OXIDATION DYES COMPRISING AROMATIC DIAMINES AND COUPLING COMPONENTS

Karl-Josef Boosen, Düsseldorf-Holthausen, and Peter Berth, Düsseldorf-Benrath, Germany, assignors to Theranemisch Chemische Therapeutische Gesellschaft m.b.H., Düsseldorf, Germany

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14 Claims

ABSTRACT OF THE DISCLOSURE

A composition for treatment of human hair comprising a substantially 0.1 to 5.0 weight percent aqueous solution of a developer plus a coupling agent in quantities ranging from substantially equimolar to a slight excess of the developer; said developer having the formula

![Chemical Structure](image)

wherein R1 and R2 individually are selected from the group consisting of hydrogen, lower hydroxyalkyls, beta methyl sulfonamidoethyl, hydroxyethyls, lower alkyls and interconnected lower alkyls; R3 is selected from the group consisting of hydrogen, lower alkyl and lower alkoxy; R4 is lower alkyl; and X is selected from the group consisting of —COOH, —SO3H, —PO3H2 and —PO4H2, their water soluble salts, their acid amides and esters with aliphatic alcohols having 1–4 carbon atoms; said coupling agent being selected from the group consisting of o- and m-phenylenediamine; o- and m-amino phenol; o- and m-toluylenediamine; o-anisidine; 2,4-diaminoanisole; 2,4-diaminoxanisole; 2,4-diaminophenol; pyrogallol; resorcinol; pyrocatechol; alphametaphthol; amioresorcinol; 1,5 - aminoxyderynaphthalene; and 1,8-diaminodihydroxyphenanthrene; and a method for use thereof.

The invention relates to agents and compositions for the dyeing of hair. More particularly, it relates to such agents based on oxidation dyes and is suited for the dyeing of human hair, especially living human hair.

The use of oxidation dyes for the coloring of human hair has long been known. The coloring components used frequently are aromatic diamines, especially p-phenylenediamine, with or without such known coupling components as phenol. These compounds are converted on the hair into dyes by oxidation either by the influence of atmospheric oxygen or particularly with chemical oxidizers such as hydrogen peroxide.

These known hair dyeing agents have the disadvantage that they can be removed from the hair only with difficulty. Moreover, phenylene diamines have undesirable physiological effects on susceptible persons.

It is the object of the invention to devise hair coloring agents based on oxidation dyes which are free of these drawbacks. The object is attained by employing coloring agents for use on human hair, including living hair which are based on oxidation dyes characterized by a content of compounds having the generic Formula 1

![Chemical Structure](image)

wherein R1 and R2 individually denote hydrogen or lower alkyls which may be interconnected or substituted; R3 is hydrogen or a lower alkyl or alkoxy; R4 is a lower alkyl; and X is a hydrophilic π-electron containing group.

These compounds of Formula 1 further are bound to coupling components or agents for the purpose of dyeing hair.

Groups containing hydrophilic π-electrons usable for the purpose at hand are —COOH, —SO3H, —PO3H2 and —PO4H2 under certain conditions in the form of their water soluble salts or in the form of the corresponding acid amides or esters of lower aliphatic alcohols having 1–4 carbon atoms.

When the groups containing hydrophilic π-electrons are used in the form of their water-soluble salts, especially their alkali salts are of advantage, i.e., their sodium and potassium salts, also the ammonium salts and those formed with organic bases, especially mono-, di- and triethanolamine.

The alkyl radicals in the compounds named as Formula 1, which hereinafter will be referred to as developer components, may be linear or branched. Preferred substituted alkyl radicals are hydroxyalkyl or beta-methylsulfonamidoethyl groups. "Lower alkyls" are those in the present case which contain 1–5 carbon atoms, and preferably 1 to 3. Preferred compounds are those wherein R1 and, under certain conditions, also R2 are alkyl, and R3 is hydrogen. If, however, R2 and/or R3 are hydrogen, the preferred compounds are those wherein R1 is an alkyl or alkoxy.

As stated, R2 and R3 may be interconnected and form a heterocyclic ring with the neighboring nitrogen atoms. Numerous compounds may act as coupling components for oxidation hair dyes. Particularly suited are aromatic amines and diamines, also phenols, naphthols, polyphenols and aminophenols. Of the diamines, aminophenols and phenols, ortho- and meta-compounds are preferred. The following are applicable:

- o- and m-phenylenediamine
- o- and m-anisidine
- 2,4-diaminophenol
- 2,4-diaminoanisole
- o- and m-toluidinediamine
- 2,4-diaminophenol
- pyrogallol
- resorcinol
- pyrocatechol
- aminoresorcinol
- 1,5 - 1,8-diaminodihydroxyphenanthrene

Other coupling components which preferably are employed are heterocyclic methylene couplers, i.e., compounds which contain in the heterocyclic radical a methylene group contiguous to the keto group, such as pyrazolones; furthermore so-called "open-chain methylene couplers," i.e., compounds which contain a methylene group contiguous to the keto group in the aliphatic chain, e.g., aroyl- and acylacetic acid derivatives. Suitable compounds of this type are

- 3-methylpyrazolone-(5)
- 1-phenyl-3-methylpyrazolone-(5)
- 1,3-dimethylpyrazolone-(5)
- acetoacetic acid anilide
- benzoylacetylanilide
- benzoacetonolide
- nicotinoylacetanilide

The coupling components opportunistically are employed in essentially molar quantities with respect to the developer components. However, it generally is not harmful to have the latter present in a certain excess.
Coloring of the hair can be developed, as with other oxidation dyes, by the action of atmospheric oxygen or of chemical oxidizers, such as hydrogen peroxide or its addition products, especially on urea, melamine or sodium borate.

Dyeing of the hair is carried out at temperatures of substantially 15-40°C, preferably at room temperature.

The dyes can be applied in the form of aqueous solutions, but it is preferred to use them in the form of creams or emulsions. For this purpose, the developer components can be mixed with any detergent or washing agent, especially those which are anionic or nonionic. Particularly suitable compounds are alkylbenzenesulfonates, alkylsulfonates, fatty acid ethanolamides, ethylene oxide additives on fatty acids and on fatty alcohols.

The coloring effect of the dyes named above is good in admixture with such detergents or washing agents. Thus, the hair dyes can be manufactured in the form of shampoos, particularly cream shampoos, which frequently is desired in practice.

The agents according to the invention furthermore may contain thickeners, e.g., methylcellulose, carboxymethylcellulose, starch, higher fatty alcohols, vaseline, paraffin oil or fatty acids; also perfumes, i.e., essential oils; and hair treating agents, such as pantothenic acid and cholesterol. It is a matter of course that the compatibility of all these additives named with the other components must be considered.

The additives are applied in the customary quantities. Detergents are used particularly in amounts of 0.5 to 30 weight percent, and thickeners in amounts of 0.1 to 25 weight percent, all calculated on the total composition. The concentration of the developer and coupling components, taken together, may be up to 5 percent, preferably 0.1 to 2 weight percent of the total composition.

The hair dyes according to the invention are employed preferably in an alkaline pH range, especially at a pH ranging from 8 to 9.5. They lead to colors which have good light-, wash- and rub-resistance (abrasion resistance) and, contrary to the commonly used agents based on oxidation dyes, can readily be removed from the hair by means of reducing agents such as sodium hydroxyethanesulfinate.

The developer components can be produced from the corresponding substituted diamines by reaction with halogenalkylcarboxylic acids or by reaction with SO₃ and aldehydes and further conversion into the corresponding amides or esters. The manufacture of derivatives containing phosphorus is carried out correspondingly by the reaction of substituted amines with hypophosphorous acid or with phosphorous acid and aldehydes or ketones.

The invention now will be further explained by the following examples. However, it should be understood that these are given merely by way of illustration, and not of limitation, and that changes may be made in the details without departing from the spirit and the scope of the invention as hereinafter claimed.

**EXAMPLE 1**

A solution was prepared consisting of 2 parts of a developer component having Formula 2

\[
\text{H}_2\text{C}_2\text{N}(-\text{CH}=-\text{SO}_2\text{H})\]

1 part alpha-naphthol and 0.5 part sodium sulfite in 80 parts water. The pH was adjusted with ammonia to 9.5, and the solution made up to 100 parts with water. Shortly before application, 4 parts 30% H₂O₂ were added thereto, and this solution applied for 20 minutes to naturally grey living human hair at room temperature. This was followed by rinsing and a thorough shampoo. A deep blue coloration thus was obtained.

**EXAMPLE 2**

A deep violet color was obtained when proceeding as in Example 1, but substituting an equal amount of 1-phenyl-3-methylpyrazolone-(5) for the alpha-naphthol.

**EXAMPLE 3**

The conditions of Example 1 were duplicated except that 2 parts of a developer component having Formula 3 were used and 1 part m-diaminoanisole in lieu of the alpha-naphthol. The solution dyed naturally grey hair to a strong purplish red color. The coloration was fully removed by a treatment with a 3% aqueous solution of sodium hydroxyethanesulfinate (Rongalit C).

**EXAMPLE 4**

The procedure followed was the same as in Example 1, but 2 parts of a developer component of Formula 4 and 1 part alpha-naphthol were used. Grey hair was dyed blueblack. The same color was obtained when the pH value was adjusted to 7 with ethanolamine in lieu of 9.5 with NH₃.

**EXAMPLE 5**

2 parts of a developer component having Formula 5

\[
\text{H}_2\text{C}_2\text{N}(-\text{CH}=-\text{SO}_2\text{H})\]

1 part alpha-naphthol as coupling component, 0.5 part sodium sulfite and 95 parts water were mixed to yield a dyeing solution which was adjusted to 9.5 with triethanolamine. Shortly before application, 8 parts melamine perhydrates were mixed into this solution and living naturally grey hair treated therewith for 15 minutes at room temperature. A deep blue color ensued.

**EXAMPLE 6**

A solution of 2 parts of a compound of Formula 6

\[
\text{HOCH}_2\text{CH}_3\]

1 part benzoylacetonilide and 1 part sodium sulfite in 90 parts water was thickened with 5 parts carboxymethylcellulose, adjusted to a pH of 9.5 with ammonia, and made up to 100 parts with water. The paste thus obtained was mixed with 8 parts melamine perhydrate and applied to grey hair for 20 minutes at room temperature. The hair assumed a yellowish orange color.

**EXAMPLE 7**

A cream was produced from the following ingredients:

<table>
<thead>
<tr>
<th>Parts</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty alcohols (C₁₆-C₁₈)</td>
<td>10</td>
</tr>
<tr>
<td>Fatty alcohol sulfate</td>
<td>10</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>0.5</td>
</tr>
<tr>
<td>Developer component (Formula 2)</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>70</td>
</tr>
</tbody>
</table>

The pH was adjusted to 9.5 with ammonia, and the mixture made up to 100 parts with water. 4 parts percarbamide were mixed into this cream, and the latter then applied to living human grey hair for 20 minutes at a temperature of 25°C. The hair became deep blue.
The procedure was identical with that given in the preceding example except that in lieu of 1 part alpha-naphthol, 1 part of one of the compounds named in the following table individually were used. The colors thus obtained on grey hair also are listed in the table. All colors could readily be removed from the hair by treatment with a reducing agent.

**TABLE**

<table>
<thead>
<tr>
<th>Coupling component:</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methylpyrazolone-(5)</td>
<td>Wine red.</td>
</tr>
<tr>
<td>1,3-dimethylpyrazolone-(5)</td>
<td>Bluish red.</td>
</tr>
<tr>
<td>1-methylpyrazolone-(5)</td>
<td>Wine red.</td>
</tr>
<tr>
<td>Acetoacetic acid anilide</td>
<td>Yellow-green.</td>
</tr>
<tr>
<td>Benzyloacetolactone-</td>
<td>Greenish yellow.</td>
</tr>
<tr>
<td>Nicotinoylacetic acid</td>
<td>Strong green-yellow.</td>
</tr>
<tr>
<td>1-beta-hydroxyethyl-3-methyl pyrazolone</td>
<td>Brownish red.</td>
</tr>
<tr>
<td>1,3-phenylpyrazolone-(5)</td>
<td>Wine red.</td>
</tr>
<tr>
<td>3-nicotinopyrazolone-(5)</td>
<td>Strong bluish wine red.</td>
</tr>
<tr>
<td>Acetacetic ester</td>
<td>Dull yellow-green.</td>
</tr>
<tr>
<td>Acetylacetone</td>
<td>Dull yellow-green.</td>
</tr>
<tr>
<td>Nicotinoylactetate</td>
<td>Yellowish green.</td>
</tr>
</tbody>
</table>

**EXAMPLE 9**

The developer component consisted of 2 parts of a compound of Formula 7, the coupler of 1 part resorcinol, the pH was adjusted to 8.5 with ammonia. Otherwise, the procedure as outlined in Example 1 was followed. Grey human hair attained a red-purple color.

\[ 
\text{CH}_3\text{SO}_3\text{NH} - \text{CH}_2\text{CH}_2\text{NH} - \text{CH}_2\text{SO}_3\text{H} 
\]

**EXAMPLE 10**

A hair dyeing cream was manufactured consisting of 10 parts fatty alcohol (C₁₂₋₁₈), 10 parts fatty alcohol sulfate obtained from coconut oil, 0.5 part sodium sulfite, 1 part alpha-naphthol, 70 parts water and 1 part of a developer component of Formula 8.

\[ 
\text{H}_3\text{C} \quad \text{N} \quad \text{CH} - \text{CH} - \text{P} - \text{O} - \text{H}_2
\]

The mixture was adjusted to a pH of 9.5 with ammonia and made up to 100 parts with water. 4 parts percarbamid were mixed in prior to use. Grey hair, treated with this cream for 20 minutes at room temperature obtained a deep blue color.

**EXAMPLE 11**

The composition of the hair cream prepared was the same as in Example 10, except that 1 part of a developer component of Formula 9 was used and 1 part 2,4-diaminoanisole as coupler. The cream was adjusted to a pH of 9 with ammonia. After addition of 8 parts melamine perhydrate, grey hair assumed a brown-red color after 20 minutes at room temperature.

**EXAMPLE 12**

1 part of a developer component of Formula 10, 1 part of resorcinol, 1 part sodium sulfite and 92 parts water were thickened with 5 parts carboxymethylcellulose and the paste obtained adjusted to a pH of 9.5 with ethanolamine. 4 parts percarbamid were admixed thereto, and the paste thus obtained applied to living grey human hair for 20 minutes. The hair thereby became purple-red.

**EXAMPLE 13**

When in the procedure as given in Example 3 the developer is replaced by 1 part of Formula 11, practically the same coloration is obtained.

A hair dyeing cream was produced from:

- **Parts**
  - Fatty alcohol sulfate (from coconut oil) ............ 10
  - Fatty alcohol (C₁₂₋₁₈) ............................... 10
  - Sodium sulfite ....................................... 0.5
  - Developer component Formula 12 ..................... 1
  - Alpha-naphthol ....................................... 1
  - Water .................................................. 70

The pH was adjusted to 9.0 with ethanolamine, and the mixture made up to 100 parts with water. After adding 4 parts percarbamid to the cream, the same was applied to grey hair for 20 minutes at 25°, and a deep blue coloration ensued.

We claim as our invention:

1. A composition for the oxidative treatment of human hair, said composition having good dyeing properties, light-, washing- and rub-resistance yet being readily removable from the hair by reducing treatment, which comprises a substantially 0.1-5 weight percent aqueous solution of a developer plus a coupling agent in mutual quantities ranging from substantially equimolar to a slight excess of said developer; said developer being a compound having the formula:

\[ 
\text{H}_3\text{C} \quad \text{N} \quad \text{CH} - \text{CH} - \text{S} \text{O}_3\text{H} \]

wherein R₁ and R₂ individually are selected from the group consisting of hydrogen, lower hydroxyalkyl, beta methyl sulfonamidoethyl and lower alkyl; R₃ is selected from the group consisting of hydrogen, lower alkyl and lower alkoxy; R₄ is lower alkyl; and X is selected from the group consisting of -COOH, -SO₃H, -PO₃H₂ and -PO₃H₂ their water-soluble salts, their acid amides and esters with aliphatic alcohols having 1-4 carbon atoms; said coupling agent being selected from the group consisting of o- and m-phenylenediamine; o- and m-aminophenol; o- and m-toluidinediamine; o-anisidine; 2,4-diaminoanisole; 2,4-diaminophenol; pyrogallol; resorcinol; pyrocatechol; alpha-naphthol; aminoresorcinol; 1,3-diaminohydroxynaphthalene; and 1,8-diaminohydroxynaphthalene.

2. The composition as defined in claim 1, wherein R₁ and R₂ are selected from the group consisting of hydrogen, lower alkyl and lower alkoxy.

3. The composition as defined in claim 1, wherein R₃ is hydrogen and R₄ is hydrogen.

4. The composition as defined in claim 1, wherein X is selected from the group consisting of -COOH, -SO₃H, -PO₃H₂ and -PO₃H₂.
5. The composition as defined in claim 1 wherein said composition also contains 0.5–30 weight percent of a nonionic or anionic detergent to act simultaneously as a shampoo.

6. The composition as defined in claim 4, also containing a thickener in an amount of 0.1–25 weight percent.

7. A process for the oxidative treatment of human hair with a compound having light-, washing- and rub-resistance, yet being readily removable from the hair, which comprises applying to said hair for approximately 15 to 30 minutes at a temperature ranging from substantially 15 to 40°C, a composition comprising a substantially 0.5 to 5 weight percent aqueous solution of a developer plus a coupling component in quantities relative to each other ranging from substantially equimolar to a slight excess of said developer; followed by rinsing of the hair; said developer being a compound having the formula

\[
R_1 \text{NH} - R_2 - X
\]

wherein \(R_1\) and \(R_2\) individually are selected from the group consisting of hydrogen, lower hydroxyalkyl, beta methyl sulfonamidoethyl, and lower alkyl; \(R_2\) is selected from the group consisting of hydrogen, lower alkyl and lower alkoxy; \(R_3\) is lower alkyl; and \(X\) is selected from the group consisting of \(-\text{COOH, } -\text{SO}_2\text{H, } -\text{PO}_3\text{H}_2\) and \(-\text{PO}_3\text{H}_2\), their water soluble salts, their acid amides and esters with aliphatic alcohols having 1–4 carbon atoms; said coupling agent being selected from the group consisting of \(o\)- and \(m\)-phenylenediamine; \(o\)- and \(m\)-aminophenol; \(o\)- and \(m\)-toluylenediamine; \(o\)-anisidine; \(2,4\)-diaminoanisole; \(2,4\)-diaminophenol; pyrogallol; resorcinol; pyrocatechol; alpha-naphthol; aminoresorcinol; 1,5-aminohydroxyanaphthalene; and 1,8-diaminohydroxyanaphthalene.

8. The process as defined in claim 7 wherein \(R_1\) and \(R_2\) are alkyl having 1–5 carbon atoms and \(R_3\) is hydrogen.

9. The process as defined in claim 7 wherein \(R_1\) and \(R_2\) are hydrogen and \(R_3\) is selected from the group consisting of lower alkyl and lower alkoxy.

10. The process as defined in claim 7 wherein \(X\) is selected from the group consisting of \(-\text{COOH, } -\text{SO}_2\text{H, } -\text{PO}_3\text{H}_2\) and \(-\text{PO}_3\text{H}_2\).

11. The process as defined in claim 7 wherein said treatment is induced by atmospheric oxygen.

12. The process as defined in claim 7 wherein said oxidative treatment is induced by a compound selected from the class consisting of \(\text{H}_2\text{O}_2\), percarbonide, melamine perhydrate, and sodium perborate.

13. The composition according to claim 1 wherein said developer is

\[
\begin{align*}
\text{CH}_3 \text{CH}_2 \text{NH-CH-SO_2H} \\
\text{O} \text{H}_2 \text{CH}_3 \\
\end{align*}
\]

14. The process according to claim 7 wherein said developer is

\[
\begin{align*}
\text{CH}_3 \text{CH}_2 \text{NH-CH-SO_2H} \\
\text{O} \text{H}_2 \text{CH}_3 \\
\end{align*}
\]

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V. C. CLARKE, Assistant Examiner

U.S. Cl. X.R.

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