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COLORING OF CELLULOSE-CELLULOSE TRIACETATE TEXTILES

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This invention relates to the coloring of textile materials and relates more particularly to the coloring of textile materials containing fibers of cellulose esters of low hydroxyl content and fibers of cellulose.

It is an object of this invention to provide a new and useful process for the production of colored textile materials containing fibers of cellulose esters of low hydroxyl content and cellulose fibers.

Another object of this invention is the provision of a novel process for making cross-dyed textile materials of excellent fastness to washing, to sunlight and to atmospheric influences, and of excellent dimensional stability and shrink-resistance.

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

In accordance with one aspect of this invention, a textile material comprising a blend of fibers of a cellulose ester of low hydroxyl content and cellulose fibers, such as cotton, is given a heat-treatment to develop a crystalline structure in said cellulose ester. Thereafter the textile material is given a mercerizing treatment using a strongly alkaline mercerizing bath. This causes a mercerization of the cotton or other cellulose fibers but, surprisingly and as a result of the heat-treatment, has substantially no effect on the fibers of cellulose ester of low hydroxy content. The textile material is then treated with a leuco-compound of a vat dye, as by passing the textile material through an aqueous alkaline bath containing said leuco-compound. In this step the leuco-compound, which is substantive to the cotton fibers, penetrates into said cotton fibers. Subsequent oxidation, as in air, converts the leuco-compound into an insoluble vat dye in the cotton fibers. The fibers of cellulose ester of low hydroxyl content remain unaffected by the dyeing treatment so that a cross-dyed effect is produced.

The cellulose esters of low hydroxyl content employed in the process of this invention contain not more than 0.29, preferably 0.0 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 low hydroxyl content and of correspondingly high acetyl value, e.g. an acetyl value of at least 59%, preferably 61 to 62.5%, calculated as combined acetic acid. However, other lower aliphatic acid esters of cellulose of low hydroxyl content may be employed. Examples of such esters are cellulose-propionate, cellulose butyrate, cellulose acetate-propionate, cellulose acetate-butyrate and cellulose acetate-formate.

The cellulose fibers employed in the textile material treated in accordance with this invention are preferably cotton fibers. However, if desired, other cellulose fibers may be used in place of, or in addition to, the cotton. Examples of such other cellulose fibers are those of ramie or flax.

The process of this invention may be applied to all

sorts of textile material such as yarns, circular-knitted or warp-knitted fabrics, woven fabrics and non-woven fabrics made up of randomly arranged fibers. The cellulose ester fibers and cotton or other cellulose fibers may be combined in any suitable manner. Thus, staple fibers of the cellulose ester may be blended with cotton fibers. Alternatively, yarns composed of staple fibers or continuous filaments, or both, of the cellulose ester may be combined, as by doubling, with yarns of cotton. Also, fabrics may be produced in which some of the yarns are of cotton and some are of the cellulose ester, for example, by using a cotton warp and a cellulose ester filling or by using filling yarns of cotton and of the cellulose ester alternately. Any suitable combination of these methods may be used.

The heat treatment of the textile material may be carried out in air or in any other convenient gaseous or inert liquid atmosphere or even in vacuum. Thus, the textile material may be passed through a hot air oven, or over one or more heated drums or plates, or through a bath of a suitable liquid such as a molten metal of low melting point. Heat may also be applied by means of infra-red radiation or a high frequency electrical field. When the heat-treatment is carried out in air, best results are obtained when the textile material attains a surface temperature about 210 to 220° C. for a short period of time, e.g. 5 to 30 seconds. Alternatively, the textile material may be placed in an atmosphere of saturated steam under a superatmospheric pressure of, for example, 10 to 30 p.s.i.g. or an atmosphere of superheated steam. The textile material may also be heat treated by subjecting it to the action of a liquid polyhydric alcohol, such as ethylene glycol, at a suitable elevated temperature, e.g. 140° C.

The heat treatment should be carried out for a sufficient period to develop a crystalline structure in the cellulose ester of low hydroxyl content. One indication of the attainment of the desired crystalline structure is an increase in the safe ironing temperature of the textile material. Thus, before heat treatment the safe ironing temperature of a textile fabric having a basis of cellulose acetate of low hydroxyl content is generally about 180 or 190° C., and this is raised by the heat treatment to about 230° C. or above. Other indications of the extent of heat treatment are given by study of the X-ray diffraction pattern of the cellulose ester filaments, from which a "crystalline order index" (determined as described below) may be calculated. It is preferred to heat treat the textile material to such an extent that the crystalline order index of the cellulose ester of low hydroxyl content is raised to at least 1.2, preferably 1.5 to 2.

The "crystalline order index" referred to above is obtained by calculation from curves based on X-ray diffractometer studies of samples of the cellulose ester fibers of the treated fabric. These curves are plots of intensity of the diffracted beam against the angle of the beam. Thus, the curve for cellulose triacetate has four angle being that which the diffracted X-ray beam makes pronounced peaks at angles of 8, 10, 12.6 and 16°, the with respect to the incoming X-ray beam. The degree of heat treatment will affect the sharpness of these peaks. The crystalline order index, which is an indication of the sharpness of the peaks, is the average of the ratios of each peak height to its width at half height for the four peaks mentioned above. For producing the diffractometer curves used for measuring the crystalline order index there is employed a North America Phillips Geiger Counter Diffractometer operated under the following conditions:

Radiation: Nickel filtered CuK α radiation 35 kv., 14 ma. using both voltage and ma. stabilization. Dif-

fractometer constants: 3° take-off, 1 divergence slit; .003" receiving slit (0.025°), 1° scatter slit; 2° 20/min. scanning speed. Recorder constants: Ratemeter: Scaler—8, multiplier—0.6 (full scale 240 counts/sec.). Time constant: 16. Chart speed: 0.5"/min.

As stated, the heat treatment employed in the process of this invention makes the cellulose ester resistant to saponification during mercerization. It also increases the resistance of the cellulose ester fibers to surface-saponification during the alkaline treatment involved in the vat dyeing. Such surface saponification would not only cause the cellulose ester fibers to take up the vat dye but it would also cause them to take up any urea-formaldehyde or similar resin-forming material which might be subsequently applied to increase the crease- and shrink-resistance of the cotton portion of the textile material. This absorption of the crease-proofing resin by the cellulose ester fibers would change the hand of said cellulose ester fibers and decrease their strength.

The heat treatment has the further advantage of improving the physical properties of the textile material. Thus, it effects an improvement in the resistance to glazing, in the resistance to shrinkage on pressing with moist steam, in the ability of the material to be pleated permanently, and in the resistance of the material to mussing or wrinkling on laundering. It will be understood of course that the heat treatment is preferably not continued for such a long period as to cause substantial degradation of the textile material.

While it is most convenient to heat treat the cellulose ester of low hydroxyl content material when combined with the cotton or other cellulose fibers, as described above, the procedure may be varied, if desired. Thus, the cellulose ester of low hydroxyl content material, which may be in the form of staple fiber or yarns, may be heat treated separately and then combined with the cotton fibers.

The mercerizing treatment improves the affinity of the cotton or other cellulose fibers for the leuco-compound of the vat dye. This mercerizing treatment is carried out in the manner well known in the art of cotton textiles, and comprises, for example, applying to the textile material an aqueous solution containing about 20 to 25% of sodium hydroxide, at a temperature of about 15 to 25° C. In usual commercial mercerization treatments the textile material remains in contact with the alkaline mercerizing solution for at most about one minute. In order to obtain complete penetration of the textile material in this short period of time it is desirable to give the textile material a preliminary scouring treatment, as by boiling them in dilute aqueous alkaline solution of soap or a synthetic detergent, at a pH of 9.5 or less, before the heat treatment. The rate of penetration of the mercerizing solution may also be increased by adding thereto a suitable wetting agent which is stable at the high concentration of alkali prevailing in said mercerizing solution. Alkaline salts of homologues of phenol, e.g. the sodium salt of m-cresol, are suitable wetting agents for this purpose.

In one convenient commercial preliminary treatment of a fabric composed of cotton fibers and fibers of cellulose acetate of low hydroxyl content, the fabric is first singed, then treated with an enzyme to remove any starch size from the cotton fibers. Thereafter the fabric is subjected for an appreciable period of time, e.g. 1 to 2 hours, to a boiling mildly alkaline detergent solution, such as an aqueous solution of sodium oleyl taurate or soap containing tetrasodium pyrophosphate or soda ash and having a pH of 9.5 or less. Then, if the fabric contains uncombed cotton yarns, it is bleached to remove cotton motes, as with an acid hypochlorite bleaching solution, a sodium chlorite bleaching solution, or an alkaline hydrogen peroxide bleaching solution having a pH of 9.5 or less. The fabric is then heat-treated in accordance with this invention.

The vat dyeing step of the process of this invention may be conducted in the manner conventionally employed in the vat dyeing of cotton textiles. Thus, there may be applied to the textile material an aqueous alkaline bath containing the leuco-compound of the vat dye together with a reducing agent such as sodium hydrosulfite or sodium formaldehyde sulfoxylate or the vat dye may be applied in pigment form and then reduced on the fabric. In general vat dyes of the well known cold dyeing type give best results. Examples of suitable dyes of this type are those sold under the names "Indanthrene Blue RCLN infra paste," "Indanthrene Violet FFBNA," "Veranthrene Brilliant Pink BL paste," "Ahcovat Jade Green B paste," "Indanthrene Red RK paste," "Indanthrene Scarlet RA," "Indanthrene Brown RA," "Veranthrene Blue HCGK paste," "Veranthrene Brilliant Green H3G paste," "Calcosol Yellow GL paste," and "Ponsol Yellow 5GLL paste."

The dyebath may be applied by padding or by immersion, as on the jig. Continuous vat-dyeing machines, of the type well known in the art, may be used. In using such machines the vat dye is generally deposited to the fabric in pigment form, an alkaline reducing agent is applied to the fabric to convert the vat dye to its leuco compound, and the leuco-dyed fabric is then treated to fix the dye in the oxidized form on the fabric. Thus, the leuco-dyed fabric may be treated with an oxidizing solution, such as an alkaline peroxide or perborate, or it may be treated with steam and then oxidized in air. It is desirable to maintain the treating baths alkaline, since vat acids, which are formed on acidification of the alkaline leuco-compound of the vat dye, tend to be deposited on the cellulose ester fibers. However, the vat dye may actually be applied to the textile material in the form of the vat acid, provided that this application of vat acid is done at relatively low temperatures at which there is very little tendency for the vat acid to be absorbed by the cellulose ester fibers and provided that the textile material is made alkaline shortly after the vat acid is applied, so as to convert the vat acid to the alkaline leuco-compound. In the use of the continuous dyeing machines the treating solutions are in contact with the fabric being dyed for very short times, on the order of several seconds, usually less than a minute. With such short treatment times, any of the treating temperatures and concentrations of alkali commonly employed in the vat dyeing of cotton may be employed in the practice of this invention. However, when the dyeing is carried out using a jig, where the treatment time is relatively long, it is desirable to use a temperature not over 120° F., a caustic concentration of not more than 1½ ounces of NaOH per gallon of liquid and a time of not more than about one hour.

The fibers of cellulose ester of low hydroxyl content may be left undyed or they may be colored at any time after the conclusion of the vat-dyeing procedure. Thus, the cellulose ester fibers may be colored by applying a disperse cellulose acetate dye to the vat-dyed textile material, using any of the known procedures. Preferably, since the cellulose ester of low hydroxyl content has a crystalline structure produced by heat treatment and is therefore relatively difficult to dye, the disperse cellulose acetate dye should be applied at a relatively high temperature, e.g. 95 to 98° C., or even higher under superatmospheric pressure, or in conjunction with a dyeing assistant such as orthophenyl phenol or methyl salicylate or butyl benzoate. Alternatively, the cellulose ester of low hydroxyl content may be dyed, as with a disperse cellulose acetate dye, prior to the heat treatment procedure of this invention.

The following examples are given to illustrate this invention further.

Example I

A scoured fabric of 50% cotton fibers and 50% of

fibers of cellulose acetate of 61.5% acetyl value, calculated as combined acetic acid, the fabric being so woven, in known manner, that dyeing of the cotton with the cellulose ester reserved will produce a check pattern, is heat-treated with radiant heat, so that the fabric attains a surface temperature of 215° C., for 10 seconds. Thereafter the fabric is mercerized for 30 seconds in an aqueous bath containing 22% of sodium hydroxide at a temperature of 20° C. and then, after rinsing, is padded in a continuous manner with an aqueous bath containing, per 130 gallons of the padding bath, 16¼ pounds of "Indanthrene Red RK paste" (C.I. 1162), 10 ounces of tetrasodium pyrophosphate and 10 ounces of "Nekal NF" (an alkyl aryl sulfonate wetting agent) at a temperature of 150° F. The padded fabric is then can dried, and thereafter passed through a Williams unit (a well known continuous type of machine used in vat dyeing) where it is subjected to an aqueous reducing solution at a temperature of 175° F., said solution containing, per 130 gallons of solution, 24 pounds of sodium hydrosulfite, 24 quarts of caustic soda (63° Twaddell), 1¼ pints of "Peregal O" (a nonionic wetting agent made by reacting ethylene oxide and a higher fatty alcohol to form a polyoxyethylene ether), 2 quarts of "Sandozol KB" (sulfonated Turkey red oil), 6 gallons of the padding liquor used previously, and 25 pounds of common salt. The fabric is then steamed and rinsed and allowed to oxidize in air. The product is a fabric colored in a pink check pattern with the cellulose ester fibers uncolored.

Example II

The undyed fabric of Example I is padded, after the heat-treating and mercerizing steps, with an aqueous bath having a temperature of 120° F. and containing, per 26 gallons of bath, 8 pounds of "Indanthrene Scarlet RA paste" (Pr. 449), 2 pounds of "Indanthrene Golden Yellow RKA double paste" (Pr. 292), ⅛ pint of "Nekal NF" and ½ pound of "Quadrofos" (sodium tetraphosphate). The padded fabric is then treated on a jig for 1 hour with a reducing bath having a temperature of 120° F. and containing, per 100 gallons of the reducing bath, 9 pounds 6 ounces of sodium hydroxide, 12½ pounds of sodium hydrosulfite, ½ pint of "Permaclear" (a water softening sequestering agent comprising a sodium salt of a polyaminocarboxylic acid), 1 pint of "Sandazol KB" and 1 quart of formalin (37%). Half of the sodium hydrosulfite is incorporated into this reducing bath at the beginning of the treatment and the remainder after ½ hour of treatment. The fabric is then rinsed, oxidized with an aqueous mixture of hydrogen peroxide and tetrasodium pyrophosphate having a pH of 9.0 and then treated at the boil with an aqueous solution of sodium oleyl taurate. The product is a fabric colored in a pink check pattern with the cellulose ester fibers uncolored. Analysis of the cellulose ester fibers of the finished fabric shows their acetyl value to be 61.5%.

It is to be understood that the foregoing detailed description is given merely 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 the coloring of textile materials which comprises heat-treating textile material comprising mercerizable cellulose fibers and fibers of cellulose acetate having an acetyl value of at least about 61%, calculated as combined acetic acid, to increase the crystallinity and crystalline order of said cellulose acetate to such a degree that its safe ironing temperature is increased to at least 230° C., mercerizing the heat-treated textile material, and then vat dyeing said textile material by application thereto of a vat dye in alkaline leuco form.

2. Process as set forth in claim 1 in which the mercerizing treatment is carried out by applying a solution of sodium hydroxide of about 20 to 25% concentration to said textile material, said mercerizing treatment having substantially no saponifying effect on said cellulose ester fibers which have been heat-treated, and said cellulose ester fibers being substantially undyed by the vat-dyeing.

3. Process as set forth in claim 1 in which said heat-treatment is carried out in air and the textile material attains a surface temperature of about 210 to 220° C. for a period of from 5 to 30 seconds.

4. Process as set forth in claim 1 in which said heat-treatment is carried out in an atmosphere of saturated steam at a pressure of 10 to 30 p.s.i.g.

5. Process as set forth in claim 1 in which said heat-treatment is carried out in a liquid polyhydric alcohol at a temperature of about 140° C.

6. Process as set forth in claim 1 in which the heat-treatment is carried out until the acetate fibers achieve a crystalline order of at least 1.2.

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