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(54) Title: PRODUCTION OF DYED COTTON FIBERS

(57) Abstract: In a method of dyeing and finishing cotton fibers, emulsion copolymer treated cotton fibers are prepared by contacting the fibers with an emulsion copolymer and curing the copolymer under conditions to chemically anchor the emulsion copolymer to the cotton and thereby form copolymer-treated cotton fibers. The copolymer-treated cotton fibers are then contacted with a dye material under conditions sufficient to affix at least a portion of the dye material to the copolymer component of the copolymer-treated cotton fibers and produce dyed cotton fibers. Thereafter, the dyed cotton fibers are treated with a surfactant-stabilized aqueous acrylic polymer dispersion to give the fibers a worn or vintage character.



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PRODUCTION OF DYED COTTON FIBERS**Field**

[0001] The present development relates to the production of dyed cotton fibers, in which the dyed product is imparted a “stone-washed”, vintage or worn appearance.

Background

[0002] Up until the present cotton fibers in the form of yarns and fabrics have generally been dyed with reactive, direct, sulfur, vat, or mordant dyes. Currently the industry prefers reactive dyeing for apparel as reactive dyes provide the brightest colored cotton of all the dyes. Water-soluble reactive dyes, which also provide dyeing results with good fastness-to-washing properties, can be used to dye or print hydrophilic cellulose fibers such as cotton fibers. In such procedures, the cellulose fiber -OH groups which are accessible on the fiber surface react with the fiber- reactive groups of the reactive dyes, forming a covalent fiber/dye bond.

[0003] Dyeing of cotton with reactive dyes gives good color fastness. However, reactive dyes are strongly hydrophilic leading to process inefficiencies and high costs due to the necessity of using long dyeing times with salt additions and alkali, thus allowing for the sensitive needs of reactives for high pH and high temperature conditions. Reactive dyes which do not react with cotton cellulose in the dyeing step eventually react with water and hydrolyze. This hydrolyzed dye must be removed from the cotton surface after dyeing with an after-soaping step to improve crockfastness and washfastness properties.

[0004] Another dye class commonly employed for the coloring of fabrics comprises disperse dyes, which are mainly used for the dyeing of polyester, but can also be used to dye nylon, cellulose acetate and acrylic fibers. Given their lack of affinity or substantivity for cellulose, disperse dyes cannot be readily used to dye cotton fibers and fabrics. However, some attempts have been made to provide procedures for dyeing modified cotton fibers, e.g., fabrics, with disperse dyes. For example, U.S. Patent Publication No. 2006/0048308 discloses a method of dyeing or printing cellulose-containing fiber materials using disperse dyes. Such a method comprises pre-treating the

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cellulose fiber material with a water-soluble or dispersible polyester resin and a water-soluble or dispersible acrylic binder. The polyester resin is fixed, for example, to cotton fabric with the acrylic binder and strong cross-linkers (e.g., melamine) via a pretreatment bath. The polyester impregnated fabric is then dyed with an aqueous dye bath containing disperse dye at a temperature of 130 °C under elevated pressure conditions.

[0005] In our co-pending U.S. Patent Application published as US2012/0246842 A1 on October 4, 2012 we have described a method for dyeing cotton fibers, which method comprises: (a) contacting a plurality of cotton fibers with a cellulose-reactive emulsion copolymer in order to provide a combination of emulsion copolymer and fibers; (b) curing the combination of emulsion copolymer and fibers in order to chemically anchor the emulsion copolymer to the cotton fibers via reaction of at least some cellulose-reactive monomers within said copolymer with cellulose hydroxyl moieties within the cotton fibers, to thereby form copolymer-treated cotton fibers; and thereafter (c) contacting the copolymer-treated cotton fibers with a disperse dye material under conditions which are sufficient to affix at least a portion of said disperse dye material to the copolymer component of said copolymer-treated cotton fibers.

[0006] In addition, in our co-pending U.S. Patent Application published as US2013/0000057 A1 on January 3, 2013 we have described a method for preparing indigo-dyed denim fabric, which method comprises: (a) preparing emulsion copolymer-treated warp yarn by contacting cotton yarn with a cellulose-reactive emulsion copolymer and thereafter curing the emulsion copolymer; (b) weaving or knitting the emulsion copolymer-treated cotton warp yarn into denim fabric along with untreated cotton yarn as the weft yarn to thereby prepare greige denim fabric having emulsion copolymer-treated cotton warp yarn in the warp direction only; and thereafter (c) contacting the greige denim fabric with an aqueous dispersion of an indigo dyestuff material under conditions sufficient to preferentially color the outer cross-sectional portions of the emulsion copolymer-treated warp yarn to a greater extent than the indigo dyestuff material colors the outer cross-sectional portions of the untreated cotton weft yarn, to thereby provide indigo-dyed denim fabric having a non-uniformly colored appearance.

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[0007] Dyed cotton products are subjected to a variety of post treatments to improve their physical and/or visual properties. One such post treatment is stone-washing in which the dyed material is imparted a “worn” appearance by partial removal of dye in a manner to yield a material having areas which are lighter in color (sometimes referred to as “highs and lows” or a vintage character) and softer in texture. Traditionally, stone washing is effected by washing the dyed material at 60 to 70 °C for about 60 minutes in a commercial washing machine together with pumice stones, water and a surfactant. However, conventional stone washing suffers from a number of defects in that, for example, not only does stone washing damage the fabric but also the pumice stones are expensive and tend to abrade during the process. Moreover, particulate abrasion by-products can cause significant processing and equipment problems. Particulate pumice must be manually removed from processed clothing items because it tends to accumulate in pockets, on interior surfaces, in creases and in folds. In the stone washing machine, the stones can cause overload damage to electric motors, mechanical damage to transport mechanisms and washing drums and can significantly increase the requirements for machine maintenance. The pumice stones and particulate material can clog machine drainage passages and can clog drains and sewer lines at the machine site. These problems can add significantly to the cost of doing business and to the purchase price of the goods. Moreover, although other abrasive materials, such as diatomaceous earth, have been used instead of pumice stones, these in general have proved less effective in generating the required distressed appearance.

[0008] To avoid the problems of mechanical stone washing, it is known to try to achieve the same distressed appearance by the use of chemical agents, particularly enzymes. For example, U.S. Patent No. 5,006,126 discloses a method of introducing localized areas of variation and color density into the surface of dyed cellulosic fabric by contacting the fabric with an aqueous composition consisting essentially of: (a) water; (b) at least 25 wt-% of a cellulase enzyme and at least 1,500 CMC units of cellulase enzyme per liter of aqueous composition; and (c) a buffer that can maintain the pH of the aqueous solution at about the cellulase enzyme optimum pH. However, although this treatment is said to give a variation in color density that is substantially the same as that produced by

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conventional pumice stone processing, enzymes digest the underlying cellulosic fabric thereby decreasing its strength. In addition, enzymatic processes are generally difficult to control.

[0009] There is therefore a need for a process for producing dyed fabrics with a worn or distressed appearance which reduces or obviates the need for mechanical stone washing.

[0010] According to the present invention, it has now been found that if an emulsion treated and dyed material, such as disclosed in U.S. patent publications Nos. US2012/0246842 A1 and US2013/0000057 A1, is subjected to a specific post treatment with an acrylic emulsion composition, the material can be given the desired “worn” appearance characteristic of stone washing either without or with a much reduced stone washing treatment.

Summary

[0011] In one aspect, the invention resides in a method of dyeing and finishing cotton fibers, which method comprises:

(a) preparing emulsion copolymer treated cotton fibers by contacting the fibers with an emulsion copolymer and curing the copolymer under conditions to chemically anchor the emulsion copolymer to the cotton and thereby form copolymer-treated cotton fibers;

b) contacting said copolymer-treated cotton fibers with a dye material under conditions sufficient to affix at least a portion of said dye material to the copolymer component of said copolymer-treated cotton fibers and produce dyed cotton fibers; and then

(c) treating the dyed cotton fibers with a surfactant-stabilized aqueous acrylic polymer dispersion.

[0012] Generally, the treating (c) is conducted at a temperature of 25 °C to 80 °C, such as 30 °C to 60 °C, for a period of at least 5 minutes, such as 15 to 45 minutes.

[0013] Typically, the acrylic polymer dispersion employed in (c) is diluted to about 0.05 to about 0.30 wt % solids, preferably to about 0.05 to about 0.15 wt % solids.

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[0014] In one embodiment, the acrylic polymer is formed from a monomer composition comprising one or more (meth)alkyl acrylate monomers wherein the alkyl group has from 1 to 12 carbon atoms. Optionally, the monomer composition further comprises from 5 to 20 % by weight, such as from 5 to 10 % by weight, of acrylonitrile based on the total weight of monomers in the composition.

[0015] Conveniently, the surfactant stabilizer for the acrylic polymer comprises an anionic surfactant.

[0016] In one embodiment, the method further comprises (d) stone washing the dyed cotton fibers at a temperature of 10 °C to 80 °C, such as 25 °C to 50 °C, for a period of less than 30 minutes, for example for 15 to 30 minutes.

[0017] Generally, the emulsion copolymer employed in (a) is selected from vinyl ester-based, acrylic-based, styrene/acrylic-based and styrene/butadiene-based emulsion copolymers and mixtures thereof.

[0018] In one embodiment, the emulsion copolymer employed in (a) is a vinyl acetate-ethylene copolymer comprising from 60 wt% to 95 wt% of vinyl acetate and from 5 wt% to 40 wt% of ethylene, based on total monomers therein.

[0019] In another embodiment, the emulsion copolymer employed in (a) is an acrylic emulsion copolymer which comprises at least two different types of (meth)acrylate co-monomers., for example ethyl acrylate and butyl acrylate co-monomers.

[0020] Conveniently, the emulsion copolymer employed in (a) comprises from 0.1 wt% to 10 wt%, based on total monomers in the copolymer, of one or more ethylenically unsaturated cross-linking co-monomers having at least one amide, epoxy, or alkoxysilane group.

[0021] Conveniently, the emulsion copolymer employed in (a) comprises from 0.1 wt% to 10 wt%, based on total monomers in the copolymer, of one of more multifunctional external cross-linking co-monomers selected from diallyl adipate, triallyl cyanurate, butanediol diacrylate, allyl methacrylate, and combinations of said cross-linking co-monomers.

DETAILED DESCRIPTION.

[0022] Described herein is method of producing dyed cotton fibers, whether in the form of yarn, fabric or garments, which not only allows the use of disperse dyes in the dying operation but also employs a post treatment step which imparts to the fibers the “worn” or “vintage” appearance characteristic of stone washing either without or with a much reduced stone washing treatment. In addition, the post treatment step has little or no adverse effect on the integrity of the cotton fibers unlike most existing chemical methods of duplicating the stone washing process.

Cotton Fibrous Material

[0023] Cotton is a fluffy staple fiber that grows in a boll, or protective capsule, around the seeds of cotton plants. The chemical composition of cotton is generally about 91% cellulose and 7.85 % water with the balance being protoplasm, pectins, waxes fatty substances and mineral salts.

[0024] Cotton fiber is generally spun into yarn or thread and used to make a soft, breathable textile fabric. “Textiles” and like terminology refer to yarns, fabrics, sewing threads, finished garments and so forth. Fabrics may be knit or woven fabrics made of cotton fibrous material. Garments may be apparel and industrial garments. The terms “fabrics” and “textiles” also include home goods such as linens, drapery, and upholstery (automotive, boating, airline included) made of the cotton fibrous materials described herein.

[0025] It is well known that cotton fibers can be combined with other fiber types when fashioned and used in the form of yarns, fabrics, textiles and garments. Typically cotton can be combined with other natural fiber types such as silk, linen, wool, angora and mohair. It is also well known that cotton can also be combined with synthetic and semi-synthetic fiber types such as polyester fibers, aramid fibers, polyamide (nylon) fibers, acrylic (acrylonitrile) fibers, spandexes, rayons, Tencel and cellulose acetate fibers. The cotton fibrous materials which are dyed and treated by the method described herein can contain minor amounts (less than 50 wt%) of fiber types other than cotton. However, the best dyeing results obtained using the method described herein are

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achieved when the yarns, fabrics, textile, garments, etc., contain no fibers other than cotton. Accordingly, preferred for use in the method herein are yarns, fabrics, textiles and garments which are 100% cotton.

Emulsion Copolymer Pretreatment

[0026] In the present process, the cotton fibrous material is contacted, prior to dyeing, with a selected type of emulsion copolymer. Such emulsion copolymers include those which have conventionally been used as textile finishing agents. Such emulsion copolymers include those described in detail in U.S. Patent Publication No. 2011/0005008, which is incorporated by reference herein in its entirety.

[0027] Suitable types of emulsion copolymers for use in the present process include vinyl ester-based, acrylic-based, styrene/acrylic-based or styrene/butadiene-based emulsion copolymers. The emulsions are generally aqueous emulsions. Such copolymers typically can also contain minor amounts of cross-linking or emulsion stabilizing co-monomers. Such co-monomers can, for example, in and of themselves or in combination with external cross-linking agents, make the emulsion copolymers used herein cellulose-reactive during the curing step described below.

[0028] One preferred type of emulsion copolymer comprises the vinyl ester-based copolymers selected from vinyl acetate-ethylene copolymers, vinyl acetate-vinyl versatate; vinyl acetate-acrylic copolymers, and combinations of these copolymer types. Vinyl acetate-ethylene (VAE) emulsion copolymers are well-known. Such VAE copolymers useful herein can comprise from about 60 wt% to about 95 wt% of vinyl acetate and from about 5 wt% to about 40 wt% of ethylene, based on total monomers therein. More preferably, VAE copolymers will comprise from about 70 wt% to about 90 wt% of vinyl acetate and from about 8 wt% to about 15 wt% of ethylene, based on total monomers therein.

[0029] Another preferred type of emulsion copolymer for use in the method herein comprises acrylic emulsion copolymers made of acrylic ester co-monomers. The alkyl acrylates that can be used to prepare the acrylic ester copolymer emulsions include alkyl acrylates and alkyl methacrylates containing 1 to 12, preferably 1 to 10 carbon atoms in

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the alkyl group. The polymer backbone in the acrylic ester copolymer can be either hydrophilic or hydrophobic and it can comprise polymerized soft monomers and/or hard monomers. The soft and hard monomers are monomers which, when polymerized, produce soft or hard polymers, or polymers in between. Preferred soft acrylic ester monomers are selected from alkyl acrylates containing 2 to 8 carbon atoms in the alkyl group and include ethyl acrylate, propyl acrylate, n-butyl acrylate, and 2-ethylhexyl acrylate. The hard acrylic ester monomers are selected from alkyl methacrylates containing up to 3 carbon atoms in the alkyl group and from non-acrylic monomers such as styrene and substituted styrenes, acrylonitrile, vinylchloride, and generally any compatible monomer the homopolymer of which has a Tg above 50° C. Preferred acrylic ester monomers are selected from alkyl acrylates and methacrylates containing 1 to 12 carbon atoms in the alkyl group, especially ethyl acrylate and butyl acrylate.

[0030] The emulsion copolymer will frequently contain, in addition to the main co-monomers, minor amounts of co-monomers which can provide cross-linking with both cellulose hydroxyl moieties within the cotton fibers and cross-linking within the copolymer itself. Such cross-linking co-monomers are unsaturated so as to polymerize into the copolymer backbone and will also contain at least one functional group containing nitrogen, oxygen or silicon atoms.

[0031] Thus the emulsion copolymers herein can comprise from about 0.1 wt% to about 10 wt%, based on total monomers in the copolymer, of one or more ethylenically unsaturated cross-linking co-monomers having, for example, at least one amide, epoxy, or alkoxy silane group. Examples of such suitable self cross-linking co-monomers include N-methylol (meth)acrylamide and esters thereof, N-vinylpyrrolidinone, dimethylaminoethyl acrylate, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, vinyl glycidyl ether, acryloxy-propyltri(alkoxy)silanes, methacryloxypropyltri(alkoxy)silanes, vinyltrialkoxysilanes, vinylmethyldialkoxysilanes and combinations of these cross-linkable co-monomers.

[0032] The emulsion copolymer can also contain, in addition to the main co-monomers and self cross-linking co-monomers, minor amounts of multifunctional external cross-linking co-monomers. Thus the copolymers used herein can optionally

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comprise from about 0.1 wt% to about 10 wt%, based on total monomers in the copolymer, of one or more of these multifunctional cross-linking co-monomers. Examples of suitable multifunctional cross-linking co-monomers include diallyl adipate, triallyl cyanurate, butanediol diacrylate, allyl methacrylate and combinations thereof.

[0033] Suitable cellulose-reactive emulsion copolymers can be prepared in conventional fashion using known emulsion polymerization techniques and raw materials. In general, such emulsion copolymers can be prepared by polymerizing appropriate co-monomers in appropriate amounts in an aqueous reaction mixture using conventional polymerization initiators and catalysts and conventional polymerization conditions. The copolymer emulsions so prepared can be stabilized with suitable emulsifiers (surfactants) and/or protective colloids.

[0034] Pretreating the cotton fibers with the emulsion copolymers initially involves contacting the fibers with the aqueous emulsion at a temperature of 40 °C to 60 °C so that the insoluble emulsion copolymer is deposited or “exhausted” onto the cotton fibers, substantially without reaction with the fibers. Such contact generally involves immersion of the cotton fibrous material in a treatment bath which can be made by diluting an aqueous emulsion copolymer dispersion to a solids content of from about 2 wt% to about 10 wt%, more preferably from about 3 wt% to about 6 wt%. Such treatment baths will also have a pH of from about 3 to about 7, more preferably from about 5 to about 7.

[0035] Yarn can be treated with saturating liquors (called “pad baths”) with a nip roll squeeze after each bath saturation. Yarn can also be treated in “package” form with the saturating liquor. Woven goods can be pad bath finished in continuous stenter (open width) frames or with batch processes such as, piece dyeing, jet, beck, jigger or paddle machines. Knit goods can be processed in the same machinery (both continuous and batch) as woven, just under different conditions. For garments, industrial garment washing machines may be used. Optional application methods include manual processes such as spraying or manual wet add-on techniques.

[0036] In one embodiment, cotton fabric can be contacted with the emulsion copolymer-containing treatment bath in a continuous padding operation run at a pad pressure of from about 0.3 bar to about 2.5 bar and at a pad speed of from about 0.25 to

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about 1 m/minute. More preferably, such a continuous padding operation can be run at a pad pressure of from about 0.9 bar to about 1.1 bar and at a pad speed of from about 0.3 to about 0.6 m/minute. (Commercial production speeds can be considerably higher, for example from about 10 to about 30 meters/minute.)

[0037] Regardless of the method of application selected, application and processing conditions should be selected such that the cotton fibrous material has a substantially uniform distribution of the emulsion copolymer associated with it. The fiber/copolymer combination will generally contain from about 1 wt% to about 10 wt%, more preferably from about 3 wt% to about 6 wt%, of the copolymer on a dry basis.

[0038] After the fiber/copolymer combination has been formed, this combination is subjected to curing conditions which are effective to chemically anchor the emulsion copolymer to the cotton fibrous material via reaction of the copolymer with at least a portion of the hydroxyl moieties of the cellulose component of the cotton fibers. Such chemical reaction can occur via a cross-linking mechanism with the cross-linkable comonomers which will generally form part of the emulsion copolymer as hereinbefore described. Curing of the fiber/copolymer combination also will generally promote some self-cross-linking of the copolymer within the fibrous cotton materials as well.

[0039] Curing conditions for the fiber/copolymer combination will generally involve subjecting the combination to elevated temperatures of from about 140 °C to about 165 °C for a period (dwell time) of from about 0.2 to about 4 minutes. More preferably, the fiber/copolymer combination can be cured by using temperatures of from about 145 °C to about 155 °C for a period (dwell time) of from about 0.3 to about 1 minute. In addition to anchoring the copolymer to the cellulose hydroxyl groups of the cotton fibers, curing of the fiber/copolymer combination will also generally serve to remove water from this combination. Thus curing of the fiber/copolymer combination can serve to partially or even substantially completely dry the fiber/copolymer combination prior to the dyeing step of the method herein.

[0040] The treating of the cotton fibrous material with the emulsion copolymer and the subsequent curing of the fiber/copolymer combination serves to provide chemically

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modified, copolymer-treated cotton fibrous material. Such copolymer-treated cotton fibers can then be dyed using the dyes and dyeing conditions hereinafter described.

Optional Denim Fabric Formation

[0041] In one embodiment, cotton warp yarn, after the copolymer emulsion pretreatment described above and either before or after being dyed, is incorporated into cotton denim fabric with untreated weft or fill yarn, that is yarn that has not been modified by the emulsion copolymer treatment. In practice, not all of the warp yarn needs to be emulsion copolymer-treated cotton yarn and not all of the weft yarn needs to be untreated cotton yarn. Generally, at least 50% of the warp yarn in the resultant greige denim fabric should be emulsion copolymer-treated cotton yarn and at least 50% of the weft yarn should be untreated cotton yarn. Preferably, however, substantially all of the warp yarn in the fabric should be emulsion copolymer-treated cotton yarn and substantially all of the weft yarn should be untreated cotton yarn.

[0042] Cotton warp and weft yarns can be fashioned into cotton denim fabrics in accordance with the methods herein by any conventional technique known for the preparation of such denim fabrics. The method herein is compatible with cotton denim fabrics having a wide range of fabric basis weights. Cotton denim fabrics will typically have a basis weight ranging from about 3 to about 10 oz/yd².

[0043] Weaving is a common method for making cotton yarn into cotton denim fabrics. The woven cotton denim fabrics which can be indigo dyed in accordance with the dyeing methods described hereinafter include, for example, those of a basic weave, satin weave, twill weave, ripstop weave or basket weave. Denim fabrics are most commonly of the twill weave type.

[0044] Cotton yarns can also be knitted to provide a variety of denim knit fabric types prior to being dyed in accordance with the dyeing method herein. Denim knit cotton fabrics will generally be of the warp type, including tricot knits or raschel knits.

Dyeing Process

[0045] After curing, the emulsion copolymer-treated cotton fibers are contacted with a dye material under conditions sufficient to affix at least a portion of said dye material to the copolymer component of said copolymer-treated cotton fibers and produce dyed cotton fibers.

[0046] Any known dye material can be used in the dyeing step but, in one preferred embodiment, the dye is a disperse dye. Disperse dyes are insoluble in water and were originally developed for the dyeing of cellulose acetate and are water-insoluble. They are generally finely ground in the presence of a dispersing agent (surfactant) and are sold as a paste or spray-dried and sold as a powder.

[0047] Suitable disperse dyes for use in the dyeing method herein are those described under "Disperse Dyes" in the Colour Index, 3rd edition (3rd revision 1987 inclusive of Additions and Amendments up to No. 85). Such dyes include, for example, carboxylic acid group-free and/or sulfonic acid group-free nitro, amino, aminoketone, ketonimine, methine, polymethine, diphenylamine, quinoline, benzimidazole, xanthene, oxazine and coumarin dyes and especially anthraquinone and azo dyes, such as mono- or di-azo dyes. Such disperse dyes are also those described in detail in U.S. Patent Publication No. 2006/0048308. That '308 patent document, and especially its disclosure of the several structural formulas for disperse dye materials disclosed therein, is incorporated herein by reference.

[0048] The preferred types of disperse dye materials useful herein include the quinoline dyes, the anthraquinone dyes and the azo dyes. The dyeing method herein is equally useful with disperse dyes whether they are classified as high energy dyes, medium energy dyes or low energy dyes. Useful disperse dyes which can be used herein also include dyes which are especially formulated for to serve as automotive dyes, lightfast dyes or fluorescent dyes.

[0049] Generally, the copolymer-treated cotton fibers will be contacted with the disperse dye material by immersing the fibers in a dye liquor in the form of an aqueous dispersion of the disperse dye material. The aqueous dye liquor can contain, for example, from about 0.01 wt% to about 15 wt% of the disperse dye material. More preferably, the

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aqueous dye liquor can contain from about 0.5 wt% to about 5.0 wt% of the disperse dye material. The lower concentrations of the dye in the dye liquor are useful for tinting operations. Higher dye concentrations in the dye liquor, of course, produce dyed cotton fibers, yarns, fabrics and garments having more intense color.

[0050] The aqueous dye liquor will generally be contacted with the cotton fibrous material to be dyed at temperatures of from about 65 °C to about 100 °C, more preferably from about 80 °C to about 95 °C. Under such dyeing liquor temperature conditions, it is possible to carry out the dyeing step of the method herein at atmospheric pressure. Dyeing liquor pH will generally range from about 3 to about 8, more preferably from about 4 to about 7.

[0051] The dyeing step of the method herein may be carried out using either batch or continuous operations. If a batch method is employed, the copolymer-treated cotton fibrous material can be contacted with the dye liquor for a period of from about 0.25 to about 3 hours, more preferably from about 0.5 to about 1.0 hour. In batch operation, a dye liquor to fiber ratio of from about 30:1 to about 3:1 can be used. More preferably, when cotton fibers are in fabric form, liquor to fabric ratios of from about 20:1 to about 8:1 can be employed.

[0052] The aqueous dyeing liquor can optionally contain various fiber and fabric treating adjuvants besides the disperse dye material. Such adjuvants can include, for example, optical brighteners, fabric softeners, antistatic agents, antibacterial agents, anti-wrinkling agents, ironing aids, flame-retardants, enzymes, UV stabilizers, anti-foaming agents, perfumes, and the like.

[0053] In another preferred embodiment, the dye is a vat dye and in particular an indigo dye generally known as Vat Blue 1. Unlike conventional indigo dyeing processes, with the emulsion copolymer treated fibers described herein, the dyeing can be conducted without the indigo dye being converted to its reduced or leuco form and at moderate pH values of from about 9 to less than about 12, more preferably from about 10 to about 11. In addition, as in the case of disperse dyes, indigo dyeing can be at temperatures of from about 65 °C to about 100 °C, more preferably from about 80 °C to about 95 °C, under atmospheric pressure.

Post Treatment

[0054] After dyeing, the dyed cotton fibers are rinsed with water and then subjected to one or more post treatment steps to give the material a stone-washed or vintage appearance. The first, and optionally the only post-treatment step, involves treating the dyed cotton fibers with a surfactant-stabilized aqueous acrylic polymer dispersion. Suitable acrylic polymers are produced from monomer compositions comprising one or more (meth)alkyl acrylate monomers wherein the alkyl group has from 1 to 12 carbon atoms. Preferred monomer compositions include butyl acrylate, methyl methacrylate, ethyl acrylate and mixtures thereof. Optionally, the monomer composition can contain from 5 to 20 % by weight, such as from 5 to 10 % by weight, of acrylonitrile based on the total weight of monomers used to produce the acrylic polymer.

[0055] In addition, the monomer composition can contain from 1 to 10 % by weight, such as from 1 to 5 % by weight, of N-methylol (meth)acrylamide and esters thereof, N-vinylpyrrolidinone, dimethylaminoethyl acrylate, glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, vinyl glycidyl ether, acryloxy-propyltri(alkoxy)silanes, methacryloxypropyltri(alkoxy)silanes, vinyltrialkoxysilanes, vinylmethyldialkoxysilanes and combinations of these cross-linkable co-monomers.

[0056] Suitable surfactants used to stabilize the acrylic polymer dispersion are anionic surfactants, such as sodium, potassium, and ammonium salts of linear aliphatic carboxylic acids of chain length C₁₂-C₂₀, sodium hydroxyoctadecanesulfonate, sodium, potassium, and ammonium salts of hydroxy fatty acids of chain length C₁₂-C₂₀ and their sulfonation and/or sulfation and/or acetylation products, alkyl sulfates, including those in the form of triethanolamine salts, alkyl(C₁₀-C₂₀) sulfonates, alkyl(C₁₀-C₂₀) arylsulfonates, dimethyl-dialkyl (C₈-C₁₈) ammonium chloride, and their sulfonation products, lignosulfonic acid and its calcium, magnesium, sodium, and ammonium salts, resin acids, hydrogenated and dehydrogenated resin acids, and their alkali metal salts, dodecylated sodium diphenyl ether disulfonate, sodium lauryl sulfate, sulfated alkyl or aryl ethoxylate with EO degree between 1 and 10, for example ethoxylated sodium lauryl ether sulfate (EO degree 3) or a salt of a bisester, preferably of a bis-C₄-C₁₈ alkyl ester, of a sulfonated

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dicarboxylic acid having 4 to 8 carbon atoms, or a mixture of these salts, preferably sulfonated salts of esters of succinic acid, more preferably salts, such as alkali metal salts, of bis-C₄-C₁₈ alkyl esters of sulfonated succinic acid, or phosphates of polyethoxylated alkanols or alkylphenols.

[0057] In one embodiment, the surfactant-stabilized aqueous acrylic polymer dispersion is Lyoprint PBA available from Huntsman.

[0058] Generally, the post-treatment with the surfactant-stabilized aqueous acrylic polymer dispersion is conducted at a temperature of 25 °C to 80 °C, preferably 30 °C to 60 °C, for a period of at least 5 minutes, preferably 15 to 45 minutes. Generally, the acrylic polymer dispersion is diluted with water so as to contain from about 0.05 to about 0.30 wt % solids, preferably from about 0.05 to about 0.15 wt % solids, most preferably about 0.10 wt % solids.

[0059] After the acrylic emulsion post-treatment the material has a natural looking “salt and pepper” effect characteristic of worn garments. Although the reason for this result is not fully understood it is believed that the surfactant-stabilized acrylic polymer dispersion partially removes the dye from the emulsion coated fibers without adversely effecting the underlying cotton structure.

[0060] Although the post-treatment with the surfactant-stabilized acrylic polymer dispersion will often be sufficient to provide the required vintage appearance to the cotton product, it may in some cases be desirable to precede this post treatment with a mechanical stone washing treatment. In this case, however, the duration and severity of the mechanical stone washing treatment can be significantly reduced as compared with a conventional stone washing process. For example, in the present process, stone washing is conveniently conducted at a temperature of 10 °C to 80 °C, preferably 25 °C to 50 °C, for a period of less than 45 minutes, for example for 15 minutes to 30 minutes without the addition of caustic. In contrast, conventional stone washing treatments require temperatures of 75 °C to 95 °C for periods of 60 minutes to 90 minutes at pH values of 8 to 11.

[0061] The invention will now be more particularly described with reference to the following non-limiting Examples.

Example 1: Garment Exhaust Pretreatment with Garment Exhaust Dyeing and Batch Post treatment

[0062] Cotton garments prepared for dyeing are added to a garment washing machine, which is filled with water at a 20:1 liquor ratio, or 20 parts water for each part fabric. The machine is run at low (25 to 40) RPM for 5 minutes at ambient temperature for wetting of the garments. A 50% solids acrylic copolymer emulsion (composed of 89% ethyl acrylate, 8% acrylonitrile and 3% N-methylolacrylamide (NMA)) is added to create a 10% diluted solids solution. The bath temperature is ramped at 5 °F/min to 160 °F (71 °C) while running at low RPM and the machine is run at this temperature for 1 hour. The bath temperature is then ramped down to 140 °F (60 °C) and the water is removed. Complete extraction of the garments is effected for 30 seconds at 400 RPM and the garments are then removed from the washing machine for drying/curing.

[0063] Curing of the emulsion copolymer is completed on the dry garments at 120 °C to 150 °C for about 20 seconds.

[0064] The dried and cured garments are then exhaust dyed in the same garment washing machine used for the emulsion pretreatment again with the machine being filled with water to a 20:1 liquor ratio. The water is adjusted to a 4 pH with acetic acid and the machine is run for 5 minutes with low RPM to rewet the garments. The desired mixture and concentration of disperse dye is solubilized in hot water as is conventional in the art of handling dry disperse dyestuffs for use in wet processing of polyester. This dissolved dye is added to the machine after the wetting step and the resultant exhaust dye bath is ramped to 95 °C at a ramp rate of about 5 °F/min. The exhaust bath is retained at this temperature for 60 minutes, after which the bath temperature is ramped down to 140 °F (60 °C) at 5 °F/min before bath is removed. The machine is then filled with fresh water, ramped to 40 °C for rinsing, and cycled at this temperature for 15 minutes. The first rinse bath is then removed, whereafter the machine is again filled with fresh water and rinsed for 15 minutes with 25 °C water. The second rinse bath is then removed and the garments are transferred to a stone-washing machine.

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[0065] The stone-washing machine is filled with the garments and water at a 15:1 liquor ratio. Pumice stones (preferably 2-4 cm diameter stones) are added to the machine at about 2 parts stone to 1 part cotton. The stone-washing machine is run at 25 to 40 RPM for 30 minutes at 30 °C. The garments are now ready for post treatment

[0066] The stone-washed garments are placed in a garment washing machine and water is added to a 20:1 liquor ratio. 10 g/L Lyoprint® PBA (Huntsmann) is added to the bath and the machine is run at low RPM for 20 minutes at 60 °C bath temperature. After 20 minutes the bath is cooled to 30 °C and a softener package, 2% owg Siligen N-AP softener (BASF), is added to the bath. The softener package is run for 5 minutes, after which the water is removed. The garments are dried at 80 °C and are then ready for conditioning and packaging for delivery.

Example 2: Continuous Pretreatment with Continuous Dyeing

[0067] This Example employs circular knit or tubular fabric that has been pretreated by bleaching and biofinishing (enzyme) for whitening and wettability and run through a slitter to make it “open width”, or flat. This flat fabric is run through a pad bath made of an 8% diluted solid solution of the acrylic copolymer emulsion used in Example 1. The saturated cotton is then squeezed between pad rolls at a pressure to generate a wet pick up of approx. 95% to 105%. The cotton is then dried in a stenter frame at 230 °F (110 °C). The dried cotton is doffed in roll form at the end of the line and returned through another drying stenter for curing at 300 °F (149 °C) for about 60 seconds. The fabric is collected and is ready for pad dyeing.

[0068] The pretreated cotton roll is then sent through a disperse dye bath and passed between pad rolls with wet pick up and dye bath concentration adjusted for desired depth of shade. The disperse dye is prepared in the same way as in Example 1 before being added to the pad trough. The fabric is then dried at 230 °F (166 °C) or at acceptable production temperature. The fabric is then sent for production and stonewashing/post treatment using the same process as described in Example 1 above.

CLAIMS

1. A method of dyeing and finishing cotton fibers, which method comprises:
 - (a) preparing emulsion copolymer treated cotton fibers by contacting the fibers with an emulsion copolymer and curing the copolymer under conditions to chemically anchor the emulsion copolymer to the cotton and thereby form copolymer-treated cotton fibers;
 - b) contacting said copolymer-treated cotton fibers with a dye material under conditions sufficient to affix at least a portion of said dye material to the copolymer component of said copolymer-treated cotton fibers and produce dyed cotton fibers; and then
 - (c) treating the dyed cotton fibers with a surfactant-stabilized aqueous acrylic polymer dispersion.
2. The method according to Claim 1, wherein the treating (c) is conducted at a temperature of 25 °C to 80 °C for a period of at least 5 minutes.
3. The method according to Claim 1 or Claim 2, wherein the treating (c) is conducted at a temperature of 30 °C to 60 °C for a period of 15 to 45 minutes.
4. The method according to any preceding Claim, wherein the acrylic polymer dispersion employed in (c) is diluted to about 0.05 to about 0.3 % solids.
5. The method according to any preceding Claim, wherein the acrylic polymer employed in (c) is produced from a monomer composition comprising one or more (meth)alkyl acrylate monomers wherein the alkyl group has from 1 to 12 carbon atoms.
6. The method according to Claim 5, wherein the monomer composition comprises butyl acrylate, methyl methacrylate, ethyl acrylate or a mixture thereof.

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7. The method according to Claim 5 or Claim 6, wherein the monomer composition further comprises from 5 to 20 % by weight, such as from 5 to 10 % by weight, of acrylonitrile based on the total weight of monomers in the composition.
8. The method according to any preceding Claim, wherein the surfactant stabilizer for the acrylic polymer comprises an anionic surfactant.
9. The method according to any preceding Claim and further comprising:
 - (d) stone washing the dyed cotton fibers at a temperature of 10 °C to 80 °C for a period of less than 30 minutes.
10. The method according to Claim 9, wherein the stone washing is conducted at a temperature of 25 °C to 50 °C for a period of 15 minutes to 30 minutes.
11. The method according to any preceding Claim, wherein the dye material is a disperse or vat dye.
12. The method according to any preceding Claim, wherein the emulsion copolymer employed in (a) is selected from vinyl ester-based, acrylic-based, styrene/acrylic-based and styrene/butadiene-based emulsion copolymers and mixtures thereof.
13. The method according to any preceding Claim, wherein emulsion copolymer employed in (a) is a vinyl ester-based copolymer selected from vinyl acetate-ethylene copolymers, vinyl acetate-vinyl versatate; vinyl acetate-acrylic copolymers, and combinations of said copolymer types.
14. The method according to any preceding Claim, wherein the emulsion copolymer employed in (a) is a vinyl acetate-ethylene copolymer comprising from 60 wt% to 95 wt% of vinyl acetate and from 5 wt% to 40 wt% of ethylene, based on total monomers therein.

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15. The method according to any one of Claims 1 to 13, wherein the emulsion copolymer employed in (a) is an acrylic emulsion copolymer which comprises at least two different types of (meth)acrylate co-monomers, preferably ethyl acrylate and butyl acrylate co-monomers.

16. The method according to any preceding Claim wherein the emulsion copolymer employed in (a) comprises from 0.1 wt% to 10 wt%, based on total monomers in the copolymer, of one or more ethylenically unsaturated cross-linking co-monomers having at least one amide, epoxy, or alkoxysilane group.

17. The method according to any preceding Claim wherein the emulsion copolymer employed in (a) comprises from 0.1 wt% to 10 wt%, based on total monomers in the copolymer, of one or more multifunctional external cross-linking co-monomers selected from diallyl adipate, triallyl cyanurate, butanediol diacrylate, allyl methacrylate, and combinations of said cross-linking co-monomers.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/027733

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	D06P3/60	D06P5/02
	D06P1/52	D06P1/54
ADD.	D06P5/15	D06P1/16
		D06P1/22
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) D06P		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 2011/005008 A1 (SCHROOTS HARRIE P [US] ET AL) 13 January 2011 (2011-01-13) paragraphs [0003] - [0018]; claims 53-57	1-17
Y	WO 2004/016849 A1 (CIBA SC HOLDING AG [CH]; SCHEIBLI PETER [CH]) 26 February 2004 (2004-02-26) page 17, paragraph 5 page 18, paragraph 3 - page 20, paragraph 1 page 20, paragraph 5 - page 21, paragraph 3; claims	1-17
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 27 May 2013		Date of mailing of the international search report 10/06/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Koegler-Hoffmann, S

INTERNATIONAL SEARCH REPORT

International application No

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Y	WO 95/35363 A1 (IVAX IND INC [US]) 28 December 1995 (1995-12-28) claims 1,16 -----	1-17
Y	US 5 958 083 A (ONISHI MASAHIRO [JP] ET AL) 28 September 1999 (1999-09-28) column 7, line 1 - line 10 -----	1-17

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