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TEXTILE TREATING

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This application is a continuation-in-part of our co-pending application Serial Number 406,350, filed January 26, 1954, now abandoned.

This invention relates to the dyeing of cellulose acetate of very high acetyl value and relates more particularly to the production of wash-fast dyed textile materials.

As is well known, the cellulose acetate textile materials customarily employed have acetyl values of about 53.0 to 55.5%, calculated as combined acetic acid, and are soluble in acetone. It has been common practice to dye such textile materials with dispersed cellulose acetate dyestuffs to produce colored materials. However, the fastness to washing of these colored materials has not been as good as desired. Thus, for certain purposes it is necessary to have colored materials which show a fastness to washing sufficient to meet the requirements of the #3 wash fastness test of the American Association of Textile Chemists and Colorists. This test involves washing a specimen of the dyed material at 150° C. for 45 minutes under certain standard conditions and observing the change, if any, in the color of the dyed material and the staining caused by running of the dye from said material. It has generally not been possible, by the use of dispersed cellulose acetate dyestuffs, to obtain dyed cellulose acetate textile materials, particularly such textile materials dyed in full shades, capable of passing the aforementioned #3 test. In fact this #3 test is so rigorous that, generally speaking, only a very limited group of dyed materials, e.g., vat-dyed cotton or regenerated cellulose, will pass the test.

It is an important object of this invention to produce a dyed textile material having extremely good wash fastness, e.g. wash fastness sufficient to pass the aforesaid #3 A.A.T.C.C wash fastness test.

A further object of this invention is the production of novel textile materials having improved properties, such as improved wash fastness; fastness to perspiration; resistance to crocking and wet bleeding; fading and sublimation; resistance to glazing; higher safe ironing temperatures; ability to form pleats which are permanent to laundering; increased resistance to wrinkling during washing; and decreased shrinkage when the fabric is pressed in the presence of moist steam.

Another object of this invention is to produce a novel textile material of cellulose triacetate or other cellulose acetate of very high acetyl value.

Still another object of this invention is the development of an improved process for dyeing cellulose acetate of very high acetyl value rapidly and in full shades.

Other objects of this invention will be apparent from the following detailed description and claims.

In accordance with one embodiment of this invention, a textile material of cellulose acetate of very high acetyl value, i.e. of 59% to 62.5% acetyl content, calculated as combined acetic acid, is dyed at an elevated temperature in an aqueous dyebath containing a dispersed cellulose acetate dyestuff of the "high temperature, slow dyeing" type in the presence of an assistant which is substantive to the cellulose acetate of very high acetyl value, and the resulting dyed textile material is then subjected to heat treatment.

By the use of this process there are produced textile fabrics dyed in full shades, which dyed fabrics may be washed a very large number of times under the conditions of the #3 A.A.T.C.C. wash fastness test, without showing appreciable change in color or staining. In addition, this process results in a decided increase in the safe ironing temperature of the textile fabric, an improvement in its resistance to glazing, and also an improvement in its resistance to mussing and wrinkling during laundering. Also, the treatment, which does not materially alter the hand or strength of the fabric, imparts to the fabric an ability to be permanently pleated and causes a marked decrease in the degree to which the fabric will shrink when it is pressed with moist steam.

As stated, the dyeing of the cellulose acetate of very high acetyl value is carried out in a heated aqueous bath of a dispersed cellulose acetate dyestuff of the high temperature, slow dyeing type. This class of dyestuffs is well known to the art and is represented by such compounds as 2-nitro-4-sulfonanilido diphenylamine; 4'-ethoxy-2-nitrodiphenylamine-β-hydroxy-propylsulfonamide; 4-nitro-2-methoxyphenyl azo 4'-bis(betahydroxyethyl)amino-2'-acetylaminobenzene; 4-nitro-2-methylsulfonephenyl 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(hydroxy-ethylamino)-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'-methoxy benzene. These dyestuffs, as sold, are in the form of mixtures of a dispersing agent, such as sodium lignosulfonate or the sodium salt of formaldehyde-naphthalene sulfonic acid condensation product, with the actual dye material, and usually contain about 30 to 45% of the actual dye material. Commercial dyestuffs of this type include those sold under the names "Setacyl Blue G"; "Eastman Blue GLF"; "Interchemical Blue RLF–40" (Pr. 227); "Celliton Blue AF" (Pr. 227); "Red Y"; "Celliton Blue Green BA" (Pr. 229); "Eastone Red 2B–GLF"; "Amacel Red 2B"; "Amacel Yellow CW"; "Eastone Red GLF"; "Amacel Rubine IX" (Pr. 239); "Scarlet III" (Pr. 244); "Interchemical Blue BGLF–40"; "Interchemical Blue-Green BALF–40" (Pr. 229) and "Amacel Violet Blue FS1." All of these dyestuffs 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 at 80° C., they will dye said textile materials in full shades, but when the same dyestuffs 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 dyestuff.

It has been found that cellulose triacetate and other cellulose acetates of very high acetyl value are generally resistant to dyeing with the previously described dispersed

cellulose acetate dyestuffs of the high temperature slow dyeing type. For example, when "Celliton Blue AF," which is of the high temperature type, is employed as the dye-stuff for both ordinary cellulose acetate and cellulose triacetate at 80° C., under identical conditions, the depth of shade on the triacetate after two hours of dyeing is only 20 or 25% of the depth of the shade obtained on the ordinary cellulose acetate after one hour of dyeing. Some improvements can be obtained by increasing the temperature of the dyebath up to its boiling point. Thus, when the temperature of the dyebath is raised to 95° C. the depth of shade on the cellulose triacetate is increased to 30%, as compared with the 20 or 25% obtained at 80° C.

In accordance with this invention, it has been found that the rate of dyeing of cellulose triacetate and other cellulose acetates of very high acetyl value may be greatly increased by carrying out the dyeing with the aqueous dyebth in the presence of certain assistants which are substantive to said cellulose acetates. By the use of these assistants the cellulose acetates of very high acetyl value may be dyed in full shades and within commercially acceptable periods of time using dispersed cellulose acetate dyestuffs of the high temperature slow dyeing type. These full shades may be attained at temperatures well below the boiling point of the dyebath at atmospheric pressure.

The assistants employed in accordance with this invention are, as stated, substantive to the cellulose acetate of very high acetyl value. Thus, when fibers of said cellulose acetate of very high acetyl value are placed in an aqueous bath containing the assistant uniformly dispersed therein, e.g. in an aqueous bath containing 0.05 to 0.2% of the assistant based on the weight of the bath and having a temperature of 65 to 90° C., the assistant is absorbed on the fiber in a quantity which is larger, usually several times larger, than the quantity which would be absorbed by the fiber by mere imbibition of the aqueous bath, so that the concentration of said assistant in the aqueous bath is reduced. The assistant should also be a good solvent for the dyestuff and should preferably have a limited solubility in water. For example, one of the preferred assistants of this invention, tripropyl phosphate, has a water solubility of less than 0.9% at 25° C. and about 0.5% at temperatures of 50 to 95° C., while the other assistants are generally even less soluble.

Outstanding results have been obtained by using as the dyeing assistants such materials as the terpene alcohols, e.g. pine oil, and their ethers, e.g. the terpene glycol ether known as "Terposol #8," such esters as tripropyl phosphate, tributyl phosphate, triamyl phosphate, trihexyl phosphate, dioctyl acid phosphate, dimethyl phthalate, diethyl phthalate and dipropyl phthalate, diallyl phthalate, triallyl citrate, methyl salicylate, methyl benzoate, and the N,N-dihydroxyethyl amides of higher fatty acids, such as capric or lauric acids, which N,N-dihydroxyethyl amides may be prepared by reacting diethanolamine with the higher fatty acid at an elevated temperature while splitting out water. Other materials which have been found to be effective as assistants include such aromatic compounds as cumene, biphenyl, naphthalene, tetrahydronaphthalene, trichlorobenzene, cyclohexyl phenol, o-phenyl phenol, salicylic acid, benzoic acid, the monophenyl ether of ethylene glycol, the monodichlorophenyl ether of ethylene glycol, and the mono p-chlorophenyl ether of ethylene glycol, the monophenyl ether of diethylene glycol, acetophenone, dibutyl phthalate, and 2-methyl-5-ethylpyridine, and such aliphatic and cycloaliphatic materials as decanol, trioctyl phosphates, e.g. tri-n-octyl phosphate, dipropyl acid phosphate, dibutyl acid phosphate, diamyl acid phosphate, didecyl acid phosphate, dilauryl acid phosphate, dibutyl ethanolamine, diisobutyl Carbitol, "Maypon K" (a condensation product of a protein split off product and a fatty acid), "Alkamine W-30" (a fatty amine condensate), and "CRL 40229-G2125," (an ester produced by condensing lauric acid and 8 to 10 moles of ethylene oxide), and the aryl amine known as "Kar-In." However, the latter materials are not considered to be as useful generally as the previously mentioned preferred assistants, i.e. terpene alcohols and ethers, tripropyl, triamyl, trihexyl and tributyl phosphates, dimethyl, diethyl, diallyl and dipropyl phthalates, dioctyl acid phosphate, triallyl citrate, methyl salicylate, methyl benzoate, and the fatty acid-diethanol amine condensation products, since in many cases the materials are toxic; or too highly volatile; or do not sufficiently solubilize certain of the dispersed acetate dyestuffs of the high temperature type; or have some tendency to produce spotting unless added dispersing agents are present; or do not increase the dyeing rate to the same extent as said preferred assistants; or are at times deleterious to the mechanical properties and dimensions of the fabric.

Mixtures of dyeing assistants may be employed if desired. For example, excellent results have been obtained by the use of a mixture of tributyl phosphate and the condensation product of diethanolamine and capric acid, e.g. N,N-dihydroxyethyl capramide, said mixtures containing for example, at least 20%, e.g. 50%, of each of these assistants. Other mixtures of dyeing assistants which have given excellent results are, for example, a mixture of equal parts of pine oil and the aforementioned condensation product of diethanolamine and capric acid; a mixture of 40% by weight of tributyl phosphate, 40% by weight of pine oil and 20% by weight of the aforementioned condensation product of diethanolamine and capric acid; a mixture of 40% by weight of tripropyl phosphate, 40% by weight of tributyl phosphate and 20% by weight of the aforementioned condensation product of diethanolamine and capric acid.

Generally speaking, the dyebath should contain a dispersing agent in order to insure that the dye is properly dispersed. As pointed out previously, the commercially available dispersed cellulose acetate dyestuffs are preparations containing such dispersing agents in intimate mixture with the actual dye material. It is the usual practice in the dyeing of ordinary acetone-soluble cellulose acetate to incorporate into the dyebath additional amounts of dispersing agent beyond those amounts present in the commercial dyestuff. However, we have found that in the dyeing of cellulose triacetate and other cellulose acetates of very high acetyl value in the presence of assistants, the presence of an excessive amount of the dispersing agent generally causes a decrease in the rate of dyeing. Accordingly, it is usually desirable to maintain the amount of dispersing agent in the dyebath at a minimum value, commensurate with the particular dyestuff and dyeing conditions. On the other hand, certain dispersing agents having a substantivity for the fiber may be employed to aid the action of the dyeing assistant. Thus, the condensation product of diethanolamine and capric acid, which possesses some dispersing properties and detergent action, may be used to aid in the dispersing of tributyl phosphate or pine oil, for example.

When the amount of dispersing agent is too small the material may be unevenly dyed. For example, the dyed fabric may exhibit round, more heavily dyed spots when the assistant employed is not self-dispersible in water and insufficient dispersing agent is present. Accordingly, when such an assistant is used sufficient dispersing agent should be present to insure even dyeing under the particular dyeing conditions employed. Thus, in many cases a higher ratio of dispersing agent to assistant, e.g. up to about 1:5, should be used when a more concentrated dyebath is employed, as in a jig-dyeing, than when a relatively dilute dyebath is employed, as in winch dyeing. If desired, fabric showing the spots mentioned above may be treated to remove the spots by scouring the fabric thoroughly at a high temperature, e.g. 95° C., in the presence of a strong emulsifying agent, such as the nonionic reaction product of castor oil and ethylene oxide

sold under the name "Emulphor ELA–719"; the scoured spot-free fabric may then be redyed.

The dyeing assistant may be added directly to the aqueous dyebath together with the dyestuff, or it may be applied to the surfaces of the textile material before said textile material is brought into contact with the dyebath. In the latter case, the process of this invention is advantageously carried out by padding a dispersion of the dyeing assistant, e.g. an aqueous emulsion containing the assistant and a dispersing agent, onto the surfaces of a fabric comprising fibers of the cellulose acetate of very high acetyl value, and then introducing the resulting wet fabric into the dyebath.

In the practice of this invention, the aqueous dyebath is maintained at an elevated temperature, best results being obtained at temperatures of at least about 65° C. Temperatures up to the boiling point of the dyebath may be employed, and, in fact, the dyebath may be maintained under superatmospheric pressure in order that it may be heated to temperatures well above the normal boiling point of said dyebath, but this has not been found to be necessary from a practical standpoint.

The amount of assistant, the pH of the dyebath, the proportion of dyestuff in the dyebath, and the liquor ratio, i.e. the ratio of the weight of the dyebath to the weight of the fabric, may be varied widely. Thus, excellent results have been obtained when the amount of assistant in the dyebath has been varied from about 5 to 20% (based on the weight of the fabric) and when the pH of the dyebath has varied from about 6 to 9. It is preferred, of course, to employ dyebaths containing minimum amounts of the assistant. With respect to the amount of the dyestuff, this is of the same order as that generally employed in dyebaths containing dispersed cellulose acetate dyestuffs, e.g. about 0.1 to 4.0% (based on the weight of the fabric). For best results the liquor ratio should not be too high, e.g. it should not be above about 80, preferably about 50 or less, e.g. about 50 to 30 when the dyeing is carried out in a winch, since at higher liquor ratios the dyebath is generally too dilute. When methods other than winch dyeing are used for bringing the dyebath into contact with the material to be dyed, the liquor ratio is appreciably lower, e.g. about 10 in the case of package dyeing and about 5 in the case of jig dyeing.

When the assistant is applied to the textile material before the textile material is brought into contact with the dyebath, the total amount of dyeing assistant used may be reduced substantially, particularly in the case of those dyeing assistants, such as, for example, tripropyl phosphate, tributyl phosphate, dimethyl phthalate and dibutyl phthalate, which are not removed readily from the surfaces of the textile material by the dyebath. Thus, an emulsion having a concentration of about 1 to 5% of dyeing assistant may be applied to the fabric in an amount about equal to the weight of the fabric (e.g. about 75 to 100% of emulsion based on the weight of the fabric) at a temperature of, say, 20 to 60° C., before the fabric is introduced into a dyebath containing no added dyeing assistant. Though the total amount of dyeing assistant used is then only about 1 to 5%, based on the weight of the fabric, the results are equal to or better than those obtained using larger amounts, e.g. 5 to 20% of assistant, in the dyebath. In fact, when this method is used instead of the method in which the assistant is added directly to the dyebath, the rate of dyeing is generally higher so that the dyeing period is shortened considerably. With those assistants which are more easily removed from the surface of the fabric by the action of the dyebath, such as the condensation product of diethanolamine and capric acid, it is preferable to use dispersions containing a higher concentration of the assistant, e.g. about 5 to 10%, when the dispersions are applied to the fabric before the latter is brought into contact with the dyebath.

After the textile material made of cellulose triacetate or other cellulose acetate of very high acetyl value has been dyed, it is rinsed, in the manner well known in the dyeing art, to remove dyebath components other than the dyestuff and is then subjected to a heat treatment in accordance with this invention. The heat treatment has the effect of improving the wash fastness, perspiration fastness, and other properties of the textile material, e.g. safe ironing temperature, ability to take permanent pleats, glazing resistance, and moist steam pressing shrinkage.

The temperature at which the heat treatment is carried out and the period of treatment depend to some extent on the heat treating medium. Thus, when hot air is employed as a heating medium, an improvement in the properties of the textile material may be obtained by the use of temperatures of about 190° C., though optimum results are obtained at considerably higher temperatures, e.g. at temperatures of about 250° C. Thus, heat treatment of a dyed staple fiber, yarn or woven fabric of cellulose triacetate in hot air at a temperature of 190° C. for 20 minutes effects a considerable improvement in the wash fastness of the material and the safe ironing temperature of the fabric, but only a relatively minor improvement in the resistance to glazing and resistance to shrinkage on moist steam pressing, while heat treatment of the same fabric in hot air at a temperature of 250° C. for several seconds results in a very marked improvement in all of these properties. Furthermore, as will be evident from the results described in the preceding sentence, the desired improvement in the properties of the textile material may be obtained much more quickly when the higher temperatures are employed. For best results, the heat treatment should not be carried out at such temperatures and for such long periods of time as to materially impair the color, tensile strength and elongation at break, or other mechanical properties, of the textile material.

The heat treatment is a dynamic process and involves the heating up of the textile material to the elevated temperature. Actually, it is thought that the textile material need be at this elevated temperature for only a very short time and that most of the time is consumed in heating the fabric to this temperature. However, the use of heat sources having very high temperatures in order to shorten the time of treatment is not altogether practical since the outer surface of the fiber or fabric may then reach a temperature sufficiently high to cause damage before the interior of the fiber of fabric has reached the proper temperature. In addition it is very difficult to measure the exact temperatures actually attained by the fabric during heat treatment.

It will be therefore apparent that for commercial heat treatment of any particular fabric and with any particular apparatus it is best to make some simple trials in order to determine the best conditions for heat treatment. Such trials are carried out easily and quickly by exposing samples of the fabric to heat in the apparatus to be used, employing various conditions of time and temperature and by observing the characteristics of the treated samples, such as safe ironing point and extent of degradation, if any.

The textile material may be heat-treated in the relaxed condition or while it is held under tension. The heat-treatment may be carried out while the dimensions of the textile material are maintained substantially constant, as by the use of a frame or tenter. Heat-treatment in the relaxed condition results in some shrinkage of the textile material. This shrinkage is very small in the case of cellulose acetates having acetyl values above 61%. Thus, when a yarn of cellulose acetate having an acetyl value of 61.3% is heated in a relaxed condition to a temperature of 250° C. for 30 seconds and then cooled, the yarn shrinks only about 4%. The shrinkage is normally less when woven fabric, rather than yarn, is heat-treated.

The heat treatment in the relaxed condition, with ac-

companying shrinkage, is often desirable when it is necessary to avoid removal of the crimp in the fibers making up the textile material and to avoid flattening of the fabric.

The optimum times for heat treatment will depend to some extent on the weight and construction of the fabric, since, for example, a longer period of time will be required to bring the fabric to the desired elevated temperature in the case of a heavier, or more tightly woven fabric than in the case of a lighter or more loosely woven fabric. Thus a relatively light woven fabric having a weight of about 4 ounces per square yard, described more fully below, is advantageously heated in hot air at a temperature of about 230° C. for at least about 5 seconds, but not above about 1 minute in order to avoid damaging the fabric, preferably for slightly less than 1 minute. For the same fabric at temperatures of 250° C. and 270° C., the corresponding times are at least about 5 seconds and at least about 2 seconds, respectively, and not above about 30 seconds and not above about 15 seconds, respectively. When a relatively heavy fabric, having a weight of about 6½ to 7 ounces per square yard and made up of staple fibers, described more fully below, is employed, the corresponding maximum times are double those given, i.e. about 2 minutes, 1 minute and 30 seconds at temperatures of 230, 250 and 270° C., respectively, while the minimum times are about double or somewhat more than double the minimum times given for the relatively light fabric. When maximum improvement in the resistance to glazing and to shrinkage on moist steam pressing is desired, the heat treatment should be continued for as long as it is possible to do so without materially damaging the fabric. Thus, by suitable heat treatment of a fabric of a cellulose acetate having an acetyl value of 61.3%, the shrinkage on repeated moist steam pressing can be reduced to less than 4% and the tendency for the fabric to glaze on pressing and ironing can be practically eliminated.

The "relatively light fabric" referred to above is composed of yarns of 150 denier, each yarn being made up of 40 continuous filaments of cellulose triacetate. The fabric is of 2 over 1 twill construction and has 120 ends and 72 picks per inch.

The "relatively heavy fabric" referred to above is composed of staple 3 denier 2 inch long fibers, spun to 20*s* 2-ply yarn (cotton count) with a twist of 15z in the singles and 14*s* in the ply, and woven 44 ends and 42 picks per inch in a tropical suiting construction.

When saturated steam is used as the heating medium the heat treatment may be effected at lower temperatures. Thus a significant improvement in the properties of the fabric may be obtained by treating the fabric with saturated steam at a pressure of 20 pounds per square inch gauge for a period of five minutes, although a treating period of 30 minutes gives best results at this pressure. Steam at higher pressures, e.g. 30 to 50 pounds per square inch gauge may also be employed. When treating with steam it is desirable to prevent any droplets of condensate from coming in contact with the material being treated since such droplets sometimes cause spotting of the dyed material.

If desired, other heat treating media may be employed, e.g. superheated steam, hot oil or molten metal, or the textile material may be heated by subjecting it to a high frequency electric field or to infrared radiation, or the textile material may be heated by contact with hot rolls or hot platens. The heat treatment may be carried out at atmospheric, superatmospheric or even subatmospheric pressure.

Heat treatment tends to cause the fabric to stiffen slightly. This stiffness may be eliminated by subjecting the fabric to mechanical working, e.g. to the operations known as "button-breaking" or cold calendering or to wet processing, e.g. washing or decatizing. The tendency to stiffening may also be overcome by the application of a very finely divided solid material to the textile material before heat treatment; for example, a dispersion of silica, such as those anionic dispersions of one micron particles of silica known as Ludox or "Syton W–20 or DS," may be applied to the fabric for this purpose. The least stiffening of the fabric has been observed when the heat treatment is effected by the use of steam under pressure, e.g. in an autoclave.

As stated, the safe ironing temperature of the textile material is improved significantly by the heat treatment of this invention. For example, the safe ironing temperature of fabrics composed of fibers of cellulose triacetate or of cellulose acetate of acetyl value 59.5%, calculated as combined acetic acid, is not above about 190° C., e.g. about 180° C. On heat treating such fabrics in accordance with this invention the safe ironing temperature is raised by more than about 20° C., to a value of above about 220° C. or 230° C., usually above about 240° C.

The effect of the heat treatment is most pronounced in the case of those cellulose acetates having the highest acetyl values. Thus, for example, cellulose acetates having acetyl values of about 61% or 62% or higher, calculated as combined acetic acid, show greater improvements, on heat-treatment, in resistance to glazing, resistance to moist steam pressing shrinkage and in safe ironing temperature as compared with cellulose acetate of acetyl value of 59.5%, calculated as combined acetic acid. In contrast, when a fabric of ordinary cellulose acetate, e.g. of 54.5% acetyl value, is subjected to the heat-treatment of this invention the fabric is damaged severely. For optimum properties for fabrics sold on a commercial scale, the acetyl value should be at least 60% and perferably at least 61%.

In accordance with one aspect of this invention, the heat treatment may be applied to dyed textile materials in which the major portion of the dye has been absorbed only on the surface of the fibers. Thus, when certain dyeing assistants, e.g. polybasic acid esters such as tributyl phosphate, dimethyl phthalate and diethyl phthalate, are employed, it is observed that even at temperatures as low as 65° C. there is an initial "strike" of the dye onto the fiber to produce a peripherally dyed, or "surface dyed" material during the early stages of dyeing. The fiber is truly dyed as shown by the fact that examination of fiber cross-sections reveals that the dye is within the fiber, and the fact that the dye is not removed by rinsing. When this material is subjected to a heat treatment in accordance with this invention, the dyed material becomes highly fast to washing and does not crock due in part to further diffusion of dyestuff into the fiber cross section.

Heat-treatment in accordance with this invention has the additional effect of removing a large part of the dyeing assistant from the textile material. Since the dyeing assistants are substantive to the cellulose acetate of very high acetyl value, an appraciable proportion of these assistants, remains in the textile material after the dyeing operation, even after the textile material is rinsed or scoured. For example, two portions of a fabric of cellulose acetate having an acetyl value of 61.3%, which portions had been dyed, one in the presence of tributyl phosphate as the assistant and the other in the presence of tripropyl phosphate, were found, after socuring at 120° F., to have PO_4 contents, resulting from the presence of the above phosphates, of 1.64% and 1.44%, respectively. After the portions of fabric had been heated for 31 seconds by subjecting them to infra-red radiation so that their surfaces attained a temperature of about 245–255° C., their PO_4 contents were reduced to 0.12% and 0.08% respectively, due to vaporization of the phosphates. Similar results are obtained with other assistants volatile at the temperatures of heat treatment, e.g. pine oil. However, the high temperature slow dyeing cellulose acetate dyestuffs employed in this invention do not volatilize or decompose to any appreciable extent during the heat

treatment and remain substantially entirely in the textile material.

In some cases it is advantageous to scour the textile material after the heat treatment. Such scouring has been found to reduce any tendency the material may have to stain the water used for the first home- or laundry-washing thereof, presumably by the removal of a very small amount of loosely adherent dyestuff. This scouring treatment may be carried out, for example, at a temperature of 120 to 150° F. using an aqueous scouring bath containing 0.5 to 2 grams per liter of a non-ionic or anionic detergent such as "Emulphor ELA–719" or "Duponol RA."

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, 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%, 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 P30," "Ahco 111," "Ahcovel A," "Ahcovel E," "Ahcovel G," "Ahcovel NC," "Ahcovel R," "Aquex 16," "Aquex 16x," "Permel," "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 N–5." The finishing agents may be applied to the dyed material before but preferably after the heat-treating operation. However, certain finishing agents, such as the silicones, e.g. "Decetex 104," may be applied to the textile material and cured even before the dyeing without appreciably affecting the rate of dyeing. 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 apparance 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 acetate of very high acetyl value colored with certain dispersed cellulose acetate dyestuffs shows a tendency to fade on exposure to acid fumes, such as combustion gases and, in some cases on exposure to ozone. To reduce this tendency it is often desirable to apply a suitable inhibitor to the textile material. The inhibitor may be applied, for example, by including it in the dyebath, by padding on a solution or dispersion of the inhibitor before or after dyeing, or by applying the inhibitor after the heat-treatment. It is generally desirable to apply the inhibitor before the heat-treatment. Examples of suitable inhibitors are those conventionally employed for ordinary acetone-soluble cellulose acetate, such as diphenylimidazolidine, N,N'-diphenylethylenediamine, N.N'-dibenzylethyllenediamine and methyl or other alkyl substitution products thereof, diphenylbenzamidine, diphenylacetamidine, benzylethylaniline, sodium formate or "Melemine" (melamine which has been partly solubilized in water by reaction with a small amount of formaldehyde.) For prevention of fading by ozone, antioxidants, e.g. tertiary butyl hydroquinone, alkylated phenols such as "Ionol" and "Inhibitor 162," and many of the aforementioned nitrogenous inhibitors, may be employed. The amount of inhibitor is generally small, e.g. 0.5 to 3% based on the weight of the textile material.

It is found that, even without the use of an inhibitor, dyed textile material of cellulose acetate of very high acetyl value which has been heat-treated in accordance with this invention shows a much smaller tendency to fade on exposure to ozone than the same dyed fabric before heat-treatment.

As stated, heat-treated fabrics of this invention are capable of being permanently pleated. Thus, in one example, a heat-treated fabric of cellulose acetate having an acetyl value of 61.3% is accordion-pleated on a steam press using 500 pounds head pressure while steaming for 10 seconds with steam having a pressure of 50 pounds per square inch gauge; the pleats are retained on washing. Permanent pleats may also be obtained by pleating the fabric before or during the heat-treatment; for example, a fabric which has not been heat-treated may be pleated between metal rolls having a tempertaure of 350° F. and then further heat-treated, e.g. with steam at a pressure of 20 pounds per square inch gauge in an autoclave.

If desired, the cellulose acetate textile material of very high acetyl value may also be embossed with any suitable pattern before, during or after heat treatment. For example, a woven fabric of cellulose acetate of very high acetyl value which has not been heat-treated may be given a surface pattern which is fast to washing by the application of a metal embossing roller having a temperature of 400° F.

While the process of this invention has been described particularly in connection with textile materials composed entirely of fibers of cellulose acetate of very high acetyl value, 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. Such 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 acetate of very high acetyl value as well as those made up of continuous filaments of said cellulose acetate.

Although the heat treatment of this invention is of greatest value and yields optimum results when used on cellulose acetate textile materials of very acetyl value dyed with cellulose acetate dyestuffs of the high temperature slow dyeing type, it may also be applied to such high acetyl value cellulose acetate textile materials dyed with other dyestuffs, 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. In such cases the safe ironing temperature, resistance to glazing, resistance to shrinkage on moist steam pressing and ability to take permanent pleats are improved, as is the wash fastness of the material, but there

is not a sufficient improvement in the latter property to enable the material to pass the #3 A.A.T.C.C. wash fastness test. Furthermore, the materials dyed with dyes of the high temperature slow dyeing type generally possess superior resistance to gas fading, light fading and sublimation.

After the heat treatment of this invention the cellulose acetate textile materials of high acetyl value are much more resistant to dyeing than the same materials before the heat treatment. However, the rate at which the heat-treated materials take up the dye may be markedly increased by the use of the dyeing assistants previously described and by the use of higher dyebath temperatures, e.g. temperatures of 95 to 100° C. and higher.

The following examples are given to illustrate the invention further.

Example I

(*a*) A woven fabric composed of fibers of cellulose acetate having an acetyl value of 62.0 to 62.5%, calculated as combined acetic acid, said fibers having been produced by spinning a solution of said cellulose acetate in a mixture of 90% of methylene chloride and 10% of ethanol into an evaporative atmosphere, is dyed in accordance with this invention. The fabric used is of 2 over 1 twill construction weighing about 4 ounces per square yard and having 120 ends per inch and 72 picks per inch, each yarn in both weft and warp having a denier of 150 and being composed of 40 continuous filaments. The dyeing operation is carried out for one hour in an aqueous dyebath maintained at a temperature of 85° C. and containing 2% (based on the weight of the fabric) of the dyestuff "Eastman Blue GLF" (containing about 40% active dye material consisting of 1,8-dihydroxy-4-(para-beta-hydroxyethyl) anilido-5-nitro anthraquinone), 10% (based on the weight of the fabric) of tri-n-propyl phosphate, and 1% (based on the weight of the fabric) of "Igepon T Gel," a dispersing agent which comprises as its active ingredient 16% of the sodium salt of oleyl taurate. The liquor ratio, i.e. the ratio of the weight of the dyebath to the weight of the fabric, is 50. After the dyeing operation the wet fabric is rinsed for 15 minutes at 35° C. in a bath containing 2 grams per liter of soap, and dried.

Four other portions of the same fabric are dyed. The conditions of dyeing, which are different in each case, are identical with the dyeing conditions given in paragraph (*a*) above with the following exceptions:

(*b*) There is substituted for the tripropyl phosphate an equal weight of pine oil.

(*c*) There is substituted for the 10% of tripropyl phosphate, 10% (based on the weight of the fabric) of "Alrosol C," a condensation product produced by heating two moles of diethanolamine with one mole of capric acid while splitting out the water of reaction, said condensation product comprising N,N-dihydroxyethyl capramide. This condensation product is a liquid soluble in water and in organic solvents; its water solutions are clear, thin and slightly alkaline, do not gel on dilution with water and tolerate electrolytes.

(*d*) The dyebath contains no added assistant or "Igepon T," but merely the "Eastman Blue GLF" and water.

(*e*) The dyebath contains no added assistant, but merely the "Eastman Blue GLF," water and 1% (based on the weight of the fabric) of the "Igepon T."

The following table compares the results obtained in the above dyeings:

Type of Dyebath	Color of Fabric
(*a*) Tripropyl Phosphate, "Igepon T"	Deep blue shade.
(*b*) Pine oil, "Igepon T" and water	Shade almost as deep as (*a*).
(*c*) "Alrosol C" and water	Shade somewhat lighter than (*b*).
(*d*) Water	Very pale shade, much lighter than (*c*).
(*e*) "Igepon T" and water	Paler than (*d*).

Example II

The procedure of Example I (*a*), (*b*), (*c*), (*d*) and (*e*) is repeated except that the dyestuff "Celliton Blue AF" (containing about 40% of active dye material) is substituted for the "Eastman Blue GLF." The results are tabulated below:

Type of Dyebath	Color of Fabric
(*a*) Tripropyl phosphate, "Igepon T" and water.	Deep blue shade.
(*b*) Pine oil, "Igepon T" and water	Shade almost as deep as (*a*).
(*c*) "Alrosol C" and water	Shade somewhat lighter than (*b*).
(*d*) Water	Very pale shade, much lighter than (*c*).
(*e*) "Igepon T" and water	Shade about the same as (*d*).

Example III

(*a*) A woven fabric composed of fibers of cellulose acetate having an acetyl value of 62.0 to 62.5%, calculated as combined acetic acid, said fibers having been produced by spinning a solution of said cellulose acetate in an organic solvent therefor into an evaporative atmosphere, is dyed for one hour in an aqueous dyebath maintained at a temperature of 85° C. and containing 1% (based on the weight of the fabric) of the dyestuff "Eastone Red GLF," comprising 4-nitro-2-methylsulfonephenyl azo-4'-(N-beta-hydroxyethyl-N-difluoroethyl) aminobenzene, 10% (based on the weight of the fabric) of pine oil, and 1% (based on the weight of the fabric) of a dispersing agent comprising equal proportions, by weight, of the dispersing agents known as "Emulphor ELA–719" (a non-ionic product of the reaction of castor oil and ethylene oxide) and "Quadronate" (a "mahogany soap," i.e. a sodium petroleum sulfonate, of low molecular weight). The liquor ratio is 50 and the fabric is washed after the dyeing operation in a manner similar to Example I, and dried.

The other portions of the same fabric are dyed. The dyeing procedures, which are different for each of said portions, are identical with those set out in the preceding paragraph, with the following exceptions:

(*b*) There is substituted for the 10% of pine oil 10% (based on the weight of the fabric) of "Alrosol C" and the dispersing agent is omitted.

(*c*) The pine oil and dispersing agent are omitted: The results are tabulated below:

Type of Dyebath	Color of Fabric
(*a*) Pine oil, dispersing agent and water	Deep red shade.
(*b*) "Alrosol C" and water	Somewhat lighter than (*a*).
(*c*) Water	Pale red shade, much lighter than (*b*).

Example IV

The dyed fabrics of the preceeding examples (I, II and III) are heat treated in an oven in circulating hot air having a temperature of 230° C. for 60 seconds while said fabrics are held in frames to maintain their dimensions substantially constant throughout the heat treatment. The heat treated fabrics are subjected to the A.A.T.C.C. #3 wash fastness test and are found to retain their color, without appreciable change of color or staining, even after 3 repetitions of said test The heat treatment raises the safe ironing temperature of the dyed fabric by 60° C., i.e. from 180° C. to 240° C., improves the glazing resistance of the fabric, and reduces the degree of wrinkling which occurs during laundering. The heat treated fabric shrinks 9% in area after 12 pressings in moist steam, as compared with a 15% shrinkage for fabric which has not been heat-treated. The heat-treated fabric may be pleated in a steam press using a damp cloth and high mechanical press pressure, and the resulting pleats are permanent to repeated washing at 160° F.

The hand and strength of the fabric is substantially the same before and after heat treatment.

The "safe ironing temperature," referred to above, is determined by the use of a standard hand iron having a weight of five pounds and an area of its sole plate of 22½ square inches. The test is conducted by heating the iron until a selected 2-inch-square area of the sole plate adjacent the tip of the iron has the desired temperature. A 2-inch square of the fabric to be tested is placed on an ironing surface comprising a flat board covered with one inch of sponge rubber, over which are 4 layers of cotton flannel, and the iron is then placed on the fabric so that the aforesaid selected area of the sole plate coincides with the fabric. The placing of the iron is carried out by hand without any lateral motion of the iron on the fabric and without any application of hand pressure to the iron on the fabric. After the iron has rested on the fabric for exactly 10 seconds, the iron is lifted straight up off the fabric. The test is repeated with the iron heated in 10° C. increments for each test until there is evidence of damage to the fabric, e.g. until the fabric sticks to the iron, becomes boardy or changes in color. The maximum safe ironing temperature is that temperature which is 10° C. below the temperature at which the first sign of damage to the fabric occurs.

Example V

The procedure of Example I(*a*) is followed except that tri-n-butyl phosphate in the amount of 5% (based on the weight of the fabric) is used in place of the tripropyl phosphate; the dispersing agent is a mixture of ¼% (based on the weight of the fabric) of "Emulphor ELA–719" and ¼% (based on the weight of the fabric) of "Quadronate"; the dyestuff is "Amacel Rubine IX" and is used in the amount of 2% based on the weight of the fabric; and the dyeing is carried out at 80° C. The fabric is dyed a full red shade.

Example VI

A portion of the woven fabric described in Example I is dyed for 30 minutes in an aqueous dyebath maintained at a temperature of 65° C. and containing 2% (based on the weight of the fabric) of the dyestuff "Celliton Blue AF" (containing 40% active dye material), 10% (based on the weight of the fabric) of tri-n-butyl phosphate, and 0.5% (based on the weight of the fabric) of "Quadronate" and 0.5% (based on the weight of the fabric) of "Emulphor ELA–719." The tributyl phosphate, which is a liquid, is first mixed with the "Empulphor ELA–719" and "Quadronate" and the resulting paste is then mixed with the water of the dyebath. The liquor ratio is 50. After the dyeing operation the wet "surface dyed" fabric is rinsed for 15 minutes at 35° C. in a bath containing 1 gram per liter of "Igepon T Gel." The fabric is dyed a deep blue shade. When this material is subjected to a heat treatment in accordance with this invention, it becomes highly fast to washing and does not crock.

Example VII

A portion of the woven fabric described in Example I is padded at a temperature of 50° C. with a bath comprising an emulsion containing 5% by weight of tri-n-butyl phosphate, ½% of "Emulphor ELA–719," ½% of "Quadronate" and the remainder water, all of said proportions being based on the total weight of the emulsion. After the fabric has been in contact with the padding bath for 30 seconds, the fabric, carrying 100% of its weight of said emulsion, is introduced into, and maintained for ½ hour at 85° C. in, a dyebath containing 2% (based on the weight of the fabric) of "Celliton Blue AF," the liquor ratio being 50. The fabric is dyed a full blue shade.

Example VIII

Example I is repeated except that the fabric is composed of fibers of cellulose acetate having an actyl value of 59.5%, calculated as acetic acid. Substantially the same results are obtained as in Example I.

The dyed fabric is subjected to the heat treatment described in Example IV for a period of 30 seconds. Substantially the same results as in Example IV with respect to wash fastness are obtained. The safe ironing temperature is raised and the pleating characteristics, resistance to wrinkling and mussing during laundering, and resistance to pressing shrinkage in moist steam are improved, but not nearly to as great an extent as in the case of Example IV.

Example IX

50 kilograms of woven fabric is cellulose acetate of 61.3% acetyl value are placed on a jig, scoured, and dyed on the jig at a liquor ratio of 4:1 with an aqueous mixture comprising 3000 grams of "Celliton Blue AF" 390 grams of "Eastone Red GLF," 420 grams of "Amacel Yellow CW," 950 grams of diphenylimidazolidine, 50 grams of "Igepon T Gel," 100 grams of tetrasodium pyrophosphate and 2500 grams of a mixture of 400 parts by weight of tripropylphosphate, 400 parts by weight of the pine oil sold under the name "Yarmor 350" (a mixture of hydrocarbons and alcohols, distilling in the range of 190–220° C., with about 50% distilling at about 200° C., at atmospheric pressure) and 100 parts by weight of "Emulphor ELA–719." The dyeing is started at 85° C. and after 2 hours the temperature of the dyebath is raised to 95° C. Total dyeing time is 6 hours, during which time the fabric is passed from one roll of the jig, through the dyebath and rolled onto the other roll of the jig and then passed through the dyebath to the first roll, this operation being repeated several times during the dyeing period, in the conventional manner. Thereafter the fabric is scoured and washed on the jig. The fabric, dyed a heavy navy blue shade, is heat treated in a radiant heating apparatus for 30 seconds, during which time the fabric attains a temperature of 230° C., and then subjected to the A.A.T.C.C. #3 wash fastness test, during which there is no appreciable change in shade.

Example X

A fabric composed of a blend of 50% of staple fibers of cellulose acetate of 62.5% acetyl value and 50% of viscose rayon staple fibers is dyed, at a liquor ratio of 50:1, with an aqueous bath comprising 1% "Eastman Blue GLF" 2% "Eastone Red GLF," 0.75% "Interchemical Acetate Yellow HDLF–40," 0.21% "Resofix Blue GLN," 0.45% "Cuprofix Yellow GL" and 2.5% "Resofix Rubine BLN," the latter three being direct dyes for cellulose, all proportions being based on the weight of the fabric. The dyebath also contains 10%, based on the weight of the fabric, of "Alrosol C." 10%, based on the weight of the fabric, of sodium chloride is added in portions during the dyeing. The temperature of dyeing is 90° C. The fabric is dyed in a uniform medium brown shade. It is rinsed, then heat set by exposing it to radiant heat for 30 seconds, during which time the fabric attains a temperature of 220° C., and thereafter padded with an aqueous mixture in such a manner as to deposit on the fabric 0.5% by weight of "Decetex 104," 0.5% by weight of "Decetex 108" (both "Decetex" compositions being silicone finishing agents), 10% by weight of a low condensation product of 1.3 moles of formaldehyde and 1 mole of urea, 1% by weight of "Catalyst G–8" (an acidic mixture of formaldehyde and an amine hydrochloride curing catalyst for the urea-formaldehyde product) and 2% by weight of "Cuprofix 47" (a fixative agent for direct dyes on cellulose), all proportions being based on the weight of the fabric. After drying the fabric is heated at 155° C. for 8 minutes to cure the finish and then scoured.

Example XI

100 parts by weight of a fabric of cellulose acetate of 62.5% acetyl value are immersed and agitated for one

hour in a bath having a temperature of 85° C. and comprising 4000 parts by weight of water, 2 parts by weight of the dyestuff "Celliton Blue Green BA," containing about 40% by weight of active dye material and the balance dispersing agent, and 5 parts by weight of tri-n-butyl phosphate. The fabric is then rinsed in water and dried.

The resulting dyed fabric is analyzed to determine its content of tri-n-butyl phosphate and dye, and the dyebath is analyzed to determine the concentration of tri-n-butyl phosphate therein.

For comparison, the dyeing is repeated under identical conditions except that in one instance the phosphate is entirely omitted from the dyebath and, in the other cases, an equal amount of tri-n-ethyl or tri-n-propyl phosphate is employed in place of the tributyl phosphate.

The results are tablulated below:

Trialkyl phosphate	Trialkyl phosphate content of dyed fabric,[1] percent	Trialkyl phosphate concentration in dyebath after 1 hour of dyeing,[2] percent	Dye content of dyed fabric,[1] percent
None	0.00	0.00	0.22
Triethyl	0.32	0.060	0.23
Tripropyl	0.81	0.045	0.28
Tributyl	1.35	0.008	0.43

[1] Based on weight of the dyed fabric.
[2] Based on the weight of the dyebath.

Example XII

A fabric of cellulose acetate of 62.5% acetyl value is padded with an emulsion prepared by vigorously blending 99% of water and 1% of tri-n-butyl phosphate. In the padding operation the fabric is first dipped into the emulsion for 2 minutes at 25° C. and then passed between pressure pad rollers. The padded fabric, carrying an amount of emulsion equal to about 90% its own weight, is then dyed at 85° C. for 1 hour with an aqueous dispersion of 2%, based on the weight of the fabric before padding, of "Celliton Blue Green BA," at a liquor ratio of 40. The fabric is then rinsed and dried. The resulting dyed fabric is analyzed to determine its content of tri-n-butyl phosphate and dye.

For comparison, the procedure described above is repeated, using no phosphate in the padding bath, or using tri-n-ethyl phosphate or tri-n-proply phosphate in place of the tri-n-butyl phosphate, all other conditions being identical. The results are tabulated below:

Trialkyl phosphate	Trialkyl phosphate content of fabric,[1] percent	Dye content of fabric,[1] percent
None	0.0	0.22
Triethyl	0.10	0.24
Tripropyl	0.57	0.32
Tributyl	3.24	0.76

[1] Based on the weight of the dyed fabric.

Example XIII

100 parts by weight of a textile fabric of cellulose acetate of 61.3% acetyl value are immersed and agitated in a dyebath containing 5000 parts by weight of water, 3 parts by weight of "Celliton Fast Blue AF," 12.5 parts by weight of diethyl phthalate and 2.5 parts by weight of "Tween 85" (a polyoxyethylene sorbitan trioleate). The dyeing is started with the dyebath at a temperature of 60° C., which is raised to 90° C. as the dyeing progresses. The fabric is dyed in a full, very level blue shade.

Example XIV

Other examples of mixtures of dyeing assistants and dispersing agents suitable for use with the aforementioned cellulose acetate dyes of the high temperature slow dyeing type are:

(*a*)

4 parts by weight of tributyl phosphate
4 parts by weight of "Yarmor 350"
1 part by weight of "Emulphor ELA–719"

(*b*)

3 parts by weight of tributyl phosphate
3 parts by weight of tripropyl phosphate
1 part by weight of "Emulphor ELA–719"

(*c*)

3 parts by weight of tributyl phosphate
2 parts by weight of "Yarmor 350"
2 parts by weight of "Alrosol C"
1 part by weight of "Emulphor ELA–719"

(*d*)

4 parts by weight of diethyl phthalate
4 parts by weight of tripropyl phosphate
1 part by weight of "Tween 80"

(*e*)

4 parts by weight of phenyl ether of ethylene glycol
4 parts by weight of phenyl ether of diethylene glycol
0.5 part by weight of "Span 20"
0.5 part by weight of "Tween 20"

It is to be understood that the foregoing detailed decription is given merely by way of illustration and that many variatons 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 treatment of textile material, which comprises dyeing a textile material comprising fibers of cellulose acetate having an acetyl value of at least 59%, calculated as combined acetic acid, with a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in an essentially aqueous bath in the presence of about 1 to 20% on the weight of said fibers of a substantive assistant for increasing the rate of dyeing of said textile material, said assistant being substantially insoluble in water and being applied from water in up to about 10% concentration by weight.

2. Process as set out in claim 1 in which said cellulose acetate has an acetyl value of at least 61%.

3. Process as set forth in claim 1 in which said aqueous dyebath comprises a dispersion of said assistant.

4. Proces as set forth in claim 1 in which said assistant is tripropyl phosphate.

5. Process as set forth in claim 1 and including the further step of heat treating the dyed material at a temperature ranging from about 190° C. to 270° C. and discontinuing said heat treatment before any substantial damage to the textile material occurs.

6. Process as set forth in claim 1 in which said assistant comprises methyl salicylate.

7. Process as set forth in claim 1 in which said assistant comprises trichlorobenzene.

8. Process as set forth in claim 1 in which said assistant comprises biphenyl.

9. Process as set forth in claim 1 wherein said bath is present in less than about 50 times the weight of the textile material and the concentration of said assistant in said bath is at least about 1% by weight.

10. Process as set forth in claim 1 in which said assistant is applied to the textile material before said textile material is brought into contact with said aqueous dyebath.

11. Process as set forth in claim 10 in which said assistant is applied to said textile material in the form of an aqueous dispersion thereof.

12. Process as set forth in claim 1 and including the

further step of heat treating the dyed material to raise the safe ironing temperature of said material to at least 230° C. whereby the wash fastness of the dyed material is increased.

13. Process as set forth in claim 12 in which said dyed material is heat treated in air at a temperature of about 250° C., at which temperature said assistant is volatile.

14. Process for the treatment of textile material, said process comprising dyeing a textile material comprising fibers of cellulose acetate having an acetyl value of at least 59%, calculated as combined acetic acid, with a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in an essentially aqueous dyebath in the presence of about 1 to 20% on the weight of said fibers of a substantive assistant for increasing the rate of dyeing of said textile material, said assistant being substantially insoluble in water, being applied from water in up to about 10% concentration by weight and being a solvent for said dye.

15. Process for the treatment of textile material, which comprises dyeing a textile material comprising fibers of cellulose acetate having an acetyl value of at least 59%, calculated as combined acetic acid, with a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in an essentially aqueous bath in the presence of about 1 to 20% on the weight of said fibers of a substantive assistant for increasing the rate of dyeing of said textile material, said assistant comprising a member of the group consisting of terpene alcohols and ethers, being substantially insoluble in water and being applied from water in up to about 10% concentration by weight.

16. Process for the treatment of textile materials, said process comprising dyeing a textile material comprising fibers of cellulose acetate having an acetyl value of at least 59%, calculated as combined acetic acid, with a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in an essentially aqueous bath in the presence of about 1 to 20% on the weight of said fibers of a substantive assistant for increasing the rate of dyeing of said textile material, said assistant being applied from water in up to about 10% concentration by weight and comprising a phosphate ester selected from the group consisting of tripropyl phosphate, tributyl phosphate, triamyl phosphate and trihexyl phosphate.

17. Process for the treatment of textile material, which comprises dyeing a textile material comprising fibers of cellulose acetate having an acetyl value of at least 59%, calculated as combined acetic acid, with a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in an essentially aqueous bath in the presence of about 1 to 20% on the weight of said fibers of a substantive assistant for increasing the rate of dyeing of said textile material, said assistant comprising a phthalate diester of at least one alcohol selected from the group consisting of methyl, ethyl, propyl and allyl alcohols, being substantially insoluble in water and being applied from water in up to about 10% concentration by weight.

18. Process for the treatment of textile material, which comprises dyeing a textile material comprising fibers of cellulose acetate having an acetyl value of at least 59%, calculated as combined acetic acid, with a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in an essentially aqueous dyebath in the presence of about 1 to 20% on the weight of said fibers of a substantive assistant for increasing the rate of dyeing of said textile material, said assistant being substantially insoluble in water and being applied from water in up to about 10% concentration by weight, and heat-treating the resulting dyed textile material for improving the wash fastness of the dyed material so that the material meets the requirements of the #3 A.A.T.C.C. wash fastness test.

19. Process as set out in claim 18 in which the textile material is in the form of a fabric and the fabric is allowed to shrink during said heat treatment.

20. Process as set out in claim 18 in which the heat treatment is carried out in air until the safe ironing temperature of the material is raised to at least 230° C.

21. Process as set out in claim 18 in which the heat treatment is conducted in substantially saturated steam under pressure.

22. Process for the treatment of textile material, which comprises dyeing a textile material comprising fibers of cellulose acetate having an acetyl value of at least 59%, calculated as combined acetic acid, with a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in an aqueous bath in the presence of about 1 to 20% by weight of said fibers of a substantive assistant for increasing the rate of dyeing of said textile material, said assistant being insoluble in water, being applied from water in up to about 10 concentration by weight, being substantive to said fibers and being a solvent for said dye, rinsing the resulting dyed textile material in an aqueous bath, and heat-treating the rinsed material for improving the wash fastness of the dyematerial.

23. Process for the treatment of fabrics, which process comprises dyeing a fabric comprising fibers produced by spinning a solution, in an organic solvent, of cellulose acetate having an acetyl value of at least 61%, calculated as combined acetic acid, said dyeing being carried out with a heated essentially aqueous bath containing a dispersed cellulose acetate dye of the "high temperature slow dyeing type" in the presence of about 1 to 20% on the weight of said fibers of a substantive assistant for increasing the rate of dyeing of said fabric, said assistant being substantially insoluble in water, being applied from water in up to about 10% concentration by weight and being a solvent for said dye, rinsing the resulting dyed fabric in an aqueous bath, and heat treating the rinsed fabric at a temperature sufficiently high and for a sufficient period of time to improve the wash fastness to a point where the material passes the requirements of the #3 A.A.T.C.C. wash fastness test, to increase the safe ironing temperature to at least 230° C., and to substantially improve the glazing resistance, the shrinkage on moist steam pressing, the resistance to wrinkling on laundering, and the ability to take permanent pleats of said fabric, and discontinuing said heat treatment before any substantial damage to the fabric occurs.

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