaminoalkyl, dialkylaminoalkyl, piperidinoalkyl or morpholinocalkyl radical, the alkyl groups in R₄ and R₅ having from 1 to 4 carbon atoms, or alternatively R₄ and R₅ form a piperidino or morpholino group together with the nitrogen atom to which they are attached, with the proviso that R₁ and R₃ represent a
hydrogen atom if \( R_4 \) and \( R_5 \) do not represent a hydrogen atom.

B. The para-aminophenols of the general formula (III):

\[
\text{(III)}
\]

or the corresponding salts with acids, in which formula \( R_6 \) represents a hydrogen atom, an alkyl radical containing from 1 to 4 carbon atoms or a halogen atom such as, for example, chlorine or bromine.

C. Heterocyclic bases such as 2,5-diaminopyridine, 3-methyl-7-aminobenzomorpholine and 5-aminooindole.

It has been found that the use of the meta-phenylenediamines according to the invention, with at least one oxidation base mentioned under A, B and C above, makes it possible to obtain dyeing compositions which give the hair shades of good quality, which are very resistant especially to washing.

In general, the couplers according to the invention make it possible to obtain, with the para-phenylenediamines, blue colorations which are more or less rich in green or purple, and, with the para-aminophenols, red colorations. The dyeing compositions according to the invention will thus be able advantageously to contain both para-phenylenediamines and para-aminophenols.
It has been found that particularly valuable results are obtained by using, as the compounds of the formula (I) or their corresponding salts with acids, 2,4-diaminophenyl β-(β'-hydroxyethoxy)-ethyl ether, especially in the form of the dihydrochloride, or 2,4-diaminophenyl β,γ-dihydroxypropyl ether, especially in the form of the dihydrochloride.

Apart from the coupler (or couplers) of the formula (I) and the associated oxidation base (or bases), the dyeing compositions forming the subject of the invention can contain the following products, taken in isolation or in combination:

1) other known couplers, for example resorcinol, 2-methylresorcinol, meta-aminophenol, 2-methyl-5-aminophenol, 2-methyl-5-[N-(β-hydroxyethyl)-amine]-phenol, 6-hydroxybenzomorpholine, 2,6-dimethyl-3-acetylanaphenol, 2-methyl-5-carbethoxyaminophenol, 2-methoxy-5-carbethoxyaminophenol, 2-methyl-5-ureidophenol and 1-phenyl-3-methylpyrazol-5-one;

2) ortho-phenylenediamines and ortho-aminophenols optionally containing substituents on the nucleus or on the amine groups, or also ortho-diphenol, it being possible, by means of complex oxidation mechanisms, for these products to lead to new coloured compounds, either by cyclisation with themselves or by reaction with the para-phenylenediamines;

3) dyestuff precursors of the benzene series, containing,
on the nucleus, at least three substituents chosen from the group comprising hydroxyl, methoxy or amino groups, such as 2,6-diaminohydroquinone dihydrochloride, 2,6-diamino-4-[N,N-bis-(ethyl)-amino]-phenol trihydrochloride, 2,4-diaminophenol dihydrochloride, 1,2,4-trihydroxybenzene, 2,3,5-trihydroxyltoluene or 4-methoxy-2-amino-N-(β-hydroxyethyl)-aniline;

4) dyestuff precursors of the naphthalene series, such as 2-hydroxy-1,4-naphthoquinone and 5-hydroxy-1,4-naphthoquinone;

5) leuco-derivatives of indoanilines or of indophenols, such as 4,4'-dihydroxy-2-amino-5-methyldiphenylamine, 4,4'-dihydroxy-2-[N-(β-hydroxyethyl)-amino]-5-methyl-2'-chlorodiphenylamine, 2,4'-diamino-4-hydroxy-5-methyl-diphenylamine, 2,4-dihydroxy-4'-[N-(β-methoxyethyl)-amino]-diphenylamine or 2,4-dihydroxy-5-methyl-4'-[N-(β-methoxyethyl)-amino]-diphenylamine; and

6) direct dyestuffs, for example those chosen from the class of the nitro dyestuffs of the benzene series, such as 1-[N,N-bis-(β-hydroxyethyl)-amino]-3-nitro-4-(N'-methylamino)-benzene, 1-[N-methyl-N-(β-hydroxyethyl)-amino]-3-nitro-4-[N'-(β-hydroxyethyl)-amino]-benzene, 1-[N-methyl-N-(β-hydroxyethyl)-amino]-3-nitro-4-(N'-methy lamino)-benzene, 3-nitro-4-[N-(β-hydroxyethyl)-amino]-anisole, 3-nitro-4-[N-(β-hydroxyethyl)-amino]-phenol, 3-nitro-4-aminophenoxy-ethanol, 3-nitro-4-(N-methylamino)-phenoxy-ethanol or 2-[N-(β-hydroxyethyl)-
The pH of the dyeing compositions according to the invention is basic, for example between 8 and 11.5. Amongst the alkalising agents which can be used, there may be mentioned ammonia, alkylamines such as ethylamine or triethylamine, alkanolamines such as mono-, di- or tri-ethanolamine, alkylalkanolamines such as methyl-di-ethanolamine, sodium hydroxide or potassium hydroxide and sodium carbonate, potassium carbonate or ammonium carbonate. Amongst the acidifying agents which can be used, there may be mentioned lactic acid, acetic acid, tartaric acid and phosphoric acid.

The cosmetically acceptable carrier which is associated with the base(s), coupler(s) and, if appropriate, direct dyestuff(s) of the composition can comprise, apart from water, surface-active agents, organic solvents, thickening products, antioxidants, penetrating agents, foaming agents, sequestering agents, film-forming products, treating agents and perfumes.

Anionic, cationic, non-ionic and amphoteric surface-active agents, or a mixture thereof, can be added to the composition according to the invention. Amongst the surface-active agents which can be used in particular, there may be mentioned alkylbenzenesulphonates, alkyl-naphthalenesulphonates, the sulphates, ether-sulphates and sulphonates of fatty alcohols, quaternary ammonium salts such as trimethylcetylammonium bromide and cetylpyridin-
ium bromide, fatty acid diethanolamides, polyoxyethyleneated or polyglycerolated acids and alcohols and polyoxyethyleneated or polyglycerolated alkylphenols. Preferably, the surface-active agents are present in the composition according to the invention in a proportion of between 0.5 and 55% by weight and advantageously of between 4 and 40% by weight, relative to the total weight of the composition.

Organic solvents can also be added to the composition according to the invention in order to solubilise compounds which would not be sufficiently soluble in water. Amongst the solvents which can advantageously be used, examples which may be mentioned are ethanol, isopropanol, glycerol, glycols and their ethers, such as 2-butoxyethanol, ethylene glycol, propylene glycol, diethylene glycol monoethyl ether and monomethyl ether, and analogous solvents. The solvents can advantageously be present in the composition in a proportion ranging from 1 to 40% by weight and preferably of between 5 and 30% by weight, relative to the total weight of the composition.

The thickening products which can be added to the composition according to the invention can advantageously be taken from the group comprising sodium alginate, gum arabic, cellulose derivatives such as methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose and the sodium salt of carboxymethylcellulose, and acrylic
acid polymers; it is also possible to use inorganic thickeners such as bentonite. Preferably, the thickeners are present in a proportion of between 0.5 and 5% by weight, relative to the total weight of the composition, and advantageously of between 0.5 and 3% by weight.

The antioxidants which can be added to the composition according to the invention can advantageously be taken from the group comprising sodium sulphite, thio-glycolic acid, mercaptosuccinic acid, sodium bisulphite, ascorbic acid and hydroquinone. These antioxidants can be present in the composition in a proportion of between 0.05 and 1.5% by weight, relative to the total weight of the composition.

The dyeing composition according to the invention contains, at the time of use, oxidising agents such as hydrogen peroxide, urea peroxide or per-salts, for example ammonium persulphate.

The dyeing composition according to the invention can be presented in the form of a liquid, a cream, a gel or an aerosol or in any other form suitable for dyeing keratin fibres.

The present invention also relates to a hair-dyeing process which is characterised in that a composition according to the invention is mixed with an oxidising agent, in that the said mixture is applied to the hair, in that the mixture is left to act on the hair for a
period of between 5 and 45 minutes, and in that the hair is rinsed, optionally shampooed and rinsed again, and dried.

To provide a clearer understanding of the subject of the invention, several embodiments thereof will now be described by way of purely illustrative and non-limiting examples.

Example 1: Preparation of 2,4-diaminophenyl 8-(8'-hydroxyethoxy)ethyl ether dihydrochloride

The compound prepared has the following formula:

$$\text{O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH}$$

$$\text{NH}_2 \quad \text{2HCl}$$

First stage:

$$\text{OH} \quad \text{NHCOC}_3$$

Second stage:

$$\text{OK} \quad \text{NHCOC}_3$$

$$\text{OK} \quad \text{NHCOC}_3$$

$$\text{Cl-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH}$$
Third stage:

\[
\begin{align*}
O-CH_2-CH_2-O-CH_2-CH_2-OH \\
N\text{HCOCH}_3 \\
\text{NO}_2
\end{align*}
\]

\[
\rightarrow
\]

Fourth stage:

\[
\begin{align*}
O-CH_2-CH_2-O-CH_2-CH_2-OH \\
N\text{HCOCH}_3 \\
\text{HCl} \\
\text{NH}_2
\end{align*}
\]

\[
\rightarrow
\]

\[
\begin{align*}
O-CH_2-CH_2-O-CH_2-CH_2-OH \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{2HCl}
\end{align*}
\]
First step: Preparation of the potassium salt of 2-acetylamino-4-nitrophenol

2,150 ml of ethanol, containing, in solution, 133 g of 80% strength potassium hydroxide solution (1.89 mols), are cooled to -10°C; 1.89 mols (371 g) of 2-acetylamino-4-nitrophenol are then added gradually, whilst stirring and at the same time keeping the temperature below 5°C. The potassium salt precipitates. The product is filtered off, washed with ethanol and dried in vacuo at 50°C.

Second step: Preparation of 2-acetylamino-4-nitrophenyl 8-(8'-hydroxyethoxy)-ethyl ether

0.5 mol (117 g) of the potassium salt of 2-acetylamino-4-nitrophenol is introduced into 500 ml of dimethylformamide; 0.6 mol (64 ml) of diethylene glycol monochlorohydrin is then added, whilst stirring. The mixture is stirred for 8 hours at a temperature of the order of 100°C and then poured into two litres of ice-cooled water. The crude product is filtered off; it is washed with water, then with an ice-cooled normal sodium carbonate solution and finally with water.

After drying in vacuo and recrystallisation from ethanol, the expected product melts at 152°C.

Analysis of the product obtained gives the following results:
<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for $C_{12}H_{16}N_2O_6$</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
<td>50.70</td>
<td>50.88</td>
</tr>
<tr>
<td>H %</td>
<td>5.67</td>
<td>5.64</td>
</tr>
<tr>
<td>N %</td>
<td>9.86</td>
<td>9.74</td>
</tr>
<tr>
<td>O %</td>
<td>33.77</td>
<td>33.90</td>
</tr>
</tbody>
</table>

**Third step: Preparation of 2-acetylamino-4-aminophenyl $\beta$-($\beta'$-hydroxyethoxy)-ethyl ether monohydrochloride**

400 ml of ethanol (96° strength), to which 75 ml of water, 10 g of ammonium chloride and 200 g of zinc powder have been added, are heated to the reflux temperature, whilst stirring; 0.32 mol (91 g) of 2-acetylamino-4-nitrophenyl $\beta$-($\beta'$-hydroxyethoxy)-ethyl ether is then added gradually, whilst at the same time continuing the stirring. After each addition, the reaction medium is decolorised very rapidly. When the addition of the nitro derivative has ended, the heating is maintained for about ten minutes and the reaction medium is then filtered, the filtrate being collected in 30 ml of ethanol (96° strength) to which 34 ml of 36% strength hydrochloric acid have been added, and which have been cooled beforehand with the aid of a solid carbon dioxide/ethanol mixture. The expected product crystallises in the form of the hydrochloride. It is filtered off, washed with a small amount of absolute ethanol cooled to -10°C beforehand, and then dried in vacuo at 55°C.
Analysis of the product obtained gives the following results:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for $\text{C}<em>{12}\text{H}</em>{18}\text{N}<em>{2}\text{O}</em>{4}$ $\cdot$ $\text{HCl}$</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
<td>49.57</td>
<td>49.56</td>
</tr>
<tr>
<td>H %</td>
<td>6.58</td>
<td>6.50</td>
</tr>
<tr>
<td>N %</td>
<td>9.63</td>
<td>9.48</td>
</tr>
<tr>
<td>O %</td>
<td>22.01</td>
<td>21.83</td>
</tr>
<tr>
<td>Cl %</td>
<td>12.19</td>
<td>12.30</td>
</tr>
</tbody>
</table>

Fourth step: Preparation of 2,4-diaminophenyl $\beta$-($\beta'$-hydroxyethoxy)-ethyl ether dihydrochloride

0.25 mol (70.9 g) of 2-acetylamino-4-aminophenyl $\beta$-($\beta'$-hydroxyethoxy)-ethyl ether monohydrochloride is heated to the reflux temperature, whilst stirring, in 210 ml of absolute ethanol saturated with hydrogen chloride. After heating for 10 minutes, dissolution is total and the expected dihydrochloride then starts to precipitate after about half an hour. The heating is maintained for one hour in total and the reaction medium is then cooled to $0^\circ\text{C}$. The dihydrochloride is filtered off, washed with a small amount of absolute ethanol at $0^\circ\text{C}$ and then dried in vacuo at $55^\circ\text{C}$. It melts with decomposition between 180 and 185$^\circ\text{C}$.

Analysis of the product obtained gives the following results:
Example 2bis: Preparation of 2,4-diaminophenyl-B-[(β-hydroxyethoxyethoxy)ethoxy]ethyl ether dihydrochloride

The prepared compound has the following formula:

\[
\text{OCH}_2\text{CH}_{2}\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}
\]

First Stage:

\[
\text{NH}_2 + \text{NHCOCH}_3 \rightarrow \text{NHCOCH}_3
\]

Second Stage:

\[
\text{NO}_2 + \text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \rightarrow \text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}
\]

Third Stage:

\[
\text{NHCOCH}_3 + \text{Pd/C} \rightarrow \text{HCl/EtOH}
\]

\[
\text{NH}_2
\]

\[
\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}
\]

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for C\textsubscript{10}H\textsubscript{16}N\textsubscript{2}O\textsubscript{3} \cdot 2HCl</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C%} )</td>
<td>42.12</td>
<td>42.24</td>
</tr>
<tr>
<td>( \text{H%} )</td>
<td>6.36</td>
<td>6.39</td>
</tr>
<tr>
<td>( \text{N%} )</td>
<td>9.82</td>
<td>9.73</td>
</tr>
<tr>
<td>( \text{O%} )</td>
<td>16.83</td>
<td>17.07</td>
</tr>
<tr>
<td>( \text{Cl%} )</td>
<td>24.87</td>
<td>24.90-24.94</td>
</tr>
</tbody>
</table>
First Step: Preparation of the potassium salt of 2-acetylamino-4-nitrophenol

2150 ml of ethanol containing, in solution, 1.89 mols (133 g) of 80% strength potassium hydroxide solution are cooled to -10°C; 1.89 mols (371 g) of 2-acetylamino-4-nitrophenol are then added gradually, whilst stirring, and at the same time keeping the temperature below 5°C. The potassium salt precipitates. The product is filtered off, washed with ethanol and dried in vacuo at 50°C.

Second Step: Preparation of 2-acetylamino-4-nitrophenyl β-[(β′-hydroxyethoxy)ethoxy]-ethyl ether

0.2 mol (46.85 g) of the potassium salt of 2-acetylamino-4-nitrophenol is introduced into 200 ml of dimethylformamide; 0.24 mol (40.5 g) of triethylene glycol monochlorohydrin is then added, whilst stirring (boiling point = 256-258°C). The mixture is kept, whilst stirring at a temperature of about 100°C for eight hours, then it is poured into 300 ml of ice-cooled water. The crude product is filtered off; it is washed with water, then with an ice-cooled normal sodium carbonate solution and finally with water. After drying in vacuo and recrystallization in ethanol, the expected product melts at 104°C.

The analysis of the product obtained gives the following results:
### Analysis Calculated for C$_{14}$H$_{20}$O$_7$N$_2$ Found

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
<td>51.21</td>
<td>51.33</td>
<td></td>
</tr>
<tr>
<td>H %</td>
<td>6.14</td>
<td>6.19</td>
<td></td>
</tr>
<tr>
<td>N %</td>
<td>8.53</td>
<td>8.49</td>
<td></td>
</tr>
<tr>
<td>O %</td>
<td>34.11</td>
<td>33.96</td>
<td></td>
</tr>
</tbody>
</table>

**Third Step: Preparation of 2,4-diaminophenyl \(\beta\)-[\(\beta\)'-hydroxyethoxy]ethoxy]-ethyl ether dihydrochloride**

16.4 g of 10% strength palladium on carbon medium are added to 160 ml of 96° GL strength ethyl alcohol, then 0.65 mol (66 ml) of cyclohexane is added. While stirring vigorously, a suspension of 0.1 mol (32.83 g) of 2-acetylamino-4-nitrophenyl \(\beta\)-[\(\beta\)'-hydroxyethoxy]ethoxy]-ethyl ether and 60 ml of 96° GL strength ethyl alcohol are poured into this mixture. The medium is brought to reflux for two hours under nitrogen. The boiling reaction mixture is filtered, then the filtrate is brought into contact with 50 ml of 32% strength ethanol hydrochloric acid. The dihydrochloride formed is filtered. Salt formation is completed by heating under reflux for three hours the 15.2 g of the crude dihydrochloride in 150 ml of 32% strength ethanol hydrochloric acid. The medium is left to cool, and then the salt is precipitated by 500 ml of ethyl ether. The product is filtered and washed several times with ethyl ether. The product is dried in vacuo at nearly 50°C, and 7.8 g of this product are obtained having a melting point of 156°C (KÖFLER).
The analysis of the product obtained gives the following results:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for C_{12}H_{22}N_{2}O_{4}Cl_{2}</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
<td>43.78</td>
<td>43.05</td>
</tr>
<tr>
<td>H %</td>
<td>6.73</td>
<td>6.58</td>
</tr>
<tr>
<td>N %</td>
<td>8.51</td>
<td>8.29</td>
</tr>
<tr>
<td>O %</td>
<td>19.44</td>
<td>19.97</td>
</tr>
</tbody>
</table>

Example 2ter: Preparation of 2,4-diaminophenyl 3\-'(\text{R-hydroxyethoxy})-2'\-'hydroxy propyl ether dihydrochloride

The prepared compound has the following formula:

\[
\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CH}_2\text{OH}
\]

\[
\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CH}_2\text{OH}
\]

**First Stage:**

\[
\text{NHCOCH}_3
\]

**Second Stage:**

\[
\text{ClCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CH}_2\text{OH} + \text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CH}_2\text{OH}
\]

\[
\text{NHCOCH}_3
\]
**Third Stage:**

\[
\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CH}_2\text{OH} \quad \text{NHCOCH}_3 \\
\text{NO}_2 \quad \text{Pd/C} \quad \text{HCl/Ethanol} \\
\text{OCH}_2\text{CHOHCH}_2\text{OCH}_2\text{CH}_2\text{OH} \quad \text{NH}_2 \quad 2\text{HCl}
\]

**First step:** Preparation of the potassium salt of 2-acetylamino-4-nitrophenol

2150 ml of ethanol containing, in solution, 1.89 mols (133 g) of 80% strength potassium hydroxide solution are cooled to -10°C; 1.89 mols (371 g) of 2-acetylamino-4-nitrophenol are then added gradually, whilst stirring, and at the same time keeping the temperature below 5°C. The potassium salt precipitates. The product is filtered off, washed with ethanol and dried in vacuo at 50°C.

**Second step:** Preparation of (2-acetylamino-4-nitrophenyl) 3′-{(ß-hydroxyethoxy)-2′-hydroxy propyl ether

0.2 mol (46.85 g) of the potassium salt of 2-acetylamino-4-nitrophenol is introduced into 200 ml of dimentylformamide; 0.24 mol of 2-hydroxy-3-chloro propyl 2′-hydroxy ethyl ether (boiling point = 110°C/0.4 ml Hg) are then added, whilst stirring (Ref: Pretrow, Stephenson, J. Pharm. Pharmacol. 7 (1955) 198, 200).

The mixture is kept for eight hours at a temperature of about 100°C, whilst stirring, and then it is poured into 800 ml of ice-cooled water. The precipitate is filtered off, washed with water, then with a normal, ice-cooled solid solution and finally with water. After drying in
vacuo and recrystallization in acetonitrile, the expected product melts at 65°C.

The analysis of the product obtained gives the following results:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for C_{13}H_{18}O_{2}N_{2}</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
<td>49.68</td>
<td>49.59</td>
</tr>
<tr>
<td>H %</td>
<td>5.77</td>
<td>5.76</td>
</tr>
<tr>
<td>N %</td>
<td>8.91</td>
<td>8.94</td>
</tr>
<tr>
<td>O %</td>
<td>35.63</td>
<td>35.57</td>
</tr>
</tbody>
</table>

Third step: Preparation of 2,4-diaminophenyl 3'-(β-hydroxyethoxy)-2'-hydroxy propyl ether dihydrochloride

3.2 g of a palladium and carbon medium at 10% strength are added to 32 ml of ethanol at 96° GL strength, then 0.13 mol (13.2 ml) of cyclohexane is added. Whilst stirring vigorously, a suspension of 0.02 mol (6.28 g) of 2-acetylamino-4-nitro phenyl 3'-(β-hydroxyethoxy)-2'-hydroxy propyl ether and 12 ml of ethanol is added. The mixture is brought under reflux for three hours and the boiling reaction mixture is filtered. The ethanolic filtrate is then mixed with 150 ml of ethanol and 17.4 ml of ethanol hydrochloric acid at 32% strength. The entire mixture is kept under reflux for 3 hours. The total mixture is concentrated to a volume of 75 ml, then precipitated by ethyl ether. The precipitate is filtered off and rewashed with ethyl ether. The product is dried in vacuo at ambient temperature for 48 hours. A beige product is obtained which has a melting point of 207-210°C on the KÖFLER Bench.
The analysis of the product obtained gives the following results:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for $C_{11}H_{20}N_2O_4Cl_2$</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C %</td>
<td>41.92</td>
<td>41.32</td>
</tr>
<tr>
<td>H %</td>
<td>6.39</td>
<td>6.45</td>
</tr>
<tr>
<td>N %</td>
<td>8.89</td>
<td>8.80</td>
</tr>
<tr>
<td>O %</td>
<td>22.50</td>
<td>22.22</td>
</tr>
</tbody>
</table>

Example 2: Preparation of 2,4-diaminophenyl $\beta$,$\gamma$-dihydroxypropyl ether dihydrochloride

First Stage:

$\text{O-CH}_2\text{-CHOH-CH}_2\text{-OH}$

$\text{NH}_2$

$\text{NH}_2$

$\text{2HCl}$

$\text{OK}$

$\text{NHCOCH}_3$

$\text{+ ClCH}_2\text{-CHOH-CH}_2\text{OH}$

$\text{O-CH}_2\text{-CHOH-CH}_2\text{OH}$

$\text{NHCOCH}_3$

$\text{NO}_2$
Second stage:

\[
\begin{align*}
\text{O-CH}_2\text{-CHOH-CH}_2\text{OH} & \quad \text{NHCOCH}_3 \\
\text{O-CH}_2\text{-CHOH-CH}_2\text{OH} & \quad \text{NHCOCH}_3 \cdot \text{HCl}
\end{align*}
\]

Third stage:

\[
\begin{align*}
\text{O-CH}_2\text{-CHOH-CH}_2\text{OH} & \quad \text{NHCOCH}_3 \cdot \text{HCl} \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{O-CH}_2\text{-CHOH-CH}_2\text{OH} \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{O-CH}_2\text{-CHOH-CH}_2\text{OH}
\end{align*}
\]

First step: Preparation of 2-acetylamino-4-nitrophenyl 8,7-dihydroxypropyl ether

0.2 mol (46.8 g) of the potassium salt of 2-acetylamino-4-nitrophenol is introduced into 100 ml of 1-chloropropane-2,3-diol to which 20 ml of water have been added. The mixture is heated for 10 hours in a boiling water-bath. 0.1 mol (13.8 g) of potassium carbonate is added and the heating is then continued for six hours. After cooling and removal of the inorganic salts by filtration, 250 ml of ethanol (96° strength) are added to the filtrate and the mixture is then cooled overnight at 0°C. The expected product crystallises. It is filtered off and washed with ethanol, then with a normal sodium carbonate solution and then with water.

After two recrystallisations from ethanol and
drying in vacuo at 55°C, the product melts at 142°C.

Analysis of the product obtained gives the following results:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for ( \text{C}<em>{11}\text{H}</em>{14}\text{N}<em>{2}\text{O}</em>{6} )</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C%</td>
<td>48.89</td>
<td>48.77</td>
</tr>
<tr>
<td>H%</td>
<td>5.22</td>
<td>5.15</td>
</tr>
<tr>
<td>N%</td>
<td>10.37</td>
<td>10.44</td>
</tr>
<tr>
<td>O%</td>
<td>35.52</td>
<td>35.32-35.46</td>
</tr>
</tbody>
</table>

Second step: Preparation of 2-acetylamino-4-aminophenyl 
8,8-dihydroxypropyl ether hydrochloride

17 ml of ethanol (96% strength), to which 2.5 ml of \( \alpha,\beta \)-unsaturated hydrochloric acid have been added, are heated to the reflux temperature, whilst stirring; 1.33 \( \times \) 10^{-2} mols (3.6 g) of 2-acetylamino-4-nitrophenyl 8,8-dihydroxypropyl ether are then added gradually, whilst at the same time maintaining the stirring. When the addition has ended and the reaction medium is decolorised, the latter is filtered, the filtrate being collected in 1.5 ml of ethanol (96% strength) to which 1.5 ml of 35% strength hydrochloric acid have been added, cooling being carried out with the aid of an ethanol/solid carbon dioxide mixture. In the cooled filtrate, the expected product crystallises in the form of the hydrochloride. It is filtered off, washed with a small amount of absolute ethanol cooled
beforehand, and then dried in vacuo at 55°C.

Analysis of the product obtained gives the following results:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated for ( \text{C}<em>{11}\text{H}</em>{16}\text{N}_2\text{O}_4 \cdot \text{HCl} )</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C%} )</td>
<td>47.74</td>
<td>47.86</td>
</tr>
<tr>
<td>( \text{H%} )</td>
<td>6.19</td>
<td>6.26</td>
</tr>
<tr>
<td>( \text{N%} )</td>
<td>10.12</td>
<td>10.16</td>
</tr>
<tr>
<td>( \text{O%} )</td>
<td>23.13</td>
<td>23.08</td>
</tr>
<tr>
<td>( \text{Cl%} )</td>
<td>12.81</td>
<td>12.90</td>
</tr>
</tbody>
</table>

Third step: Preparation of 2,4-diaminophenyl \( \beta,\gamma \)-dihydroxypropyl ether dihydrochloride

0.195 mol (54 g) of 2-acetylaminophenyl \( \beta,\gamma \)-dihydroxypropyl ether hydrochloride is introduced into 270 ml of absolute ethanol saturated with hydrogen chloride, to which 54 ml of 12 N hydrochloric acid have been added. The reaction mixture is heated for one hour in the region of 100°C, whilst stirring. The expected dihydrochloride, which is insoluble in the hot reaction medium, is filtered off. The product is washed with a small amount of absolute ethanol saturated with hydrogen chloride, and then washed with acetone. After drying in vacuo at 55°C, it melts with decomposition between 210° and 215°C.

Analysis of the product obtained gives the following results:
Analysis Calculated for C₉H₁₄N₂O₃·2HCl Found

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C%</td>
<td>39.86</td>
<td>39.96</td>
</tr>
<tr>
<td>H%</td>
<td>5.95</td>
<td>6.04</td>
</tr>
<tr>
<td>N%</td>
<td>10.33</td>
<td>10.28</td>
</tr>
<tr>
<td>O%</td>
<td>17.70</td>
<td>17.64</td>
</tr>
<tr>
<td>Cl%</td>
<td>26.15</td>
<td>26.23</td>
</tr>
</tbody>
</table>

**Example 3:**

The following dyeing composition is prepared:

- Compound of Example 1 ..................... 2.85 g
- Para-phenylenediamine ..................... 1.08 g
- Oxyethylenated nonylphenol containing four mols of ethylene oxide, sold under the name "CEMULSOL NP4" by "RHONE POULENCE" ..................... 21 g
- Oxyethylenated nonylphenol containing nine mols of ethylene oxide, sold under the name "CEMULSOL NP9" by "RHONE POULENCE" ..................... 24 g
- Oleic acid ................................. 4 g
- 2-Butoxyethanol ............................ 3 g
- Ethanol (96⁰ strength) .................... 10 g
- Pentasodium salt of diethylenetriaminepenta-acetic acid, sold under the name "MASQUOL DTPA" ..................... 2.5 g
- Thioglycolic acid .......................... 0.6 g
- Ammonia solution (22⁰B strength) .......... 10 g
- Water .......................... q.s.p. 100 g
The pH of the composition is equal to 9.7. 100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied to 90% naturally white hair for 25 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a blue-black coloration.

Example 4:

The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound of Example 2</td>
<td>0.0057 g</td>
</tr>
<tr>
<td>Para-phenylenediamine</td>
<td>0.0027 g</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>8 g</td>
</tr>
<tr>
<td>Carboxymethylcellulose</td>
<td>2 g</td>
</tr>
<tr>
<td>Ammonium lauryl-sulphate</td>
<td>5 g</td>
</tr>
<tr>
<td>Ammonium acetate</td>
<td>1 g</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>8 g</td>
</tr>
<tr>
<td>Pentasodium salt of diethylenetriaminepenta-acetic acid, sold under the name &quot;MASQUOL DTPA&quot;</td>
<td>2 g</td>
</tr>
<tr>
<td>Thioglycolic acid</td>
<td>0.4 g</td>
</tr>
<tr>
<td>Ammonia solution (22°B strength)</td>
<td>5 g</td>
</tr>
<tr>
<td>Water, q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>

The pH of the composition is equal to 10.1. 50 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied for 30 minutes at 28°C to hair which has been bleached white beforehand, this mixture imparts to the hair, after rinsing and shampooing, a bluish
light silver coloration.

**Example 5:**

The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound of Example 2</td>
<td>0.542 g</td>
</tr>
<tr>
<td>Para-aminophenol</td>
<td>0.218 g</td>
</tr>
<tr>
<td>Acrylic acid polymer having a molecular weight</td>
<td></td>
</tr>
<tr>
<td>of 2 to 3 million, sold under the name</td>
<td></td>
</tr>
<tr>
<td>&quot;CARBOPOL 934&quot; by &quot;GOODRICH CHEMICAL CO&quot;</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11 g</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>5 g</td>
</tr>
<tr>
<td>Trimethylcetylammonium bromide</td>
<td>1 g</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid sold under</td>
<td></td>
</tr>
<tr>
<td>the name &quot;TRILON B&quot;</td>
<td>0.1 g</td>
</tr>
<tr>
<td>Ammonia solution (22°B strength)</td>
<td>10 g</td>
</tr>
<tr>
<td>Thioglycolic acid</td>
<td>0.2 g</td>
</tr>
<tr>
<td>Water q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>

The pH of the composition is equal to 10.2.

80 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied to 90% naturally white hair for 25 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a dark red coloration.

**Example 6:**

The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound of Example 1</td>
<td>1.42 g</td>
</tr>
<tr>
<td>Para-aminophenol</td>
<td>0.55 g</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>8 g</td>
</tr>
</tbody>
</table>
Propylene glycol ........................................... 8 g
Carboxymethylcellulose ................................... 2 g
Ammonium lauryl-sulphate ................................. 5 g
Pentasodium salt of diethylenetriaminepenta-
acetic acid, sold under the name
"MASQUOL DTPA" ........................................... 2 g
Thioglycolic acid ............................................ 0.4 g
Ammonia solution (22°B strength) ....................... 10 g
Water ......................................................... 100 g

The pH of the composition is equal to 10.

100 g of hydrogen peroxide of 20 volumes strength
are added at the time of use.

When applied to 90% naturally white hair for 30
minutes at 25°C, this mixture imparts to the hair, after
rinsing and shampooing, a coppery-red coloration.

Example 7:

The following dyeing composition is prepared:

Compound of Example 2 ................................. 0.271 g
4-[(N-(β-Methoxyethyl)-amino]-aniline
dihydrochloride .......................................... 0.239 g
Oxyethyleneated nonylphenol containing four
mols of ethylene oxide, sold under the name
"CEMULSOL NP4" by "RHONE POUJENC" .......... 12 g
Oxyethyleneated nonylphenol containing nine
mols of ethylene oxide, sold under the name
"CEMULSOL NP9" by "RHONE POUJENC" .......... 15 g
Oxyethyleneated oleyl alcohol containing two
mols of ethylene oxide ................................ 1.5 g
Oxyethylenated oleyl alcohol containing four mols of ethylene oxide ................................ 1.5 g
Propylene glycol .............................................. 6 g
Ethylenediaminetetraacetic acid sold under the name "TRILON B" .................................... 0.12 g
Ammonia solution (22°B strength) ................. 11 g
Thioglycolic acid .............................................. 0.6 g
Water...q.s.p. .................................................. 100 g

The pH of the composition is equal to 10.4.

100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied to 90% naturally white hair for 20 minutes at 25°C, this mixture imparts to the hair, after rinsing and shampooing, a pure blue coloration.

Example 8:

The following dyeing composition is prepared:

Compound of Example 1 ................................. 0.285 g
2,6-Dimethyl-para-phenylenediamine dihydrochloride ........................................ 0.209 g
Oxyethylenated oleyl alcohol containing two mols of ethylene oxide .............................. 4.5 g
Oxyethylenated oleyl alcohol containing four mols of ethylene oxide .............................. 4.5 g
Oxyethylenated oleylamine containing twelve mols of ethylene oxide, sold under the name "ETHOMLEN TO_{12}" by "ARMOUR HESS" .............................. 4.5 g
Dietanolamides of copra fatty acids .......... 9 g
Propylene glycol ................................ 4 g
2-Butoxyethanol ................................. 8 g
Ethanol (96° strength) ......................... 6 g
Pentasodium salt of diethylenetriaminepenta-
acetic acid, sold under the name
"MASQUOL DTPA" ............................... 2 g
Hydroquinone .................................. 0.15 g
Sodium bisulphite solution (35°B strength) ... 1.3 g
Ammonia solution (22°B strength) ............. 5 g
Water...q.s.p. .................................. 100 g

The pH of the composition is equal to 10.

100 g of hydrogen peroxide of 20 volumes strength
are added at the time of use.

When applied for 30 minutes at 28°C to hair which
has been bleached white beforehand, this mixture imparts
to the hair, after rinsing and shampooing, a slightly
purple, intense blue coloration.

Example 9:

The following dyeing composition is prepared:

Compound of Example 1 ......................... 0.012 g
Para-phenylenediamine ......................... 0.108 g
2,6-Dimethyl-para-phenylenediamine
dihydrochloride ................................. 0.0502 g
Para-aminophenol .............................. 0.155 g
2-Methyresorcinol .............................. 0.19 g
Meta-aminophenol .............................. 0.12 g

This mixture, applied to naturally white hair at 90%
strength, for 15 minutes at 35°C.
1-Phenyl-3-methylpyrazol-5-one ............... 0.09 g
3-(N-Methylamino)-4-nitrophenoxyethanol ...... 0.2 g
Oxyethyleneated nonylphenol containing four mols of ethylene oxide, sold under the name "CEMULSOL NP4" by "RHONE POULENC" ............... 12 g
Oxyethyleneated nonylphenol containing nine mols of ethylene oxide, sold under the name "CEMULSOL NP9" by "RHONE POULENC" ............... 15 g
Oxyethyleneated oleyl alcohol containing two mols of ethylene oxide ....................... 1.5 g
Oxyethyleneated oleyl alcohol containing four mols of ethylene oxide ....................... 1.5 g
Propylene glycol ................................ 6 g
Ethylenediaminetetraacetic acid sold under the name "TRILON B" .......................... 0.12 g
Ammonia solution (22°B strength) ................ 11 g
Mercaptosuccinic acid .......................... 0.2 g
Water...q.s.p. ................................ 100 g

The pH of the composition is equal to 10.4.

75 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied for 25 minutes at 30°C to hair which has been bleached white beforehand, this mixture imparts to the hair, after rinsing and shampooing, a golden sandy coloration.

Example 10:

The following dyeing composition is prepared:
Compound of Example 2 .......................... 0.065 g
Para-phenylenediamine .......................... 0.2 g
Para-aminophenol .............................. 0.4 g
N-Methyl-para-aminophenol sulphate ............... 0.31 g
2-Methylresorcinol .............................. 0.3 g
Meta-aminophenol ............................... 0.405 g
2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol .... 0.08 g
3-(N-Methylamino)-4-nitrophenoxo-ethanol .......... 0.5 g
Oxyethyleneated oleyl alcohol containing two mols of ethylene oxide .............. 4.5 g
Oxyethyleneated oleyl alcohol containing four mols of ethylene oxide .............. 4.5 g
Oxyethyleneated oleylamine containing two mols of ethylene oxide, sold under the name "ETHOMEEN TO12" by "ARMOUR HESS" .... 4.5 g
Diethanolamides of copra fatty acids ................ 9 g
Propylene glycol ................................ 4 g
2-Butoxyethanol ................................ 8 g
Ethanol (96° strength) ............................ 6 g
Pentasodium salt of diethylenetriaminepenta-acetic acid, sold under the name "MASQUOL DIPA" .... 2 g
Hydroquinone .................................. 0.15 g
Sodium bisulphite solution (35°B strength) .......... 1.3 g
Ammonia solution (22°B strength) ................... 8 g
Water... q.s.p. .................................. 100 g

The pH of the composition is equal to 10.5.

80 g of hydrogen peroxide of 20 volumes strength
are added at the time of use.

When applied for 35 minutes at 30°C to hair which has been bleached straw blond beforehand, this mixture imparts to the hair, after rinsing and shampooing, a medium chestnut coloration with a coppery sheen.

**Example II:**

The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound of Example 1</td>
<td>0.52 g</td>
</tr>
<tr>
<td>Para-phenylenediamine</td>
<td>0.6 g</td>
</tr>
<tr>
<td>Para-aminophenol</td>
<td>0.8 g</td>
</tr>
<tr>
<td>4-[N,N-Di-(β-hydroxyethyl)-amino]-aniline dihydrochloride</td>
<td>1 g</td>
</tr>
<tr>
<td>Meta-aminophenol</td>
<td>0.5 g</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>1.54 g</td>
</tr>
<tr>
<td>3-Nitro-4-aminophenol</td>
<td>0.6 g</td>
</tr>
<tr>
<td>Oxyethyleneated oleyl alcohol containing two mols of ethylene oxide</td>
<td>4.5 g</td>
</tr>
<tr>
<td>Oxyethyleneated oleyl alcohol containing four mols of ethylene oxide</td>
<td>4.5 g</td>
</tr>
<tr>
<td>Oxyethyleneated oleylamine containing twelve mols of ethylene oxide</td>
<td>4.5 g</td>
</tr>
<tr>
<td>&quot;ETHOMEEN T012&quot; by &quot;ARMOUR HESS&quot;</td>
<td>4.5 g</td>
</tr>
<tr>
<td>Diethanolamides of copra fatty acids</td>
<td>9 g</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>4 g</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>8 g</td>
</tr>
<tr>
<td>Ethanol (96° strength)</td>
<td>6 g</td>
</tr>
<tr>
<td>Pentasodium salt of diethylenetriaminepenta-</td>
<td></td>
</tr>
</tbody>
</table>

indicated in Claim 1.
acetic acid, sold under the name "MASQUOL DTPA" 2 g
Thioglycolic acid ........................................ 0.5 g
Ammonia solution (20°B strength) .................... 10 g
Water...q.s.p. .................................................. 100 g

The pH of the composition is equal to 10.3.

100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied for 30 minutes at 28°C to hair which has been bleached deep blond, this mixture imparts to the hair, after rinsing and shampooing, a brown coloration.

Example 12:

The following dyeing composition is prepared:

Compound of Example 2 ................................. 0.04 g
Para-phenylenediamine ................................ 0.955 g
Ortho-aminophenol ................................. 0.375 g
Resorcinol ............................................ 0.09 g
Meta-aminophenol ................................. 0.155 g
2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol .. 1.12 g
Cetyl/stearyl alcohol sold under the name
"ALFOL Cl6/18 E" by "CONDIA" ....................... 19 g
2-Octyldodecanol sold under the name "ENTANOL G"
by "HENKEL" ............................................ 4.5 g
Cetyl/stearyl alcohol containing fifteen mols
of ethylene oxide, sold under the name
"MERTITAL CS 15/E" by "HENKEL" ...................... 2.5 g
Ammonium lauryl-sulphate containing 30% of

or the corresponding salts with acids, in which formula R₁,
R₂ and R₃ are identical or different and represent a
active ingredient ........................................ 12 g
Polymer based on repeat units of the formula

\[
\begin{aligned}
\left( \begin{array}{c}
\text{N} \\
\text{CH}_3 \\
\text{CH}_2 \\
\text{Cl}
\end{array} \right)
& \left( \begin{array}{c}
\text{N} \\
\text{CH}_3 \\
\text{CH}_2 \\
\text{Cl}
\end{array} \right) \\
& \left( \begin{array}{c}
\text{N} \\
\text{CH}_3 \\
\text{CH}_2 \\
\text{Cl}
\end{array} \right)
\end{aligned}
\]

.......................................................... 4 g
Benzyl alcohol .............................................. 2 g
Ammonia solution (220B strength) .................. 11 g
Ethylenediaminetetraacetic acid sold under
the name "TRILON B" ................................. 1 g
Sodium bisulphite solution (d=1.3) ............... 1.2 g
Water... q.s.p. ............................................ 100 g

The pH of the composition is equal to 10.2.
100 g of hydrogen peroxide of 20 volumes strength
are added at the time of use.

When applied for 20 minutes at 25°C to hair which
has been bleached straw yellow, this mixture imparts to
the hair, after rinsing and shampooing, a purple-black
coloration.

Example 12:

The following dyeing composition is prepared:

Compound of Example 1 .............................. 0.1 g
Para-phenylenediamine ............................. 0.31 g
Para-aminophenol ................................. 0.4 g
4-((N-Methylamino)-phenol sulphate ............ 0.4 g
Resorcinol ............................................ 0.5 g
Meta-aminophenol ............................... 0.3 g
2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol ... 0.41 g
2-Isopropyl-6-nitroaniline .................. 0.81 g
Cetyl/stearyl alcohol sold under the name "ALFOL C16/18 E" by "CONDEA" .............. 8 g
Sodium cetyl-/stearyl-sulphate sold under the name "LANETTE WAX E" by "HENKEL" .......... 0.5 g
Oxyethyleneated castor oil sold under the name "CEMULSOL B" by "RHÔNE POUENC" ............ 1 g
Oleyl diethanolamide .......................... 1.5 g
Pentasodium salt of diethylenetriaminepenta-acetic acid, sold under the name "MASQUOL DTPA" 2.5 g
Thioglycolic acid ......................... 0.5 g
Hydroquinone ................................. 0.15 g
Ammonia solution (22°B strength) ........... 11 g
Water .......... q.s.p. .......................... 100 g

The pH of the composition is equal to 10.4.

100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied for 30 minutes at 30°C to hair which has been bleached white, this mixture imparts to the hair, after rinsing and shampooing, a coppery medium chestnut coloration.

**Example 14:**

The following dyeing composition is prepared:

Compound of Example 1 .................. 0.0143 g
4-[N-(β-Methoxyethyl)-amino]-aniline dihydro-chloride .......................... 0.0120 g
Acrylic acid polymer having a molecular weight of 2 to 3 million, sold under the name "CARBOPOL 934" by "GOODRICH CHEMICAL CO" .......... 1.5 g
Ethanol (96° strength) ........................................ 11 g
2-Butoxyethanol ........................................... 5 g
Trimethylcetylammonium bromide ...................... 1 g
Ethylenediaminetetraacetic acid sold under the name "TRILON B" ............................................. 0.1 g
Ammonia solution (22°B strength) ...................... 10 g
Thioglycolic acid ........................................... 0.2 g
Water...q.s.p. .............................................. 100 g

The pH of the composition is equal to 10.2.

20 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied for 30 minutes at 30°C to hair which has been bleached white, this mixture imparts to the hair, after rinsing and shampooing, a silvery light turquoise-blue coloration.

Example 15:

The following dyeing composition is prepared:

Compound of Example 1 ............................. 0.055 g
Para-phenylenediamine ............................. 0.058 g
Para-aminophenol ................................. 0.5 g
Resorcinol ........................................... 0.4 g
Meta-aminophenol ................................ 0.103 g
2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol ... 0.05 g
3-Nitro-4-(N-methylamino)-N,N-di-(β-hydroxy-
ethyl-aniline ................................................. 0.31 g
Oxyethyleneated nonylphenol containing four
mols of ethylene oxide, sold under the name
"REMCOPAL 334" by "GERLAND" ......................... 12 g
Oxyethyleneated nonylphenol containing nine
mols of ethylene oxide, sold under the name
"REMCOPAL 349" by "GERLAND" ......................... 15 g
Oxyethyleneated oleyl alcohol containing two
mols of ethylene oxide ................................... 1.5 g
Oxyethyleneated oleyl alcohol containing four
mols of ethylene oxide ................................... 1.5 g
Propylene glycol ............................................ 6 g
Sodium bisulphite solution (35°B strength) ........ 1.2 g
Ethylenediaminetetraacetic acid sold under
the name "TRILON B" ........................................ 0.12 g
Triethanolamine ............................................. pH 8.5
Water, q.s.p ................................................. 100 g

70 g of hydrogen peroxide of 20 volumes strength
are added at the time of use.

When applied for 25 minutes at 28°C to hair which
has been bleached white, this mixture imparts to the
hair, after rinsing and shampooing, a hazel coloration.

**Example 16**

The following dyeing composition is prepared:

- Compound of Example 1 ................................. 1.3 g
- Para-phenylenediamine .............................. 1.61 g
- Para-aminophenol .................................. 0.8 g
2,4-Diaminophenoxy-ethanol dihydrochloride .... 0.2 g
2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol .. 0.803 g
Resorcinol ........................................ 0.81 g
Meta-aminophenol .................................. 0.9 g
Oxyethyleneated nonylphenol containing four mols of ethylene oxide, sold under the name "CEMULSOL NP4" by "RHONE POULENC" 21 g
Oxyethyleneated nonylphenol containing nine mols of ethylene oxide, sold under the name "CEMULSOL NP9" by "RHONE POULENC" 24 g
Oleic acid ........................................... 4 g
2-Butoxyethanol .................................... 3 g
Ethanol (96° strength) ............................. 10 g
Pentasodium salt of diethylenetriaminepentaacetic acid, sold under the name "MASQUOL DTPA" 2.5 g
Thioglycolic acid .................................. 0.6 g
Ammonia solution (22°B strength) .................. 10 g
Water...q.s.p. .................................... 100 g

The pH of the composition is equal to 9.5.
120 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied for 25 minutes at 28°C to hair which has been bleached straw yellow, this mixture imparts to the hair, after rinsing and shampooing, a raven black coloration.

Example 17:
The following dyeing composition is prepared:
<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound of Example 1</td>
<td>0.252 g</td>
</tr>
<tr>
<td>4-[(β-Methoxyethyl)-amino]aniline dihydrochloride</td>
<td>0.6 g</td>
</tr>
<tr>
<td>2,6-Dimethyl-para-phenylenediamine dihydrochloride</td>
<td>0.2 g</td>
</tr>
<tr>
<td>Para-aminophenol</td>
<td>0.6 g</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>0.905 g</td>
</tr>
<tr>
<td>Meta-aminophenol</td>
<td>0.435 g</td>
</tr>
<tr>
<td>2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol</td>
<td>0.2 g</td>
</tr>
<tr>
<td>6-Hydroxybenzomorpholine</td>
<td>0.435 g</td>
</tr>
<tr>
<td>2-Methyl-4-amino-5-nitrophenol</td>
<td>0.703 g</td>
</tr>
<tr>
<td>Oxyethyleneated nonylphenol containing four mols of ethylene oxide, sold under the name &quot;CEMULSOL NP4&quot; by &quot;RHONE POULENC&quot;</td>
<td>12 g</td>
</tr>
<tr>
<td>Oxyethyleneated nonylphenol containing nine mols of ethylene oxide, sold under the name &quot;CEMULSOL NP9&quot; by &quot;RHONE POULENC&quot;</td>
<td>15 g</td>
</tr>
<tr>
<td>Oleyl alcohol containing two mols of ethylene oxide</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Oleyl alcohol containing four mols of ethylene oxide</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>6 g</td>
</tr>
<tr>
<td>Ethylenediaminetetraacetic acid sold under the name &quot;TRILON B&quot;</td>
<td>0.12 g</td>
</tr>
<tr>
<td>Ammonia solution (22°B strength)</td>
<td>11 g</td>
</tr>
<tr>
<td>Thioglycolic acid</td>
<td>0.6 g</td>
</tr>
<tr>
<td>Water... q.s.p.</td>
<td>100 g</td>
</tr>
</tbody>
</table>
The pH of the composition is equal to 9.9. 100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied to 90% naturally white hair for 30 minutes at 30°C, this mixture imparts to the hair, after rinsing and shampooing, a coppery light chestnut coloration.

Example 18:

The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound of Example 1</td>
<td>0.306 g</td>
</tr>
<tr>
<td>Para-phenylenediamine</td>
<td>0.307 g</td>
</tr>
<tr>
<td>4-[N-(β-Methoxyethyl)-amino]-aniline dihydrochloride</td>
<td>0.15 g</td>
</tr>
<tr>
<td>2-Methylresorcinol</td>
<td>0.405 g</td>
</tr>
<tr>
<td>2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol</td>
<td>0.115 g</td>
</tr>
<tr>
<td>2,4-Diaminophenoxy-ethanol dihydrochloride</td>
<td>0.106 g</td>
</tr>
<tr>
<td>2-Amino-3-nitrophenol</td>
<td>0.203 g</td>
</tr>
<tr>
<td>Cetyl/stearyl alcohol sold under the name</td>
<td></td>
</tr>
<tr>
<td>&quot;ALFOL Cl6/18 E&quot; by &quot;CONDEA&quot;</td>
<td>8 g</td>
</tr>
<tr>
<td>Sodium cetyl-/stearyl-sulphate sold under the name &quot;LANETTE WAX E&quot; by &quot;HENKEL&quot;</td>
<td>0.5 g</td>
</tr>
<tr>
<td>Oxyethyleneated castor oil sold under the name &quot;CEMULSOL B&quot; by &quot;RHONE POULENC&quot;</td>
<td>1 g</td>
</tr>
<tr>
<td>Oleyl diethanolamide</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Pentasodium salt of diethylenetriaminepenta-acetic acid, sold under the name &quot;MASQUOL DTPA&quot;</td>
<td>2.5 g</td>
</tr>
<tr>
<td>Thioglycolic acid</td>
<td>0.5 g</td>
</tr>
</tbody>
</table>
Hydroquinone ........................................ 0.15 g
Ammonia solution (22°B strength) .............. 11 g
Water... q.s.p. ..................................... 100 g

The pH of the composition is equal to 10.3.

90 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied to 90% naturally white hair for 25 minutes at 25°C, this mixture imparts to the hair, after rinsing and shampooing, a charcoal grey coloration.

Example 19:

The following dyeing composition is prepared:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound of Example 2</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Compound of Example 1</td>
<td>0.42 g</td>
</tr>
<tr>
<td>Para-phenylenediamine</td>
<td>0.62 g</td>
</tr>
<tr>
<td>4-[N,N-Di-(β-hydroxyethyl)-amino]-aniline dihydrochloride</td>
<td>0.42 g</td>
</tr>
<tr>
<td>Para-aminophenol</td>
<td>3.705 g</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>0.81 g</td>
</tr>
<tr>
<td>2-Methyl-5-[N-(β-hydroxyethyl)-amino]-phenol</td>
<td>0.21 g</td>
</tr>
<tr>
<td>2-Amino-3-nitrophenol</td>
<td>0.61 g</td>
</tr>
<tr>
<td>Cetyl/stearyl alcohol sold under the name &quot;ALFOL C16/18 E&quot; by &quot;CONDEA&quot;</td>
<td>8 g</td>
</tr>
<tr>
<td>Sodium cetyl-/stearyl-sulphate sold under the name &quot;LANETTE WAX E&quot; by &quot;HENKEL&quot;</td>
<td>0.5 g</td>
</tr>
<tr>
<td>Oxyethyleneated castor oil sold under the name &quot;CENULSOL B&quot; by &quot;RHONE POULENCE&quot;</td>
<td>1 g</td>
</tr>
<tr>
<td>Oleyl diethanolamide</td>
<td>1.5 g</td>
</tr>
</tbody>
</table>
Pentasodium salt of diethylenetriaminepenta-acetic acid, sold under the name "MASQUOL DTPA" 2.5 g
Thioglycolic acid................................. 0.5 g
Hydroquinone .................................. 0.15g
Ammonia solution (22°B strength) ............ 11 g
Water... q.s.p. .................................. 100 g

The pH of the composition is equal to 10.1.

100 g of hydrogen peroxide of 20 volumes strength are added at the time of use.

When applied to 90% naturally white hair for 20 minutes at 28°C, this mixture imparts to the hair, after rinsing and shampooing, a very dark brown coloration.

Of course, the embodiments referred to above in no way imply a limitation and will be able to form the subject of any desirable modifications without thereby going outside the scope of the invention.

Example 20:

The following dyeing composition is prepared:

Compound of example 2bis......................... 0.496 g
Para-aminophenol ................................. 0.218 g
Butyl glycol ..................................... 5 g
Diethylenated lauric alcohol containing 10.5 mols of ethylene oxide .................... 5 g
Ammonia at 22°B strength ......................... 6 g
Water ... q.s.p. .................................. 100 g

The pH is equal to 10.3.

At the time of use, 25 g of oxygenated water of 20 volumes strength are added.
This mixture, applied to naturally white hair at 90% strength, for 15 minutes at 25°C, imparts to the hair a rosewood colour, after rinsing and shampooing.

Example 21:
The following dyeing composition is prepared:

- Compound of example 2ter .................. 1.57 g
- Para-aminophenol ......................... 0.55 g
- 2-butoxy ethanol ......................... 8 g
- Propylene glycol ......................... 8 g
- Carboxymethyl cellulose .................. 2 g
- Ammonium lauryl sulphate ............... 5 g
- Pentasodium salt of diethylene-triamine-penta-acetic acid, sold under the name "MASQUOL DTPA" 2 g
- Thioglycolic acid ......................... 0.4 g
- Ammonia at 22° B strength ................ 10 g
- Water ... q.s.p. ....................... 100 g

The pH of the composition is equal to 9.8.

At the time of use, 100 g of oxygenated water at 20 volumes strength are added.

This mixture, applied to naturally white hair at 90% strength for 30 minutes at ambient temperature, confers to it a sustained rosewood coloration, after rinsing and shampooing.
The following dyeing composition is prepared:

- **Hair**: at 90% volume, 100 g of dye is applied to the hair at 20 volumes.

- **Forming and Holding**: at 8 volumes, 5.5 g of holding is added.

- **Construction**: at 8 volumes, 2 g of holding is added.

- **Precipitating**: at 8 volumes, 0.4 g of precipitating is added.

- **Stabilizing**: at 8 volumes, 0.5 g of stabilizing is added.

The following cycling composition is prepared:

- **Rinsing**: at 8 volumes, 2 g of rinsing is added.

The following washing composition is prepared:

- **Water**: at 10 volumes, 0.12 g of water is added.

The following treatment composition is prepared:

- **Treatment**: at 1 volume, 0.12 g of treatment is added.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Chemical compound of the general formula (I):

\[
\text{OZ} \quad \text{NH}_2 \\
\text{NH}_2
\]

in which formula Z represents either a polyhydroxyalkyl radical in which the alkyl group contains from 3 to 6 carbon atoms, the said radical containing 2 or 3 hydroxyl groups, or an alkyl chain interrupted by at least one oxygen atom and containing at least one to three hydroxyl groups, the said alkyl chain containing from 4 to 8 carbon atoms, or the corresponding salts with acids.

2. Compound according to Claim 1, characterised in that Z represents a \(\beta\)-(\(\beta\')-hydroxyethoxy)-ethyl radical.

3. Compound according to Claim 1, characterised in that Z represents a \(\beta\),\(\gamma\)-dihydroxypropyl radical.

4. Process for the preparation of the compounds according to one of Claims 1 to 3, characterised in that a halogen derivative of the formula X-Z, X being a halogen and Z having the meanings indicated in Claim 1 for the definition of the general formula (I), is reacted with an alkali metal salt of 2-acetylamino-4-nitrophenol so as to condense the radical Z onto the nucleus, an alkali metal halide being eliminated, the nitro group of the product obtained is then reduced and, finally, the product is deacetylated to obtain a compound of the formula (I) as
indicated in Claim 1.

5. Process according to Claim 4, characterised in that the halogen \( X \) is chlorine and in that the alkali metal of the phenate used as the starting material is potassium.

6. Process according to one of Claims 4 or 5, characterised in that the reduction of the nitro group is carried out in alcoholic solution, under reflux, by means of zinc powder in the presence of ammonium chloride.

7. Dyeing composition for keratin fibres, and in particular for hair, the said composition containing at least one oxidation base, in a cosmetically acceptable carrier, characterised in that it contains, as the coupler, at least one compound of the formula \((\text{I})\) or a corresponding salt with an acid.

8. Composition according to Claim 7, characterised in that the meta-phenylenediamines of the formula \((\text{I})\) are present therein in a proportion of between 0.001 and 2.85% by weight, relative to the total weight of the composition.

9. Composition according to one of Claims 7 or 8, characterised in that it contains, as the oxidation base, at least one para-phenylenediamine of the general formula \((\text{II})\):

\[
\begin{align*}
\text{N} & \quad \text{R}_5 \\
\text{R}_1 & \quad \text{R}_4 \\
\text{R}_2 & \quad \text{R}_3 \\
\text{NH}_2 & \quad \text{R}_6
\end{align*}
\]
or the corresponding salts with acids, in which formula $R_1$, $R_2$ and $R_3$ are identical or different and represent a hydrogen atom, an alkyl radical having from 1 to 4 carbon atoms or an alkoxy radical having from 1 to 2 carbon atoms, and $R_4$ and $R_5$ are identical or different and represent a hydrogen atom, an alkyl or hydroxyalkyl radical, an alkoxyalkyl radical in which the alkoxy group contains from 1 to 2 carbon atoms, or a carbamylalkyl, mesylaminoalkyl, aminalkyl, monoalkylaminoalkyl, dialkylaminoalkyl, piperidinoalkyl or morpholinoalkyl radical, the alkyl groups in $R_4$ and $R_5$ having from 1 to 4 carbon atoms, or alternatively $R_4$ and $R_5$ form a piperidino or morpholino group together with the nitrogen atom to which they are attached, with the proviso that $R_1$ and $R_3$ represent a hydrogen atom if $R_4$ and $R_5$ do not represent a hydrogen atom.

11. Composition according to one of Claims 7 to 9, characterised in that it contains, as the oxidation base, at least one para-aminophenol of the general formula (III):

```
       OH
      /  \      R_6
     /    \     \\
   NH_2   N
```

or the corresponding salts with acids, in which formula $R_6$ represents a hydrogen atom, an alkyl radical containing from 1 to 4 carbon atoms or a halogen atom.

11. Composition according to one of Claims 7 to 10, characterised in that it contains at least one heterocyclic base as the oxidation base.
12. Composition according to Claim 11, characterised in that it contains, as the oxidation base, 2,5-diamino-pyridine and/or 3-methyl-7-aminobenzomorpholine and/or 5-aminoindole.

13. Composition according to one of Claims 7 to 12, characterised in that it contains at least one coupler taken from the group comprising resorcinol, 2-methyl-resorcinol, meta-aminophenol, 2-methyl-5-aminophenol, 2-methyl-5-[N-(β-hydroxyethyl)-amino]-phenol, 6-hydroxy-benzomorpholine, 2,6-dimethyl-3-acetyaminophenol, 2-methyl-5-carbethoxyaminophenol, 2-methoxy-5-carbethoxyaminophenol, 2-methyl-5-ureidophenol and 1-phenyl-3-methylpyrazol-5-one.

14. Composition according to one of Claims 7 to 13, characterised in that it contains ortho-diphenol or at least one ortho-phenylenediamine or at least one ortho-aminophenol optionally containing substituents on the nucleus or on the amine groups.

15. Composition according to one of Claims 7 to 14, characterised in that it contains at least one dyestuff precursor of the benzene series, containing, on the nucleus, at least three substituents chosen from hydroxyl, methoxy or amino groups.

16. Composition according to one of Claims 7 to 15, characterised in that it contains at least one dyestuff precursor of the naphthalene series.
17. Composition according to one of Claims 7 to 16, characterised in that it contains at least one leuco-derivative of indoaniline or of indophenol.

18. Composition according to one of Claims 7 to 17, characterised in that it contains at least one direct dye-stuff.

19. Composition according to one of Claims 7 to 18, characterised in that its pH is between 8 and 11.5.

20. Composition according to Claim 19, characterised in that it contains, as the alkalising agent, at least one product taken from the group comprising ammonia, alkylamines, alkanolamines, alkylalkanolamines, sodium hydroxide or potassium hydroxide and alkali metal carbonates.

21. Composition according to Claim 19, characterised in that it contains at least one acidifying agent taken from the group comprising lactic acid, acetic acid, tartaric acid and phosphoric acid.

22. Composition according to one of Claims 7 to 21, characterised in that its cosmetically acceptable carrier comprises, apart from water, at least one product taken from the group comprising surface-active agents, organic solvents, thickening products, antioxidants, penetrating agents, foaming agents, sequestering agents, film-forming products, treating agents and perfumes.

23. Composition according to Claim 22, characterised
in that it contains at least one surface-active agent taken from the group comprising alkylbenzenesulphonates, alkyl-
naphthalenesulphonates, the sulphates, ether-sulphates and sulphonates of fatty alcohols, quaternary ammonium salts, fatty acid diethanolamides, polyoxyethyleneated or polygly-
cerolated alkylphenols.

24. Composition according to one of Claims 22 or 23, characterised in that it contains from 0.5 to 55% by weight of surface-active agents, relative to the total weight of the composition.

25. Composition according to Claim 22, characterised in that it contains at least one organic solvent taken from the group comprising ethanol, isopropanol, glycerol, glycols and their ethers and diethylene glycol and its ethers.

26. Composition according to one of Claims 22 or 25, characterised in that it contains from 1 to 40% by weight of organic solvent(s), relative to the total weight of the composition.

27. Composition according to Claim 22, characterised in that it contains at least one thickening product taken from the group comprising sodium alginate, gum arabic, cellulose derivatives, acrylic acid polymers and bentonite.

28. Composition according to one of Claims 22 or 27, characterised in that it contains between 0.5 and 5% by weight of thickener(s), relative to the total weight of the composition.
Composition according to Claim 22, characterised in that it contains at least one antioxidant taken from the group comprising sodium sulphite, thioglycolic acid, mercaptosuccinic acid, sodium bisulphite, ascorbic acid and hydroquinone.

Composition according to one of Claims 22 or 29, characterised in that it contains between 0.05 and 1.5% of antioxidant(s), relative to the total weight of the composition.

Hair-dyeing process using a dyeing composition according to one of Claims 7 to 30, characterised in that a composition according to one of Claims 7 to 29 is mixed with an oxidising agent, in that the said mixture is then applied to the hair, in that the said mixture is left to act on the hair for a period of between 5 and 45 minutes, and in that the hair is rinsed, optionally shampooed and rinsed again, and dried.

Process according to Claim 31, characterised in that the oxidising agent mixed with the composition is taken from the group comprising hydrogen peroxide, urea peroxide and per-salts.

Process according to one of Claims 31 or 32, characterised in that the composition mixed with the oxidising
The following dyeing composition is prepared:

agent is presented in the form of a liquid, a cream, a gel or an aerosol.

DATED this 9th day of October, 1984.

L'OREAL

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JM:BB