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MODIFICATION OF REACTIVE HYDROGEN- AND HALOGEN-CONTAINING MATERIALS WITH THIOXANE DIOXIDE

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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 (i.e. increasing, rendering more permanent, etc.) dimensional and shape retention properties variously referred to as wet and/or dry crease resistance, crease angle retention, crease recovery, wrinkle resistance, winkle recovery, dimensional stability, "wash-and-wearability," swelling resistance, shrinkage resistance, tensile strength, retention of creases, pleats, glazed, embossed and other mechanical defects, and the like, in addition to other properties such as resistance, to attack by moths, mildew and the like, washing, laundry bleaches and sours, chlorine retention, industrial gases and other environmental conditions, development of objectionable odors, yellowing or other discoloration, hydrolysis, heat and/or abrasion, and the like. The invention also relates to improved fibrous material produced by such method.

Crease resistant finishing agents for fibrous material, particularly cellulosic material such as cotton, have recently become very popular and a large proportion of such material now provided to the trade have been treated with such agents for the production of so called "wash and wear" effects and the like. Such agents are generally resinous, which involves a number of disadvantages including unduly high costs, a tendency to stiffen and otherwise undesirably change the character and properties of the fibrous material and the like. Further, considerable room for improvement of such agents remains with respect to other properties of the type referred to above. Previously developed nonresinous agents have for the most part been subject to a number of similar disadvantages, in addition to undesirable toxicity and the like.

It is an object of this invention to provide a process for improving the properties of fibrous material which will not be subject to one or more of the above disadvantages. Another object of this invention is the provision of improved fibrous material treated by such a process. 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 fibrous material with an aqueous alkaline medium containing 1,4-thioxane dioxide and then drying and curing the treated material at a temperature of at least about 250° F. It has been found that the process of this invention enables the attainment of substantially permanent effects with respect to improved properties of the above described type.

It is generally recognized that optimum dimensional and shape retention properties are imparted to fibrous material such as cotton by treatment with a di-functional reactive agent whereby adjacent cellulose or other polymer chains are cross-linked. It was most surprising to find such an agent from among the cyclic ether class. Ethers are considered extremely stable to alkaline attack and most especially so are six-membered cyclic ethers. That 1,4-thioxane dioxide could impart such desirable dimensional and shape retention properties to fibrous material was therefore quite unexpected. This six-membered cycle ether is a known compound and is extremely stable to heat and to strong oxidation as with chromic acid.

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.

The concentration of the 1,4-thioxane dioxide 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 character of the fibrous material, the properties desired, and the like. The aqueous medium may be applied to the 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 followed 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 dimensional and shape retention properties are obtained by so conducting the process as to provide the fibrous material with about 1 to 10% of 1,4-thioxane dioxide by weight of the material.

Following 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 will generally vary inversely with the temperature, although of course both temperature and duration will depend upon the fibrous material being treated, the results desired, etc. In general, the curing step will usually range up to 5 minutes or more at 250° F. to as little as 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 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 and the like. For white materials it is usually desirable to apply a bleaching treatment to the cured fibrous materials directly or, if desired, after an intermediate washing.

The process of this invention may be applied to the fibrous material in the natural state (unbleached), or to such material which has been bleached white or colored in any manner and with any desired dyestuff or pigment. The alkaline curing step required in the present process often results in discoloration or yellowing of the fibrous material. This is particularly troublesome in the processing of white fibrous material. In accordance with the expedient disclosed and claimed in the copending application of Freyermuth and Mayhew, Ser. No. 96,704, filed Mar. 20, 1961, such discoloration 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 tetra-

borates 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 amines such as mono-, di- and tri-methylamine, -ethylamine-, -propylamine, -butylamine, -octylamine, -cyclohexylamine, mono-, di-, and tri-ethanolamine, -propanolamine, -butanolamine, and -octanolamine, aromatic amines such as benzylamine, heterocyclic amines such as 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 added to the aqueous alkaline medium containing 1,4-thioxane dioxide 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, proportons of about 0.03 to 5.0% of the boron-containing compound by weight in the aqueous alkaline treating medium 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 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 present process may also advantageously be employed for simultaneously dyeing the fibrous material with a reactive dyestuff. Such dyestuffs may be of any type, inorganic but generally organic, containing a reactive atom or group, capable of reacting with the fiber being treated in the above described aqueous alkaline treating medium and/or in 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 pyrimidine ring and dyestuffs containing a β-halogenopropionyl, β-haloethylsulfonyl, β-halogenoethylsulfamyl, β-sulfatoethylsulfonyl, β-phosphatoethylsulfonyl, β-acyloxyethylsulfonyl, β-hydroxyethylsulfonyl, chloroacetylamino, β-(chloromethyl) - β-sulfato-ethyl-sulfamyl, vinyl sulfone, alkyl phosphite, or sulphon fluoride radical. Such radicals, particularly those containing a sulphonyl group, may if desired be nuclearly substituted either directly to the sulfonyl group or through a methylene or other linkage. Specific examples of such dyestuffs are described in British No. 209,723 in Examples 1 and 2, British No. 298,484 in Example 1, British Nos. 456,343, 460,224, 733,471, 740,533, 775,308, 772,030, 774,925, 780,591, 781,930, 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, 2,657,205, 2,670,265, 2,728,762, 2,743,267, 2,766,231, 2,784,204, etc. U.S. 2,895,785 also discloses methods for dyeing textiles with reactive dyestuffs followed by an alkaline heating step.

For simultaneously dyeing the fibrous material as described above, a suitable amount of reactive dyestuff is included in the above described aqueous alkaline treating medium and the process otherwise carried out unchanged. The concentration of reactive dyestuff to be included in the aqueous medium is of course a matter of choice obvious to skilled dyers, and may range from about 0.05 to 2 or 3% in the aqueous medium depending upon the dyestuff, the shade desired, etc.

The mechanism by which the process of this invention yields the desired improved properties is not clearly understood, although it apparently involves a splitting of the thioxane ring to produce in situ in the fibrous material a di-functional aliphatic compound which reacts with and cross-links adjacent fiber molecules. 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 fibers containing reactive or replaceable atoms or groups 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 cellulose fibers of natural or synthetic type such as cotton, linen, wool, paper, regenerated cellulose and the like. The 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 cellulose, the process of this invention may be employed for improving other 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, partially hydrolyzed cellulose acetate and polyvinyl acetate, polyvinyl chloride, and mixtures, copolymers and graft polymers thereof. Mixed fabrics and fibers may likewise be so treated. The process of the present invention finds its greatest advantage in the treatment of white felts and woven fabrics, particularly cotton shirting, sheetwear, apparel, and the like. When employed for simultaneously dyeing the material, brighter, truer and faster shades of dyeings are obtainable. When applied to previously dyed or pigmented material, improved fastness properties are obtainable. It will be understood that the present process may be applied to 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 fibrous material with such a finish enables more permanent effects due to simultaneous reaction or cross-linking of the 1,4-thioxane dioxide 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.

EXAMPLE I

Springs Mills Shirting S/073 was immersed in a solu-

tion containing 10 g. 1,4-thioxane dioxide, 3.0 g. soda ash, 0.5 g. borax (sodium tetraborate decahydrate) and 86.5 g. water. The fabric was then passed between squeeze rollers set at such a pressure that the weight of solution retained was 80% of the weight of dry untreated fabric. The fabric was then dried at 175 to 180° F. and then heat cured at about 360° F. for about 90 seconds. The fabric was then bleached in a 1% hydrogen peroxide solution, rinsed with plain water, and ironed dry. The fabric was then conditioned for 48 hours at about 48% relative humidity. When tested by A.S.T.M. test method D1295–53T, the treated fabric had a dry crease recovery angle of 194° and a wet crease recovery angle of 237° as compared with dry and wet crease recovery angles of, respectively, 164° and 191°, for untreated fabric.

EXAMPLE II

The process of Example I was repeated except that the borax was omitted. The treated fabric had dry and wet crease recovery angles of, respectively, 188° and 230°, and was slightly yellower than the product of Example I above.

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 fibrous material while retaining the fiber structure thereof comprising treating fibrous material containing a member of the group consisting of reactive hydrogen atoms and reactive halide atoms with an aqueous alkaline medium containing about 0.5 to 50% by weight of 1,4-thioxane dioxide and then drying and curing the treated material at a temperature of at least about 250° F.

2. A process for improving the properties of fibrous material while retaining the fiber structure thereof comprising treating fibrous material containing a member of the group consisting of reactive hydrogen atoms and reactive halide atoms with an aqueous alkaline medium containing about 0.5 to 50% by weight of 1,4-thioxane dioxide and an alkaline reacting substance selected from the group consisting of alkali metal hydroxides, carbonates, bicarbonates, phosphates, silicates, borates, and acetates, and then drying and curing the treated material at a temperature of at least about 250° F.

3. A process as defined in claim 2 wherein said alkaline reacting substance is sodium carbonate.

4. A process for improving the properties of fibrous material while retaining the fiber structure thereof comprising treating fibrous material containing a member of the group consisting of reactive hydrogen atoms and reactive halide atoms with an aqueous alkaline medium containing about 0.5 to 50% by weight of 1,4-thioxane dioxide and a boron-containing compound, and then drying and curing the treated material at a temperature of at least about 250° F.

5. A process as defined in claim 4 wherein said boron-containing compound is selected from the group consisting of metal, ammonium, and amine borates and borohydrides.

6. A process as defined in claim 4 wherein said boron-containing compound is an alkali metal borate.

7. A process as defined in claim 4 wherein said boron-containing compound is sodium tetraborate.

8. A process as defined in claim 4 wherein said boron-containing compound is sodium borohydride.

9. A process for improving the properties of fibrous material while retaining the fiber structure thereof comprising treating cellulose fibrous material with an aqueous alkaline medium containing about 0.5 to 50% by weight of 1,4-thioxane dioxide and then drying and curing the treated material at a temperature of at least about 250° F.

10. A process for improving the properties of fibrous material while retaining the fiber structure thereof comprising treating cellulose fibrous material with an aqueous alkaline medium containing about 0.5 to 50% by weight of 1,4-thioxane dioxide and an alkaline reacting substance selected from the group consisting of alkali metal hydroxides, carbonates, bicarbonates, phosphates, silicates, borates, and acetates, and then drying and curing the treated material at a temperature of at least about 250° F.

11. A process as defined in claim 10 wherein said alkaline reacting substance is sodium carbonate.

12. A process for improving the properties of fibrous material while retaining the fiber structure thereof comprising treating cellulose fibrous material with an aqueous alkaline medium containing about 0.5 to 50% by weight of 1,4-thioxane dioxide and a boron-containing compound, and then drying and curing the treated material at a temperature of at least about 250° F.

13. A process as defined in claim 12 wherein said boron-containing compound is selected from the group consisting of metal, ammonium, and amine borates and borohydrides.

14. A process as defined in claim 12 wherein said boron-containing compound is an alkali metal borate.

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

16. A process as defined in claim 12 wherein said boron-containing compound is sodium borohydride.

17. A process for cross-linking a hydroxyl group containing polymer which comprises heating said polymer with about 1–10% by weight of thioxane dioxide in the presence of about .5–8% by weight of an alkaline catalyst to react the thioxane dioxide with the hydroxyl groups of the polymer.

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