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# UNITED STATES PATENT OFFICE

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## 1,3-DIPHENYLIMIDAZOLIDINE AND CERTAIN DERIVATIVES THEREOF USED AS ACID FADING INHIBITORS

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12 Claims. (Cl. 8—61)

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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 water-insoluble 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

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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.

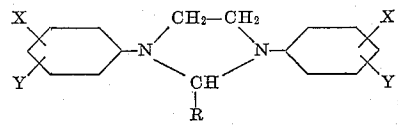
Moreover, since the dyeing is often carried out at elevated temperatures, it is necessary that the compounds employed have a sufficiently high melting point to avoid fusion in the dye bath. When such fusion occurs, the molten compound forms an oil which generally separates from the dispersion and dissolves a substantial portion of the dispersed water-insoluble 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 imidazolidine derivatives, specifically 1,3-diphenylimidazolidine and certain derivatives thereof, are highly effective acid fading inhibitors when applied in minor amounts to textile materials containing organic derivatives of cellulose colored with organic dyestuffs. For the purposes of this invention, we employ compounds of the aforesaid class which are colorless, substantially insoluble in water, and which remain solid at temperatures of the aqueous dye-baths in which they are employed.

The acid fading inhibitors of this invention are 1,3-diphenylimidazolidine which may contain non-solubilizing nuclear substituent groups or radicals such as halogen, alkyl, nitro, cyano and similar groups in the phenyl residues, and/or aliphatic, aromatic, or heterocyclic radicals in the 2-position of the imidazolidine ring, the latter radicals being unsubstituted or containing such non-solubilizing substituents as are suitable for

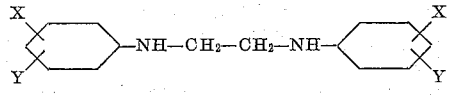
inclusion in the phenyl radicals, e. g., halogen, alkyl, nitro and cyano groups.

Thus, the acid fading inhibitors of this invention are represented by the general formula



wherein X and Y are nuclear substituents selected from the group consisting of hydrogen and non-solubilizing groups and radicals (e. g., alkyl, halogen, nitro, and cyano groups), and R is selected from the group consisting of hydrogen, alkyl, aryl, and heterocyclic radicals which are free of solubilizing substituents.

The aforesaid compounds can be prepared by reacting an aldehyde of the formula R.CHO with an NN'-diphenyl-ethylenediamine of the formula



wherein X and Y are nuclear substituents selected from the group consisting of hydrogen and non-solubilizing groups and radicals (e. g., alkyl, halogen, nitro, and cyano groups), and R is selected from the group consisting of hydrogen, alkyl, aryl, and heterocyclic radicals which are free of solubilizing substituents. For example, as disclosed by Moos in Berichte Der Deutchen Chemischen Gesellschaft, vol. 20, page 732, 1,2,3-triphenylimidazolidine can be prepared by heating benzaldehyde with NN'-diphenyl-ethylenediamine to boiling temperatures. The resulting imidazole derivative can be purified by recrystallization from alcohol, petroleum ether, benzene or other suitable solvents. 2-methyl-1,3-diphenyl-imidazolidine can be prepared in an analogous manner by substituting acetaldehyde for benzaldehyde in the aforesaid procedure, and 2-furyl-1,3-ditolylimidazolidine can be similarly prepared from furfural and NN'-ditolyl-ethylenediamine.

The resulting compounds have been found eminently satisfactory as acid fading inhibitors for use in accordance with this invention. They have been found to possess not only all of the desired properties required in general for acid fading inhibitors but, in addition, can be advantageously applied to textile materials containing organic derivatives of cellulose 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 in water, and fast to dry-cleaning of the textile materials with the usual dry-cleaning solvents, so that they withstand the effects of usual cleaning operations of materials in which they are incorporated 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 our 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 water-insoluble 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 inhibitor of our invention which can be employed may be varied within rather wide limits. Thus, we have found them to be fully effective in amounts corresponding to about 1% by weight of the quantity of organic derivative of cellulose subjected to treatment therewith, and can be applied from a dye-bath or treatment bath containing said compounds in concentrations from 0.01 to 0.1%, such amounts being, for example, of the order of 1 to 5 times the amount of dyestuff employed. These proportions 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 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 illustrate the manner in which a number of acid fading inhibitors of our invention can be used.

*Example I*

1 to 2 parts of 2-methyl-1,3-diphenylimidazolidine 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 a 5% aqueous solution of N,N-oleyl-methyl-taurine 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 45–55° C. One hundred parts of cellulose acetate silk in the form of yarn or fabric is immersed in the dye-bath, the temperature gradually raised to 80–90° C., and the material worked in the dye-bath at this temperature for an hour. When the dyeing operation is complete, the cellulose acetate material is removed from the dye-bath, washed with a dilute aqueous soap solution, rinsed with water and dried.

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 by a Bunsen burner.

Similar results are obtained when other cellulose acetate dyes of the anthraquinone or azo series, especially dyestuffs yielding blue coloration, are substituted for the blue amino-anthraquinone dyestuff of the foregoing example;

and/or upon substituting a corresponding amount of another water-insoluble 1,3-diphenylimidazolidine of the general formula hereinbefore set forth, for the 2-methyl-1,3-diphenylimidazolidine of the example.

*Example II*

1 to 2 parts of 2-furyl-1,3-ditolylimidazolidine are dissolved, as in the preceding example, in a mixture of equal parts of alcohol and acetone, and 40 parts of a 5% aqueous solution of N,N-oleyl-methyl-taurine sodium salt, or another suitable saponaceous dispersing agent, are added. The resulting concentrated dispersion of the 1,3-ditolylimidazolidine derivative is diluted with 5000 parts of water at 45–55° C., 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° C., and thereafter at the same temperature for a period of ½ to 1 hour. The cellulose acetate silk is then removed, washed with dilute aqueous soap solution, rinsed with water and dried. The blue coloration of the dyed material thus obtained shows excellent resistance to acid fading, similar to that obtained in the case of the dyed material of Example I, as indicated by subjecting it to a similar test involving prolonged exposure to the fumes of a Bunsen burner burning illuminating gas.

Cellulose acetate materials dyed with other dyestuffs, particularly those of the blue range, can be treated in the same manner as in the foregoing example, and other 1,3-diphenylimidazolidines can be employed instead of the 2-furyl-1,3-ditolylimidazolidine of the example, with similarly advantageous rsults.

*Example III*

1 to 2 parts of 1,2,3-triphenylimidazolidine and 0.6 part of 1,4-di-(2'-hydroxyethylamino)-anthraquinone (a blue cellulose acetate dyestuff) are dissolved in a small quantity of a solvent composed of equal proportions of alcohol and acetone, and 40 parts of a 5% aqueous solution of N,N-oleyl-methyl taurine 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 110–130° F. 100 parts of cellulose acetate silk fabric are immersed in the dye-bath, and the temperature is gradually raised to 175–195° F., the cellulose acetate material being worked in the bath for one hour at the latter temperature. When the dyeing operation is complete, the cellulose acetate material is removed from the dye-bath, washed with dilute aqueous soap solution, rinsed with water and dried.

The blue coloration of the cellulose acetate material, dyed in the foregoing manner, shows excellent resistance to acid fumes when tested in the manner described in the preceding example.

Colorations on textile materials containing or made up of organic derivatives of cellulose other than cellulose acetate, e. g. other cellulose esters, or ethers such as ethyl cellulose, can be rendered fast to acid fading in the same manner in the foregoing examples. Similarly, colorations produced with other dyestuffs than those of the type employed in the examples are improved to a similar degree.

Furthermore, instead of the specific acid fading inhibitors employed in the examples, other compounds corresponding to the general formula



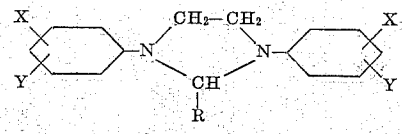
hereinbefore set forth can be used in like manner with equally advantageous results.

If desired, the treatment of Example II can be applied to undyed textile materials containing organic derivatives of cellulose, before carrying out a dyeing operation thereon in order to render the resulting 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 of water-insoluble dyestuffs on organic derivatives of cellulose in textile materials, which colorations are normally subject to fading when exposed to acid fumes, which comprises incorporating in such material a colorless water insoluble 1,3-diphenylimidazolidine having the general formula



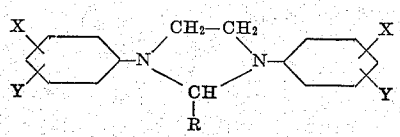
wherein X and Y are nuclear substituents selected from the group consisting of hydrogen, alkyl, halo, nitro and cyano groups, and R is selected from the group consisting of hydrogen, alkyl, aryl, and furyl radicals which are free of solubilizing substituents.

2. The process for increasing the resistance to acid fading of colorations of water-insoluble dyestuffs on organic derivatives of cellulose in textile materials, which colorations are normally subject to fading when exposed to acid fumes, which comprises incorporating in such material 2-methyl-1,3-diphenylimidazolidine.

3. The process for increasing the resistance to acid fading of colorations of water-insoluble dyestuffs on organic derivatives of cellulose in textile materials, which colorations are normally subject to fading when exposed to acid fumes, which comprises incorporating in such material 2-furyl-1,3-ditolylimidazolidine.

4. The process for increasing the resistance to acid fading of colorations of water-insoluble dyestuffs on organic derivatives of cellulose in textile materials, which colorations are normally subject to fading when exposed to acid fumes, which comprises incorporating in such material 1,2,3-triphenylimidazolidine.

5. Textile material comprising dyed fibers of an organic derivative of cellulose dyed with a water-insoluble dyestuff yielding colorations on said fibers normally subject to fading when exposed to acid fumes, having incorporated in said fibers a colorless water-insoluble 1,3-diphenylimidazolidine having the general formula



wherein X and Y are nuclear substituents selected from the group consisting of hydrogen, alkyl, halo, nitro and cyano groups, and R is selected from the group consisting of hydrogen, alkyl, aryl, and furyl radicals which are free of solubilizing substituents.

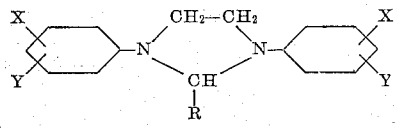
6. Textile material comprising dyed fibers of an organic derivative of cellulose dyed with a water-insoluble dyestuff yielding colorations on said fibers normally subject to fading when ex-

posed to acid fumes, having incorporated in said fibers 2-methyl-1,3-diphenyimidazolidine.

7. Textile material comprising dyed fibers of an organic derivative of cellulose dyed with a water-insoluble dyestuff yielding colorations on said fibers normally subject to fading when exposed to acid fumes, having incorporated in said fibers 2-furyl-1,3-ditolylimidazolidine.

8. Textile material comprising dyed fibers of an organic derivative of cellulose dyed with a water-insoluble dyestuff yielding colorations on said fibers normally subject to fading when exposed to acid fumes, having incorporated in said fibers 1,2,3-triphenyimidazolidine.

9. In a process for dyeing textile material containing an organic derivative of cellulose, the improvement which comprises dispersing a colorless water-insoluble 1,3-diphenylimidazolidine having the general formula



wherein X and Y are nuclear substituents selected from the group consisting of hydrogen, alkyl, halo, nitro and cyano groups, and R is selected from the group consisting of hydrogen, alkyl, aryl, and furyl radicals which are free of solubilizing substituents, in a dye-bath containing a water-insoluble dyestuff for said organic derivative of cellulose, yielding colorations thereon which are normally subject to fading when exposed to acid fumes, and working said material in the resulting bath until dyeing is complete.

10. In a process for dyeing textile material containing an organic derivative of cellulose, the improvement which comprises dispersing 2-methyl-1,3-diphenylimidazolidine in a dye-bath containing a water-insoluble dyestuff for said organic derivative of cellulose, yielding colorations thereon which are normally subject to fading when exposed to acid fumes, and working said material in the resulting bath until dyeing is complete.



11. In a process for dyeing textile material containing an organic derivative of cellulose, the improvement which comprises dispersing 2-furyl-1,3-ditolylimidazolidine in a dye-bath containing a water-insoluble dyestuff for said organic derivative of cellulose, yielding colorations thereon which are normally subject to fading when exposed to acid fumes, and working said material in the resulting bath until dyeing is complete.

12. In a process for dyeing textile material containing an organic derivative of cellulose, the improvement which comprises dispersing 1,2,3-triphenylimidazolidine in a dye-bath containing a water-insoluble dyestuff for said organic derivative of cellulose, yielding colorations thereon which are normally subject to fading when exposed to acid fumes, and working said material in the resulting bath until dyeing is complete.

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ALFRED GUENTHER.


## REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,930,232 | Ellis | Oct. 10, 1933 |
| 2,083,122 | Olpin | June 8, 1937 |
| 2,148,655 | Seymour | Feb. 28, 1939 |
| 2,176,506 | McNally | Oct. 17, 1939 |
| 2,255,090 | Tinker | Sept. 9, 1941 |
| 2,298,401 | McNally | Oct. 13, 1942 |
| 2,340,375 | Giles | Feb. 1, 1944 |
| 2,416,380 | Collie | Feb. 25, 1947 |