AZO COMPOUNDS FOR DYEING HUMAN HAIR

Karl-Josef Boosen, Dusseldorf-Holthausen, Germany, assignor to Therachemisch chemische therapeutische Gesellschaft m.b.H., Dusseldorf, Germany

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ABSTRACT OF THE DISCLOSURE

Agents for dyeing of human hair which are of the directly fixing type and are applicable at room temperature. The active ingredients are substituted aminobenzenes and can be combined, if desired, with other direct dyes, such as anthraquinone dyes. The dyestuffs preferably are applied in the form of a neutral to slightly alkaline cream which additionally may contain a shampoo, permanent waving agents, perfumes, and mixtures thereof.

The invention relates to agents for the dyeing of human hair and, more particularly, to agents based on certain azo compounds, as will hereinafter be more fully described, said agents being suited for application at room temperature.

Aside from dyestuffs which solely function on human hair in the presence of oxidizers, e.g., H₂O₂ or perborates, directly-fixing agents are used, e.g., certain anthraquinone derivatives.

Upon the employment of directly fixing dyes it is particularly desirable in practice to carry out the dyeing of human hair without any pretreatment and in the absence of heating implements, such as heating caps or the like.

It now has been found that agents for the dyeing of human hair is described below have these properties. They contain dyes which hereinafter will be described in detail. The novel agents are characterized by a content of compounds having the generic Formula 1

\[
\begin{align*}
R_1 & \quad N=\quad N=\quad N=\quad X=\quad N=\quad R_2 \\
\end{align*}
\]

wherein R₁ and R₂ individually may denote hydrogen or a lower alkyl or alkanol group, each preferably having 1 to 3 carbon atoms; X may be phenylene or naphthylene group. Such compounds can be produced by diazotization of phenylenediamines followed by a reaction with the corresponding amines. Specifically, the following compounds are suitable for the purpose: 2,2'-diaminoazobenzene; 4,4'-diaminoazobenzene; 2,4'-diaminoazobenzene; 4-amino-4'-N-hydroxyethylaminomazobenzene; 4,4'-diaminophenylazomethane; or 4-amino-4'-dimethylaminomazobenzene.

It has furthermore been found that the above-named agents are compatible with other known directly-fixing hair dyes, especially anthraquinone dyes. Especially suitable are those anthraquinone dyes which are free of acid groups in the anthraquinone ring and which contain, in lieu of a hydrogen atom in the ring, a hetero atom which,

in turn, is linked to a hydrocarbon group. The latter is an aliphatic group interrupted once or repeatedly by a heteroatom.

Also, those anthraquinone dyes can be used to great advantage which are free of acid groups in the ring and contain an oxygen or nitrogen in the ring in lieu of a hydrogen, which in turn is linked to a hydrocarbon group or a heterocyclic ring having a secondary or tertiary nitrogen.

Anthraquinone compounds of the compositions described in the preceding two paragraphs have been disclosed in assignee's co-pending application Ser. No. 174,377, filed Feb. 20, 1962, now U.S. Patent 3,192,177, and in an application having the same assignee, filed simultaneously herewith, respectively.

The agents according to the instant invention can be mixed with any desired wetting and dispersing agents, washing agents and detergents, preferably with those which are anionic or nonionic. Alkylbenzenesulfonates, fatty alcohol sulfates, alkylsulfonates, fatty acid etholamines, ethylene adducts on fatty acids and fatty alcohols are applicable.

The fixing power of the dyestuffs according to the invention remains good in admixture with these materials.

Hence, the dyes can be manufactured in the form of shampoos, especially of cream shampoos, as is frequently desired in practice.

Thickeners, e.g., methylcellulose or starch, higher fatty alcohols, vaseline, paraffin oil, essential oils, and hair grooming agents, such as pantethenic acid and cholesterol, may be admixed to the agents.

These additives are to be present in the customary quantities. For the wetting and dispersing agents and detergents, this ranges from 0.5 to 30 percent by weight, calculated on the total composition; thickeners are to be added in amounts of 0.1 to 25 percent by weight, on the total composition. The concentration of the dyes is up to 5 percent by weight, on the total composition, and preferably 0.1 to 2 percent.

Finally, permanent waving agents also can be incorporated in the novel hair dyes according to the invention. These permanent waving agents are based on substances containing mercapto groups, such as thioglycolic acid, thiolaetic acid, mercapto-butane- or mercaptopropanesulfonic acid. They may be entered in the dyeing compounds during initial manufacture since the dyes are not affected thereby and have the great advantage of being stable on prolonged storage.

The new dyes according to the invention impart color to human hair without the application of heating devices such as heating caps, since they act at temperatures below 40° C., and preferably at room temperature. The dyeing agents can be adjusted to a pH of 7—10, the preferred range being 8.5—9.5. They may be employed for dyeing grey hair or to redy dyed hair. The colors attained are extremely resistant to washing and rubbing. Permanent waves may be applied to hair dyed with the materials according to the invention with practically no change in color or hue.

Finally, the hair dyes according to the invention have a particularly good fixing strength on the hair.

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 numerous changes may be
Example 1

1.0 part 2,2'-diaminoazobenzene was worked into a cream having shampooing properties, by heating 4.5 parts each of cetyl alcohol and stearyl alcohol, 1.5 parts fatty alcohol mixture (C_{12}-C_{18}), and 10 parts fatty alcohol sulfate (C_{16}-C_{18}) at 98°, adding the dyestuff, emulsifying with water to 95 parts, and cooling to room temperature with agitation. After adjusting the pH to 9.5 with ammonia, the mixture was made up to 100 parts with water.

The cream thus obtained imparted to naturally grey human hair a strong orange color.

Example 2

1 part 4,4'-diaminoazobenzene is worked into a cream by heating to 98° 5 parts each of cetyl and stearyl alcohol, 2 parts wool fat, and 12 parts fatty alcohol sulfate (C_{16}-C_{18}), adding the dye, emulsifying with water to 95 parts, and stirring while cooling to room temperature. After adjustment of the pH to 8.5, the mixture was made up to 100 parts with water.

Grey hair dyed at room temperature within substantially 20 minutes became yellow-red and was highly resistant in its color retention to washing.

Example 3

0.6 part 2,2'-diaminoazobenzene, 0.1 part of a dye having Formula 2

\[
\text{Formula 2: } \begin{array}{c}
\text{O} \\
\text{N} \\
\text{H}_2 \\
\text{O} \\
\end{array}
\]

and 0.3 part of a dye of Formula 3

\[
\text{Formula 3: } \begin{array}{c}
\text{O} \\
\text{H}_2 \\
\text{O} \\
\end{array}
\]

were incorporated in a cream as described in Example 1.

Living human hair treated with the mixture thus obtained for 20 minutes at 25° assumed a natural dark brown color.

Example 4

Upon dyeing of grey hair with a substance of the composition as given in the preceding example, but with the proportions as named below, a strong dark brown color was obtained in 20 minutes at 25° C.

The dyes used were:

- 2,2'-diaminobenzene: 0.25 parts
- Formula 2: 0.30 parts
- Formula 3: 0.40 parts

Example 5

Naturally grey hair was treated for 20 minutes at room temperature with an aqueous solution of 1.2 percent of Formula 4

\[
\text{Formula 4: } \begin{array}{c}
\text{H}_2 \text{N} \\
\text{N} \\
\text{N} \\
\text{H} \\
\end{array}
\]

The hair assumed a yellow-red color.

Example 6

In a hair dyeing cream as described in Example 1, in lieu of the dye named therein, 1 part 4-amino-4'-dimethylaminobenzene was incorporated. Hair dyed with this agent at room temperature obtained a lemon-yellow color.

Example 7

A yellow-brown color was obtained at 25° and for 20 minutes of grey hair dyed with an agent of a composition as named in Example 2, but containing as dye, in lieu of the one named therein, the same amount of Formula 5

\[
\text{Formula 5: } \begin{array}{c}
\text{H}_2 \text{N} \\
\text{N} \\
\text{N} \\
\text{H} \\
\end{array}
\]

The times named in the preceding examples for application of the agents merely are illustrative, and application times of 15 to 30 minutes can be employed.

1. A process for dyeing of human hair which comprises applying to said hair for substantially 15 to 30 minutes and substantially at room temperature a cream having a pH of substantially 7 to 10 and containing as active dyeing ingredient an effective amount of a compound having the formula

\[
\text{Formula 6: } \begin{array}{c}
\text{R}_1 \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{R}_3 \\
\end{array}
\]

wherein R_1 and R_2 individually are selected from the group consisting of hydrogen, lower alkyl having 1 to 3 carbon atoms, and alkylamino having 1 to 3 carbon atoms; and X is selected from the group consisting of phenylethlynylene and naphthylene.

2. A process for dyeing of human hair which comprises applying to said hair for substantially 15 to 30 minutes and substantially at room temperature a cream having a pH of substantially 7 to 10 and containing as active dyeing ingredient, 0.1 to 5 percent by weight, calculated on total composition, of an effective amount of a compound having the formula

\[
\text{Formula 7: } \begin{array}{c}
\text{R}_1 \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{R}_3 \\
\end{array}
\]

wherein R_1 and R_2 individually are selected from the group consisting of hydrogen, lower alkyl having 1 to 3 carbon atoms, and alkylamino having 1 to 3 carbon atoms; and X is selected from the group consisting of phenylethlynylene and naphthylene.

3. A process for dyeing of human hair which comprises applying to said hair substantially at room temperature and for substantially 15 to 30 minutes a cream having a pH of substantially 7 to 10 and containing as active ingredient an effective amount of a substance selected from the group consisting of 2,2'-diamino-azobenzene; 4,4'-diaminoazobenzene; 2,4'-diaminoazobenzene; 2,4'-diamino-phenoxylaminophenylamine; and 4-amino-4'-dimethylaminobenzene.

4. A process for dyeing of human hair which comprises applying to said hair substantially at room temperature and for substantially 15 to 30 minutes a cream having a pH of substantially 7 to 10 and containing as active ingredient 0.1 to 5 percent by weight, calculated on total composition, of a substance selected from the group consisting of 2,2'-diamino-azobenzene; 4,4'-diamino-
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ALBERT T. MEYERS, Primary Examiner.

V. CLARKE, Assistant Examiner.