INHIBITING CELLULOSE FIBER YELLOWING IN ALKALINE PROCESSING AT ELEVATED TEMPERATURES THROUGH UTILIZATION OF BORON SALTS

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3 Claims

This invention relates to a method for the treatment of fibrous material, and more particularly to a method for reducing the tendency of fibrous materials to discolor or darken when cured at elevated temperatures in the presence of an alkalizing agent.

A number of alkaline heat-curing methods for fibrous materials are known, as for example treatments involving the application of certain crease-proofing or wash-and-wear agents, reactive dyestuffs and other functional substances. In most of these processes, a chemical reaction takes place between the treating agent (including reactive dyes) and the fiber as a result of which the agent becomes chemically bound to the fiber. In these processes, an alkalizing agent or alkaline-reacting material is employed as a catalyst, acid-binding agent, or for some other purpose.

Substantially all of these alkaline heat-curing methods are subject to a more or less troublesome side effect in that the action of the alkaline material on the fiber at the high temperatures necessary in such methods produces varying amounts of discoloration depending upon the curing temperature and the duration of the curing step. The color produced may vary from light yellow to tan or even to brownish shades (assuming of course that the fiber is originally substantially white).

The color produced by the action of the alkaline material in such heat-curing methods may be destroyed or eliminated by bleaching, as with oxidizing agents such as hydrogen peroxide, sodium hypochlorite and the like. The more color formed during the heat-curing treatment the more difficult becomes the bleaching operation. Sodium hypochlorite solution performs better than hydrogen peroxide in this bleaching operation but it is less desirable because of undesirable side reactions which may occur. For example, in the dyeing of fibers with reactive dyestuffs, or in the simultaneous treatment of fibers with cross-linking agents (for crease-proofing, water repellency, etc.) and optical brighteners or reactive dyestuffs, the brightener and/or dyestuff may be more or less destroyed by the oxidizing bleaching agent. If the amount of color produced during such alkaline heat-curing methods is too large, it becomes too difficult to bleach with oxidizing agents such as hydrogen peroxide, the bleaching operation becoming too time-consuming and commercially unfeasible.

It is an object of this invention to provide an alkaline heat-curing method for fibrous material which will not be subject to the above disadvantages. Another object of this invention is the provision of an alkaline heat-curing method for fibrous materials with a reduced tendency to discoloration. Still another object of this invention is the provision of a process involving treatment of fibrous materials in an alkaline medium followed by drying and heat-curing the treated fibrous materials which process has a reduced tendency to discolor the fibrous materials. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the present invention which is based upon the discovery that when the heat-curing step is carried out in the presence of a boron-containing compound, the above described tendency of the fibrous material to discolor is unexpectedly reduced or eliminated. More particularly, the invention broadly comprises the step of heat-curing the fibrous material in the presence of a boron-containing compound at a temperature of at least about 250° F. It has been unexpectedly found that even when the use of a boron-containing compound in the alkaline heat-curing of fibrous materials does not completely eliminate color formation, the minimizing effect is great enough to permit commercially preferred bleaching of residual color with oxidizing agents such as hydrogen peroxide or oxidizing agents that do not cause undesirable secondary degradations.

Since the mechanism of the discoloration of fibrous material during alkaline heat-curing treatments is not fully understood, the effect of reducing such color formation by the use of boron-containing compounds cannot be fully explained. The mechanism by which such boron-containing compounds function to reduce such discoloration is rendered even more 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 in the present process 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, propanamide and the like, and phenols, thiophenols, cresols, naphthols, and the like.

A preferred group of boron-containing compounds operative herein are the ammonium, and metal (including alkaline earth metal and alkali metal) borates such as the metabolates, 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 amines such as mono-, di- and tri-methylamine, ethylamine-, propylamine, butylamine, -octylamine, -cyclohexylamine, mono-, di- and tri-ethanolamine, -propylanolamine, -butan-olamine and -octanolamine, aromatic amines such as benzyllamine, heterocyclic amines such as morpholine, 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 invention is effected by adding the boron-containing compound to the aqueous alkaline medium containing the functional agent (e.g. brightener or reactive dyestuff, cross-linking, crease-proofing, wash and wear agent, etc.) in an amount sufficient to obtain the desired reduction in discoloration. This amount will be readily ascertainable in any particular instance by routine experimentation. While the reduction in discoloration varies directly with the amount of boron-containing compound employed in the aqueous
alkaline treating medium, such increased amounts may sometimes be accompanied by a diminution in the effectiveness of the functional agent being applied. For example, when the functional agent is a crease-proofing agent or cross-linking agent, increased amounts of boron-containing compound in some instances result in progressively decreasing effectiveness of the functional agent. In such instances a compromise will have to be made by sacrificing some degree of crease-proofing effect in favor of reduced discoloration, or vice versa. Usually, proportions of about 10.03 to 5.0% of boron-containing compound by weight in the aqueous alkaline treating medium will suffice in most instances. The optimum amount to be employed in any particular instance will depend upon the particular boron-containing compound employed, the functional agent being applied to the fibrous material, the result desired, etc. Thus, the borohydrides are extremely effective in relatively small amounts in the lower part of the aforementioned range, and may be employed in proportions of about 0.03 to 0.08% in the aqueous alkaline medium. The borates are generally employed in higher concentrations of about 0.1 to 5%, preferably about 0.1 to 1% in the aqueous medium.

The process of this invention is highly effective when employed in the fiber-improving process disclosed and claimed in our said copending application Ser. No. 12,509, and the disclosure of which is herein incorporated by reference. Saidcopending application broadens and closes a process comprising treating fibrous materials with an aqueous alkaline medium containing a compound of the formula

$$\text{HOCH}_2\text{CH}_2\text{SO}_4\left(\text{R}^1\text{X}\right)_{m} \left(\text{R}^2\text{SO}_3\right)_{n} + \text{CH}_2\text{CH}_2\text{OH}$$

wherein X is a divalent radical selected from the group consisting of —O— and —SO$_3$—; R$^1$ and R$^2$ are selected from the group consisting of phenylene 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 250°F. In the above formula, the alkaline groups may be methylene, ethylene, and normal and isomeric propylene and butylene. The preferred compound employed in such process is 2,2'-sulfonylethylene dihydrochloride, but other compounds coming within the scope of said formula generically or specifically disclosed in our said copending application may also be employed. The process in said copending application produces an easy-care and wash and wear reactive finish or fibrous materials. It imparts wet and dry crease resistance in addition to increased resistance to washing, laundry soaps, mildew damage, moth damage, shrinkage, chlorine retention, odor and/or dying.

When employed in the process of said copending application, the present invention is carried into effect by adding the boron-containing compound to the aqueous alkaline medium, in the form of a solution, emulsion, suspension or other type of dispersion, containing the desired amount of crease-proofing agent. The latter amount is not critical and may range from about 0.5 to 50% or more dependent upon the manner of application of the aqueous medium to the fibrous material, the particular crease-proofing agent employed, the properties desired, and the like. The medium, if not already alkaline, is rendered alkaline by addition of any suitable alkaline reacting substance such as sodium or potassium hydroxide, carbonate, bicarbonate, phosphate 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. Sodium carbonate or bicarbonate is preferred for this purpose. The aqueous medium may be applied to the fibrous material by immersion, padding, spraying, printing or any other process desired, either separately or otherwise. For overall effects, it is preferred to apply an excess of the aqueous alkaline medium followed by a squeezing step with a liquor pick-up of about 30% or less to 100% or more by weight of the fiber. For printing purposes the aqueous alkaline medium may be appropriately thickened in known manner.

Following the application of the aqueous alkaline medium to the fibrous material, the treated material is dried and then cured at a temperature of at least about 250°F. The duration of the curing step will generally vary inversely with the temperature although of course the temperature and duration would depend upon the type of fiber being treated, the identity of the crease-proofing agent, the results desired, etc. In general the curing step will usually range up to 5 minutes or more at 250°F to about 15 seconds or less at 500°F. Too high a curing temperature and/or duration causes fiber damage and is to be avoided. These maximum permissible conditions are readily determinable in any 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 and the like. For white materials, it is usually desirable to apply a bleaching treatment of the cured fibrous materials directly or, if desired, after an intermediate washing.

The present process is of course also applicable for reducing discoloration occurring in the application of any other type of crease-proofing or wash and wear agent, reactive dyestuff, or any other functional agent. Involving the use of an aqueous alkaline treating medium followed by an alkaline heat-curing step, or in any such application wherein the alkalinity is first developed during the heat-curing step.

Reactive dyestuffs are dyestuffs of any type, inorganic but generally organic, containing a reactive atom or group capable of reacting with the fiber being dyed. The present process is useful in applying such reactive dyestuffs which are applied from an alkaline medium or from a medium containing a compound which develops alkalinity during the subsequent heat-curing step. As examples of classes of such reactive dyestuffs, which may be nitro dyestuffs, dyestuffs of the azo, anthraquinone, phthalocyanine or any other series, including inorganic, which dyestuffs may be metal free or may contain metal in complex union, there may be mentioned dyestuffs containing an s-triazinyl radical carrying one or two chlorine or bromine atoms directly attached to the triazine ring, dyestuffs containing a pyrimidyl radical carrying one or two chlorine or bromine atoms directly attached to the pyrimidone ring and dyestuffs containing a beta-halo-glycosopropionyl, beta-haloketopropionyl, beta-ethyloxethylamphenyl, beta-sulfatoethylsulphenyl, beta-hydroxyethylsulphenyl, chloroacetaldehyde, beta-(chloromethyl)-beta-sulfato-ethylsulffamyl, vinyl sulfone, alkyl phosphate, or sulphon fluoride radical. Such radicals, particularly those containing a sulphonyl group, may if desired be nuclearily substituted either directly to the sulphon group or through a methylene or other linkage. Specific examples of such dyestuffs are described in British Nos. 209,723 in Examples 1 and 2, British No. 298,484 in Example 1, British Nos. 546,343, 460,224, 753,471, 740,533, 755,308, 772,030, 774,929, 780,590, 785,120, and 785,222, French Nos. 901,187, and 907,103, Belgian Nos. 497,065, 543,214, 543,215, 543,216, and U.S. Nos. 1,935,929, 2,151,857, 2,424,493, 2,434,150, 2,637,205, 2,670,265, 2,728,762, 2,743,267, 2,766,231, 2,784,240, etc. U.S. 2,895,785 also disclose methods for dyeing textiles with reactive dyestuffs followed by an alkaline heating step.

The present process is employed in reactive dyeing processes in similar manner to its employment in crease-proofing, wash and wear processes. Normally, an aqueous medium containing the reactive dyestuff, boron-containing compound, and an aqueous relaxing substance or substrate developing alkalinity during the subsequent heat-curing step, is applied to the fibrous material to be dyed.
The concentration of dyestuff is of course a matter of choice obvious to skilled dyers, and may range from .05 to 2 or 3% in the treating medium. The invention is also useful in a simultaneous reactive dyeing and crease-proofing process.

The process of this invention may similarly be employed in any process for treating fibrous material with resins or any other substance or substances intra-reactive, inter-reactive or reactive with the fiber or otherwise, involving an alkaline heat-curing step.

The process of this invention has been found to be highly effective in fiber-improving and reactive dyeing processes applied to cellulose fibers of natural or synthetic type, such as cotton, linen, wood, paper, regenerated cellulose and the like. The fibrous material may be in any of the usual forms and in natural bulk, interwoven 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 cellulose, the process of this invention may be employed for improving other fibers, including natural and synthetic polymides such as wool, silk, casein, zell, nylon and polyurethane fibers and fibers containing recurring carboxylic or cyano groups or the like in the polymer chain. The process of the present invention finds its greatest advantage in the treatment of white fibrous material, particularly cotton, silk, or wool, etc. When employed in a dyeing process, it enables the attainment of brighter and truer shades of dyeings. It will be understood that the present process may be applied to fibrous materials in conjunction with other assistants in addition to the functional agents described above, as for example optical brighteners, stabilizers, softeners, surface active agents, reactive bacteriostatics, etc.

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.

**Example I**

Cotton print cloth (80 x 80) was padded through an aqueous solution containing 2% sodium carbonate, 12.5% 2,2'-sulfonyldiethanol and 0.2% sodium tetaborate deca-hydrate (Na₂B₄O₇·10H₂O), commonly known as borax. The pressure on the squeeze rolls had been previously adjusted so that the pickup of the solution was 80% of the weight of the fabric. The fabric was dried and then subjected to heat-curing for three minutes at 300°F. A light cream color was developed which partially washed out upon soaking and the remainder easily bleached with oxidizing agents such as sodium hypochlorite or hydrogen peroxide. The treated fabric possessed excellent crease recovery properties.

**Control example**

The procedure of Example I was followed except that the sodium tetraborate was omitted. The heat-cured fabric with dark buff in color. This color was much more difficult to remove by washing and bleaching than that produced by the heat-curing treatment of Example I.

**Example II**

The procedure of Example I was followed except that 1.0% sodium perborate was used in place of 0.2% sodium tetraborate. The effect of the perborate in lessening the color of the cured cloth was roughly equivalent to the tetraborate, and markedly superior to the Control Example.

**Example III**

The procedure of Example I was followed except that 0.06% sodium borohydride was used in place of 0.2% sodium tetraborate. The effect of minimizing color was about the same as Example I.
8. A method as defined in claim 7 wherein said boron-containing salt is an alkali metal borate.

9. A cellulosic material produced by the process of claim 7.

10. An aqueous treating medium for cellulosic materials comprising a bis(β-hydroxyethyl)sulfone, an alkaline catalyst and a water-soluble, boron-containing salt.

11. A medium as defined in claim 10 wherein said boron-containing compound is an alkali metal borate.

12. A medium as defined in claim 10 wherein said boron-containing compound is sodium tetraborate.

13. A medium as defined in claim 10 wherein said boron-containing compound is sodium borohydride.

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