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3,544,363

DYED TEXTILE MATERIALS HAVING IMPROVED WET FASTNESS PROPERTIES AND METHOD OF PRODUCING SAME

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Claims priority, application Switzerland, Nov. 9, 1965, 15,411/65

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U.S. Cl. 117-139.5

5 Claims

ABSTRACT OF THE DISCLOSURE

Textile cellulosic materials dyed or printed with sulfur dyestuffs and having improved wet fastness properties, wherein the materials contain from 0.1 to 5.0% by weight, based on the dry weight of the material, of a bis- or poly- α,β -halohydrin compound containing at least one basic nitrogen atom.

This application is a continuation of our copending application Ser. No. 592,722, filed Nov. 8, 1966, now abandoned.

The invention in this application relates to the dyeing of fibrous cellulosic textile materials such as fabrics, and yarn, and more particularly, to a process and composition for treating sulfur-dyed cellulosic textiles to improve their wet fastness and their tensile strength.

In French Patent No. 1,352,583 and its Canadian counterpart Patent No. 734,324, which are commonly assigned with the present application, there is disclosed a process for improving the wet fastness properties of cellulosic textile fibers and fabrics dyed or printed with sulfur dyes by after-treatment of the freshly prepared dyeings or prints, subsequent to short rinsing and prior to their oxidation, with polyfunctional substances that yield stable reaction products together with the dyestuffs. The process disclosed in these two patents requires treatment of the dyed textile materials prior to their oxidation whereas the process of the present invention may be applied to the dyed textile materials either prior to or after oxidation.

One of the characterizing and most important aspects of the present invention is the treatment of the dyed textile materials with compounds containing at least one basic nitrogen atom. This is in contradistinction to the compounds disclosed in the above French and Canadian patents which do not contain basic nitrogen atoms. We have discovered that the basic nitrogen atom compounds when applied to dyed textile material effect substantial improvement in the wet fastness properties and in the tensile strength properties, as compared with the textile materials treated in accordance with the above French and Canadian patents.

More specifically, we have found that the improved wet fastness may be obtained by impregnating the dyed or printed textile materials, after rinsing, and either prior to or subsequent to oxidation, with 0.1 to 5.0% by weight, based on the weight of the dry textile materials, of an aliphatic or heterocyclic water-soluble bis- or poly- α,β -halohydrin compound containing at least one basic nitrogen atom.

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The nitrogen-containing halohydrins of the present invention are prepared by combining a halohydrin, such as epichlorohydrin, with a basic nitrogen compound, for example, in a suitable solvent, and then heating the mixture for a sufficient period of time to form a reaction product, after which the solvent may be removed from the product by distillation. The resultant reaction product is then applied to the dyed textile materials in a suitable manner, such as from an aqueous treating bath. The aqueous bath preferably may contain a basic compound so that the textile materials are impregnated under alkaline conditions. After impregnation of the fabrics, they may be subjected to conventional finishing treatments.

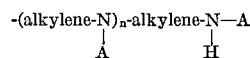
Water-soluble, nitrogenous bis- or poly- α,β -halohydrins suitable for use in the present invention are, for example, those obtained by reacting an epihalohydrin with ammonia or an amine of the general formula



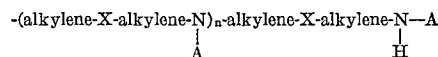
wherein

A represents hydrogen or an alkyl or hydroxyalkyl group of from 1 to 5 carbon atoms; and

R represents an alkyl or hydroxyalkyl group of from 1 to 5 carbon atoms; an



group, or an



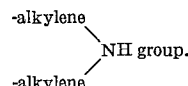
group, wherein

X may be oxygen or sulfur; and

n is an integer from 0 through 5;

or wherein

R and A may together represent an



Examples of amines corresponding to the above formula which may be used in the present invention are: methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, monohydroxyethylamine, monohydroxypropylamine, ethylenediamine, diaminopropanes, diaminobutanes, diaminohexanes, 3,3'-diaminodipropyl ether, piperazine, monohydroxyethyl-ethylene diamine, dihydroxyethylethylene diamine, diethylene triamine, dipropylene triamine, triethylene tetramine and the like.

In addition to improved wet fastness properties the water-soluble nitrogenous bis- or poly- α,β -halohydrins of the present invention also achieve a substantial reduction in loss of tensile strength which may occur during the storage of textile materials dyed or printed with sulfur dyes, and in particular, with Sulfur Black.

The following examples are given for the purpose of illustrating the present invention. Unless otherwise stated, temperatures are given in degrees Centigrade and percentages are percentages by weight based on the dry weight of the textile material to be dyed.

EXAMPLE 1

Cotton fabric is dyed in a conventional dyebath containing 5% Immedial Supra Yellow GWL (Color Index: Sulfur Yellow 5, constitution described in Collection Czechoslov. Chem. Commun., vol. 27 (1962), page 1553/48), 3.75 g./l. crystallized sodium sulfide, 4 g./l. calcined

sodium carbonate and 10 g./l. calcined Glauber's salt (liquor ratio 1:20). After rinsing, the fabric is introduced into a liquor containing 3% of a reaction product of ammonia and epichlorohydrin, the preparation of which is described below. By the addition of a sodium carbonate solution the liquor is adjusted to a pH of 10, then heated to 90–95° in the course of 20 minutes and kept at this temperature for 10 minutes. Subsequently, the fabric is thoroughly rinsed.

The examination of the fastness to washing with perborate, made in accordance to DIN 54015 (German Industrial Standards Method 54015), and the fastness to boiling with sodium carbonate, made in accordance to DIN 54031, indicates a substantially better result than that of a similarly dyed fabric without aftertreatment or one which is aftertreated in accordance with above-mentioned French Patent No. 1,352,583 and Canadian Patent No. 734,324. The fastness to washing in the presence of reducing substances, such as, for example, dextrin, is also considerably improved in the case of the cotton fabric aftertreated as disclosed in Example 1.

The reaction product used as the aftertreating agent is prepared in the following manner:

To a solution of 185 g. epichlorohydrin in 200 cc. methanol at 25–30° is added, dropwise, over a period of 3 hours, a solution of 17 g. of ammonia in 200 cc. of methanol. The mixture is stirred for 2 hours at 25–30°, heated to 70° over a 3 hour period, and kept at this temperature for 2 additional hours. The methanol is removed by vacuum distillation at 50–60° to produce 202 grams of a highly viscous oil reaction product that is easily soluble in water. For further purification, the product may be repeatedly dissolved in methanol and precipitated with ether.

A similarly effective aftertreatment product is obtained by an analogous reaction of 277 g. epichlorohydrin, dissolved in 300 cc. methanol, with a solution of 17 g. ammonia in 200 cc. methanol.

EXAMPLE 2

Cotton fabric is dyed in the usual manner in a dye bath containing 4% Hydron Blue R for Sol (Color Index: Vat Blue 43, CI No. 53630), 9 cc./l. sodium hydroxide solution of 33° Bé., and 4 g./l. hydrosulfite (liquor ratio 1:20). After rinsing the fabric, an aqueous solution having a pH of 10 and containing 20 g./l. of a reaction product of n-butylamine and epichlorohydrin, prepared as indicated below, is padded onto the fabric in such a manner that 2% of the product goes onto the fabric. Thereupon, the material is steamed for 2 minutes, thoroughly rinsed, and finished. The treated fabric, when compared with similarly dyed fabrics not aftertreated or those treated in accordance with the above French and Canadian patents, exhibits substantially improved wet fastness properties and, in particular, a good fastness to boiling with sodium carbonate and to washing with peroxide.

The aftertreatment reaction product may be prepared as follows:

A solution of 73 g. butylamine in 100 cc. ethanol, at 25°, is slowly added, dropwise, to 185 g. epichlorohydrin. Thereafter, the solution is heated to 60–65° over a 2 hour period and kept at this temperature for a further 2 hours. Subsequently, the ethanol is distilled off the solution and the limpid yellowish oil reaction product obtained is easily soluble in water.

A product having a similar effect may be obtained by reacting in an analogous manner 61 g. monoethanolamine with 185 g. epichlorohydrin.

EXAMPLE 3

A cellulosic fabric is dyed in usual manner in a dye bath containing 8% Indocarbon CL for Sol (Color Index: Sulfur Black 11, CI No. 53290), 8 g./l. crystallized sodium sulfide, 8 g./l. calcined sodium carbonate, and

20 g./l. calcined Glauber's salt (liquor ratio 1:10). After rinsing, the fabric is treated in a liquor containing a 2% reaction product of a diamine and epichlorohydrin, prepared as described below. The liquor, which was adjusted to a pH of 10 by addition of sodium carbonate solution, is then heated to 90–95° over a period of 30 minutes and kept at this temperature for 10 additional minutes. After thorough rinsing, the treated fabric is finished in the usual manner and possesses wet fastness properties, particularly those in respect to washing in the presence of dextrin, which are substantially improved over those of a similarly dyed fabric which is not aftertreated or one which is aftertreated in accordance with the above French and Canadian patents.

For the aftertreatment of the above-dyed fabric, the following reaction products may be employed: epichlorohydrin and ethylene diamine in a molar ratio of 2:1, 3:1, and 4:1; also the corresponding products from the reaction of epichlorohydrin with 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, or 3,3'-diaminodipropyl ether; additional, the reaction product of 3 mols epichlorohydrin with 1 mol monohydroxyethyl-ethylene diamine or with N,N'-bis-(3-chloro-2-hydroxypropyl)-piperazine can be used.

These reaction products may be prepared in the following manner.

A solution of 1 mole of the amine in 150 cc. water is slowly added, dropwise, at room temperature, to the required amount of epichlorohydrine. The mixture is then heated to 60–70° in the course of 2 to 3 hours and the reaction is terminated by 2 hours' heating at this temperature. After elimination of the water by the distillation under reduced pressure, the above reaction products are obtained in their pure form.

EXAMPLE 4

A cotton fabric is dyed in a 90° dye bath containing 10% Hydrosol Black B (Color Index: Solubilized Sulfur Black, CI No. 53186), 2.5 g./l. calcined sodium carbonate, 2.5 g./l. sodium sulfhydrate and 10 g./l. calcined Glauber's salt (liquor ratio 1:20). After rinsing, the fabric is treated for 10 minutes at 30° in a liquor containing 4% of a reaction product of 4 mols epichlorohydrin and 1 mol 3,3'-diamino-dipropyl ether, and 2% sodium carbonate. Subsequently, the liquor is heated to 90° in the course of 20 minutes and then kept at this temperature for a further 10 minutes. Thereafter, the fabric is rinsed, acidified with 2 cc./l. acetic acid of a 60% concentration, and dried.

To test the storability, ropes of an untreated dyed material and of a dyed material aftertreated in the manner described above are treated for 6 hours, at 135°, in a damp atmosphere, according to the AATCC-method B/93 (AATCC Annual Registered 1963) and the tensile strength is determined both prior and subsequent to this treatment. The results of the tests indicated below show that the rope aftertreated in accordance with the present invention possesses and retains a higher tensile strength than a similarly dyed untreated rope.

Cotton rope dyed with 10% hydrosol black B	Tensile strength in gms. prior to artificial aging	Tensile strength in gms. subsequent to artificial aging	Residual tensile strength in percent after artificial aging
(a) Untreated.....	594	122	21
(b) Aftertreatment according to Example 4.	633	530	84

EXAMPLE 5

Cotton cheeses are dyed in a 90° dye bath containing 10% Indocarbon CL conc. (Color Index: Sulfur Black II, CI No. 53290), 30 g./l. crystallized sodium sulfide, 4 g./l. calcined sodium carbonate and 20 g./l. calcined Glauber's salt (liquor ratio 1:10). The dyed material is rinsed with cold water, filtered off with suction, and treated in a liquor (ratio of 1:10) containing 3% (re-

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lated to the dry weight of the fabric) of a reaction product of 5 mols epichlorohydrin and 1 mol diethylene triamine, and 1% calcined sodium carbonate, during which time the temperature is raised from 30° to 90° in the course of 20 minutes and then kept at 90° for 10 minutes; subsequently, the fabric is thoroughly rinsed. The cheeses thus obtained possess very good wet fastness properties, in particular, a very good fastness to washing with peroxide and dextrin, as well as a good fastness to storing, which property is also retained when the dyeing is aftertreated in an acid liquor or brightened.

In place of the above-mentioned reaction product, the following products can likewise successfully be employed: reaction products of 5 mols epichlorohydrin and 1 mol dipropylene triamine, 6 mols epichlorohydrin with 1 mol triethylene tetramine, 7 mols epichlorohydrin with 1 mol tetraethylene pentamine, and 8 mols epichlorohydrin with 1 mol pentaethylene hexamine.

These products are prepared in accordance with the methods described in the above examples.

EXAMPLE 6

A cotton fabric is dyed in a dyebath containing 5% Hydrosol Yellow RR (Color Index: Solubilized Sulfur Yellow 2, CI, No. 53121), 3.75 g./l. crystallized sodium sulfide, 4 g./l. calcined sodium carbonate, and 10 g./l. Glauber's salt (liquor ratio 1:20). After rinsing, the fabric is introduced into an aqueous bath containing 3% of one of the reaction products mentioned in the second paragraph of Example 3, and 1.5% calcined sodium carbonate. The temperature of the bath is raised from 30° to 90° in the course of 10 minutes and then kept at 90° for 5 minutes. The fabric is then removed and thoroughly rinsed. The thus dyed and aftertreated fabric yields a satisfactory result in washing in accordance with AATCC Test Method No. 3, as well as a substantially improved fastness to washing in accordance with DIN 54011 and peroxide washing in accordance with DIN 54015 when compared with an untreated fabric or one treated in accordance with the above French and Canadian patents. The fabric which is not aftertreated, but is oxidized in the usual manner with a solution of dichromate in acetic acid, stains to a high extent an undyed fabric which is concurrently washed in accordance with AATCC Test Method No. 3. The result of the AATCC Test Method No. 3 washing of the aftertreated fabric is also satisfactory when the reaction product is applied subsequently to oxidation of the fabric with a solution of dichromate in acetic acid.

EXAMPLE 7

A cotton fabric is dyed in a dyebath containing 4% Hydrosol Supra Blue B (Color Index: Solubilized Sulfur Blue 7, CI No. 53441), 3 g./l. crystallized sodium sulfide, 4 g./l. calcined sodium carbonate and 10 g./l. calcined Glauber's salt (liquor ratio 1:20). After rinsing and squeezing off, the fabric is treated in a liquor containing 3% of the reaction product mentioned in the first paragraph of Example 4 and 1.5% calcined sodium carbonate. The temperature of the liquor is raised from 30° to 60° in the course of 10 minutes and then kept at 60° for a further 10 minutes. Subsequently, the fabric is thoroughly rinsed. The dyed and aftertreated fabric yields a satisfactory result in washing according to AATCC Test Method No. 3, as well as substantially improved fastness to washing in accordance with DIN 54011 and peroxide

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washing in accordance with DIN 54015 when compared with fabrics which are not aftertreated or oxidized in the usual manner with a solution of dichromate in acetic acid.

Various modifications may be made in the above-described materials, chemicals, process conditions, etc., without departing from the scope of this invention as set forth in the appended claims.

That which is claimed is:

1. A method of improving the wet fastness properties of textile cellulosic materials which have been dyed or printed with sulfur dyestuffs which comprises the steps of impregnating the dyed or printed materials, after rinsing and prior to or subsequent to oxidation, with 0.1 to 5.0% by weight, based on the dry weight of the cellulosic material, of a bis- or poly- α,β -halohydrin compound formed by the reaction of epichlorohydrin and ethylene diamine.

2. A textile product comprising a cellulosic fibrous material dyed with a sulfur dyestuff and having improved wet fastness and tensile strength properties, and containing from 0.1 to 5.0%, based on the dry weight of the material, of a basic nitrogenous polyalkylene polyamine polyhalohydrin compound.

3. A textile product as defined in claim 2 and in which the basic nitrogenous compound is a reaction product of an epichlorohydrin and ethylene diamine.

4. A method for improving the wet fastness properties of textile cellulosic materials which have been previously dyed or printed with sulfur dyestuffs, comprising impregnating said sulfur dye dyed or printed material with a basic nitrogenous polyalkylene polyamine polyhalohydrin compound.

5. A method of improving the wet fastness properties of textile cellulosic materials which have been dyed or printed with sulfur dyestuffs which comprises the step of impregnating the dyed or printed material either before or after oxidation with 0.1 to 5.0% by weight, based on the dry weight of the cellulosic material, of an aliphatic or heterocyclic water-soluble bis- (or) poly- α,β -halohydrin compound containing at least one basic nitrogen atom, whereby the cellulosic material treated with the basic nitrogen containing compound possesses substantially greater wet fastness and tensile strength properties.

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U.S. CI. X.R.

8—37, 74, 84; 117—143, 155

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,544,363 Dated December 1, 1970

Inventor(s) Hermann Rath et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:
Column 1, line 35, after "fabrics," insert --fibers, --. Column 3, line 32, "bly" should be --ly--. Column 3, line 64, after "off" insert --from--. Column 4, line 21, "additional" should be --additionally--. Column 4, line 26, the period (.) should be a colon (:). Column 4, line 27, "mole" should be --mol--. Column 4, line 53, "Registered" should be --Register--. Column 5, line 25, after "53121)" the period should be a comma (,). Column 6, Claim 5, line 39, "(or)" should be --or--.

**SIGNED AND
SEALED
MAR 9 1971**

(SEAL)

Attest:

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Commissioner of Patent**