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DIAMINOANTHRAQUINONES AND THEIR USE AS HUMAN HAIR DYES

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ABSTRACT OF THE DISCLOSURE

Agents for dyeing of human hair at room temperature which have as active ingredient diaminoanthraquinone compounds which are devoid of acid groups in the ring; a hydrogen atom in the ring is replaced by oxygen or nitrogen which is linked to a hydrocarbon group which, in turn, is linked to a secondary or tertiary nitrogen in an aliphatic chain or in a pyridine-type ring. The agents can be combined with wetting agents, thickeners, perfumes and permanent waving agents and can be applied in the form of a cream.

The invention relates to agents for dyeing of human hair and, more particularly, to certain substituted anthraquinone dyes, as hereinafter will become more apparent. These dyes have the advantage that they can be employed substantially at room temperature.

The use of certain anthraquinone derivatives for the dyeing of human hair is known. These derivatives contain, e.g., amino-, hydroxyl-, carboxyl- or sulfo groups in the nucleus.

In the practical application of these known compounds it becomes necessary to accomplish the dyeing of the hair at temperatures ranging from 40 to 60° C. Hence, heating caps or similar devices must be employed on the hair. It has also been established that the strength of these dyes diminishes greatly when they are incorporated in creams or pastes, as frequently is the case in practice.

It now has been found that hair dyeing agents containing anthraquinone compounds as described hereinafter in detail, surprisingly do not exhibit the above-named drawbacks. The novel hair dyes are characterized by a content of anthraquinone compounds which are free of acid groups in the nucleus and which contain a side chain consisting of a hydrocarbon radical connected to the nucleus by way of an oxygen or nitrogen atom, this hydrocarbon radical further containing a secondary or, preferably, tertiary nitrogen atom in an aliphatic chain or else in a heterocyclic ring. Of the anthraquinone dyes especially those are suited which contain a hydrocarbon group of the formula



wherein n equals 1-4, and X denotes one of the following groups: $-C_6H_4N$; $-N(CH_3)_2$; $-NH(CH_2)_3NH_2$;

$-NH(CH_2)_2NH_2$; $-NH(CH_2)_2OH$; $-NH-CO-NH_2$; or $-NH-CS-NH_2$.

These anthraquinone derivatives can be manufactured by reacting aminoanthraquinones which contain a reactive halogen atom, an NO_2 - or OH group, with compounds which contain in an aliphatic chain or in a heterocyclic ring at least a secondary, but preferably a tertiary, nitrogen group.

Furthermore, these compounds must contain a group capable of reacting with the substituted anthraquinone, e.g., an OH group, an NH_2 group or a halogen atom.

Accordingly the following compounds are to be considered, amongst others: pyridine-2-carbinol; pyridine-2-

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ethanol; 4-picolyamine; 2-picolychloride; dimethylaminoethanol; N-beta-oxethylpropanediamine-(1,3); ethanol-isopropanolamine; diethylenetriamine; triethylenetetramine; beta-oxethylurea; beta-oxethylthiourea; 3-allyloxy-2-oxypropylamine - (1); N-beta-aminoethylmorpholine; and N-beta-oxethylmorpholine.

The aminoanthraquinone radical must be free from acid groups in the nucleus, such as hydroxyl-, carboxyl- or sulfo-groups. However, it may contain other substituents, such as halogen or nitro groups. The hair dyes can be mixed with any desired wetting, dispersing and washing agents, preferably however with those which are anionic or nonionic. Suitable wetting, dispersing and washing agents are, e.g., alkylbenzenesulfates, fatty alcohol sulfates, alkylsulfonates, fatty acid ethanolamides, ethylene adducts on fatty acids and fatty alcohols.

The fixing quality of the dyes according to the invention remains good on the hair when admixed with the agents named above and does not diminish to any practical extent. Therefore, these dyes can be manufactured in the form of shampoos, particularly cream shampoos, which frequently are desirable in practice.

Furthermore, thickeners, such as methylcellulose, starch, higher fatty alcohols, vaseline, paraffin oil, fatty acids; also essential oils and hair grooming agents, e.g., pantothenic acid and cholesterol, can be admixed.

The additives are employed in the customary quantities. For the wetting, dispersing and washing agents, amounts from 0.5 to 30 percent by weight, and for thickeners amounts of 0.1 to 25 percent, by weight, all calculated on the total composition, are used. The concentration of the dyestuffs according to the invention in the mixtures, depending upon end use, ranges up to 5 percent by weight of the total composition, preferably 0.1 to 2 percent.

Finally, permanent waving agents, known per se, also can be admixed to the novel hair dyeing agents. These permanent waving materials are based on compounds containing mercapto groups, e.g., thioglycolic acid, thiolactic acid, mercaptopropane- or mercaptobutanesulfonic acid. The novel hair dyes can be produced with these additives since the dyes have the advantage of stability even in the presence of the materials named so that storage presents no problem, even over prolonged periods of time.

Human hair can be dyed with these novel hair dyeing agents without the aid of heating caps or similar devices since temperatures below 40° C., and preferably room temperature, are required for the dyeing process. The pH of the agents may range from 7 to 10, preferably from 8.5 to 9.5. The agents can be used for dyeing naturally grey hair or for redyeing dyed hair from one color to another. The hair thus dyed is not affected by repeated washing nor by rubbing or other friction. When a permanent wave treatment is imparted to hair dyed with the agents according to this invention, a change in color or hue does not occur. Finally, the fixing of the color on the hair is very good.

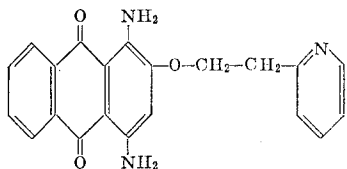
The invention now will be further illustrated by the following examples. However, it should be understood that this is given merely by way of explanation, and not of limitation, and that numerous changes may be made in the details without departing from the spirit and the scope of the invention as hereinafter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

All parts given in the examples are parts by weight, temperatures are degrees centigrade.

EXAMPLE 1

27.2 parts 1,4-diamino-2-chloroanthraquinone were stirred with 100 parts pyridine-2-ethanol and 4.4 parts powdered NaOH for 8 hours at 100° and for another 16 hours at 130°. The excess pyridine-2-ethanol then was

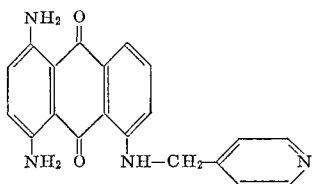
vacuum-distilled, the crude reaction mixture stirred with 100 parts water and suction-filtered. The residue was treated for 10 minutes at 98° with 2,500 parts water and 75 parts concentrated HCl, suction-filtered at 20° and dried. 23 parts of a blue powder were obtained having a melting point of 193–202° and having the following structure (Formula 1):



1 part of the 1,4-amino-2-[2'-pyridine]-ethoxy)-anthraquinone thus obtained was worked into a shampoo cream, in the following manner: 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) were heated at 98°, the dye added, the mixture emulsified with enough water to make 95 parts and cooled to room temperature with agitation. The pH was adjusted to 9.5 with ammonia, and the mixture made up to 100 parts of water. The cream thus obtained produced a strong and clear red color on naturally grey hair at 25° when applied for approximately 20 minutes. Ensuing shampooing of the hair did not diminish the red color.

EXAMPLE 2

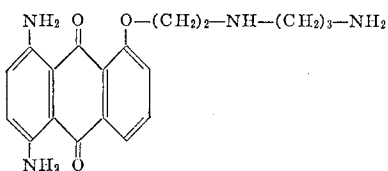
28.4 parts 1,4-diamino-5-nitroanthraquinone were dissolved in 150 parts dimethylformamide, 10.8 parts 4-picolylamine and 4.4 parts powdered NaOH added, and the mixture stirred for 12 hours on a bath of a temperature of 100°. The solvent then was vacuum-distilled, the residue stirred in water, neutralized with dilute acetic acid, and suction-filtered. After drying, 24.8 parts of a blue dyestuff were obtained having a melting point of 185–186° and the Formula 2:



1 part of this dyestuff was worked into a cream in the following manner: 5 parts each of cetyl and stearyl alcohol, 2 parts wool fat and 12 parts fatty alcohol sulfate (C₁₆–C₁₈) were heated at 98°, the dye added, the mixture emulsified with water to make 95 parts and cooled with agitation to room temperature. After adjustment of the pH to 7, the mixture was made up to 100 parts with water. The cream thus produced dyed naturally grey hair a strong blue within 20 minutes at 25°.

EXAMPLE 3

14.2 parts 1,4-diamino-5-nitroanthraquinone were reacted with 100 parts N-beta-oxethylpropanediamine-(1,3) and 2.2 parts powdered NaOH at 50° for 24 hours. The reaction mixture was poured into 1,200 parts water and suction-filtered. After drying at 50° in vacuo, 12 parts of a blue powder were obtained having the constitution as shown in Formula 3:

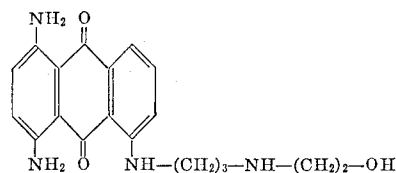


1 part of this dye was mixed into a washing cream as described in the preceding example, except that the pH was adjusted to 8. Grey hair treated with the resultant cream

at room temperature attained a strong blue color with a slight red hue.

EXAMPLE 4

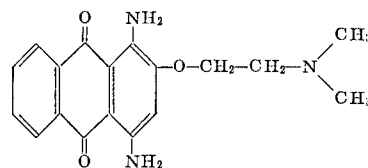
34 parts 1,4-diamino-5-nitroanthraquinone and 135 parts N-beta-oxethylpropanediamine-(1,3) were reacted at 30° for 15 hours, and were allowed to stand for another 48 hours at room temperature. In contrast to the preceding example, no addition of NaOH was made. Thereafter, the reaction mixture was poured into 500 parts ice water, suction-filtered and dried. 33 parts of blue powder of Formula 4 thus were obtained:



1 part of this dye was incorporated in a hair wash cream as described in Example 1. Naturally grey hair dyed therewith assumed a blue color.

EXAMPLE 5

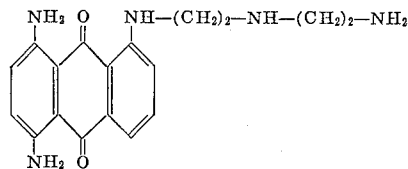
13.5 parts 1,4-diamino-2-chloroanthraquinone were heated with 50 parts N,N-beta-dimethylaminoethanol and 2.2 parts powdered NaOH at a bath temperature of 100° for 8 hours and for another 16 hours at a bath temperature of 130°. The excess dimethylaminoethanol then was vacuum-distilled, the residue stirred with 200 parts water for 15 minutes, suction-filtered and dried. 10.5 parts of a bluish-red dye were obtained having the Formula 5:



Naturally grey hair treated with a hair wash cream as described in Example 1 but containing dye (5) produced strongly red hair at 25° within 20 minutes.

EXAMPLE 6

14.2 parts 1,4-diamino-5-nitroanthraquinone were reacted with 100 parts diethylenetriamine at 70° for 15 hours. The reaction mixture was poured into 1000 parts water and suction-filtered. After drying at 60° in vacuo, 15 parts of a dark blue powder were obtained having the Formula 6:



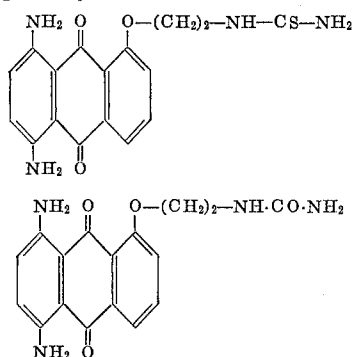
1 part of this dye was mixed into a hair wash cream as described in Example 1, except that the pH was adjusted to 9.5. Grey hair treated with this cream attained a clear blue color.

EXAMPLE 7

14.2 parts 1,4-diamino-5-nitroanthraquinone were reacted with 7.1 parts beta-oxethylthiourea (respectively 6.8 parts beta-oxethylurea) and 2.4 parts powdered NaOH in 100 parts benzene at 80° for 10 hours. Benzene was removed in vacuo, the residue was treated with diluted HCl and suction-filtered. 15 parts of a blue powder were ob-

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tained having the following constitution as shown in Formula 7 respectively 8:



Grey hair dyed with a cream containing one of these two dyestuffs at a pH of 9 attained a blue color with a slight red hue.

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.

We claim as our invention:

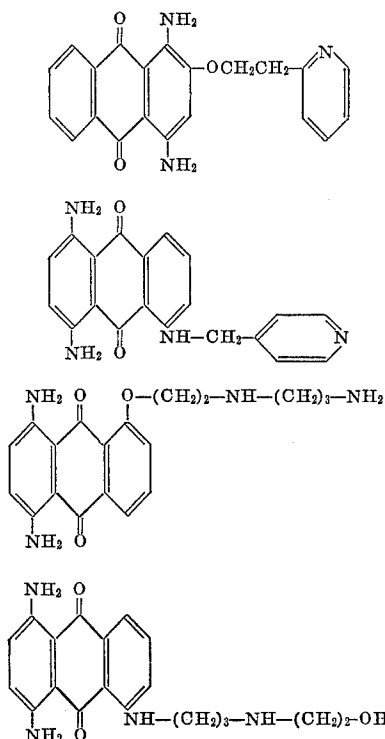
1. 1,4-diaminoanthraquinone free of hydroxyl-, carboxyl- and sulfo-groups in the anthraquinone ring; a hydrogen atom in said ring being replaced by an atom selected from the group consisting of oxygen and nitrogen; said atom being linked to a group



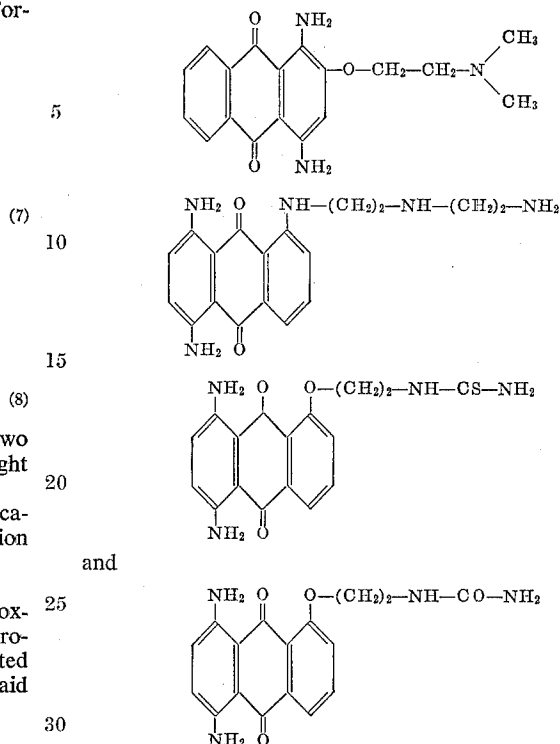
wherein n is a whole number from 1 to 4 and X is selected from the group consisting of $-C_5H_4N$; $-N(CH_3)_2$; $-NH(CH_2)_3NH_2$; $-NH(CH_2)_2NH_2$; $-NH(CH_2)_2OH$; $-NH-CO-NH_2$; and $-NH-CS-NH_2$.

2. A human hair dyeing composition comprising from 0.1 to 5 percent by weight, calculated on the total composition, of the 1,4-diaminoanthraquinone as defined in claim 1 in a cream composed of a substance selected from the group consisting of wetting agents, thickeners, essential oils permanent waving agents and mixtures thereof.

3. A compound selected from the group consisting

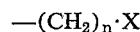


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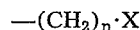
and

4. 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 composition having as the active ingredient an effective amount of 1,4-diaminoanthraquinone free of hydroxyl-, carboxyl-, sulfo-groups in the anthraquinone ring; a hydrogen in said ring being replaced by an atom selected from the group consisting of oxygen and nitrogen; said atom being linked to a group



wherein n is a whole number from 1 to 4 and X is selected from the group consisting of $-C_5H_4N$; $-N(CH_3)_2$; $-NH(CH_2)_3NH_2$; $-NH(CH_2)_2NH_2$; $-NH(CH_2)_2OH$; $-NH-CO-NH_2$; and $-NH-CS-NH_2$.

5. 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 the active ingredient 0.1 to 5 percent by weight, calculated on total composition, of 1,4-diaminoanthraquinone free of hydroxyl-, carboxyl- and sulfo-groups in the anthraquinone ring; a hydrogen in said ring being replaced by an atom selected from the group consisting of oxygen and nitrogen; said atom being linked to a group



wherein n is a whole number from 1 to 4 and X is selected from the group consisting of $-C_5H_4N$; $-N(CH_3)_2$; $-NH(CH_2)_3NH_2$; $-NH(CH_2)_2NH_2$; $-NH(CH_2)_2OH$; $-NH-CO-NH_2$; and $-NH-CS-NH_2$.

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