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TEXTILE TREATMENT

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This invention relates to textile materials and relates more particularly to the treatment of textile material having a basis of a cellulose ester of low hydroxyl content.

It is an object of this invention to provide a new and efficient process for the heat treatment of textile material having a basis of a cellulose ester of low hydroxyl content.

Another object of this invention is the provision of a novel process for the dyeing of textile material having a basis of a cellulose ester of low hydroxyl content.

Other objects of this invention will be apparent from the following detailed description and claims. In this description and claims all proportions are by weight unless otherwise indicated.

In accordance with one aspect of this invention textile material having a basis of a cellulose ester of low hydroxyl content is treated by immersing the material in a heated liquid bath of a polyhydric alcohol. The treatment results in an increase in the crystal size and crystalline orderliness of the cellulose ester. It also raises the safe ironing point of the material as well as its resistance to glazing and its resistance to shrinkage on pressing with moist steam, and improves its dimensional stability on laundering. Advantageously, a dye of the dispersed cellulose acetate type is dissolved in the bath of polyhydric alcohol. This results in the dyeing of the textile material, even in heavy shades, after only a few seconds, exposure to the heated bath.

The cellulose esters of low hydroxyl content employed in the process of this invention contain at most 0.29, preferably zero to 0.12, alcoholic hydroxyl groups per anhydroglucose unit in the cellulose molecules thereof. Best results are obtained by the use of cellulose acetate of very high acetyl value, e.g. an acetyl value of at least 59%, preferably 61 to 62.5%, calculated as combined acetic acid. Other lower aliphatic acid esters of cellulose of low hydroxyl content may be employed; for example, the propionate, butyrate, mixed acetate-propionate, mixed acetate-butyrate and mixed acetate-formate esters of cellulose.

Best results have been attained in the process of this invention by the use of treating baths comprising ethylene glycol. However, other polyhydric alcohols such as diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, glycerol, triethanolamine, diethanolamine, 1,4-butylene glycol or 1,3-butylene glycol, or mixtures of any two or more of these polyhydric alcohols may be used if desired.

As stated, the treating bath may contain a dispersed cellulose acetate dye. It is preferably to employ those dyes which are of the known "high temperature slow dyeing" type, since the use of this type of dye yields colored textile materials of increased fastness to washing. Examples of dyes of this type are such compounds as 2-nitro-4-sulfonanilido diphenylamine, 4'-ethoxy-2-nitrodiphenylamine-β-hydroxypropylsulfonamide, 4-nitro-2-methoxyphenyl azo 4'-bis(beta-hydroxyethyl) amino-2'-acetylaminobenzene, 4-nitro-2-methyl-sulfonephenyl azo 4'-(N-beta-hydroxy-ethyl-N-difluoroethyl) aminobenzene, 4-nitro-2-chlorophenyl azo 4'-bis(beta-hydroxyethyl) amino-2'-methylbenzene, 1-hydroxyethylamino-4-hydroxyethylamino-5-hydroxy-8-hydroxy anthraquinone, 4-nitrophenyl azo 4'-di-β-hydroxyethylamino-2'-acetaminobenzene, a mixture of 1,4-di(hydroxyethylamino)-5,8-dihydroxy anthraquinone and 1-amino-4-anilido anthraquinone, 1,5-dihydroxy-8-nitro-4-(meta-alpha-hydroxyethyl) anilido anthraquinone, 1,8-dihydroxy-4-(para-beta-hydroxyethyl) anilido-5-nitro anthraquinone, 1-amino-4-anilido anthraquinone, and 2,4-dinitro-6-chlorophenyl azo 4'-bis(hydroxyethyl) amino-2'-acetylamino-5'-methoxybenzene. Preferably the dye should be used in the "oil-color" form which contains little or no added dispersing agent. Examples of suitable commercial dyes of this type are those sold under the trademarks Latyl, Eastone, Celanthrene and Lenra. All of these dyes are characterized by the fact that when applied to the ordinary cellulose acetate textile materials, of 53 to 55.5% acetyl value, under certain standard conditions in aqueous medium and at 80° C., they will dye said textile materials in full shades, but when the same dyes are applied to the same textile materials under said standard conditions at a lower temperature, i.e. 60° C., the textile materials will be dyed only to a small extent, e.g. in shades whose depths are only about 65% or less of the depths of the full shades. The standard conditions mentioned above involve a treatment of 1 part by weight of the fabric in 50 parts by weight of an aqueous dyebath comprising 0.5 gram per liter of soap, e.g. sodium oleate, and 1% (based on the weight of the fabric) of dye.

While best results are obtained by the use of the dyes of the high temperature, slow dyeing type described above, this invention may also be practiced using other dispersed cellulose acetate dyes, e.g. with low temperature or medium temperature types of dispersed cellulose acetate dyestuffs such as 2-nitro-4-sulfonamido diphenylamine, p-nitrophenyl azo diethyl aniline or 1-amino-4-hydroxy anthraquinone.

The presence of certain polyhydric alcohols, such as triethanolamine, in the treating bath makes it possible to use vay dyes as the coloring agents therein, the triethanolamine providing both the alkalinity and the reductive environment which is desirable for the application of this type of dye. Examples of vat dyes which may be used are anthraquinone Vat Golden Orange G (C.I. 1096) and anthraquinone Vat Jade Green (C.I. 1101).

The proportion of dye in the treating bath may be varied in accordance with the depth of shade desired. Suitable proportions are, for example, 1 to 5%, based on the weight of liquid, with a liquid:fabric ratio of 10:1 to 20:1.

The optimum temperature of the treating bath and the optimum time of immersion of the textile material therein depend to some extent on the type of polyhydric alcohol used. Thus, with ethylene glycol, temperatures of about 130 to 170° C., preferably 145 to 155° C., and treating times of about 8 to 12 seconds have been found suitable for the treatment of fabrics comprising filaments of cellulose acetate of acetyl value 61 to 62% (e.g. 61.5%), calculated as combined acetic acid. In the case of glycerol, temperatures of 180 to 200° C. are most suitable, with the 8 to 12 second period of treatment, for the same fabric. Preferably, the temperature of treatment is not so high as to stiffen, weaken, embrittle, or otherwise degrade the textile material.

The textile material may be physically held to constant dimensions, or even stretched in one or more directions, during its immersion in the heated treating bath. Preferably, however, it is allowed to relax during treatment. It is found that treatment of the material, in fabric form, in the relaxed condition with the heated polyhydric alcohol results in a relatively large (e.g. 8 to 15%) shrinkage of the fabric, which is very desirable in many cases. The extent of shrinkage is of course, dependent on the fabric construction and the relatively large shrinkage makes it possible to change a thinly

woven, sleazy fabric into a denser fabric of improved hand and durability. The wet or dry heat treatments employed heretofore did not cause shrinkage of the same order of magnitude, even when the fabric was permitted to relax freely during the treatment.

In one convenient process the fabric is passed through driven feed rolls and then downward into one leg of a U-shaped passageway containing the heated bath of polyhydric alcohol, then up through the polyhydric alcohol bath in the other leg of said U-shaped passageway and through driven squeeze rolls mounted above the level of the treating bath. The squeeze rolls, which serve to remove much of the polyhydric alcohol from the fabric, may be driven at a lower peripheral speed than the feed rolls. The liquid is supplied from an inlet near the point where the fabric enters the U-shaped passageway and is discharged from an outlet near the point where the fabric leaves the passageway, the movement of the fabric through the passageway being assisted by the movement of the liquid therethrough and the fabric being in a relaxed state during its movement through the passageway. After the fabric leaves the squeeze rolls it is washed, as with hot water, to remove adhering polyhydric alcohol. A subsequent scouring with an aqueous solution containing soap or other detergent removes surface dyestuff.

As stated, the treatment with the heated liquid bath of polyhydric alcohol containing a dye increases the crystal size and crystalline orderliness of the cellulose ester and also raises the safe ironing point of the material, as well as its resistance to glazing and its resistance to shrinkage on pressing with moist steam. This treatment also increases the penetration of the dye into the material. However, the dyed material will not generally pass such severe tests as the #3 A.A.T.C.C. wash-fastness test, involving washing at 160° F., since at such elevated washing temperatures it tends to lose a small portion of the dispersed cellulose acetate dye and to color the wash water. To further improve the wash-fastness of the dyed material it may be treated with a strong stripping agent, such as an aqueous solution of sodium hydrosulfite, of, for example, 0.5 to 1 gram per liter concentration, which removes all of the dye available at the surface of the dyed material. Another method of improving the wash-fastness involves giving the dyed material a heat treatment. Thus, the dyed material may be subjected to infra-red radiation, to hot air, or to direct contact with hot rolls. Suitable temperatures for such heat treatment are, for example 210 to 235° C.

In accordance with another aspect of this invention, the textile material is treated with the heated polyhydric alcohol in the absence of the dye to increase the crystal size and crystalline orderliness of the material and to improve its safe ironing temperature and other properties described above. That is, the treatment serves to heat-set the material but does not color it. The heat-set material may thereafter be dyed or printed in any desired manner, as by the process described in the copending application of Salvin et al., Ser. No. 472,758, filed December 2, 1954, now U.S. Patent No. 2,982,597, or the copending application of Fortess et al., Ser. No. 445,449, filed April 13, 1953. It is found, unexpectedly, that the heat-set material produced by the treatment with a polyhydric alcohol is much more receptive to dyeing than material produced by the usual dry heat-setting procedures (e.g. by treatment with hot air or with infra-red radiation, or by contact with hot rolls) even though the latter materials have the same crystal size, crystalline orderliness, safe ironing temperature (e.g. about 220° C. or higher) and other thermal properties as the heat-set material of this invention. To obtain the best wash-fastness of the resulting dyed material it should be given a subsequent treatment after dyeing, such as a stripping treatment, as with sodium hydrosulfite, to remove the less adherent dye, or a heat treatment, in the same manner as described above in the discussion of the subsequent treatment of those materails which have been treated in a single step with both dye and polyhydric alcohol.

In accordance with another aspect of this invention, the treatment with the bath of polyhydric alcohol containing a dye is applied to textile material, having a basis of cellulose ester of low hydroxyl content, which has previously been subjected to one of the usual heat-setting procedures mentioned above. It is found that the heat-set material, which may be dyed only with difficulty by ordinary dyeing methods, becomes colored very rapidly and also shrinks when immersed in the heated bath of polyhydric alcohol containing the dye. This procedure may be applied not only to heat-set material which is undyed, but also to material which has been dyed either before or after heat-setting, thus causing a redyeing of the material, in the same color or a different color, as desired. To obtain the best wash-fastness the product should be given a stripping treatment or a subsequent heat-treatment as previously described.

Any of the usual finishing agents may be applied to textile materials produced in accordance with this invention. For example, there may be applied to the textile material a silicone finish composed of a polysiloxane containing methyl or other hydrocarbon groups and, preferably, also hydrogen atoms, directly attached to the silicon atoms. Other finishing agents which may be applied include waxy polyethylene, waxy sulfonated fatty materials, waxy cationic long chain amine compounds, finely-divided silica, finely-divided titanium dioxide, and resinous or resin-forming condensation products such as the reaction products of melamine, stearamide, and formaldehyde. Other resinous or resin-forming condensation products which may be applied include the reaction products of formaldehyde with urea or thiourea or substituted and cyclic ureas such as ethylene urea, or melamine, and alkylation products of such reaction products, e.g. dimethoxymethyl urea, trimethoxymethyl melamine or N,N'-dimethoxymethyl ethylene urea. The amount of finishing agent applied is relatively small, e.g. about ¼ to 2%, based on the weight of the textile material, and the finishing agent is most conveniently used by applying to the textile material an aqueous dispersion of said finishing agent, following which the textile material is dried and, when it is necessary to cure said finishing agent as in the case of silicones or resinous condensation products, then baked at an elevated temperature. Suitable finishing agents are sold under the names "Decetex 102," "Decetex 104," "Decetex 108," "Hydropruf," "Repelletex P 30," "Ahco III," "Ahcovel A," "Ahcovel E," "Ahcovel G," "Ahcovel NC," "Ahcovel R," "Aquex 16," "Aquex 16x," "Permel," "Permel B," "Aerotex Softener H," "Paropon R," General Electric's "Silicone 81386," "Syton W–20," "Dullatone," "Aerotex Resin 801," "Aerotex Cream 450," "Rhonite R–1," and "Rhonite R–2." Those finishing agents which act as surface lubricants, e.g. the silicones, the waxy polyethylenes and other waxy softeners, and the condensation products of melamine, formaldehyde and stearamide, increase greatly the resistance of the dyed textile material to abrasion, which abrasion sometimes causes fragments of fibers to break off and thus gives the appearance of crocking. Such finishing agents also improve the tear strength of the material. Combinations of finishing agents may be employed, e.g. combinations of silicones or waxy polyethylenes with urea-formaldehyde or melamine-formaldehyde condensation products, or combinations of dispersed finely-divided silica and silicones together, if desired, with urea—or melamine—formaldehyde condensation products.

Cellulose esters of low hydroxyl content colored with certain dispersed cellulose acetate dyes show a tendency to fade on exposure to combustion gases or similar fumes and, in some cases, on exposure to ozone. To reduce this tendency it may be desirable to apply a suitable inhibitor,

such as diphenyl imidazolidine or diphenyl ethylenediamine, to the textile material. Conveniently, the inhibitor, which has a substantial affinity for the textile material, may be applied by dispersing it in the aqueous bath used for removing surface dyestuff from the material after the treatment with the polyhydric alcohol. The amount of inhibitor is generally small, e.g. 0.5 to 2% based on the weight of the textile material.

While the process of this invention has been described particularly in connection with textile materials composed entirely of fibers of cellulose ester of low hydroxyl content, it is also applicable to other textile materials comprising such fibers, e.g. to materials made up of blends of such fibers and other fibrous materials, such as wool, cotton, rayon, glass fibers and asbestos. These blends may be dyed under such conditions that all types of fibers in the blend are colored at the same time or they may be dyed in stages so as to color the different types of fibers successively. The blends of fibers may be cross-dyed or union-dyed. The process of this invention is applicable to textile materials made up of staple fibers of cellulose ester of low hydroxyl content as well as those made up of continuous filaments of said cellulose ester. It may be applied to yarns, woven textiles, ordinary knitted materials, warp knitted materials, unspun staple fibers, etc.

The following examples are given to illustrate this invention further.

Example I

An uncolored woven fabric composed of fibers of cellulose acetate of acetyl value 61.5%, calcaulated as combined acetic acid, is immersed in a bath of ethylene glycol maintained at a temperature of 150° C. and containing 0.4% Latyl Blue BG (a 1,4-diamino, 2,3-diamide anthraquinone), 0.3% Eastone Red GLF (4-nitro-2-methylsulfone phenyl azo 4'-(N-beta-hydroxyethyl-N-difluoroethyl) aminobenzene) and 0.3% Latyl Yellow YL (2-nitro-4-sulfonanilido diphenylamine), based on the weight of ethylene glycol, for 10 seconds. The fabric is permitted to relax while in the bath and the adherent glycol and dyestuff are removed from the fabric by scouring in a 1% aqueous solution of soap at 160° F. The fabric is colored a medium gray shade and has a safe-ironing temperature of 250° C., compared with an initial safe-ironing temperature of 180° C. before the treatment. It also has excellent glazing resistance and shrinks less than 2% in area on steam pressing with a Hoffman press or on machine washing.

Example II

The colored fabric produced in accordance with Example I is treated in a bath containing 1 gram per liter of sodium hydrosulfite and 1 gram per liter of the dispersing agent known as "Emulphor ELA 719" (non-ionic product of reactor of castor oil and ethylene oxide) at 180° F. for 1 hour. The resulting gray fabric passes the #3 A.A.T.C.C. washfastness test involving washing at 160° F.

Example III

The colored fabric of Example I is passed on a pin frame through a radiant heater for 10 seconds during which the temperature of the fabric is raised to 435° F. (224° C.). The fabric is then washed, in relaxed condition, in an aqueous bath at 170° F. The properties of the resultant fabric are substantially the same as those of the fabric produced in Example II.

Example IV

Example I is repeated except that glycerol is used in place of ethylene glycol and the temperature of the bath is 200° C.

Example V

Example I is repeated except that 1,2-propylene glycol is used in place of the ethylene glycol and the temperature of the bath is 130° C.

Example VI

Example I is repeated except that a mixture of 50 parts of 1,2-propylene glycol and 50 parts of triethanolamine is used in place of the ethylene glycol and the temperature of the bath is 180° C.

Example VII

Example I is repeated except that diethylene glycol is used in place of ethylene glycol and the temperature of the bath is 140° C.

The fabrics produced in Examples IV to VII are substantially the same as those produced in Example I.

It is to be understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for improving the properties of cellulose ester textile material, which comprises impregnating a textile fabric comprising filamentary material of cellulose triacetate of at least 59% acetyl value, calculated as combined acetic acid, with a hot bath of a glycol of the group consisting of ethylene glycol, propylene glycol and diethylene glycol, at a temperature of about 130 to 170° C. for a time sufficient to raise the safe ironing temperature of textile fabric of cellulose triacetate of at least 59% acetyl value, calculated as combined acetic acid, from an initial safe ironing temperature of 180° C. to a final safe ironing temperature of about 220 to 250° C.

2. Process as set forth in claim 1 in which said cellulose triacetate has an acetyl value of at least about 61%, calculated as combined acetic acid.

3. Process as set forth in claim 2 in which said textile material is allowed to shrink in said bath.

4. Process as set forth in claim 2 in which said polyhydric alcohol is ethylene glycol.

5. Process as set forth in claim 4 and in which said textile fabric is immersed in said bath for a time not above about 12 seconds.

6. Process as set forth in claim 2 in which said polyhydric alcohol is diethylene glycol.

7. Process as set forth in claim 2 in which said polyhydric alcohol is 1,2-propylene glycol.

8. Process as set forth in claim 1 in which said bath contains dissolved therein a dye for said cellulose triacetate, the dye being inert to said glycol, and said cellulose triacetate being colored by said process.

9. Process as set forth in claim 8 in which said cellulose triacetate has an acetyl value of at least about 61%, calculated as combined acetic acid.

10. Process as set forth in claim 9 in which said dye is a dispersed cellulose acetate dye.

11. Process as set forth in claim 9 in which said material is thereafter treated with aqueous sodium hydrosulfite to strip loosely adherent dye from said material and increase the washfastness thereof.

12. Process as set forth in claim 9 in which said material is thereafter heat treated in dry condition to improve the washfastness thereof.

13. Process as set forth in claim 1 in which said treated material is thereafter dyed with an aqueous bath of a dispersed cellulose acetate dyestuff.

14. Process as set forth in claim 1 in which said glycol has triethanolamine admixed therewith.

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8

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