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ACID FADING INHIBITION USING
N-BENZYLATED AMINO-TRIAZOLES
AND -TETRAZOLES

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1

2

This invention relates to improvements in the dyeing of textile materials containing organic derivatives of cellulose (i. e., cellulose esters and ethers, such as cellulose acetate, ethyl cellulose, and the like), whereby the colorations thereon are rendered fast to acid fading (also known as "atmospheric" or "gas" fading).

Many of the dyestuffs yielding desirable shades on organic derivatives of cellulose in textile materials, and having satisfactory fastness to light, washing and other agencies, have been found to be sensitive to fading upon prolonged exposure to acid fumes, particularly the combustion products of coal, gas and other fuels, which are present in minor concentration in the atmosphere, particularly in urban communities. In some cases, the brightness of the dyeing is dulled, while in others a marked change in the shade of the coloration occurs. This is especially true of colorations produced with anthraquinone dyes, particularly those yielding valuable blue colorations on organic derivatives of cellulose. When textile materials dyed with these compounds are exposed to acid fumes, the coloration changes to one of a reddish or brownish cast, and on continued exposure may change to a pink coloration. This effect limits to a considerable extent the usefulness of such dyestuffs, which are otherwise highly satisfactory. Sensitivity to acid fumes is not restricted to anthraquinone dyes, but is likewise noticeable in the case of dyestuffs belonging to other classes.

Numerous proposals have been made to overcome acid fading, ordinarily involving the application to the textile material of compounds or compositions intended to prevent such fading of the coloration. Such compounds or compositions are referred to herein as acid fading inhibitors.

For commercial use, an acid fading inhibitor should be colorless, adapted to withstand prolonged exposure to light and/or combustion gases without discoloration, fast to dry-cleaning and wet-washing, odorless, and non-toxic in the sense that it causes no skin irritations when materials treated therewith are worn. While most of the acid fading inhibitors heretofore proposed satisfy a number of these requirements, in most cases they are defective in some of said requirements, whereby their usefulness is considerably impaired. In particular, most of the compounds suggested heretofore are subject to discoloration on exposure to acid fumes and/or to light, so that they cannot be used on goods dyed in light colors or having white designs or backgrounds

thereon. Many of the proposed materials are too soluble in water or in dry-cleaning solvents so that they are largely removed when textile materials treated therewith are subjected to customary cleansing treatments.

In addition, from the standpoint of economy and convenience, it is highly desirable that the acid fading inhibitors be applicable to the goods to be dyed together with the dyestuff, so that a separate pre-treatment or after-treatment can be avoided. For this purpose, the compounds employed must have suitable solubility properties, e. g., they should be insoluble but dispersible in water, and should possess a natural affinity for organic derivatives of cellulose.

Moreover, since the dyeing is often carried out at elevated temperatures, it is necessary that the compounds employed have a sufficiently high melting point to avoid fusion in the dye bath. When such fusion occurs, the molten compound forms an oil which generally separates from the dispersion and dissolves a substantial portion of the dispersed dyestuff. The resulting liquid oil-dye mixture is generally deposited on the goods to be dyed, forming unsightly spots or streaks. While many of the disclosures in the prior art of acid fading inhibitors indicate that they can be applied to textile materials at any time during the processing thereof, including simultaneous application with the dyestuff, many of the suggested compounds are liquid at ordinary temperatures or are solids of such low melting point that they are substantially useless for application from a dye bath under the usual conditions of commercial dyeing.

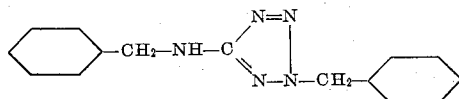
We have discovered that certain derivatives of triazoles and tetrazoles or in other words, derivatives of monocyclic-azoles having not more than two carbon atoms in the azole nucleus, the remaining members of said nucleus being nitrogen atoms, particularly N-substituted derivatives of 5-amino-tetrazole and of 3-amino-1,2,4-triazole (i. e., C-amino triazoles and -tetrazoles) are highly effective acid fading inhibitors when applied in minor amounts to textile materials containing organic derivatives of cellulose. For the purposes of this invention, we employ preferably compounds of the aforesaid class which are colorless, substantially insoluble in water, and which remain solid at temperatures of aqueous dye baths in which they are employed.

A preferred class of acid fading inhibitors of this invention is illustrated by benzlation products of 5-amino-tetrazole and of 3-amino-1,2,4-triazole, including derivatives which con-

3

tain substituents, such as chlorine, alkyl, hydroxyl, alkoxy, nitro or diethylamino groups in the benzene nucleus of the benzyl radical or radicals.

For example, so-called α -dibenzyl-5-amino-tetrazole, first described by Thiele and Ingle in *Annalen der Chemie* 287, page 255 (1895), which can be prepared by reaction of an excess of benzylchloride with 5-amino-tetrazole in the presence or absence of an inert solvent, such as dichlorobenzene, and having the probable formula



has been found eminently satisfactory as an acid fading inhibitor for use in accordance with this invention. Similarly, benzylation products of 3-amino-1,2,4-triazole, prepared in an analogous manner, e. g., the dibenzyl-3-amino-1,2,4-triazole, having a melting point of 127° C., are likewise highly satisfactory for the purpose of the invention.

These materials not only possess all of the desired properties required in general for acid fading inhibitors, but, in addition, can be advantageously applied to textile materials from a dye bath together with the dyestuff. Thus, they are colorless, are not discolored on prolonged exposure to light or combustion gases, are insoluble not only in water but also in dry-cleaning solvents, so that they withstand the effects of usual cleaning operations without loss of their effectiveness. Moreover, they are odorless and non-irritating to the skin when incorporated in textile materials. In addition, they can be readily dispersed in water in the same manner as is usual for dyestuffs employed for coloring organic cellulose derivatives, have no tendency to liquefy in the dye bath at the temperatures ordinarily employed, and show a natural affinity for organic derivatives of cellulose.

Application of the acid fading inhibitors of my invention to textile materials containing organic derivatives of cellulose may be carried out by treatment of the goods with an aqueous dispersion of the inhibitor before or after the dyeing, but is most conveniently and economically carried out simultaneously with the dyeing. Thus, the inhibitors of this invention can be dispersed in the aqueous bath by any of the methods commonly used for similar dispersion of dyestuffs adapted for dyeing organic derivatives of cellulose. For instance, they may be dissolved together with the dyestuff in a water-miscible solvent, and brought into dispersion by addition of a concentrated aqueous solution of a dispersing agent having soap-like properties and/or protective colloid action, whereupon the resulting mixture can be diluted with sufficient water to yield a dye bath of the desired concentration.

The amount of acid fading inhibitors of my invention which can be employed may be varied within wide limits, but in general concentrations in the dye bath of the order of 0.01 to 0.1%, and generally of the order of 1 to 5 times the amount of dyestuff used, have been found adequate and highly satisfactory to provide the desired fastness properties in the dyed material.

The temperature of the dye bath may be chosen to suit the dyestuff and the textile material to be dyed. Thus, the dyeing may be carried

4

out at any desired temperature up to about 80-90° C. without injuring the dispersion and without production of spots or streaks from fusion of the acid fading inhibitor.

The following examples wherein parts and percentages are by weight and temperatures are in degrees centigrade illustrate use of the preferred acid fading inhibitors of my invention.

Example I

1 to 2 parts of α -dibenzyl-5-amino-tetrazole and 0.6 part of a blue cellulose acetate dye consisting essentially of 1-(2'-hydroxy-ethylamino)-4-(monomethylamino)-anthraquinone are dissolved in a small quantity of a solvent composed of equal proportions of alcohol and acetone, or another suitable water-miscible solvent, and 40 parts of 5% aqueous solution of N,N-oleyl-methyl-aurine sodium salt, or of another suitable saponaceous dispersing agent, are added to the aforesaid solution. The resulting mixture is diluted with 5000 parts of warm water at a temperature of 45 to 55°. 100 parts of cellulose acetate silk in the form of yarn or fabric is worked in the dye bath, and the temperature is gradually raised to 80 to 90°. When the dyeing operation is complete, the cellulose acetate material is removed from the dye bath, washed with dilute aqueous soap solution, rinsed and dried. The blue coloration of the cellulose acetate silk, dyed in the foregoing manner shows excellent resistance to acid fumes, as demonstrated by a test wherein the dyed material was exposed for a prolonged period to the combustion products of illuminating gas, produced in a Bunsen burner.

Similar results are obtained when other cellulose acetate dyes of the anthraquinone, azo or other series, especially dyestuffs yielding a blue coloration, are substituted for the blue amino anthraquinone dyestuff of the foregoing example; and/or upon substituting a corresponding amount of dibenzyl-3-amino-1,2,4-triazole (melting point ca. 125°) or a crude benzylation product of 3-amino-1,2,4-triazole for the α -dibenzyl-5-amino-tetrazole of the above example.

Example II

1 to 2 parts of α -dibenzyl-5-amino-tetrazole are dissolved, as in the preceding example, in a mixture of equal parts of alcohol and acetone, and 40 parts of 5% aqueous solution of N,N-oleyl-methyl-aurine sodium salt or other suitable saponaceous dispersing agent, are added. The resulting concentrated dispersion of the tetrazole derivative is diluted with 5000 parts of water at 45 to 55° and 100 parts of cellulose acetate silk, previously dyed with 1,4-di(monomethylamino)-anthraquinone are worked in the bath while gradually raising the temperature to 80°, and thereafter, for a period of ½ to 1 hour. The cellulose acetate silk is then removed, washed with dilute aqueous soap solution, rinsed and dried. The dyed material thus obtained shows excellent resistance to acid fading, similar to that obtained in the dyed material of Example I, upon subjecting it to a corresponding test involving exposure to the fumes of a Bunsen burner.

Cellulose acetate materials dyed with other dyestuffs can be treated in the same manner as in the foregoing example, and dibenzyl-3-amino-1,2,4-triazole (melting point ca. 125°) or the crude benzylation product of 3-amino-1,2,4-triazole can

be employed instead of α -dibenzyl-5-amino-tetrazole, with similarly advantageous results.

In either of the foregoing examples, substitution products of the benzylated amino tetrazole or triazole can be employed, wherein the benzyl radical contains substituents, such as chlorine, alkyl, hydroxyl, alkoxy, nitro, dialkylamino groups, and the like, or combinations of two or more such groups, in the benzene nucleus.

Similarly, the treatment of Example II may be applied to undyed textile materials containing organic derivatives of cellulose, before carrying out the dyeing operation in order to render the coloration fast to acid fumes.

The acid fading inhibitors of this invention can be applied singly, or combinations of two or more inhibitors can be used.

We claim:

1. The process for increasing the resistance to acid fading of colorations on textile material comprising an organic derivative of cellulose, which comprises incorporating in such material a water insoluble, solid, colorless N-benzylated derivative of a compound of the class consisting of 3-amino-1,2,4-triazole and 5-amino-tetrazole.

2. The process for increasing the resistance to acid fading of colorations on textile material comprising an organic derivative of cellulose, which comprises incorporating in such material α -dibenzyl-5-amino-tetrazole.

3. The process for increasing the resistance to acid fading of colorations on textile material comprising an organic derivative of cellulose, which comprises incorporating in such material dibenzyl-3-amino-1,2,4-triazole.

4. Textile material comprising dyed fibers of an organic derivative of cellulose, having incorporated in said fibers a water insoluble, solid, colorless N-benzylated derivative of a compound of the class consisting of 3-amino-1,2,4-triazole and 5-amino-tetrazole.

5. Textile material comprising dyed fibers of an organic derivative of cellulose, having α -dibenzyl-5-amino-tetrazole incorporated in said fibers.

6. Textile material comprising dyed fibers of an organic derivative of cellulose, having dibenzyl-3-amino-1,2,4-triazole incorporated in said fibers.

7. In a process for dyeing textile material containing an organic derivative of cellulose, the improvement which comprises dispersing a water insoluble, solid, colorless N-benzylated derivative of a compound of the class consisting of 3-amino-1,2,4-triazole and 5-amino-tetrazole in a dye bath containing a water insoluble dyestuff for said organic derivative of cellulose, and working said material in the resulting bath until dyeing is complete.

8. In a process for dyeing textile material containing an organic derivative of cellulose, the improvement which comprises dispersing α -dibenzyl-5-amino-tetrazole in a dye bath containing a water insoluble dyestuff for said organic derivative of cellulose, and working said material in the resulting bath until dyeing is complete.

9. In a process for dyeing textile material containing an organic derivative of cellulose, the improvement which comprises dispersing dibenzyl-3-amino-1,2,4-triazole in a dye bath containing a water insoluble dyestuff for said organic derivative of cellulose, and working said material in the resulting bath until dyeing is complete.

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