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MERCAPTANS FOR BOOSTING THE DYEING OF HUMAN HAIR WITH DIRECT DYES

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U.S. Cl. 8—10.1 24 Claims

ABSTRACT OF THE DISCLOSURE

A process is disclosed for improving the coloring of human hair, especially living human hair, with direct dyes by the use of mercaptans which are insoluble or difficultly soluble in water. The mercaptans are mercaptocarboxylic acid esters and amides. Emulsions or dispersions of the mercaptans can be used to treat the hair prior to dyeing or they can be combined with the dyeing composition.

The invention relates to substances which boost the activity of dyeing agents for human hair, and more particularly to so-called direct dyes, applied to living human hair.

It has previously been proposed to improve the action of direct dyes on human hair, by treating the hair, prior to dyeing, with readily water-soluble mercapto compounds, such as thioglycolic acid or its alkali or ammonia salts. However, in practice the production of uniform and reproducible coloring had met with difficulties because discoloration of the hair occurs. It therefore has also been suggested to carry out an ensuing treatment with oxidizing agents, such as hydrogen peroxide. However, this is an involved procedure and eliminates the advantages of the use of direct dyes which, by themselves, do not require the addition of oxidizers. Another considerable drawback upon the use of the known water-soluble mercapto compounds, e.g., thioglycolic acid or its alkali or ammonium salts, consists in the lack of storability of mixtures thereof with direct dyes.

The object of the invention is to present a process and agents for its accomplishment which facilitate coloring of human hair with direct dyes while avoiding the above-named disadvantages. This can be attained by treating the hair with aqueous dispersions or emulsions of mercaptans which are insoluble or difficultly soluble in water.

Mercaptans of this kind which lend themselves to the purpose are particularly mercaptocarboxylic acid esters, preferably alpha- and beta-mercaptocarboxylic acids, and/or mercaptocarboxylic acid amides.

To be considered therefore are such compounds as thioglycolic acid esters, thiolactic acid esters and beta-mercaptopropionic acid esters of primary, secondary and tertiary mono- and bivalent alcohols, such as methyl-, dodecyl-, citronellyl-, tertiary heptyl alcohol, ethylene glycol monoethyl ether, diethylene glycol, cyclohexanol and phenol; furthermore, thioglycolic acid diethanolamide, thioglycolic acid - bis - (beta-hydroxyethoxyethyl)-amide and thioglycolic acid formamide.

In many instances the esters of thioglycolic acids, of thiolactic acid and of mercaptopropionic acid with alcohols such as ethyl-, propyl-, butyl-, isobutyl-, hexyl-, isoheptyl-, isooctyl-, octyl- and tetrafurfuryl alcohol and with diethyleneglycol monoethyl ether have proved especially applicable.

Of the mercaptocarboxylic acid amides, thioglycolic acid cyclohexylamide and N,N'-bis-(mercaptoacetyl)-1,6-hexamethylenediamine are especially to be mentioned.

The process can be carried out in such a manner that the hair first is treated with an emulsion or dispersion of the insoluble or difficultly soluble substituted mercaptans named, followed by rinsing of the hair and dyeing with the direct dyes in the conventional manner.

Direct dyes suitable for the purpose are nonionic compounds based upon anthraquinone or aminoanthraquinone or azo dyes. Particularly, those dyestuffs named in British Pat. 957,119 can be employed or those sold under the name Celliton (registered trademark).

Anionic direct dyes also are applicable, especially those based on acid azo dyes and triarylmethane dyes and also corresponding anthraquinone and aminoanthraquinone dyes.

Finally, cationic dyestuffs which dye directly also can be employed.

The dyes are employed in the conventional quantities of 0.1 to 5 weight percent, preferably 0.5 to 3 percent. However, when the effect of increased color intensity is not desired, the booster agents according to the invention facilitate a substantial decrease in the amount of dyestuff required, in some cases down to 1/10 the amount otherwise used.

The booster liquids in the form of emulsions or dispersions containing the water-insoluble or difficultly soluble substituted mercaptans also can be applied as the last rinse after shampooing of the hair to be dyed. The concentration of the active ingredients in all instances is approximately 0.1 to 10 weight percent, and preferably 1 to 5 percent.

If desired, the booster treatment can also be combined with the dyeing process. The booster agents, in this case, are incorporated in the dyeing compounds either upon their manufacture or shortly before application. It goes without saying that chemical compatibilities of the booster with the other materials present must be considered. It is feasible not to use just one of the water-insoluble or difficultly soluble substituted mercaptans, but a mixture of several such compounds.

The pH value of the dispersions or emulsions containing these boosters can be adapted to the prevailing conditions. Equally good results are obtained when the pretreatment liquid or the last rinse after shampooing is not alkaline, but neutral or acid.

The agents can be mixed with any desired wetting agents, detergents and washing agents, especially those which are anionic or nonionic. Suitable wetting agents, detergents and washing agents are especially alkylbenzene sulfonates, fatty alcohol sulfates, alkylsulfonates, fatty acid ethanolamides, addition products of ethylene oxide on fatty acids and fatty alcohols.

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

These admixtures are employed in the quantities customary for the purpose. Wetting agents and detergents particularly are employed at 0.5 to 30 weight percent, thickeners in amounts of 0.1 to 25 weight percent, calculated on the total composition. The concentration of the direct dyes depending upon the purpose amounts to up to 5 weight percent, preferably however to 0.1 to 2 weight percent, also calculated on the total composition.

The advantage of the novel process according to the invention reside in the feasibility of considerably reducing the amount of dye to be used without materially detracting from the color intensity; or, when using the customary amounts of dyestuff, to increase the intensity considerably. Other advantages are that not only the action of the dye on the human hair is improved, but that resistance to abrasion and rubbing ensues. The singular effects named to a certain extent depend upon the

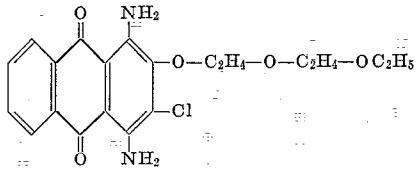
boosting agent used and especially on the kind of dyestuff employed.

Finally, a particularly great advantage is found in the fact that mixtures of direct dyes with the water-insoluble or difficultly soluble substituted mercaptans named are storable for great lengths of time. These mixtures advantageously are used in practice in the form of creams or pastes. Hair dyes containing water-soluble mercapto compounds cannot be stored for any length of time (see, e.g., Example 7 below).

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 hereinatfer claimed.

EXAMPLE 1

A strand of naturally greyed human hair was saturated with a 1 weight percent aqueous solution of a dyestuff having Formula 1



(1)

The solution had been adjusted to a pH of 9.5 with aqueous ammonia and was allowed to act on the hair for 20 minutes at room temperature. This was followed by shampooing and rinsing. The hair thus treated had a light red color.

When the dyeing solution was fortified with 1 weight percent thioglycolic acid isobutylester, dispersed therein, a brilliant deep red color was attained.

EXAMPLE 2

A dyeing cream was prepared from 8 weight parts cetylstearyl alcohol, 2 weight parts fatty alcohol C_{12}–C_{14}, 9 weight parts fatty alcohol sulfate C_{12}–C_{18} by heating these components to 80° C., adding 0.2 weight part 2,2'-diaminoazobenzene, 0.4 weight part 4,4'-diaminoazobenzene, 0.4 weight part 1,4-diamino-5-(1',4',7'-trioxanonyl)-anthraquinone, and 2 weight parts thioglycolic acid isopropylester, and emulsified at this temperature with 70 parts water of like temperature. After cooling to 40° C., the pH was adjusted to 9.5, and the emulsion made up to 100 parts with water. The dyeing cream thus obtained colored living human grey hair to a beautiful dark brown.

With the same dyeing process, but without the addition of the thioglycolic acid isopropylester, a brown color also was obtained which, however, had a much weaker hue.

EXAMPLE 3

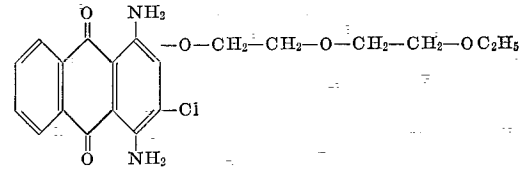
Aqueous solutions or dispersions, respectively, were produced containing as dyestuff 1,4-diamino-2-chloro-3-(1',4',7'-trioxanonyl-anthraquinone and as a booster 5 weight percent of one of the compounds listed in Table 1. The pH of these dispersions was adjusted to 9.5 with ammonia. Grey hair was treated with these coloring baths for 20 minutes at room temperature, rinsed with water and shampooed.

In all instances the color obtained was a distinct improvement over the light red color which was produced in the like process but without the boosters named.

Corresponding results were obtained when, in lieu of the dyestuff named, a dye was used as listed in Table 2.

EXAMPLE 4

A strand of grey hair was dyed with a 1 weight percent aqueous dispersion of a dyestuff having Formula 2



(2)

which had been adjusted to a pH of 9.5 with ammonia. The dye was allowed to act for 20 minutes at room temperature, and the hair was then shampooed. A light red color was obtained.

An intensively brilliant red color ensued when, at otherwise like working conditions, the hair was treated, prior to dyeing, with an aqueous-ammoniacal emulsion of 5 weight percent thioglycolic acid tertiary-butyl ester of a pH of 9.5 for 20 minutes at room temperature.

Similar results were obtained when the pretreatment with the thioglycolic acid tertiary-butyl ester emulsion was carried out when this emulsion had a pH of 2 or of 7.

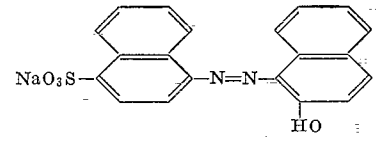
EXAMPLE 5

Aqueous dispersions were produced containing as a cationic dyestuff 0.3 weight percent crystal violet and as booster one of the compounds named in Table 3 in the amounts named therein. The dispersions were adjusted to a pH of 9.5 with ammonia. Living grey human hair was treated with these dispersions for 20 minutes at room temperature. After completed dyeing the hair was shampooed and dried.

In all instances, considerable improvement was attained over the light purple color which resulted from like treatment with the same compounds which did not contain the booster agents.

EXAMPLE 6

A strand of naturally grey human hair was dyed by immersion in an aqueous-ammoniacal fatty alcohol-fatty alcohol sulfate emulsion of a pH of 9.5 for one minute at room temperature. This emulsion further contained 5 weight percent thioglycolic acid tetrahydrofurfuryl ester. After squeezing out the excess of the emulsion, the hair was dyed for 20 minutes with an aqueous solution of a dyestuff having Formula 3



(3)

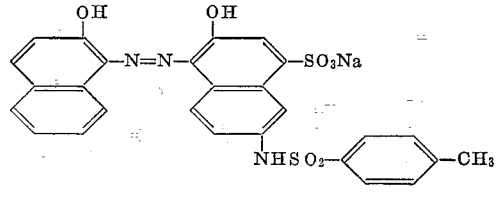
having a pH of 9.5. After dyeing, the hair was shampooed, rinsed and dried. It had a brilliant red color. Changes in the time of action of the pretreatment to between 10 seconds and 30 minutes effected corresponding differences in the shading of the coloring obtained.

Without the boosting action of the thioglycolic acid tetrahydrofurfuryl ester, the red coloring was considerably weaker in all instances.

A brilliant red color also was obtained when the pretreatment bath had a pH of 2 or of 7.

EXAMPLE 7

Naturally grey living human hair was treated for 20 minutes at room temperature with a solution containing 1 weight percent of a dyestuff having Formula 4



(4)

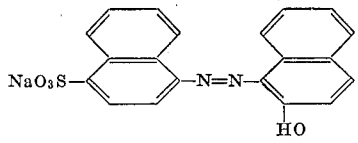
adjusted to a pH of 9.5 with ammonia. A weak grey-green coloration of the hair resulted therefrom.

When the hair was treated under like conditions but with simultaneous incorporation of 5 weight percent thioglycolic acid isopropyl ester in the dyeing solution, a deep green color was obtained.

Practically the same result was obtained when the dyestuff containing the mercaptan had been stored for approximately 6 months prior to application. In contradistinction, if in lieu of the booster, thioglycolic acid ester, thioglycolic acid itself is used, the dyeing agent is not even storable for 3 days.

EXAMPLE 8

Grey hair was treated with an aqueous solution containing 1 weight percent of a dye having Formula 3 (see also Example 6)



(3)

adjusted to a pH of 2.5, for 20 minutes at room temperature. The hair assumed a weak red color.

A strong red color was obtained when, at otherwise like treatment, the dyeing solution contained 5 weight percent thioglycolic acid hexyl ester.

TABLE 1

No.	Material
1	Thioglycolic acid methyl ester.
2	Thioglycolic acid ethyl ester.
3	Thioglycolic acid propyl ester.
4	Thioglycolic acid butyl ester.
5	Thioglycolic acid hexyl ester.
6	Thioglycolic acid octyl ester.
7	Thioglycolic acid dodecyl ester.
8	Thioglycolic acid tetrahydrofurfuryl ester.
9	Thioglycolic acid citronellyl ester.
10	Thioglycolic acid isopropyl ester.
11	Thioglycolic acid isobutyl ester.
12	Thioglycolic acid isoheptyl ester.
13	Thioglycolic acid isooctyl ester.
14	Thioglycolic acid tertiary-butyl ester.
15	Thioglycolic acid tertiary-heptyl ester.
16	Thioglycolic acid ethylene glycol monoethyl ether ester.
17	Thioglycolic acid diethylene glycol ester.
18	Thioglycolic acid diethylene glycol monoethyl ether ester.
19	Thioglycolic acid phenyl ester.
20	Thiolactic acid ethyl ester.
21	Beta-mercaptopropionic acid butyl ester.
22	Thioglycolic acid cyclohexamide.
23	N,N′-bis-(mercaptoacetyl)-1,6-hexamethylenediamine.

TABLE 2

Name of dye	Color Index No.
Supracene Red G	17045
Supracene Red B	17070
Supracene Violet 4 BF	62020
Supracene Blue GE	Acid Blue 66
Isolane Grey BRLS	Acid Black 140

TABLE 3

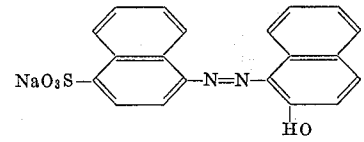
No.	Material	Weight percent
1	Thioglycolic acid diethanolamide	3
2	Thioglycolic acid hydroxyethoxyethylamide	1
3	Thioglycolic acid-di-(hydroxyethoxyethyl)-amide	2

TABLE 4

No.	Material	Weight percent
1	Thioglycolic acid ethyl ester	3
2	Thioglycolic acid hexyl ester	3
3	Thioglycolic acid tetrahydrofurfuryl ester	3
4	Thioglycolic acid isopropyl ester	3
5	Thioglycolic acid tertiary-butyl ester	3
6	Thioglycolic acid diethylene glycol ester	3
7	Thiolactic isopropyl ester	3
8	Beta-mercaptopropionic acid ethyl ester	3
9	Thioglycolic acid cyclohexylamide	5
10	Thioglycolic acid diethanolamide	5
11	N,N′-bis-(mercaptoacetyl)-1,6-hexamethylenediamine	5

EXAMPLE 9

Coloring baths were produced containing 1 weight percent of an anionic dyestuff having Formula 3 (see Examples 6 and 8)



(3)

and further containing as booster one of the compounds listed in Table 4 in the quantities named therein. The dyeing liquid was adjusted to a pH of 9.5 with aqueous ammonia.

Living human hair was dyed by treating it with these liquids for 20 minutes at room temperature. After dyeing, the hair was shampooed and dried. In all instances, the coloration was a considerable improvement over the weak red color obtained under the same conditions but without the presence of the booster in the dyeing liquid.

What is claimed is:

1. A process for boosting the action of a direct dye on human hair which comprises treating said hair substantially at room temperature with a dispersion of substantially 0.1 to 10 weight percent of compounds selected from the group consisting of water-insoluble or difficultly soluble esters of thioglycolic acid, thiolactic acid, beta mercaptopropionic acid with primary, secondary and tertiary mono and divalent alcohols; thioglycolic acid diethanolamide, thioglycolic acid mono and dihydroxyethyl amide, thioglycolic acid formamide, thioglycolic acid cyclohexamide, N,N¹-bis-(mercaptoacetyl)-1,6-hexamethylene diamine, and mixtures thereof and thereafter applying said dye.

2. A process according to claim **1** wherein said alcohols are citronellyl alcohol, mono and diethylene glycol monoethyl ether, diethylene glycol, cyclohexanol, phenol, tetrafurfuryl alcohol, or mixtures thereof.

3. A process according to claim **1**, in which said compound is thioglycolic acid ethyl ester.

4. A process according to claim **1**, in which said compound is thioglycolic acid butyl ester.

5. A process according to claim **1**, in which said compound is thioglycolic acid dodecyl ester.

6. A process according to claim **1**, in which said compound is thioglycolic acid isopropyl ester.

7. A process according to claim **1**, in which said compound is thioglycolic acid isobutyl ester.

8. A process according to claim **1**, in which said compound is thioglycolic acid isooctyl ester.

9. A process according to claim **1**, in which said compound is thioglycolic acid tertiary-butyl ester.

10. A process according to claim **1**, in which said compound is thioglycolic acid tertiary-heptyl ester.

11. A process according to claim **1**, in which said compound is thiolactic acid ethyl ester.

12. A process according to claim **1**, in which said compound is beta-mercaptopropionic acid butyl ester.

13. A process for boosting the action of a direct dye on human hair which comprises treating said hair substantially at room temperature with the application of said dye in a dispersion of substantially 0.1 to 10 weight percent of compounds selected from the group consisting of water-insoluble or difficultly soluble esters of thioglycolic acid, thiolactic acid, beta mercaptopropionic acid with primary, secondary and tertiary mono and divalent alcohols; thioglycolic acid diethanolamide, thioglycolic acid mono and dihydroxyethoxyethyl amide, thioglycolic acid formamide, thioglycolic acid cyclohexamide, N,N¹-bis-(mercaptoacetyl)-16-hexamethylene diamine, and mixtures thereof.

14. A process according to claim **13** wherein said alcohols are citronellyl alcohol mono and diethylene glycol

monoethyl ether, diethylene glycol, cyclohexanol, phenol, tetrafurfuryl alcohol or mixtures thereof.

15. A process according to claim 13 in which said compound is thioglycolic acid ethyl ester.

16. A process according to claim 13, in which said compound is thioglycolic acid butyl ester.

17. A process according to claim 13, in which said compound is thioglycolic acid dodecyl ester.

18. A process according to claim 13, in which said compound is thioglycolic acid isopropyl ester.

19. A process according to claim 13, in which said compound is thioglycolic acid isobutyl ester.

20. A process according to claim 13, in which said compound is thioglycolic acid isooctyl ester.

21. A process according to claim 13, in which said compound is thioglycolic acid tertiary-butyl ester.

22. A process according to claim 13, in which said compound is thioglycolic acid tertiary-heptyl ester.

23. A process according to claim 13, in which said compound is thiolactic acid ethyl ester.

24. A process according to claim 13, in which said compound is beta-mercaptopropionic acid butyl ester.

References Cited

UNITED STATES PATENTS

2,577,711	12/1951	McDonough	167—87.1X
2,615,782	10/1952	Haefele	167—87.1X
2,615,828	10/1952	Haefele	167—87.1

FOREIGN PATENTS

833,809	4/1960	Great Britain	167—88
906,526	9/1962	Great Britain	167—88

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