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3,482,923

DYEING OF HUMAN HAIR WITH CATIONIC DIRECT DYES

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Int. Cl. A61k 7/12
U.S. Cl. 8—10.1 14 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to the improved dyeing of hair, particularly human hair, with cationic direct dyestuffs. The dyeing is improved by ketones, esters, pyridine and derivatives thereof, as well as ethylene glycol carbonate, tetrahydrothiophene dioxide and thionaphthene.

The invention relates to boosters for cationic direct dyestuffs which facilitate the dyeing of hair, more particularly human hair, and to a process for their application.

For the dyeing of hair so-called oxidation dyes are employed on a large scale, such as aromatic diamines, aminophenols or polyhydroxy compounds. However, direct dyes also have been used which have the advantage not to require the addition of oxidizers upon application. It is known from the textile industry that dyeing and the qualities of the coloring obtained thereby can frequently be improved by means of particularly high or low pH values, elevated temperatures or extension of the time of application. Upon dyeing of hair, and particularly living human hair, such methods evidently cannot be employed. Moreover, it often is necessary to apply entirely new dyes as agents for dyeing of human hair, and this is especially true for direct dyes.

It also has been attempted to improve the usefulness especially of such dyes of limited solubility, by the addition of materials as butanol, benzyl alcohol or addition products of phenols or alcohols on ethylene oxide. However, it has been found that success has been limited to very few instances.

It is the object of the invention to present agents and a process for their application which facilitate ready dyeing of hair, particularly living human hair, with cationic direct dyestuffs, i.e., to improve the quality of the color, its intensity and resistance to rubbing and abrasion. All this is attained, according to the invention, by treating the hair with solutions, dispersions or emulsions of compounds of the following series:

(a) ketones having 5 to 10 carbon atoms;
(b) esters of saturated aliphatic and aromatic carboxylic acids having 2 to 8 carbon atoms with alcohols having 1 to 8 carbon atoms;
(c) pyridine and its derivatives;
(d) ethylene glycol carbonate, tetrahydrothiophene dioxide, thionaphthene.

Treatment of the hair can be carried out by rinsing it with a solution or emulsion containing one or more of the compounds named above, followed by dyeing with the direct dyes in the conventional manner. However, it is equally feasible to wash the hair first and to add the agents to the last rinse directly. The concentration of the agents ranges from 0.1 to 10 weight percent, preferably 1 to 5 percent. The temperatures are 15 to 40° C., preferably room temperature.

If desired, this treatment furthermore can be combined with the actual dyeing by incorporating the compounds

named in the dyeing preparation, either during the production of the latter or else shortly before its application to the hair. Concentrations and temperatures are the same as named above.

The advantages of this novel process are found in the fact that frequently the quantity of dyestuff to be applied can materially be reduced without sacrificing the intensity of the dye. It also is feasible in many instances to increase the color intensity considerably with the process according to the invention when initially a rather weak coloration is present.

A further advantage is the increase in the resistance to abrasion and rubbing with simultaneous improvement of the dyeing process.

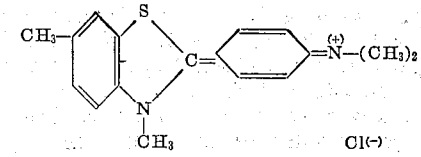
The single effects depend, to a certain extent, on the booster used and on the characteristics of the dyestuff itself, but it has been established that the improvements named have been attained in all instances. For practical application, the compounds named below are particularly interesting from a technological and economical point of view. They are special representatives of (a)–(c) above, but are not presented to be a limitation:

(a) cyclopentanone, cyclohexanone, 2-ethylcyclohexanone, 2-propylcyclohexanone, acetophenone, p-methoxyacetophenone;
(b) propylacetate, butylacetate, amylacetate, isoamylacetate, octylacetate, cyclohexylacetate, propylbutyrate, ethylbenzoate, p-nitrobenzoic acid methyl ester, diethyloxalate, diethylmalonate, dimethyladipate, diethylphthalate;
(c) pyridine-2-carbinol, pyridine-2-thiocarbinol pyridine-3-carbinol, pyridine-2-ethanol, pyridine-2-aldoxime, pyridine-2,6-dicarboxylic acid, nicotinic acid, isonicotinic acid thioamide, pyridine-2-carboxylic acid-n-butyl ester, pyridyl-3-acrylic acid, 2-cyanopyridine, 2-picolylamine, 2-picolylmethylamine, piperidine, piperazine hydrate, 2,2'-pyridil.

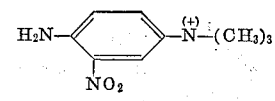
If desired, mixtures of these compounds can be used, especially mixtures of compounds of the same group. It goes without saying that the mutual chemical compatibility and that with other possibly present materials must be considered.

The pH value of the solutions containing these boosters can be adapted to a large measure to the prevailing requirements and desires. Good results have been obtained with preparing solutions and/or last rinses which were not alkaline, but acid or neutral.

Suitable cationic direct dyestuffs are those commonly known for the purpose at hand, especially those based upon triphenylmethane, azines, oxazine and thiazine. Particularly well known compounds are crystal violet, fuchsin, methylene blue or else compounds having Formulae 1 and 2:



(1)



(2)

The dyes are applied in the conventional concentrations of 0.1 to 5. weight percent, and preferably 0.5 to 3

percent. If, however, the effect of an increased color intensity is not desired, the commonly employed quantities can greatly be decreased, in some instances down to approximately 1/10 of the usual amount, with the process according to the invention.

The hair dyes can be mixed with wetting agents, detergents and washing agents, especially with those which are nonionic. Aminooxides, fatty acid ethanolamides, addition products of ethylene oxide on fatty acids and fatty alcohols are especially suited.

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

These additives are incorporated in the commonly used quantities. As wetting agent or detergent amounts of 0.5–30 weight percent, as thickeners 0.1–25 weight percent, are preferred, calculated on the total composition. The concentration of the dyes, depending upon the purpose, amounts to up to 5 weight percent, preferably however, 0.1 to 2 weight percent, calculated on the total composition.

The invention now will be further illustrated by the following Examples.

EXAMPLE 1

Naturally greyed human living hair was washed with a shampoo and rinsed repeatedly. The last rinse water contained 5 weight percent N-methylpicolinic acid thioamide. The hair then was treated with a dyeing cream containing as cation-active dye 0.1 weight percent fuchsin. The pH of the cream was 9.5, the time of application 30 minutes at room temperature. A good red-purple color was obtained whose intensity was considerably stronger than that of hair which had been treated in the same manner with the exception that the additive to the last rinse water had been omitted.

A considerable boost in the color intensity also occurred when the hair to be dyed, prior to dyeing, was rinsed with an aqueous solution of 3 weight percent methylpicolinic acid thioamide.

EXAMPLE 2

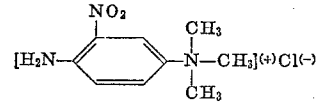
Grey hair was treated with an aqueous-ammoniacal 0.1 weight percent fuchsin solution of a pH of 9.5 at room temperature. A red coloration thereby was obtained.

A considerable stronger deep red color resulted when the same grey hair, prior to dyeing in the same manner, was treated for 5 minutes at room temperature with an aqueous-ammoniacal 5 weight percent suspension of N-methylpicolinic acid thioamide.

Practically the same result is obtained when the rinse with the above suspension is carried out with the suspension reacting neutral or at pH of 2.

EXAMPLE 3

A hair dye in cream form was prepared by heating 10 weight parts cetyl-stearyl alcohol and 8 parts lauryldimethylaminooxide to 80° C. and emulsifying with 60 weight parts water of like temperature. After cooling, a solution of 1 weight part of a dyestuff having Formula 3 in 15 parts water was added, the pH adjusted to 9 with aqueous ammonia, and the solution made up to 100 weight parts with water. The cream thus obtained dyed grey hair yellow within 30 minutes at room temperature.

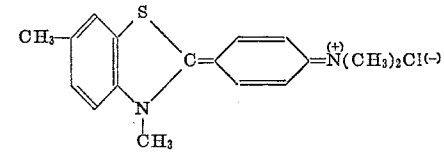


(3)

When the cream as described above further contained 5 weight percent p-aminoacetophenone, the hair assumed a brilliant yellow color of much higher intensity.

EXAMPLE 4

A hair dyeing agent in gel form was prepared by dissolving 2 weight parts of a dyestuff having Formula 4



(4)

in a transparent paste consisting of 10 weight parts of equal amounts of cetyl and stearyl alcohol and 15 weight parts of the reaction product of lauryl alcohol with 10 mols ethylene oxide and 73 parts water. This gel paste dyed hair weakly yellow within 30 minutes at room temperature.

When in this dyeing agent simultaneously 3 weight parts pyridine-2-aldehyde were incorporated, a strong yellow color developed under the same conditions.

A strong yellow color also is obtained when the amount of dyestuff is decreased from 2 weight parts to 1 weight part and additionally 5 weight parts dimethyladipate are incorporated in the dyeing agent.

EXAMPLE 5

A dyeing agent as described in the preceding example was prepared except that as dyestuff 0.5 weight parts fuchsin were employed. Grey hair was treated with the agent for 25 minutes at body temperature and assumed a red color.

The color becomes brilliantly red-purple when the dyeing cream also contains 4 weight parts acetophenone.

EXAMPLE 6

Aqueous solutions were produced containing as cationic dyestuff 0.3 weight percent crystal violet and, as a further additive, one of the compounds listed, together with the appropriate quantities to be used, in Table 1. The solutions were adjusted to a pH of 9.5 with aqueous ammonia. Grey human hair was treated with these compounds for 20 minutes at room temperature, followed by shampooing and drying.

In all instances, the coloring was substantially improved over the light purple color obtained under otherwise equal operating conditions, but without the additives named in Table 1.

Corresponding results were obtained when, in lieu of the crystal violet, a dye was used as named and indexed in Table 2.

TABLE 1

No.	Material	Weight percent
1	Cyclopentanone	3
2	Cyclohexanone	4
3	2-ethylcyclohexanone	5
4	2-propylcyclohexanone	3
5	Acetophenone	4
6	p-Methoxyacetophenone	5
7	Propylacetate	7
8	Butylacetate	4
9	Amylacetate	5
10	Isoamylacetate	5
11	Octylacetate	5
12	Cyclohexylacetate	6
13	Propylbutyrate	1
14	Ethylbenzoate	3
15	p-Nitrobenzoic acid methyl ester	2
16	Diethyloxalate	4
17	Diethylmalonate	2
18	Dimethyladipate	4
19	Diethylphthalate	3
20	Pyridine-2-carbinol	4
21	Pyridine-2-thiocarbinol	0.5
22	Pyridine-3-carbinol	5
23	Pyridine-2-ethanol	2
24	Pyridine-2-aldehyde	2
25	Pyridine-2-aldoxime	4
26	Pyridine-2,6-dicarboxylic acid	3
27	Nicotinic acid	1

TABLE 1.—Continued

No.	Material	Weight percent
28	Isonicotinic acid thiomide	1
29	Pyridine-2-carboxylic acid-n-butyl-ester.	1
30	Pyridyl-3-acrylic acid	4
31	2-cyanopyridine	3
32	2-picolylamine	2
33	2-picolylmethylamine	2
34	Piperidine	4
35	Piperazine hydrate	4
36	2,2'-pyridil	2
37	Ethyleneglycol carbonate	2
38	Thionaphthene	2
39	Pyridine	4

TABLE 2

Dyestuff	Color Index No.
Victoria Blue R	44 040
Astrazone Yellow 3G	48 055
Rhodamine B Extra	45 170
Astradiamond Green GX	42 040
Rhodamine 4 GD	45 160

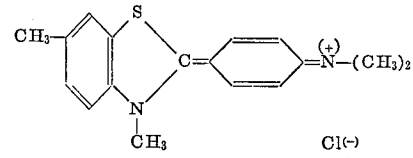
Dyes named in U.S. Patent 3,100,739.

What is claimed is:

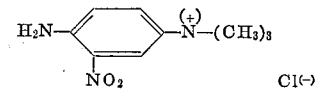
1. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair prior to the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of compounds taken from the class consisting of

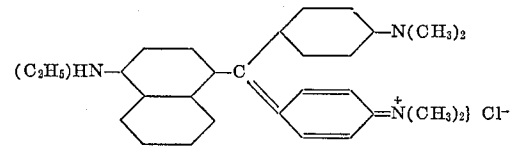
cyclopentanone, cyclohexanone, 2-ethyl cyclohexanone, 2-propyl cyclohexanone, acetophenone, p-methoxy acetophenone, and mixtures thereof.

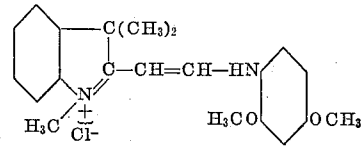
2. A process according to claim 1 wherein said dye is taken from the class consisting of crystal violet, fuchsin, methylene blue,

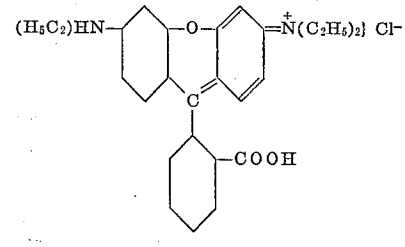


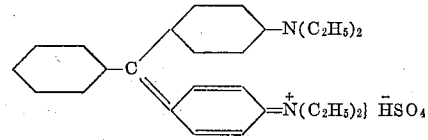
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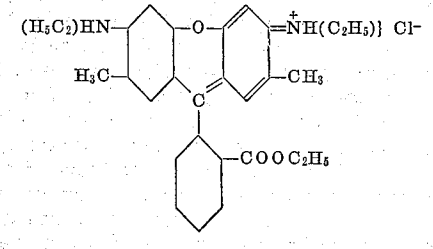












3. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair prior to the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of compounds taken from the class consisting of pyridine-2-carbinol, pyridine - 2 - thiocarbinol, pyridine-3-carbinol, pyridine-2-ethanol, pyridine-2-aldehyde, pyridine-2-aldoxime, pyridine-2,6-dicarboxylic acid, nicotinic acid, isonicotinic acid thioamide, pyridine-2-carboxylic acid-n-butylester, pyridyl-3-acrylic acid, 2-cyanopyridine, 2-picolylamine, 2-picolylmethylamine, piperidine, piperazine hydrate, 2,2'-pyridil, and mixtures thereof.

4. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair

prior to the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of compounds taken from the class consisting of ethylene glycol carbonate, tetrahydrothiophene dioxide, thionaphthene, and mixtures thereof.

5. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair prior to the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of cyclohexyl acetate.

6. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair prior to the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of p-nitro benzoic acid methyl ester.

7. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair prior to the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of diethyl phthalate.

8. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair simultaneously with the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of compounds taken from the class consisting of cyclopentanone, cyclohexanone, 2-ethyl cyclohexanone, 2-propyl cyclohexanone, acetophenone, p-methoxy acetophenone, and mixtures thereof.

9. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair simultaneously with the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of compounds taken from the class consisting of pyridine - 2 - carbinol, pyridine-2-thiocarbinol, pyridine-3-carbinol, pyridine - 2 - ethanol, pyridine-2-aldehyde, pyridine-2-aldoxime, pyridine-2,6-dicarboxylic acid, nicotinic acid, isonicotinic acid thioamide, pyridine-2-carboxylic acid-n-butylester, pyridyl-3-acrylic acid, 2-cyanopyridine, 2 - picolylamine, 2 - picolylmethylamine, piperidine, piperazine hydrate, 2,2'-pyridil, and mixtures thereof.

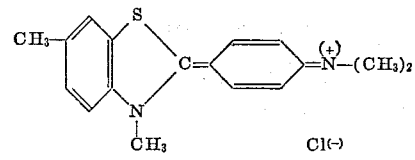
10. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair simultaneously with the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of compounds taken from the class consisting of ethylene glycol carbonate, tetrahydrothiophene dioxide, thionaphthene, and mixtures thereof.

11. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair simultaneously with the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of cyclohexyl acetate.

12. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair simultaneously with the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of p-nitro benzoic acid methyl ester.

13. A process for boosting the action of a cationic direct dye on human hair which comprises treating said hair simultaneously with the application of said dye with a liquid selected from the group consisting of aqueous solutions and dispersions at temperatures of substantially 15° to 40° C., said liquids containing substantially 0.5 to 10 weight percent of diethyl phthalate.

14. A process according to claim **8** wherein said dye is taken from the class consisting of crystal violet, fuchsin, methylene blue,



and

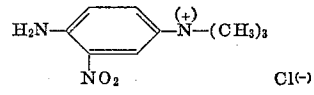
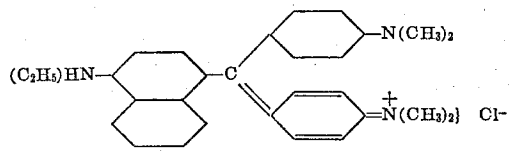
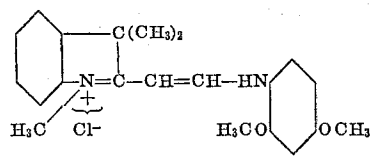
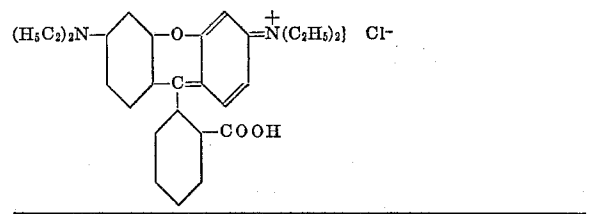
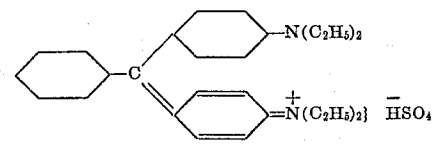
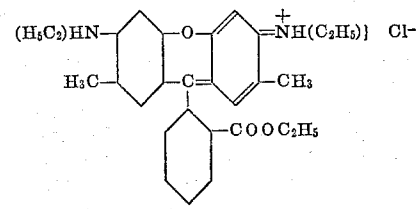


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Victoria Blue R	44 040
	
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Rhodamine B Extra	45 170
	
Astradiamond Green GX	42 040
	
Rhodamine 4 GD	45 160
	

Dyes named in U.S. Patent 3,100,739.

(References on following page)

9

References Cited

UNITED STATES PATENTS

2,069,215	2/1937	Chambers	8—85 X
2,585,610	2/1952	Wittwer	8—10

FOREIGN PATENTS

239,365	7/1962	Australia.

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U.S. Cl. X.R.

8—10, 83, 85, 92, 93