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**WATER SOLUBLE AMINOANTHRAQUINONE
HAIR DYES**

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8 Claims. (Cl. 167—88)

ABSTRACT OF THE DISCLOSURE

Hair dyeing agents applicable at room temperature and resistant to fading. The agents are based on substituted aminoanthraquinones, whereby the substituents render the compounds water-soluble. Methods for the production of the agents are described.

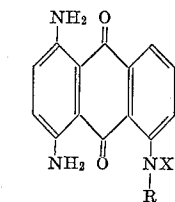
The invention relates to agents for dyeing of human hair and, more particularly, to dyeing agents based on anthraquinone of a constitution which permits their application substantially at room temperature.

The employment of so-called oxidation dyes which contain aromatic diamines or polyphenols for dyeing of human hair is known. These dyes have the disadvantage that they must be developed with the aid of oxidizers, such as H₂O₂ or perborates.

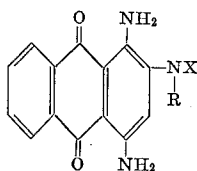
It therefore has been attempted to use hair dyes containing directly acting dyes, e.g., anthraquinone derivatives which are substituted in the nucleus by amino-, hydroxyl-, carboxyl- or sulfo groups.

In the practical application of these anthraquinone compounds known for dyeing of human hair dyeing at temperatures ranging from 40 to 60° C. is required. It therefore becomes necessary to use heating caps and similar devices on the human head to attain the required temperatures. Moreover, the hitherto known anthraquinone hair dyes are difficultly soluble so that they had been employed solely as dispersion dyes.

It now has been found that the drawbacks named above are not encountered with the agents according to the instant invention. Therein, amino-anthraquinone dyes are employed having the generic Formulae 1 and/or 2;



(1)



(2)

wherein R is hydrogen or an alkyl group having 1-3 carbon atoms, and X is an aliphatic group having 1-6 carbon atoms or else a phenyl group containing a further group rendering the compound water-soluble.

Of the anthraquinone dyestuffs to be considered for the purpose, those are especially suited which contain

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a water-soluble group such as —SO₃H, —OH or —COOH. It is understood that the corresponding alkali- or ammonium salts and also the mono- and diethanol-amino salts can be employed equally well.

Compounds of the kind named above can be produced e.g., by reacting 1,4-diamino-5-nitroanthraquinone or 2-chloro-1,4-diaminoanthraquinone with such compounds as aminobenzoic acid, sulfanilic acid or such aminocarboxylic acids as alpha- or beta- alanine. Aminoalkylsulfonic acids, such as taurine or N-methyltaurine, also can be used. The reactions are carried out in the presence of solid alkali hydroxide in solvents such as nitrobenzene.

The dyes can be mixed with any desired wetting, dispersing and washing agents, especially those of anionic or nonionic character. Particularly to be considered are alkylbenzene sulfonates, fatty alcohol sulfates, alkyl sulfonates, fatty acid ethanalamides, ethylene adducts on fatty acids and fatty alcohols.

The dyeability of the dyeing agents named above remains good even in mixture with the wetting or washing agents. This facilitates the production of the hair dyeing agents in the form of shampoos, especially of cream shampoos. The latter often are desired in practice.

Furthermore, thickeners may be added to the agents according to the invention e.g., methylcellulose, starch, higher fatty alcohols, vaseline, paraffin oil, fatty acids; also essential oils and hair grooming agents, such as pantothenic acid or cholesterol.

The additives named are admixed in the commonly used quantities. Wetting or dispersing agents are present in quantities of 0.5-30 percent by weight, thickeners in amounts of 0.1-25 percent by weight, calculated on the total composition. The concentration of the dyes themselves amounts to up to 5 percent by weight, but preferably 0.1 to 2 percent, of the total composition.

Finally, permanent waving agents, known per se, may be added to the novel hair dyeing agents. These waving agents are based on compounds containing mercapto groups, e.g., thioglycolic acid, thiolactic acid, mercaptopropane- or mercaptobutanesulfonic acid. The hair dyeing agents may be produced containing these additives since the dyestuffs are stable in their presence.

The new hair dyeing agents allow dyeing of human hair without resorting to heating caps or similar devices since they are applied at temperatures below 40° C., and preferably at room temperature. Their pH may range from 7 to 10, preferably from 8.5 to 9.5. The agents may serve for coloring gray hair or for applying a new color to any color hair. The hair thus dyed is extremely resistant to fading due to washing or friction, e.g., rubbing. When a permanent wave is applied to hair thus dyed, a change in the color or hue does not occur. The dyes fix well on human hair and, in any of the mixtures described above, can be stored practically indefinitely.

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 made in the details without departing from the spirit and the scope of the invention as hereinafter claimed.

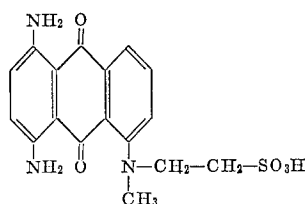
All parts given in the examples are parts by weight.

Example 1

11.4 parts 1,4-diamino-5-nitroanthraquinone, 11 parts N-methyltaurine and 0.8 part powdered NaOH were mixed into 60 parts nitrobenzene and the temperature held at 50° C. for one-half hour. After that, the mixture was heated at 100° C. for 12 hours. The reaction mixture then was refined by separating the nitrobenzene and alkali.

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The dye thus obtained had the Formula 3



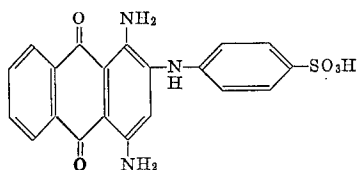
and imparted to gray hair a strong blue color with a purplish hue when applied for 20 minutes at 25° C. in an ammonia solution of a pH of 9.5.

Example 2

8 parts of a fatty alcohol mixture (C₁₂-C₁₈) and 10 parts fatty alcohol sulfate (C₁₆-C₁₈) were heated to 90° C. and emulsified with 60 parts water. Into this emulsion the dye obtained as described in Example 1, together with 1 part NH₄OH and 8 parts water, were stirred. A cream thus was obtained having a pH of substantially 9.5. This cream, applied to naturally gray hair, dyed the same purple-blue at room temperature. The hair had a strong hue and did not discolor upon washing.

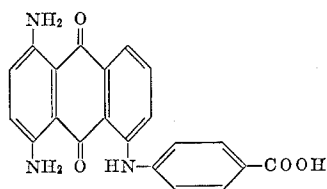
Example 3

Hair of red color is obtained when the cream described in Example 2, in lieu of the dye used therein, contains an anthraquinone dye of Formula 4:



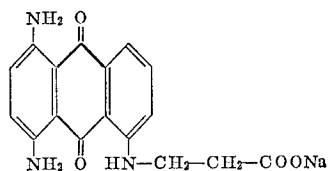
Example 4

10 parts fatty alcohol (C₁₆-C₁₈), 2 parts wool fat, and 12 parts fatty alcohol sulfate (C₁₆-C₁₈) were heated to 98° C., and 1 part of an anthraquinone dye of Formula 5 added:



The mixture then was emulsified in 75 parts water and cooled to room temperature under agitation. The pH of the cream was adjusted to 8. This cream dyed naturally gray hair purple-blue at room temperature within a treatment time of 20 minutes.

A similar hair color was obtained by incorporating, in lieu of dye (5), dye (6) of the following constitution:

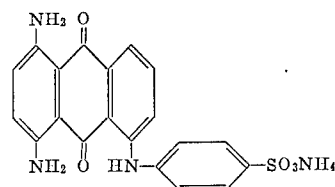


Example 5

1 part anthraquinone dye of Formula 7 was incorporated in a shampoo cream. The latter had been produced by heating a mixture of 4.5 parts cetyl alcohol, 4.5 parts stearyl alcohol, 1.5 parts fatty alcohol mixture (C₁₂-C₁₈) and 10 parts fatty alcohol sulfate (C₁₆-C₁₈), to 98° C., addition of the dye and emulsification with 78 parts water. The pH of the cream was adjusted to 9.5 with ammonia.

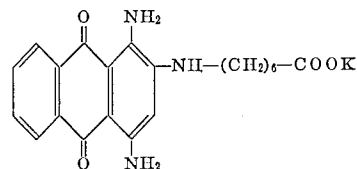
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Naturally grey hair treated with this cream at room temperature, assumed a mauve color within 20 minutes.



Example 6

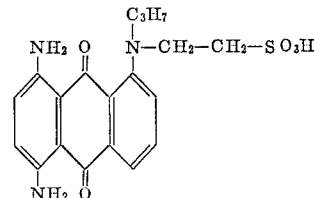
Hair of red color is obtained when the cream described in Example 5, in lieu of the dye used therein, contains an anthraquinone dye of Formula 8:



This dye is produced by reacting 2-chloro-1,4-diaminoanthraquinone with (omega)-amino-heptylic acid. The reaction is carried out in the presence of solid potassium hydroxide and in solvents such as xylene.

Example 7

1 part of anthraquinone dye of formula

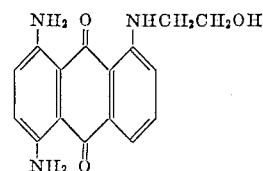


was mixed into a hair cream as described in Example 5, except that the pH was adjusted to 8.5. This cream dyed naturally grey hair blue at room temperature within a treatment of 15 minutes. The dye is produced by reacting 1,4-diamino-5-nitroanthraquinone with N-propyl-taurin in presence of solid NaOH and nitrobenzene as solvent.

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.

Example 8

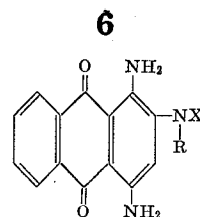
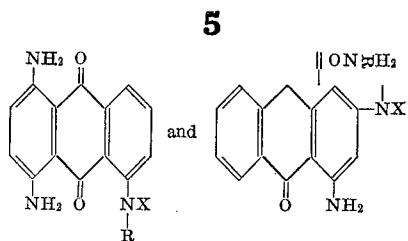
14.1 parts of 1,4-diamino-5-nitroanthraquinone and 50 parts monoethanolamine were mixed and the temperature held at 70° C. for 15 hours under stirring. After that, the surplus of monoethanolamine was distilled in vacuo, thereafter 50 parts water were added and the reaction mixture neutralized with aqueous HCl, filtered and the residue was dried at 80° C. in vacuo. The dye thus obtained had the Formula 10



1 part of this dye was incorporated in a shampoo creme as described in Example 2. The pH of the cream was adjusted to 9.5 with ammonia. This cream dyed naturally gray hair strong blue at room temperature within treatment of 30 minutes.

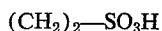
We claim as our invention:

1. Agents for the deying of human hair substantially at room temperature comprising compounds selected from the group consisting of

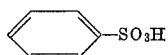


wherein R is selected from the group consisting of hydrogen and alkyl having 1 to 3 carbon atoms; and X is selected from the group consisting of alkylene of 1 to 6 carbon atoms and phenyl, said alkylene and phenyl having an end group selected from sulfo-, hydroxyl- and carboxyl, and their alkali metal, ammonium, mono- and diethanolamine salts.

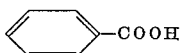
2. The agents as defined in claim 1, wherein X is



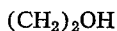
3. The agents as defined in claim 1, wherein X is



4. The agents as defined in claim 1, wherein X is

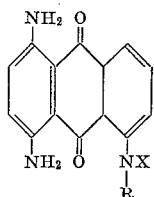


5. The agents as defined in claim 1, wherein X is



6. The agents as defined in claim 1, wherein said compounds are incorporated in amounts from 0.1 to 5 percent by weight, calculated on the total composition, in a cream composed of substances selected from the group consisting of nonionic and anionic surfactants, thickeners, essential oils, hair grooming agents, permanent waving agents, and mixtures thereof.

7. A process for the dyeing of human hair which comprises applying to said hair for approximately 15 to 30 minutes and substantially at room temperature a cream having as active dyeing ingredient an effective amount of a compound selected from the group consisting of



and

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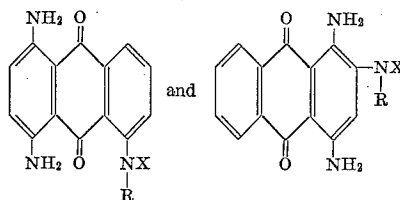
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wherein R is selected from the group consisting of hydrogen and alkyl having 1-3 carbon atoms, and X is selected from the group consisting of alkylene of 1 to 6 carbon atoms and phenyl, said alkylene and phenyl having an end group selected from sulfo, hydroxyl and carboxyl, and their alkali metal, ammonium, mono- and diethanolamine salts.

8. A process for the dyeing of human hair which comprises applying to said hair for approximately 15 to 30 minutes and substantially at room temperature a cream having as active dyeing ingredient 0.1 to 5 percent by weight, calculated on total composition, of a compound selected from the group consisting of



wherein R is selected from the group consisting of hydrogen and alkyl having 1-3 carbon atoms, and X is selected from the group consisting of alkylene of 1 to 6 carbon atoms and phenyl, said alkylene and phenyl having an end group selected from sulfo, hydroxyl and carboxyl, and their alkali metal, ammonium, mono- and diethanolamine salts.

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