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FIBER IMPROVING PROCESS AND PRODUCT

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This invention relates to a method for improving the properties of fibrous material and more particularly to a method for improving the dye fastness properties, mechanical properties, and resistance to deteriorating influences of dyed (including printed) fibrous material.

It is known that the wet fastness properties of dyeings and prints which have been prepared by use of diverse types of dyestuffs, particularly substantive water soluble dyestuffs known as direct dyestuffs, may be increased by aftertreatment with resinous aldehyde condensation products. However, said known aftertreatments have for the most part not been entirely satisfactory, involving as they do a number of disadvantages including unduly high costs, a tendency to stiffen and otherwise undesirably change the character of the properties of the fibrous material and the like. Further, in a number of cases, the wet fastness of the treated dyeings and prints have not been improved to the desired extent. Similarly, such aftertreatments have often adversely affected the shade and/or light fastness of fibrous material which has been dyed or printed with vat, direct and other colors.

It is an object of this invention to provide a process for improving the properties of dyed fibrous material which will not be subject to one or more of the above disadvantages. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by this invention which comprises treatment of dyed (including printed) fibrous material with an aqueous alkaline medium containing a compound of the formula

$$HOCH_2CH_2-SO_2-\left(R^1-X\right)_n\left(R^2-SO_2\right)_m-CH_2CH_2OH$$

wherein X is a divalent radical selected from the group consisting of —O—, —SO_2—, and —NR^3—; R^1 and R^2 are selected from the group consisting of phenylene and lower alkylene groups of 1 to 4 carbon atoms; R^3 is selected from the group consisting of H and lower alkylene groups of 1 to 4 carbon atoms; n has a value of 0 to 4; and m has a value of 0 to 1, n being 0 when m is 0; and then drying and curing the treated material at a temperature of at least about 220° F., preferably at least about 240° F.

Although direct dyestuffs constitute a large and well-known class of dyestuffs, they are inherently poor in wet fastness properties whereby their use has been precluded in a number of applications requiring dyeings and prints with good wet fastness properties. Such direct dyestufis are generally of the anionic type resulting from the presence therein of carboxylic or sulfonic groups. It will be understood that the term "direct dyestuff" also includes those direct dyestuffs which are metallizable, i.e. with chromium, cobalt, copper, etc., by reason of containing metallizable groups capable of forming complexes with metals. Highly satisfactory results are attained when such metallizable groups consist of an o,o'-dihydroxy configuration relative to an azo bridge, or an o-hydroxy carboxylic configuration relative to an azo bridge as contained, for example, in azo dyestuffs produced with a p-amino salicylic acid diazo component. It has been unexpectedly found that the process of this invention enables the production of fibrous material dyed with direct dyestuffs having improved wet fastness properties, i.e. the colors are relatively unaffected by wet treatments such as rinsing,

washing, boiling, treatment with laundry bleaches and sours, etc. Similarly, in contrast to previously mentioned aftertreatments, fibrous materials dyed with vat dyestuffs may be aftertreated by the process of this invention without detrimentally affecting the shade, light fastness and/or other properties of the dyed material. Similar improvements are attainable when applying the process of this invention to fibrous material dyed with any other types of dyestuffs, including azoics and the like.

As a further feature of this invention, the present process results in a simultaneous improvement (i.e. increasing, rendering more permanent, etc.) in the dimensional and shape retention properties of the dyed fibrous material variously referred to as wet and/or dry crease resistance, crease angle retention, crease recovery, wrinkle resistance, wrinkle recovery, dimensional stability, wash-and-wearability, swelling resistance, shrinkage resistance, tensile strength, retention of creases, pleats, glazed, embossed, and other mechanical effects, and the like in addition to other properties such as resistance to attack by moths, mildew, and other pests and the like, chlorine retention, industrial gases and other environmental conditions, development of objectionable odors, yellowing or other discolorations, hydrolysis, heat and/or abrasion, and the like.

A preferred compound for use in this invention is 2,2'-sulfonyldiethanol, several methods for the preparation of which have been described in the literature. This compound corresponds to the above formula wherein n and m are both 0.

Another preferred group of compounds for use in this invention are those of the above formula wherein n and m each has a value of 1, R^1 and R^2 are lower alkylene radicals and X is —O—. For example, the compound wherein n and m are each 1, X is —O— and R^1 and R^2 are ethylene radicals, which compound may be referred to as oxy-2,2'-bis(ethyl-2-sulfonylethanol), is also highly effective for use in the present process. Similar results are obtained with the related compounds wherein R^1 and R^2 are methylene, propylene or butylene or the like.

Other compounds of the above formula may be employed wherein n has a value of 1 to 4; m is 1; R^1 and R^2 may be the same or different and may be methylene, ethylene, propylene, butylene, or phenylene, and R^3 may be methylene, ethylene, propylene, or butylene. It will be understood that when R^1 and/or R^2 are phenylene radicals, the phenylene ring may be substituted by one or more substituents such as lower alkyl, e.g. methyl, ethyl and the like; lower alkoxy, e.g. methoxy, ethoxy, and the like; nitro, amino, halogen, e.g. bromo and chloro; or the like depending on the desired function of the aftertreating agent. Similarly, such divalent phenylene radical may be linked in ortho, meta or para position, if desired through lower alkylene groups to the SO_2 and X radicals shown in the formula. The following are illustrative of additional compounds of the above formula operative in the present process:

$HOCH_2CH_2SO_2-(C_2H_4O)_4-C_2H_4-SO_2CH_2CH_2OH$

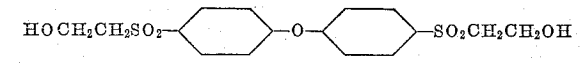
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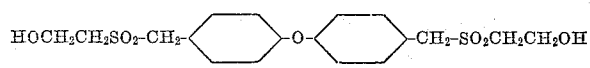
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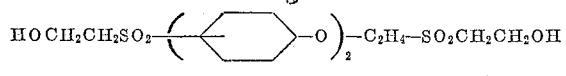
$HOCH_2CH_2SO_2-CH_2-O-CH_2-SO_2CH_2CH_2OH$

$HOCH_2CH_2SO_2-CH_2-O-C_2H_4-SO_2CH_2CH_2OH$

$HOCH_2CH_2SO_2-C_2H_4-SO_2-C_2H_4-SO_2CH_2CH_2OH$

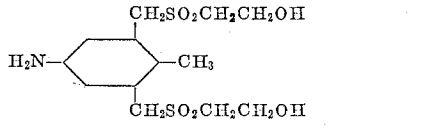






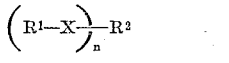


p-Xylylene-α^1,α^4-bis-(2-sulfonylethanol)



5-amino-2-methyl-m-xylylene-α^1,α^3-bis-(2-sulfonylethanol)

Representative compounds in the above groups may conveniently be prepared by halogenating or chloromethylating the R^1 and R^2 moieties in a compound of the formula



reacting the resulting di- or poly-halogen or -chloromethyl substituted intermediate with at least two moles of mercaptoethanol and then oxidizing the resulting disulfide to the disulfone. If X in the starting compound is —S—, it will be oxidized to the sulfone in the final oxidation.

In carrying out the process of this invention, the aqueous medium may be in the form of a solution, emulsion, suspension or other type of dispersion at any temperature ranging from room temperature to the boiling point of the medium. The medium is rendered alkaline, when necessary, by the addition of any suitable alkaline reacting substance, preferably an alkali metal (sodium, potassium, lithium, etc.) hydroxide, carbonate, bicarbonate, phosphate, silicate, borate, acetate or the like, or an organic base such as triethanolamine or the like, in an amount sufficient to yield a pH of about 7.5 to 10.5 or more. Such amount may range from less than 0.5% up to 8% or more in the medium. The alkali metal carbonates are preferred. Other alkaline reacting substances may be employed, including sodium sulfide, dipotassium tartrate, disodium phthalate, and the like. It will be understood that as an equivalent method of carrying out the present aftertreating process, any of the above described alkaline reacting substances may be applied to the dyed fibrous material immediately before or after application thereto of an aqueous medium containing a compound of the above defined formula.

The concentration of the treating agent in the aqueous alkaline medium is not particularly critical and may range from about 0.5 to 50% or more depending upon the manner of application to the fibrous material, the particular agent employed, the properties desired, and the like. The aqueous medium may be applied to the dyed fibrous material by immersion, padding, spraying, printing or any other desired manner, continuously or otherwise. For overall effects, it is preferred to apply an excess of the aqueous alkaline medium following by a squeezing step with a liquor pickup of about 30% or less to 100% or more by weight of the fiber. For printing or other decorative purposes, the aqueous alkaline medium may be appropriately thickened in known manner. In general, optimum dye fastness, crease resistant and crease angle retention properties are obtained by carrying out the treating process in such manner as to provide the dyed fibrous material with about 1 to 10% of the treating agent by weight of the dyed fibrous material.

Following application of the aqueous alkaline medium to the dyed fibrous material, the treated material is dried and then cured at a temperature of at least about 220° F., preferably at least about 240° F. The duration of the curing step will generally vary inversely with the temperature although of course the temperature and duration will depend upon the type of fiber being treated, the identity of the treating agent, the results desired, etc. In general, the curing step will usually range up to ten minutes or more at 220° F. to as little as 15 seconds or less at 475 to 500° F. Too high a curing temperature and/or duration causes fiber damage and is to be avoided. The optimum curing temperature and duration may be readily determined by routine experimentation in any particular instance.

Following the curing step, the treated fibrous material may be simply washed and/or bleached in known manner with the usual oxidizing agents such as sodium hypochlorite, hydrogen peroxide or the like. Such bleaching is often desirable since, as mentioned below, the curing step may darken, dull or discolor the shade of the original dyeing. As a corollary, the fibrous material subjected to treatment in accordance with this invention should be dyed with a dyestuff resistant to alkaline curing at the above temperatures, and to the above bleaching agents.

The above mentioned discoloration, darkening, or dulling tendencies of the curing step can be minimized or eliminated by including in the aqueous alkaline medium a boron-containing compound. The mechanism by which such boron-containing compounds function to reduce discoloration is difficult to postulate in view of the fact that perborate compounds are considered to have an oxidizing effect, alkali metal borohydrides are reducing agents, and alkali metal tetraborates such as borax are neither. The nature of the boron-containing compound employed to reduce discoloration is accordingly immaterial. Thus, there may be employed boric acid and fluoroboric acid and their metal, ammonium and amine salts, and boron fluoride addition products with such compounds as diethyl ether, water, lower alcohols such as methanol, ethanol, propanol, and the like, ammonia, aliphatic and aromatic amines such as ethylamine, aniline and the like, carboxylic acids such as acetic, propionic, stearic, and benzoic, and the like, amides such as acetamide, propionamide and the like, and phenols, thiophenols, cresols, naphthols, and the like.

A preferred group of boron-containing compounds operative herein are the ammonium, amine and metal (including also alkaline earth metal and alkali metal) borates such as the metaborates, perborates, and tetraborates. The alkali metal borates such as those of sodium and potassium are preferred because of their economy, availability, solubility properties, etc. Other such operative boron-containing compounds are the borates of aliphatic, aromatic and heterocyclic amines such as mono-, di- and tri-methylamine, -ethylamine, -propylamine, -butylamine, -octylamine, -cyclohexylamine, mono-, di-, and tri-ethanolamine, -propanolamine, -butanolamine, octanolamine, benzylamine, morpholine, piperidine, pyridine, and the like, and metals such as calcium, magnesium, zinc, manganese, aluminum, barium, copper, iron, nickel, tin, and the like.

Another preferred group of boron-containing compounds are the borohydrides of the same cations as referred to in the preceding paragraph with respect to the borates. Those preferred are the alkali metal borohydrides, particularly sodium borohydride.

The above described boron-containing compound is applied to the dyed fibrous material together with a compound of the above formula and/or alkaline reacting catalyst in an amount sufficient to obtain the desired reduction in discoloration, which amount, will be readily ascertainable in any particular instance by routine experimentation. Usually, an aqueous medium containing about 0.03 to 5% of the boron-containing compound will suffice in most instances. The borohydrides are extremely effective in relatively small amounts in the lower part of the aforementioned range and may be employed in concentrations of about 0.03 to 0.08%. The borates are generally employed in higher concentrations of about 0.01 to 5%, preferably about 0.1 to 1%.

The mechanism by which the process of this invention yields the desired improved properties is not clearly un-

derstood, although it apparently involves a cross-linking reaction between one molecule of a compound of the above formula and two reactive sites in the fiber molecules containing dyestuff molecules whereby the dyestuff is simultaneously fixed and the fiber properties improved as described above. Most effective reaction and cross-linking occurs with hydroxy groups in fibrous material such as cellulose, polyvinyl alcohol, partially hydrolyzed polyvinyl acetate and cellulose acetate, and the like. Reaction also occurs with other dyed fibers containing reactive or replaceable atoms or groups in the fiber such as hydrogen or halogen or the like, or with fibers containing unsaturated linkages.

The process of this invention has been found to be highly effective for improving the properties of dyed cellulosic fibers of natural or synthetic type such as cotton, linen, wood, paper, regenerated cellulose, and the like. The dyed fibrous material may be in any of the usual forms and in natural bulk, interwoven, knitted or felted form as for example in the form of staple fiber or continuous filaments in bulk form or in the form of tow, rope, yarns, slubbings, warps, fabrics, felts, and the like, and treated as a wound package, running length, fibrous stock, bulk, etc. In addition to dyed cellulose and its derivatives, the process of this invention may be employed for improving other dyed fibers including natural and synthetic proteinaceous fibers such as wool, silk, leather, animal hides and skins, casein, and zein, polyamides such as nylon and polypyrrolidone, polyurethanes, polyesters, copolymers or homopolymers containing recurring carboxylic or cyano groups, polyvinyl alcohol, polyvinyl chloride, partially hydrolyzed cellulose acetate and polyvinyl acetate, and mixtures, copolymers and graft polymers thereof. Mixed dyed fabrics and fibers, and dyed fabrics and fibers mixed with undyed fabrics and fibers may likewise be so treated. It will be understood that the term "dyed" as applied to the fibrous material treated in accordance with this invention is inclusive of material which has been colored overall or discontinuously (e.g. printed) with one or a mixture of dyes, pigments, etc.

It will be understood that the present process may be applied to dyed fibrous material in conjunction with other substances in addition to the functional agents described above, as for example optical brighteners, stabilizers, softeners, surface active agents, reactive bacteriostats, finishes such as starch, polyvinyl alcohol and the like. Previous or simultaneous treatment of the dyed fibrous material with such a finish enables more permanent effects due to simultaneous reaction or cross-linking of compounds of the above formula therewith.

The following examples are only illustrative of the present invention and are not to be regarded as limitative. All parts and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

Bleached and mercerized (2.85 yard/lb.) cotton sheeting was dyed by conventional batch dyeing procedures with the direct dyestuffs listed in the table below, using 1.0% dyestuff by weight of the fiber and using common salt to aid in exhausting the dyestuff on to the fiber. Excess dyestuff was removed by rinsing in cold water and the dyed material dried by pressing with an electric iron. A portion of each dyeing thus produced was treated by padding with a solution containing

	Percent
2,2'-sulfonyldiethanol, 38.5% aqueous solution	29.7
Sodium carbonate	2.3
Borax (sodium tetraborate decahydrate)	0.3
Water	67.7

The treated dyeing was then passed through squeeze rollers adjusted for a pickup of about 70% by weight of the dry fabric, dried at 175° F., and cured at 360° F. for 90 seconds. The cured fabric was then bleached with 1% active hydrogen peroxide solution at 180° F., rinsed and ironed dry.

Both the treated and untreated (control) portions of the dyed fabrics were then subjected to the No. 2 AATCC wash test (1960 Technical Manual of the American Association of Textile Chemists and Colorists, page 92). The results of the wash tests are shown in the table below, from which it will be apparent that the wash fastness of dyed fabric treated with 2,2'-sulfonyldiethanol in accordance with this invention is considerably improved over that of the untreated dyed fabric. There is less shade change due to washing and less staining of the cellulosic fibers in the test cloth present in the wash test with respect to the dyed fabric treated with 2,2'-sulfonyldiethanol as compared with the untreated dyed fabric. In the table a rating of 1 indicates severe change or destruction of shade and excessive staining of cotton test cloth. Increased ratings indicate increased resistance to color change and staining, a rating of 5 indicating no change of color and no staining.

Example	Dyestuff	Untreated (Control)		Treated with 2,2'-Sulfonyldiethanol	
		Color Change	Staining of Cotton Test Cloth	Color Change	Staining of Cotton Test Cloth
1	Fastusol Yellow GGA-CF (C.I. Direct Yellow 26).	4	2-3	4	3-4
2	Fastusol Yellow GAP Extra (C.I. Direct Yellow 44).	2-3	2	4	3-4
3	Fastusol Yellow LRRA Conc. (C.I. Direct Yellow 28).	3	3	4	4
4	Fastusol Yellow LRTP (C.I. Direct Yellow 28).	3	3-4	4	4-5
5	Fastusol Orange L7G (C.I. Direct Orange 34).	1-2	2	4-5	4-5
6	Fastusol Orange LGGA (C.I. Direct Orange 39).	2-3	2	4	4-5
7	Fastusol Orange L3RA (C.I. Direct Orange 37).	2-3	2	4-5	4
8	Fastusol Red 4BA (C.I. Direct Red 81).	1	1	4-5	2-3
9	Fastusol Red 8B-CF (C.I. Direct Red 80).	1	2	3	4
10	Fastusol Blue GA Extra CF (C.I. Direct Blue 78).	2-3	2	2-3	4
11	Fastusol Blue LBRRA Extra Conc. (C.I. Direct Blue 71).	2	2	4-5	4-5
12	Fastusol Turquoise Blue LGA (C.I. Direct Blue 86).	1	3-4	5	4-5
13	Fastusol Brown 3RL (C.I. Direct Red 84).	2	2	3-4	3
14	Fastusol Brown LBRSA (C.I. Direct Brown 95).	1	1	3	2
15	Fastusol Gray LRA (C.I. Direct Black 75).	3	4	3	5

When tested by A.S.T.M. test method D1295–53T, the dyed fibrous material treated by the process of this invention was found to have greatly increased dry and wet crease recovery angles as compared with the untreated dyed fabrics.

This invention has been disclosed with respect to certain preferred embodiments and it is to be understood that various modifications and variations thereof obvious to persons skilled in the art are to be included within the spirit and purview of this invention and the scope of the appended claims.

We claim:

1. A process for improving the properties of fiber containing a member of the group consisting of reactive hydrogen and halogen atoms and unsaturated linkages and dyed with a non-fiber reactive dyestuff comprising treating such dyed fiber with an aqueous alkaline medium containing a compound of the formula

$$HOCH_2CH_2-SO_2-\left(R^1-X\right)_n\left(R^2-SO_2\right)_m-CH_2CH_2OH$$

wherein X is a divalent radical selected from the group consisting of —O—, —SO_2—, and —NR^3—; R^1 and R^2

are selected from the group consisting of phenylene and lower alkylene groups of 1 to 4 carbon atoms; R^3 is selected from the group consisting of H and lower alkylene groups of 1 to 4 carbon atoms; n has a value of 0 to 4; and m has a value of 0 to 1, n being 0 when m is 0; and then drying and curing the treated material at a temperature of at least about 220° F.

2. A process as defined in claim 1 wherein said fiber is cellulosic.

3. A process as defined in claim 1 in which said compound is 2,2'-sulfonyldiethanol.

4. A process as defined in claim 1 in which said compound is oxy-2,2'-bis-(ethyl-2-sulfonylethanol).

5. A process as defined in claim 1 in which said compound is p-xylylene-α^1,α^4-bis-(2-sulfonylethanol).

6. A process as defined in claim 1 in which said compound is 5-amino-2-methyl-m-xylylene-α^1,α^3-bis - (2 - sulfonylethanol).

7. A process for improving the properties of fibrous material containing a member of the group consisting of reactive hydrogen and halogen atoms and unsaturated linkages and dyed with a direct dyestuff comprising treating such dyed material with an aqueous alkaline medium containing a compound of the formula

$$HOCH_2CH_2-SO_2-\left(R^1-X\right)_n\left(R^2-SO_2\right)_m-CH_2CH_2OH$$

wherein X is a divalent radical selected from the group consisting of —O—, —SO_2—, and —NR^3—; R^1 and R^2 are selected from the group consisting of phenylene and lower alkylene groups of 1 to 4 carbon atoms; R^3 is selected from the group consisting of H and lower alkylene groups of 1 to 4 carbon atoms; n has a value of 0 to 4; and m has a value of 0 to 1, n being 0 when m is 0; and then drying and curing the treated material at a temperature of at least about 220° F.

8. A process as defined in claim 1 in which said fibrous material is cellulosic.

9. A process as defined in claim 7 in which said compound is 2,2'-sulfonyldiethanol.

10. A process as defined in claim 7 in which said compound is oxy-2,2'-bis-(ethyl-2-sulfonylethanol).

11. A process as defined in claim 7 in which said compound is p-xylylene-α^1,α^4-bis-(2-sulfonylethanol).

12. A process as defined in claim 7 in which said compound is 5-amino-2-methyl-m-xylylene-α^1,α^3-bis-(2 - sulfonylethanol).

13. A process for improving the properties of cellulosic fibrous material dyed with a non-fiber reactive dyestuff comprising treating such dyed material with an aqueous alkaline medium containing 2,2'-sulfonyldiethanol and then drying and curing the treated material at a temperature of at least about 220° F.

14. A process as defined in claim 13 wherein the material subjected to treatment is dyed with a direct dyestuff.

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